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Alan R. Katritzky

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Edited by

ALAN R. KATRITZKY

Kenan Professor of Chemistry
Department of Chemistry
University of Florida
Gainesville, Florida

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BRANKO STANOVNIK, MIHA TIŠLER, ALAN R. KATRITZKY, AND OLGA V. DENISKO

Contributors

Numbers in parentheses indicate the pages on which the authors' contributions begin.

Olga V. Denisko (253), Florida Center for Heterocyclic Compounds, Department of Chemistry, University of Florida, Gainesville, Florida 32611-7200, email: Odenisko@chem.ufl.edu

Ahmed Hashem (107), Department of Chemistry, Ain Shams University, Abassia, Cairo, Egypt

Alan R. Katritzky (253), Florida Center for Heterocyclic Compounds, Department of Chemistry, University of Florida, Gainesville, Florida 32611-7200, email: katritzky@chem.ufl.edu

Erich Kleinpeter (107), Institut für Organische Chemie und Strukturanalytik, Universität Potsdam, D-14415 Potsdam, Germany, email: kp@chem.uni-potsdam.de

Guntram Rauhut (1), Institut für Theoretische Chemie, Universität Stuttgart, D-70569 Stuttgart, Germany, email: rauhut@theochem.uni-stuttgart.de

Alexander P. Sadimenko (167), Department of Chemistry, University of Fort Hare, Baysville, East London 5241, Republic of South Africa, email: asadimenko@ufh.ac.za, sashok@xsinet.co.za

Branko Stanovnik (253), Faculty of Chemistry and Chemical Technology, University of Ljubljana, 1000 Ljubljana, Slovenia, email: branko.stanovnik@uni-lj.si

Miha Tišler (253), Faculty of Chemistry and Chemical Technology, University of Ljubljana, 1000 Ljubljana, Slovenia, email: miha.tisler@uni-lj.si

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Preface

Volume 81 of *Advances in Heterocyclic Chemistry* consists of four chapters. G. Rauhut (University of Stuttgart, Germany) provides a contemporary overview of methods and results for the computation of heteroatom-rich five- and six-membered ring systems, covering many advances in MO theory made over the last decade. The review will be useful to a wide range of heterocyclic chemists.

A. Hashem (Ain Shams University, Egypt) and E. Kleinpeter (University of Potsdam, Germany) summarize the chemistry of 2(5*H*)-furanones, commonly known as butenolides, which has seen fast growth in the 1990s. The volume continues with a further chapter in the continuing survey by A. P. Sadimenko (University of Fort Hare, South Africa) of the organometallic chemistry of heterocycles. The present chapter covers pyrazolylborates and related ligands and is the first attempt to treat their organometallic complexes systematically. It follows previous chapters by the same author in Volumes 78, 79, and 80 of *Advances.*

The volume ends with a chapter by B. Stanovnik and M. Tišler of the University of Ljubljana, Slovenia, and A. R. Katritzky and O. V. Denisko of the University of Florida on the annular tautomerism of six-membered ring heterocycles. This represents a further installment in our comprehensive update of heteroaromatic tautomerism, which was the subject of several chapters in Volumes 79 and 80 of this series.

ALAN R. KATRITZKY

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ADVANCES IN HETEROCYCLIC CHEMISTRY, VOL. 81

Recent Advances in Computing Heteroatom-Rich Five- and Six-Membered Ring Systems

GUNTRAM RAUHUT

Institut für Theoretische Chemie, Universität Stuttgart, D-70569 Stuttgart, Germany

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I. Introduction

Recent developments in computer technology in combination with increasingly accurate quantum chemical methods allow for the detailed investigation of molecular reactions, properties, and bulk effects. However, studies of systems with several (adjacent) heteroatoms are hampered owing to strong electron correlation effects, spin contamination in open-shell molecules, and strong charge polarization which requires very flexible basis sets. These problems limit the reliability of semiempirical methods and simple Hartree–Fock *ab initio* calculations for this class of molecules. Nevertheless, many questions could be solved based on such calculations. But the accuracy of modern gradient-corrected density functionals and a new generation of fast *ab initio* post-Hartree–Fock methods allow the investigation of molecules of up to 50 atoms on standard personal computers at much higher levels. Since these methods now permit a quantitative interpretation rather than a qualitative one, computational chemistry has become increasingly important in traditional heterocyclic chemistry, life sciences, and drug design. It is thus the purpose of this contribution to provide an overview of the recent advances of modern quantum chemical methods in heterocyclic chemistry. Many of these methods are no longer "blackbox" in nature, they require a sound knowledge of quantum mechanics. Thus particular care must attend the choice of method and the interpretation of results. The last aspect is even more important when reference data are lacking.

The choice for the correct method depends on several parameters. (1) What do I want to know? (2) How large is the system I am interested in? (3) What are my computer resources? The first aspect leads to a preselection of the computational methods in principle. For instance, if one is interested in computing a UV spectrum, one may choose several standard methods including (1) time-dependent density functional theory (TD-DFT), (2) equation-of-motion coupled-cluster theory [EOM-CCSD(T)], (3) multireference perturbation theory (CASPT2), or (4) configuration-interaction methods (CISD and MRCI). These methods differ strongly with respect to their computational demands and accuracy. For a good guess, TD-DFT will be sufficient in most cases. If one wants to predict experimentally unknown data of a difficult system, EOM-CCSD(T) or MRCI calculations may be more reliable. However, if the molecule is large or possesses a strongly delocalized π system, these methods may be prohibitive, so that TD-DFT remains the only feasible choice. The size of the molecule is not the only factor that influences the method; another is the choice of the basis set. Much larger basis sets are required for anions than for neutral species, thus very demanding methods cannot be afforded very often. Therefore, the computer architecture finally determines the level of accuracy and hence the choice of the method. Consequently, many applications are still out of range even for the fastest supercomputers and thus require the development of new quantum chemical methods. A short example may

illustrate this. An energy calculation of indene at the coupled-cluster, CCSD(T), level with a satisfying cc-pVTZ basis (i.e., 388 basis functions) may need one day (which would require a multiprocessor high-performance computer). Because the number of operations in the CCSD(T) approaches scales with the seventh order with respect to the number of basis functions N [i.e. $O(N^7)$], the calculation of the corresponding dimer would require about 128 days. Extrapolating the extreme increase in computer power by assuming an optimistic annual processor speedup by a factor of 2, one would have to wait for at least 5 years until this calculation becomes feasible by virtue of developments in modern computer technology. Therefore, there is still a strong need for faster algorithms, especially for high-level *ab initio* methods. Among the most promising concepts is the local correlation approach introduced by Pulay and Saebø [83CPL151, 84JCP1901, 87JCP914]. The principal ideas of Pulay's approximations can be applied to any existing *ab initio* method and are already available up to local CCSD(T) level. For instance, the conventional MP2 approach scales with the fifth order of the basis functions, while the local MP2 (LMP2) scales with an order of about 1.5. This means that the calculation of the correlation calculation is no longer the dominating step, but rather the Hartree–Fock iterations, which scale effectively with an order of 2.3. However, new developments have also led to a linear scaling of this method. On average, the local correlation calculations are as accurate as conventional methods, and thus much larger systems can be computed owing to the tremendous reduction of CPU time. In other words, if a Hartree–Fock calculation can be performed, there are essentially no arguments for not performing an MP2 calculation.

Whereas density functional methods are widely used by experimentally working heterocyclists, high-level *ab initio* methods are mainly the tools of computational chemists, since the latter offer the possibility of a systematic improvement of the results. It is one of the major drawbacks of the density functional theory that the accuracy of the results depends solely on the exchange-correlation functional, which is parametrized on physical models and thus may fail in certain situations. The most prominent example in this respect is the absence of long-range dispersion interactions as they are of particular importance for the calculation of molecular clusters [94CPL175]. Nevertheless, DFT functionals provide excellent results for molecular geometries and vibrational frequencies. Consequently, a combination of DFT and high-level *ab initio* calculations has proven to be the most successful in computational chemistry. Owing to the much higher accuracy of the mentioned methods, the following sections will primarily focus on computational studies that deal with DFT or post-HF methods. This is necessary because heterocycles with at least two heteroatoms are usually much more sensitive to the theoretical level than are hydrocarbons or simple heterocycles. Since the power of quantum chemical methods as an interpretive tool has been recognized by very many research groups, this review is restricted to the last few years and to the heteroatoms N, O, and S. Moreover, in addition to chemical aspects, computational details are provided in

most cases. Very often, quantum chemical methods were used for the investigation of molecular properties rather than for studying the reactivity of a species. Consequently, this review differs from others by a stronger emphasis on the physical properties of a molecule.

II. Recommendations

The following sections provide examples of recent quantum chemical studies in heterocyclic chemistry. As can be seen from these studies, the quality of the results depends strongly on the applied methods and the knowledge of the users. Since most of the readers of this book are experimentalists whose primary focus is not quantum chemistry but experimental heterocyclic chemistry that should be supported by quantum chemical calculations, it is the purpose of this section to provide some crude guidelines for the less experienced users on how to use modern quantum chemical methods.

The recommendations provided below are grounded on the following premises: (1) The user has access to a standard personal computer (PC) rather than high-performance workstations. (2) The fast-growing efficiency of modern PCs enables *ab initio* investigations of systems up to 50 atoms with few limitations at the moment. Within the next five years, much larger systems can be envisaged. (3) Well established quantum chemical methods, such as the perturbational MP2 approach, will be replaced by more efficient variants. For example, with respect to the standard MP2 method, much larger systems can be studied using the RI-MP2 [93CPL359, 97TCA331], LT-MP2 [92JCP489, 99JCP3660], LMP2 [87JCP914, 98JCP5185], and related methods [95JCP1481, 98CPL102]. These methods certainly will be preferred over the conventional methods in the near future. (4) Multiprocessor PCs can run quantum chemical calculations in parallel, permitting the study of much larger systems. (5) Recommendations can be provided only for standard applications. For more detailed aspects, collaborations with computational chemistry groups are highly recommended. This usually prevents misinterpretations of computational results and enables the use of more sophisticated methods.

Certainly, in ten years these recommendations will cause readers to smile; therefore, they must be considered my personal view in December 2000, which should not be generalized immoderately.

Basis Sets: For determining structural parameters, basis sets of at least double-ζ quality should be used. The most popular basis sets of this quality are Pople's 6-31G** [71JCP724] and Dunning's cc-pVDZ bases [89JCP1007]. In any case, the basis should include polarization functions (i.e., 6-31G** vs. 6-31G). For the study of through-space interactions (e.g., molecular clusters) diffuse functions should be added (i.e., 6-31++G** or aug-cc-pVDZ [92JCP6769]). In many cases, it is sufficient to augment only a subset of atoms with diffuse functions. Geometry

optimizations with STO-3G or 3-21G bases are outdated and do not have any justification even for systems of 50 atoms or more.

Energy single point calculations require larger basis sets than those used in geometry optimizations. Although the computer architecture often prohibits basis sets of augmented triple-ζ quality (i.e., 6-311++G(2df,2pd) [80JCP650] or aug-cc-pVTZ [92JCP6769]), one may use these bases as a goal. Reasonable compromises are the 6-311+G(2d,p) and aug-cc-pVTZ(f,d) bases (the latter basis describes a standard aug-cc-pVTZ basis without *f*-functions on nonhydrogen atoms and without *d*-functions on hydrogens). Diffuse functions are generally less important than polarization functions, but are of particular importance for certain applications: Whenever the outer region of the electron cloud must be well described (anions, through-space interactions, polarizabilities, etc.), diffuse functions need to be added.

In general, the basis set should be in balance with the computational method: A highly sophisticated method [e.g., CCSD(T)] in combination with a small basis or a low-level method [e.g., Hartree–Fock (HF)] in combination with a very large basis may be useful only in very specific cases. Consequently, increasing the basis set should be done while increasing the quality of the post-HF approach for a better representation of the electron correlation.

Geometry Optimizations: Density functional theory (DFT) has been proven to provide reliable geometries for most molecules. Since DFT calculations are only moderately more expensive than simple Hartree–Fock calculations, density functional theory should be the preferred choice. As widely acknowledged, the hybrid B3-LYP exchange-correlation functional [88PR(B)785, 93JCP5648] has proved particularly successful in reproducing structural parameters, although even this functional leads to a marginal overestimation of bond lengths [95JPC3093]. Among the most promising exchange-correlation functionals of the new generation are the B97 [97JCP8554] and the HCTH [00JCP1670] functionals. However, experience with these functionals is still very limited.

In certain cases, when geometric parameters depend strongly on dispersive energy contributions—as in the calculation of stacked nucleobases—DFT should not be used, since current density functionals do not account for long-range effects [94CPL175]. In these cases, MP2 geometry optimizations are recommended. In the context of intermolecular interactions, one should keep in mind that intermolecular distances are contaminated by BSSE effects; i.e., the incompleteness of the basis set leads to distances being too short [94CRV1873]. This problem can be circumvented by modern LMP2 geometry optimizations [98JPC(A)5997].

Usually, geometries of transition states are significantly more sensitive with respect to method than are structures of stable species. Since electron correlation effects are of particular importance for these structures, the determination of transition states at the Hartree–Fock level should be avoided. It is recommended to compare the structural parameters of transition states obtained from different methods (for instance DFT and MP2) in order not to be misled.

Energy Considerations: The question of how to obtain reliable energies (e.g., to distinguish different tautomers of a specific compound) essentially is the question for the most appropriate method. In most cases, the answer is given by the speed of the available computer; but as a rule of thumb, one should allow at least the same timeframe for an energy single point calculation as needed for the underlying geometry optimization of the molecule. The entrance level should be a DFT or MP2 calculation. Note that in most modern program packages the MP2 calculation is less demanding than the corresponding HF calculation. If the computer permits more demanding calculations, a useful hierarchy of the methods is MP2–MP4(SDQ)–CCSD–CCSD(T). Note that B3-LYP relative energies are not as reliable as B3-LYP geometries. Usually, B3-LYP calculations lead to an underestimation of activation barriers [96CPL558]. In many cases, MP2 energies for transition states are still not reliable. The average absolute error of both methods (MP2 and B3-LYP) with respect to relative reaction energies is still above 5 kcal/mol and thus far beyond chemical accuracy. Interaction energies in molecular clusters should be corrected for BSSE effects [94CRV1873] which can easily be achieved by the counterpoise method of Boys and Bernardi [70MP553].

In some cases, the nature of a transition state gives rise to multireference calculations, while the corresponding educts and products can be described by single reference wavefunctions. This holds true in particular for homolytic bond-breaking processes. In this case, CASPT2 or MRCI+Q calculations are recommended, which require a sound knowledge of quantum chemistry and are thus the preferred methods of experts. Alternatives are given by the easy-to-use spin-unrestricted methods (UDFT, UMP2, etc.), but for heterocycles these calculations are often troublesome owing to severe spin contamination. Very often, however, DFT calculations are surprisingly insensitive with respect to multireference effects, which can be attributed to the fact that nondynamic electron correlation effects are partly accounted for in the exchange functional [97JCP5007]. Moreover, CCSD(T) calculations are also fairly robust with respect to multireference effects, and most programs provide a diagnostic in combination with CCSD(T) calculations in order to judge the importance of these effects [89IJQS199].

Vibrational Spectra: Many of the papers quoted below deal with the determination of vibrational spectra. The method of choice is B3-LYP density functional theory. In most cases, MP2 vibrational spectra are less accurate. In order to allow for a comparison between computed frequencies within the harmonic approximation and anharmonic experimental fundamentals, calculated frequencies should be scaled by an empirical factor. This procedure accounts for systematic errors and improves the results considerably. The easiest procedure is to scale all frequencies by the same factor, e.g., 0.963 for B3-LYP/6-31G* computed frequencies [95JPC3093]. A more sophisticated but still pragmatic approach is the SQM method [83JA7073], in which the underlying force constants (in internal coordinates) are scaled by different scaling factors.

This leads to a remarkable improvement over the uniformly scaled frequencies, and many programs are available for this task.

Excited States: The investigation of excited states is usually a tedious task and often requires non-blackbox methods. However, recent advances in method development allow the investigation of electronic spectra via single-reference methods (e.g., time-dependent DFT [96CPL454] and equation-of-motion coupled-cluster methods). The use of these methods is very simple while yielding very promising results. More commonly, multireference methods are used for the investigation of electronic spectra. Among these methods, the CASPT2 approach has proved quite successful. Simple CIS calculations must be considered outdated and cannot be recommended anymore.

Investigation of Reaction Paths: The entire investigation of reaction paths is certainly one of the most demanding tasks in quantum chemistry. Since a chemical reaction is mainly characterized by the transition state, its determination is of particular importance (*vide supra:* Geometry Optimizations and Energy Considerations) and should be done very carefully. Investigations of reaction paths that involve bond-breaking and/or bond-forming processes at the Hartree–Fock level are of limited use. Electron correlation effects need to be included in any case.

Many computational studies in heterocyclic chemistry deal with proton transfer reactions between different tautomeric structures. Activation energies of these reactions obtained from quantum chemical calculations need further corrections, since tunneling effects may lower the effective barriers considerably. These effects can either be estimated by simple models or computed more precisely via the determination of the transmission coefficients within the framework of variational transition state calculations [92CPC235, 93JA2408].

Solvent Effects: Solvent effects can either be simulated by a self-consistent reaction field approach (SCRF) in which the chemical environment is modeled by a polarizable continuum [94CRV2027, 99CRV2161] or by an explicit inclusion of solvent molecules in the quantum chemical calculation (supermolecular approach). A definite recommendation of one of these methods cannot be given here. While results can be obtained easily by the different SCRF approaches, the quality of these results is usually below that obtained from a supermolecular approach. It is often preferable to consider the numbers obtained from SCRF calculations (e.g., solvation enthalpies) indicatively as trends rather than quantitatively. On the other hand, supermolecular calculation suffer from exceedingly long geometry optimizations because the potential energy surfaces are in general very flat for these intermolecular parameters. In order to combine the advantages of both methods, a quite successful approach is the implicit inclusion of just a very few solvent molecules and to model the remaining bulk effects by the continuum approach.

Population Analyses: Population analyses are used to gain a detailed understanding of the electronic properties of a molecule. A common feature of most of these analytic tools is the definition of atomic charges. Because there is no

clearcut border between two bonded atoms, the definitions of the different atomic charges differ considerably. Moreover, atomic charges are usually strongly basis set–dependent. Therefore, an interpretation of atomic charges should be restricted to relative atomic charges within one method and basis set. For the interpretation of electronic properties, the NBO [83JCP4066, 88CRV899] and AIM [90MI1] analyses are superior to the Mulliken population analysis and are thus recommended.

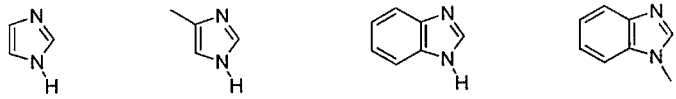
Moreover, many studies use the nature and shape of molecular orbitals for interpreting electronic effects. However, it should be kept in mind that the total energy of a molecule is invariant with respect to the occupied molecular orbitals. In other words, occupied molecular orbitals may strongly mix with each other without changing the energy of the system. Therefore, the interpretation of orbital shapes usually is not a unique source of information.

III. Five-Membered Rings with Two Heteroatoms

A. Imidazoles

Imidazoles have been studied computationally by many groups, and an excellent overview of the literature until 1994 is given by Grimmett [96MI1]. The geometry of imidazole **1** (Scheme 1) has been determined at the B3-LYP/6-31G* and MP2/6-31G* levels [98JPC(B)4488, 98JST41], which show very good agreement with experimental gas-phase and crystal data.

5-Aminoimidazole-4-imides computed at the B3-LYP/6-311+G(d,p) level differ from other imidazoles due to their long C—C bond (>1.5 Å) [97JPR735]. The substituents introduced significantly reduce the aromaticity of the ring system, which is reverted to antiaromaticity in the case of protonated species. Owing to the well-known catalytic properties of imidazole **1** and its occurrence in many bioorganic molecules (e.g., histidine; *vide infra*), particular attention has been paid to the molecule's ability to establish very strong hydrogen bonds. In this respect, neutral and charged complexes with water [98JPC(A)3782, 99JST27], ammonia [98JPC(B)4488], and a wide range of other agents [98JPC(B)4488] have been computed. Intramolecular hydrogen bonding (IMHB) has been investigated for 2-(2′-hydroxyphenyl)imidazole **2** derivatives and urocanic acid [(*Z*)-3-(1′*H*-imidazol-4′(5′)-yl)propenoic acid] **3** (see Schemes 2 and 10). Based on GIAO calculations,



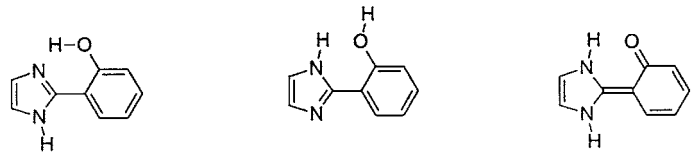
1 **4** **5** **6**

Scheme 1

correlations between the length of the hydrogen bond in a protonated imidazole–water complex and the difference in the ^{13}C chemical shifts of the two carbon atoms were established [98JPC(B)4488]. Most remarkably, simple Hartree–Fock theory provides a better basis for this correlation than B3-LYP. Recently, however, Handy and coworkers showed that a slight modification of the parameters of the hybrid B3-LYP functional yields GIAO data that are very close to the most accurate GIAO/CCSD(T) values [99CPL475]. The influence of environmental effects on the proton transfer reaction between imidazole and water was found to be substantial [00JPC(A)8283]. Other correlations than the one mentioned above were found between the interaction energy of the hydrogen bond and Mulliken bond orders, the difference in Mulliken charges, frequency shifts, and bond lengths [99JST27]. Calculations of the imidazole–tetramethylammonium complex show that the preferred orientation is characterized by an $N^+ \cdots N$ interaction (MP2: 16.3 kcal/mol) and not by a cation–π interaction as in other aromatic molecules (e.g., pyrrole, MP2: 10.7 kcal/mol) [97JCC2012]. A DFT study of complexes of the ammonium cation with imidazole and other heterocycles indicates that cation–π complexes (with NH_4^+ above the ring plane) will be formed when the heterocycle has no localized lone pairs [99JCS(P2)2615].

The vibrational spectra of the two different tautomers of 4-methylimidazole **4,** protonated **4,** and deprotonated **4** were studied by DFT calculations [00JPC(B) 4253]. An analysis of the spectra showed that the C_4—C_5 and C_5—N_1 stretching bands may serve as indicators for the protonation site and form in enzymes. Infrared vibrational spectra of matrix-isolated imidazole, benzimidazole **5,** 1-methylbenzimidazole **6,** and their complexes with water were analyzed and assigned by comparing the experimental spectra with the IR frequencies and intensities computed by *ab initio* and DFT methods [97JPC(A)2397, 98JPC(A)4863]. B3-LYP/6-31++G** frequencies of the monomers were scaled according to the SQM procedure [83JA7073] and mean deviations account for only 10 and 8 cm^{-1} for **5** and **6,** respectively. Frequency shifts of the vibrational modes directly involved in the H bond of the water complex are nicely reproduced by the B3-LYP functional. Hydrogen bond interaction energies are reported. Solvation effects modeled by self-consistent reaction field methods (SCRF) were found to have a strong impact on the IMHB in neutral **3** [98JST185]. Strong IMHBs in 2-(2′-hydroxyphenyl)imidazole **2** are responsible for the planarity of the molecule [98JST193]. The preferred tautomer of this species is the *cis*-enol form **2a,** which is more stable than the *trans*-enol **2b** or the keto forms **2c** (Scheme 2) [98JPC(A)10736].

As must be expected for all these studies of long-range interactions, large basis sets with diffuse functions in combination with correlation methods (at least MP2) are mandatory. DFT calculations were performed in order to determine the preferred addition site of OH to protonated 4-ethylimidazole [99JPC(A)1283]. As supported by computed hyperfine coupling constants, the OH radical adds

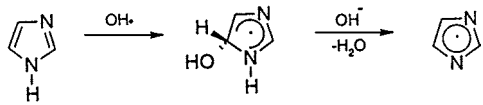


2a **2b** **2c**

SCHEME 2

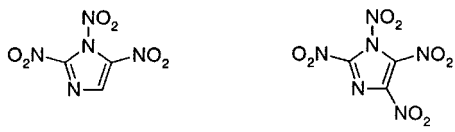
primarily to the C_5 position. The mechanism of the hydroxyl radical addition to imidazole with a subsequent elimination of water to form the 1-dehydroimidazolyl radical **7** has been studied at the B3-LYP and MP2/6-311G(2df,p) levels (Scheme 3) [99JPC(B)5598]. Again, the C_5 position is the preferred addition site. However, while the MP2 calculations predict a low activation barrier for the addition, the DFT calculations result in a barrier-free addition. Conformational studies were performed for several nitroimidazoles [98JST41]. As must be expected, the height of the rotational barrier of the nitro group(s) critically depends on the computational method. Electron correlation effects covered by QCISD(T) calculations lower the barrier with respect to simple HF results by more than 4 kcal/mol. Nitroimidazoles with a nitro group connected to the ring nitrogen appear to be particularly sensitive with respect to electron correlation. This is revealed in an extreme dependence of the N—N bond length with respect to the level of theory [99IJQ145]. For 1,2,5-trinitroimidazole **8** and 1,2,4,5-tetranitroimidazole **9** (Scheme 4), the critical bond lengths are shown in Table I.

Deviations of this magnitude are very unusual but can also be found for other sensitive heterocycles, such as 1,2,5-oxadiazole-2-oxides. Although the authors



1 **7**

SCHEME 3



8 **9**

SCHEME 4

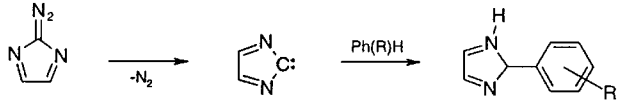
TABLE I
N—N BOND LENGTHS [Å, 6-31G(d,p) BASIS] OF 1,2,5- (**8**) AND 1,2,4,5-NITROIMIDAZOLE (**9**) IN DEPENDENCE ON THE COMPUTATIONAL LEVEL[a]

Method	**8**	**9**
HF	1.438	1.411
MP2	1.737	1.824
B-LYP	1.752	1.825
B3-LYP	1.578	1.643

[a]Data taken from Cho and Park [99IJQ145]. Reprinted by permission of John Wiley & Sons, Inc.

do not report any experimental values for bond lengths of these explosives, it is most likely that B3-LYP represents the highly polarized N—N bond best. A reactive intermediate obtained from photolyzing 2-diazo-2*H*-imidazole shows a similar though less pronounced sensitivity to the level of theory (Scheme 5): The geometric parameters of 2*H*-imidazol-2-ylidene **10** vary considerably, leading to different molecular point groups [99CEJ1590].

Moreover, the singlet and triplet states of the intermediate are very close in energy, most likely requiring multireference methods for an accurate determination of the energy gap between the two spin states. However, a comparison of the computed vibrational frequencies of the singlet and triplet structures with an experimental matrix isolation spectrum clearly identifies the singlet state as the molecular ground state. Related studies have been performed for 4*H*-imidazol-4-ylidene [00EJO2535]. 2,3-Dihydroimidazol-2-ylidene can be generated via decarboxylation of 1*H*-imidazole-2-carboxylic acid **11** (Scheme 6) [98EJO1517]. The lowest-energy rotamer of **11** shows an IMHB between the carboxylic hydrogen and the nitrogen lone pair. At the B3-LYP/6-311G(d,p) level the activation barrier of the decarboxylation was computed to be about 21 kcal/mol. A hydrogen transfer in the gas phase of the resulting 2,3-dihydroimidazol-2-ylidene toward imidazole was computed to have a barrier of 41 kcal/mol. Tunneling corrections were not estimated. A study on the *E*/*Z* conformational equilibrium of carbimazole **12** shows that the *E* conformer **12b** is slightly stabilized (Scheme 7) [98JCS(P2)1159].



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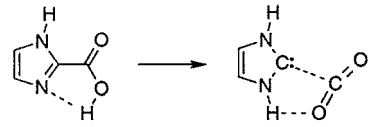
SCHEME 5

However, polar solvents shift the equilibrium toward the *Z* conformer **12a,** which has a significantly larger dipole moment.

The influence of an *ortho*-imidazole substituent on the bond dissociation energy of the O—H bond in phenol was studied by DFT calculations [00IJQ714]. The imidazole ring is twisted with respect to the phenol ring by 59° and causes a decrease of the bond dissociation energy by about −1 kcal/mol with respect to the unsubstituted molecule only.

The electronic spectrum of imidazole was studied at the CASSCF and CASPT2 levels [96JPC6484]. In the gas phase the first and second $\pi \rightarrow \pi^*$ excited singlet states were computed to occur at 6.72 and 7.15 eV, respectively. Upon solvation simulated by an SCRF procedure, a large bathochromic shift to 6.32 and 6.53 eV, respectively, is observed. In contrast, a small hypsochromic shift was found for protonated imidazole. Nuclear quadrupole coupling (NQC) has been investigated for a small series of imidazole derivatives and model systems for coenzyme B_{12} and cob(II)alamin [99JPC(B)8618]. A comparison of 12 methods (DFT and *ab initio*) showed that the PW91P86 functional in combination with a 6-311++G(2d,2p) basis yields data that are in very good agreement with experimental results. Since solvent effects have a strong impact on the NQC parameters, calculations require the first solvation shell to be explicitly included, while long-range effects can be described satisfactorily by standard SCRF continuum models. Asymmetry parameters are more sensitive and should be considered mainly on a qualitative basis rather than a quantitative one. Absolute and relative pK_A values for the (de)protonation of nitrogen on the imidazole ring can be obtained with an average deviation of 0.8 units from experiment [97JPC(A)10075]. However, the determination is hampered by calculating the free energy change associated with the deprotonation. Comparably high levels of theory, G2(MP2), are necessary in order to yield reliable data. Other computational studies on imidazoles concern the aromaticity



11

SCHEME 6

12a **12b**

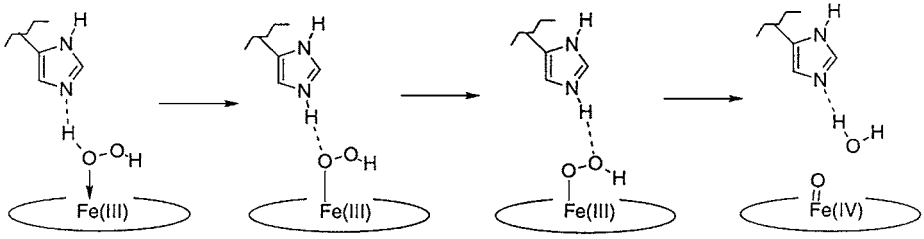
SCHEME 7

and geometric parameters of 2-pyridin-1-yl-1*H*-benzimidazole [99JST163b], the molecular properties of biotin model structures [98JST79, 99JPC(A)2851], and the structural parameters of substituted hydantoins [98JST47, 99JST105]. For the interactions between imidazole and metal cations, see Refs. [97JST55, 99IC6089, 00JPC(A)2238, 00JPC(B)6662, 00OM403]. For further work, see also Refs. [99CEJ3616, 00CEJ2350, 00JA9120, 00JOM45, 00JST227].

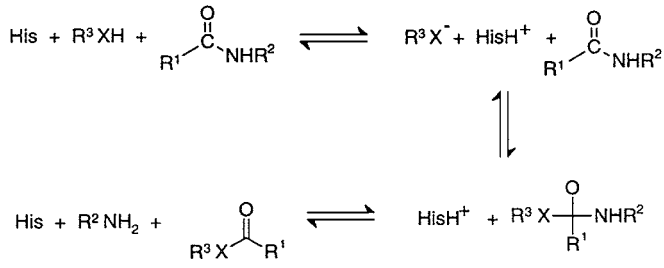
Histidine: Many contributions to the literature deal with the simulation of biologically relevant aspects of imidazole which is usually used as a model compound for histidine [97JST221, 98JA4006, 98JPC(B)6635, 99JA6984, 99JA10178, 99JA10389, 99IC940, 99MP571, 00IJQ44a, 00IJQ71, 00IJQ331, 00JA1492, 00JA8539, 00JPC(B)2148]. Since most of these biochemical studies usually focus on different aspects than properties and reactivity of heterocycles, they will not be covered in full in this review.

DFT calculations on the hyperfine coupling constants of ethyl imidazole as a model for histidine support experimental results that the preferred histidine radical is formed by OH addition at the C_5 position [00JPC(A)9144]. The reaction mechanism of compound I formation in heme peroxidases has been investigated at the B3-LYP level [99JA10178]. The reaction starts with a proton transfer from the peroxide to the distal histidine and a subsequent proton back donation from the histidine to the second oxygen of the peroxide (Scheme 8).

This results in a simultaneous breaking of the peroxide O—O bond. A computational study on the base-catalyzed methanolysis of formamide (serving as a reference reaction of serine protease) using histidine as a general base indicates that the first reaction step is characterized by a proton transfer while the second is the nucleophilic attack (Scheme 9) [00IJQ44a]. However, the potential energy surface is comparably flat and allows for a concerted mechanism also. The proton transfer from tyrosine to histidine upon oxidation has been modeled by a phenoxyl–imidazolium complex [98JA11732]. B3-LYP calculations show that one-electron oxidation leads to a spontaneous transfer of the phenolic proton to **1.** The computed coupling constants of this complex are in nice agreement with those determined experimentally for tyrosyl radicals involved in the oxygen evolution complex of photosystem II. The mechanism for serine hydrolase–catalyzed



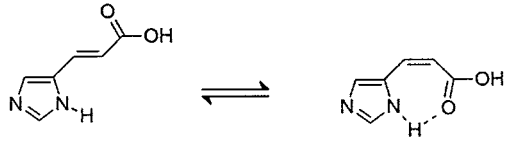
SCHEME 8



His = Histidine; X = O,S

SCHEME 9

ester hydrolysis has been modeled by a system consisting of the formate anion, imidazole, and methanol [98IJQ89]. The oxyanion hole was represented by two water molecules. Using the B3-LYP functional, the authors determined the barrier of the rate-limiting acylation step to be 13.4 kcal/mol and of the deacylation step to be 9.6 kcal/mol. Four possible intermediates in the coupled electron/proton transfer of the copper zinc superoxide dismutase and protonation cycles were investigated at the DFT level [99IC940]. The finding that the structural changes during the reduction and protonation of the active site require little energy is consistent with experimental observations. Tryptophan–histidine adducts were simulated by substituted indole–imidazole complexes at the MP2 level [98JPC(A)6152, 99IJQ175, 99TCA143, 00JPC(B)1108]. Hydrogen-bonded T-shaped structures and stacked arrangements were found to be significantly stabilized. Since dispersion interactions are important for the orientation of the molecules, diffuse basis functions and BSSE corrections are mandatory. Urocanic acid **3,** a metabolite of histidine, was studied at the CASSCF level [99IJQ25]. The authors conclude that the torsional barrier of the double bond of the propenoic acid moiety in neutral **3** is considerably lower in the T_1 and S_1 states than in the electronic ground state. Moreover, the *cis* isomer **3a** of both the neutral and the anionic **3** is lower in energy than the *trans* conformer **3b** in the S_0, S_1, and T_1 states (Scheme 10).



3b **3a**

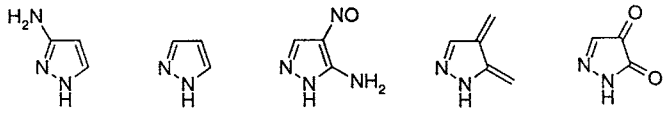
SCHEME 10

An MP2/6-311++G(d,p) study on the tautomers and conformers of histamine **13** is in excellent agreement with results obtained from jet spectroscopy [98JA10724]. The structural properties and the vibrational spectrum of the histamine monocation in aqueous solution were studied at the Hartree–Fock and DFT levels [98IJQ117, 00JPC(A)2120]. An assignment of all fundamental vibrations is provided. NMR shielding constants of **13** and its monocation were studied by Mazurek *et al.* [97JST435]. An activation mechanism of the histamine H_3 receptor has been studied by Kovalainen *et al.* [00JA6989]. They found that transferring a proton from the protonated side-chain amino group to the imidazole ring reduces the pK_a value of the imidazole H(N) atom to a range where the proton can be released.

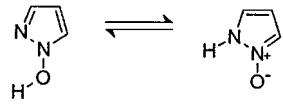
B. PYRAZOLES

Pyrazoles can be classified as aromatic heterocycles. However, the aromaticity of these compounds varies significantly depending on the substituents attached to the ring. Nuclear-independent chemical shifts (NICS) are a comparatively new but very successful measure of aromaticity [96JA6317]. While NICS below -3 ppm refer to aromatic systems, positive values above $+3$ ppm indicate antiaromatic rings. NICS values have been computed for a wide range of substituted pyrazoles [98H157, 98T12295], a selection of which is shown in Scheme 11. The dramatic decrease in aromaticity upon introduction of substituents being connected to the ring system by double bonds has also been investigated for other heterocycles, such as imidazoles [97JPR735]. Moreover, considering the physical properties of pyrazoles, Duflot *et al.* [98JCP5308] compared experimental core-excitation spectra with *ab initio* data. Force constants and vibrational frequencies of some pyrazole derivatives and transition metal complexes were calculated based on nonredundant natural internal coordinates [98JST17].

The influence of N_1 substituents upon structural parameters and energies has been investigated in detail [95T7045, 98JST255, 99PCCP5113]. Calculated B3-LYP isotropic shieldings (GIAO) are reported for most of these structures. Additionally, the hydrogen transfer from 1-hydroxypyrazole **14a** to pyrazole-*N*-oxide **14b** has been studied in detail (Scheme 12).



SCHEME 11

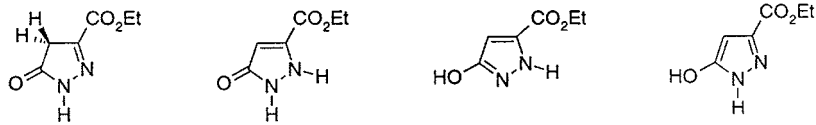


14a **14b**

SCHEME 12

In the gas phase **14a** was found to be −16.0 kcal/mol (MP2/6-31G*) more stable than the *N*-oxide **14b** and 55.1 kcal/mol lower in energy than the transition state. Tunneling corrections were not applied to this value. A similar high barrier of 47.3 kcal/mol was found for the proton shift in pyrazole [98JCS(P2)2497] which can formally be considered a [1,5]-sigmatropic reaction. This barrier refers to an intramolecular rearrangement in the gas phase. Based on experimental data, the activation barrier in solution was determined to be much lower, being in the range of 10–14 kcal/mol. Therefore, the hydrogen transfer in pyrazoles most likely involves solvent molecules. The same reaction has been investigated for fluoropyrazoles [99H355] and 3-ethoxycarbonyl-5-hydroxypyrazole [98JST71]. At the MP2/6-311G(d,p) level, 3-fluoropyrazole is more stable than 5-fluoropyrazole by −3.5 kcal/mol, and 3,4-difluoropyrazole is stabilized by −3.9 kcal/mol with respect to 4,5-difluoropyrazole. 3-Ethoxycarbonyl-5-hydroxypyrazole **15** is one of four tautomers that can be obtained due to hydrogen transfer (Scheme 13). In agreement with experimental solid-state ^{13}C NMR data, the preferred tautomer is 3-hydroxy-5-ethoxycarbonylpyrazole **15c.**

The Diels–Alder reactions of 4*H*-pyrazole **16** with different dienophiles (ethylene, formaldehyde, formaldimine, *cis*-diazene, *trans*-diazene, and nitrosyl hydride) were studied in a series of papers by Jursic [95JOC4721, 95JST229, 98JST117]. At the MP2/6-31G* level, the activation barrier of the endo N—H addition of *cis*-diazene was computed to be 15.5 kcal/mol lower than the corresponding barrier of ethylene. A significant speedup of the addition of ethylene to **16** can be achieved by protonation. Using perturbation theory up to the MP4 level and different density functionals, the difference in the activation barrier was calculated to about 14 kcal/mol. Since **16** is significantly destabilized with respect



15a **15b** **15c** **15d**

SCHEME 13

to 2*H*-pyrazole, the former compound needs to be stabilized by substituents in the 3 and 5 positions. This can be accomplished by condensation of malonic esters with hydrazine (Scheme 14).

RHF/6-31G* calculations led to the conclusion that **17** is not a minimum on the potential energy surface (Scheme 15) [00JCS(P1)2731]. Geometry optimization converged to **18** with a C_6—C_{7a} distance of 1.59 Å.

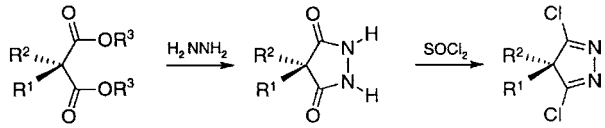
Further computational studies on pyrazoles cover the reduction of water to H_2 by diorganopalladium(II) complexes of tris(pyrazol-1-yl)borate [97OM5331] and the pseudorotational equilibrium of the cyclopentane ring in the pyrazolo[4,3-*c*]pyridine carbaribo-*C*-nucleoside [98JA2508]. (See also [99CEJ3603, 99JCS(D) 4087, 99NJC1231, 00JA9338, 00OL2679].)

C. OXAZOLES

A comparison of MP2/6-31G* structural parameters of 1,2-oxazole **19** (isoxazole) and 1,3-oxazole **20** with microwave data is provided by Kassimi *et al.* (Scheme 16) [96JPC8752]. The general agreement is excellent. The same authors investigated dipole moments, quadrupole moments, octopole moments, and dipole polarizabilities of **19** and **20** together with several oxadiazoles and oxatriazoles [96JPC8752, 99JPC(A)10009]. For the mean polarizability of these species, they found the approximative formula

$$\bar{\alpha} = \tfrac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \approx 30.5 + 4.5 n_{\mathrm{H}} \tag{1}$$

In this approximation the mean polarizability $\bar{\alpha}$ is given in atomic units and n_{H} is the number of hydrogen atoms. They founda mean absolute error of 1.2% and



SCHEME 14

17 **18**

SCHEME 15

19 **20**

SCHEME 16

a maximum error of 3.5%. For the measure of the polarizability anisotropy, $\Delta_1\alpha$, as provided by the difference between the in-plane and out-of-plane components, they found a relation of similar accuracy:

$$\Delta_1\alpha \approx 15.75 + 1.54n_{\mathrm{H}} - 1.1n_{\mathrm{O}} \tag{2}$$

Density functional studies on core-electron binding energies (CEBE), [98JCP8950] show that CEBEs are very molecule-specific and thus may serve as spectroscopic fingerprints. Although there are no experimental CEBE data for oxazoles, a comparison of experimental with theoretical data could be performed for many other molecules. The authors report absolute mean deviations of 0.2 eV for a set of 150 CEBEs. The investigation of the vibrational spectra of **19, 20,** and 1,2-thiazole and their deuterated isotopomers in terms of normal mode analyses has been accomplished by El-Azhary and Suter [95JCR(S)354, 95JPC12751]. They based their studies on harmonic MP2/6-31G** force fields.

DFT calculations confirmed the experimental findings that 2-ZnCl-1,3-oxazole **21** prefers a closed-ring structure while the corresponding 2-Li-1,3-oxazole **22** is not stable and prefers an acyclic structure (Scheme 17) [98CEJ814]. NBO analyses showed that the orbital of the C—M (M = Li, Zn) bond is $sp^{1.9}$-hybridized in the Zn species and $sp^{1.0}$ in the lithiated compound. Correspondingly, the hybridizations of the C—O bond orbital are $sp^{2.5}$ and $sp^{3.6}$, respectively, leading to a longer C—O bond in the Li species than in the ZnCl species.

Van der Waals complexes between an argon atom and **19** or **20** were investigated [95JPC12466, 96JPC14298] up to MP4(SDTQ) level using specifically adapted basis sets. It was found that the argon prefers a position above the ring rather than in the ring plane. These complexes, which are predominantly stabilized by dispersion and exchange repulsion interactions, are stabilized by about −0.9 kcal/mol only. The proton affinity of **20** is higher than that of 1,3-thiazole but lower than that of imidazole [91JCC1142]. C—H bond dissociation energies computed at the B3-LYP/6-31G* level were found to be higher for the cleavage of the C_4—H bond than

21 **22**

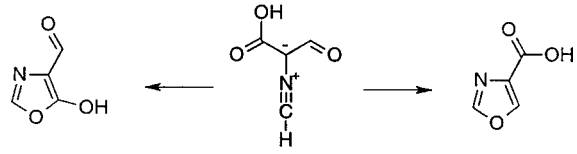
SCHEME 17

the C_2—H or C_5—H bonds [99JA491]. A database approach and MP2/6-31G** calculations on oxazoles, oxadiazoles, and other heterocycles revealed that the ring nitrogen in oxazole is a significantly better proton acceptor than the oxygen [97JCC2060]. The oxygen atom in the α position in **19** leads to a weaker hydrogen bond to the nitrogen atom than the oxygen in the β position in **20.** This effect is reversed with a hydrogen bond to the ring oxygen atom: A nitrogen in the β position has a stronger impact on the hydrogen bond than a nitrogen in the α position.

As in the case of benzothiazoles and benzimidazoles, the excited-state proton transfer in 2-(2′-hydroxyphenyl)benzoxazole was studied both experimentally and computationally. The results closely resemble the observations for the other species: The *cis*-enol form is preferred in the S_0 ground state and the *cis*-keto form in the S_1 excited state. Moreover, the proton transfer appears to be due to vibrational relaxation rather than thermal activation, suggesting that the aromatic ring has an impact on the transfer reaction of these systems [95JPC12456, 99JST255].

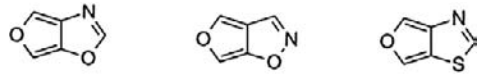
The cyclizations of conjugated nitrile ylides forming substituted oxazoles and thiazoles were computed up to the MP4/6-311+G** level [00JOC47]. Relative to **23,** oxazole-4-carboxylic acid **24** is stabilized by about −38.1 kcal/mol (Scheme 18).

The formation of **19** via a 1,3-dipolar cycloaddition of fulminic acid to ethyne has been studied by Karadakov *et al.* [98TCA222]. The concerted reaction path follows a heterolytic route, during which three orbital pairs corresponding to three distinct bonds in the reactants shift simultaneously to create the two new bonds closing the isoxazole ring and a nitrogen lone pair. The activation barrier was computed to be 12.2 kcal/mol at the CASPT2 level and 16.7 kcal/mol at the MP4(SDQ) level. Diels–Alder reactions of oxazole and isoxazole were investigated by several groups [92JOC3753, 94JCS(P2)1877, 96JCS(P2)1021]. MP2/6-31G* *ab initio* calculations confirm the general rule that Diels–Alder reactions do not occur when two heteroatoms are directly bonded so that one heteroatom appears at a bridgehead in the cycloadduct. Consequently, the activation energy of a Diels–Alder reaction with ethylene was found to be significantly higher for **19** than for **20.** Moreover, the reaction of the latter compound is strongly exothermic while the other is endothermic by about 4.0 kcal/mol. Studying cycloadditions of **20,** the activation barriers were determined for a set of different dienophiles by Jursic *et al.* [94JCS(P2)1877]. According to the calculations, the most reactive



23 **24**

SCHEME 18



25 **26** **27**

SCHEME 19

dienophile is nitrosyl hydride ($E_a = 2.7$ kcal/mol), while the highest barrier was computed for formaldehyde ($E_a = 21.7$ kcal/mol). Since MP2 has a slight tendency to underestimate the reaction barriers of Diels–Alder reactions, most recent studies use DFT rather than MP2 calculations for a crude scan of the hypersurface. Friedrichsen and coworkers [98JOC7680] investigated the Diels–Alder reaction of furo[3,4-*d*]oxazole; of course, in these cases the reaction occurs at the furan moiety rather than the oxazole. Absolute energies and geometric parameters of furo[3,4-*d*]oxazole **25,** furo[3,4-*d*]isoxazole **26,** furo[3,4-*d*]thiazole **27,** and furo[3,4-*b*]indole are reported (Scheme 19). The same group investigated the hydrogen transfer in 5-hydroxycyclohepta [1,2-*d*]isoxazole-4(7*H*)-one [96JCS(P1)1035]. Conformational studies were undertaken for 3-formyl-4,5-dihydro-1,3-oxazole and 3-formyl-2,3-dihydro-1,3-oxazole and their protonated analogs [92HCA1095].

It was found that the unimolecular rearrangement of *N*-acetylarylnitrenium ions toward C-protonated benzoxazoles operates only for singlet states (Scheme 20) [00JA5588]. At the DFT level the reaction shown in Scheme 20 has a barrier of about 7 kcal/mol only and is exothermic by about −16 kcal/mol. Optimizations on the lowest triplet potential energy surface immediately open up the ring structure of **28.** The dissociation of the oxazolidine radical cation **29** was studied up to the G2(MP2) level [00JA525]. Between the different reaction channels the formation of the formaldonitrone radical cation **30** is particularly interesting since the fragmentation of this species was found to be hindered by significant activation barriers (Scheme 21).

An investigation of the reactions of *cis*- and *trans*-2-methyl-4-phenyloxazoline-5-methylcarboxylate **31** with an azide anion shows that the transition state of the

28

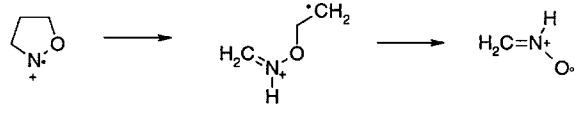
SCHEME 20

cis conformer is about 4 kcal/mol higher in energy; consequently, the reaction proceeds preferably via the *trans* isomer (Scheme 22) [00OL1243].

The addition of O_2 to oxazolyl radicals and their further fragmentation has been investigated up to the UCCSD(T) level [00JPC(A)6324]. Analogous studies were performed for diazines (see Scheme 59). MP2 and B3-LYP calculations on the tautomeric forms of 2-amino-2-oxazoline show that the amino form is stabilized by about −2 kcal/mol with respect to the imino form [99JST209]. Vertical ionization energies were computed for 2-methyloxazoline and some bisoxazolines [99JCS(P2)2455]. The rotational barriers in oxazolidine-3-carbaldehydes were analyzed by the atoms-in-molecules approach [99CJC1340], and 3-acryloyl-1,3-oxazolidin-2-one was used for the complexation of 1,4-butanediol-$TiCl_2$ [98JOC2321]. For further work on oxazoles and related substances, see Refs. [99OM4900, 00T3857, 00TA1543].

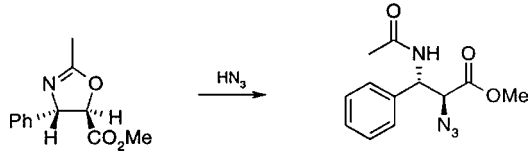
D. THIAZOLES

The vibrational spectra of thiazole and its [2-D], [4-D], and [2,5-D_2] isotopomers were investigated at the MP2/6-31G** level, and a comparison with experimental spectra [95JCR(S)174] is provided. Paying respect to the different internal coordinates, several scaling factors were used to yield very good agreement with the experimental results. Vibrational intensities of out-of-plane modes were poorly represented at the MP2 level but are in nice agreement for the in-plane modes. The IR spectrum of benzothiazole was investigated at the SQM/B3-LYP/6-31G*



29 **30**

SCHEME 21



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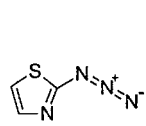
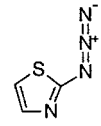
SCHEME 22



32a



32b

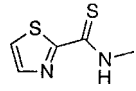
SCHEME 23

level. With respect to experimental data, the rms deviation for all in-plane modes was computed to 5.8 cm^{-1} and 4.1 cm^{-1} for all out-of-plane modes [99JCP5710]. Deviations for benzoxazole are even smaller.

A study of the relative stability of *trans*-2-azidothiazole **32b** with respect to the corresponding *cis* conformer **32a** showed that **32b** is destabilized in the gas phase but appears to be the more stable conformer in solution (Scheme 23). The stability increases with increasing polarity of the solvent [98JA4723].

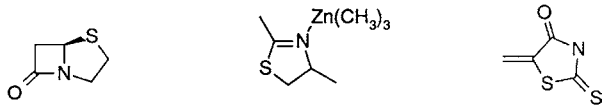
A reliable calculation of polarizabilities requires an adequate description of the outer part of the electron density. For this reason Kassimi and Lin [98JPC(A)9906] used augmented basis sets of triple-ζ quality to study polarizabilities and dipole moments of thiazoles and thiadiazoles. They expect their results to be reliable within 5%. In addition, the authors provide MP2/6-31G** geometries for most of their structures. Hyperpolarizabilities for substituted thiazoles obtained from calculations at lower levels are also provided [99MI2].

The excited-state intramolecular proton transfer (ESIPT) in 2-(2′-hydroxyphenyl)benzothiazole has been studied by several groups [93JPC11385, 98CPL521, 98JPC(A)1560]. Comparison with the ESIPT in related systems [i.e., 2-(2′-hydroxyphenyl)benzimidazole and 2-(2′-hydroxyphenyl)benzoxazole] is provided. While the *cis*-enol form is the preferred species in the S_0 ground state, it is the *cis*-keto form in the first excited S_1 state. According to simple Hartree–Fock calculations, the thioamide moiety of *N*-methylthioamide-1,2-thiazole **33** is coplanar to the heterocyclic ring (Scheme 24) [99JST21]. However, higher substitution patterns of the thiamide group such as those occurring in *N*-dimethylthioamide-1,2-thiazole or in *N*-diethylthioamide-1,2-thiazole lead to an out-of-plane distortion of about 12 to 14 degrees as obtained from HF/3-21G* calculations. Larger basis sets and electron correlation effects possibly may alter these values.



33

SCHEME 24



34 **35** **36**

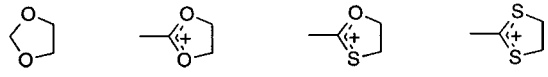
SCHEME 25

Salzner *et al.* investigated thiazole oligomers (up to six thiazole units) in order to estimate band gaps, ionization potentials, and electron affinities for polythiazoles and other heterocycles [98JPC(A)2572]. They used a modified B3-P86 exchange correlation functional that includes 30% of the Hartree–Fock exchange. Using this pragmatic approach, they were able to reproduce vertical excitation energies within ± 0.25 eV of the corresponding experimental results in solution. Compound **34** has been used as a model for penicillin (Scheme 25). Calculations up to the MP4(SDQ)/6-31G** level indicate that the axial conformer is stabilized by about -1.2 kcal/mol [99JST177]. The barrier height for the pseudorotation was predicted to be about 2 kcal/mol only, giving rise to a fast interconversion between the two conformers. The computed changes of ^{1}H and ^{15}N chemical shifts upon the coordination of $Zn(NH_3)_3^{2+}$ to 2,5-dimethyl-1,3-thiazolidine **35** indicate that the Zn^{2+} prefers the nitrogen rather than the sulfur for coordination (Scheme 25) [00JCC1].

Further computational studies on thiazoles concern the search for new synthons [99JOM98], the reaction of thiazolidine with the dimethoxyborinium ion [99JOC3213], the structure and relative energies of methylidene rhodanine **36** (Scheme 25) [97JST227], and those of 1-methylthiazolidine-2,4-dione [99IJQ97]. See also Refs. [00CPL115, 00ICA73, 00JCS(P2)1081, 00T1701].

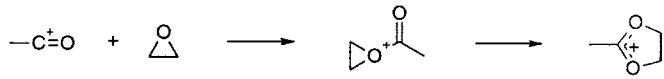
E. DIOXOLES AND OXATHIOLES

The core-electron binding energies (CEBEs) of dioxolane **37** and five other $C_3H_6O_2$ structural isomers were computed at the DFT level and were compared with X-ray photoelectron spectra (Scheme 26) [00IJQ44a]. The results are in a good agreement with an average deviation of 0.15 eV. MP2/6-311G(d,p) calculations were used to study the gas phase Meerwein reactions of acylium or thioacylium ions with epoxides or thioepoxides yielding 1,3-dioxolanylium **38,**



37 **38** **39** **40**

SCHEME 26



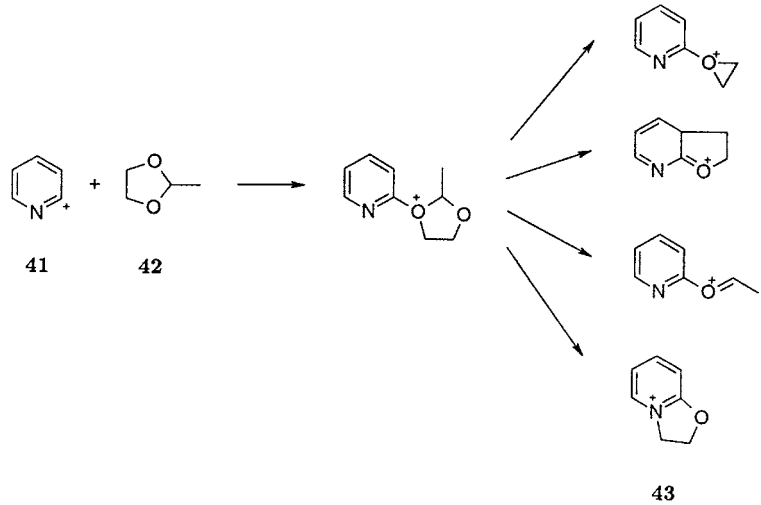
38

SCHEME 27

1,3-oxathiolanylium **39,** and 1,3-dithiolanylium ions **40,** respectively (Scheme 27) [00CEJ897]. The initial acylation is more favored for thioepoxides than for epoxides and the most stable product of the ring expansion is **38.** At the same level of theory, Eberlin and coworkers investigated the reaction of the 2-pyridyl cation **41** with 2-methyl-1,3-dioxolane **42** (Scheme 28) [98CEJ1161]. The resulting dihydrooxazolopyridyl cation **43** is significantly more stable than any alternative products. An investigation of the transacetalization reaction of **42** with phosphonium ions [$CH_3P^+(O)OCH_3$ and $CH_3OP^+(O)OCH_3$] indicates that the initial electrophilic association is responsible for the overall high exothermicity (Scheme 29).

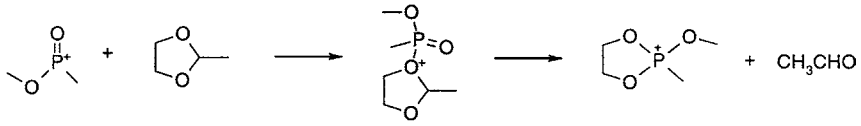
Using dioxolane as a substituent in the 1,3-dipolar cycloaddition of diazomethane with olefinic double bonds, it was found that the bulky dioxolane ring plays a major role in the diastereoselection [00JOC388].

Tietze *et al.* investigated the Diels–Alder reaction between **44** and 2-methylbut-2-ene at the B3-LYP/6-31G* level (Scheme 30) [98EJO2733].



41 **42** **43**

SCHEME 28



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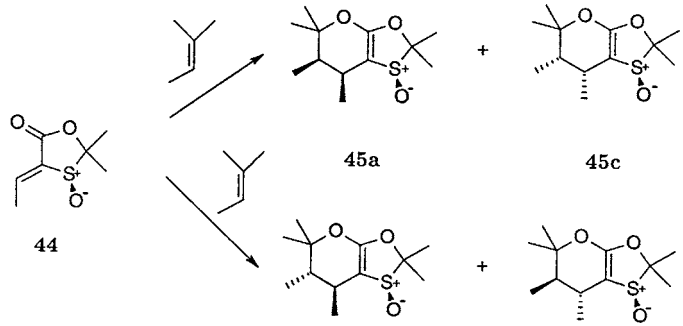
SCHEME 29



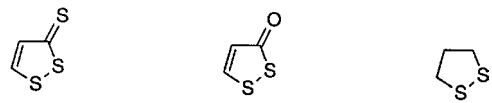
44 **45a** **45c** **45b** **45d**

SCHEME 30

Owing to the two different kinds of stereoselectivity, four products are possible for this reaction. However, calculations of the corresponding transition states show that **45a** is the kinetically favored species.

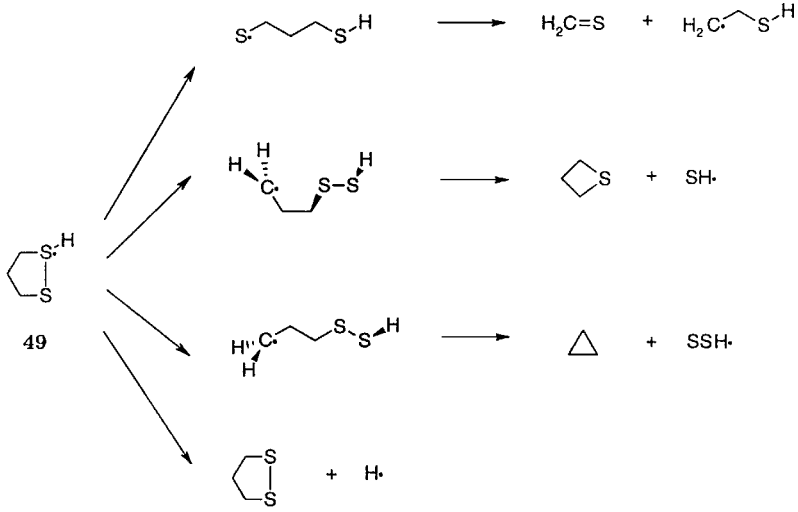
F. DITHIOLES

The vibrational spectra of 1,2-dithiole-3-thione **46** and 1,2-dithiol-3-one **47** were computed at the DFT and MP2 levels (Scheme 31) [98VS77]. Most remarkably, the uniformly scaled MP2 fundamentals are in better agreement with experimental data than the corresponding DFT frequencies.



46 **47** **48**

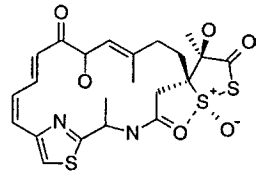
SCHEME 31



SCHEME 32

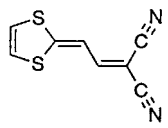
The nature of the S—S bond in 1,2-dithiolane **48** and its conformational flexibility were investigated at the MP2 level [97JST171]. The three-electron two-center S—S π-bond was found to play an important role in stabilizing the five-membered ring of the corresponding radical cation of **48.** A PMP2 and DFT study of the hydrogen atom addition to **48** indicates that the reaction is exothermic by about −28 kcal/mol and proceeds via a rear attack without an energy barrier [00JA2361]. Different fragmentation reaction paths of the resulting adduct **49** were investigated in detail, as shown in Scheme 32.

Wu and Greer investigated the S—O through-space interaction in leinamycin **50** using different 1,2-dithiolan-3-one 1-oxides as model compounds (Scheme 33) [00JOC4883]. They conclude that the 1,5 S—O interaction causes the S_1 atom in leinamycin to adopt a distorted trigonal-bipyramidal geometry. According to



50

SCHEME 33



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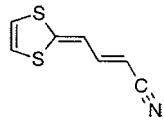
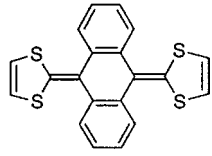


52

SCHEME 34

B3-LYP/6-31G* calculations, the stabilization is estimated to be about −6 kcal/mol. Polarizabilities, second polarizabilities, and third polarizabilities were computed for a series of bis-1,3-dithiole polymethine dyes [98EJO2747]. The electronic structure of these dyes and the conformations of **51** and **52** were studied by Moore *et al.* [98MI1] (Scheme 34). The *cis* conformer of **51** is destabilized with respect to the *trans* structure in the gas phase. In contrast, the *cis* conformer of **52** is computed to be more stable than the *trans* conformer. The vibrational frequencies and geometry of the 1,3-dithiole-2-thione-4,5-dithiolate anion were studied at the Hartree–Fock level [99CPL517]. The geometries of 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene **53** (Scheme 35) and related compounds were optimized in both planar and nonplanar conformations [98CEJ2580, 98JOC1268]. The planar structure was found to be strongly hindered by very short contacts between the sulfur atoms and the hydrogens in *peri* positions, and consequently butterfly-shaped conformations are energetically preferred. The interaction energies of tetrathiafulvalene/tetracyanoethylene complexes were studied at the MP2 and DFT levels [98CCC1223]. A laterally displaced complex is preferred over a vertically stacked orientation. Further computational studies on dithioles concern the molecular properties of metal dithiolenes [98IC1368, 98IC3154, 98JCS(D)3731, 99EJIC1995, 99IC1401, 99ICA180, 99JOM125, 00ICA94] and the structures of diiodine adducts of 1,3-dithiacyclohexane-2-thione and 4,5-ethylenedithio-1,3-dithiole-2-thione [99IC4626]. Moreover, several studies focus on large ring systems with more than two sulfur atoms [98CJC1093, 98JOC8192, 99JPR202].



53

SCHEME 35

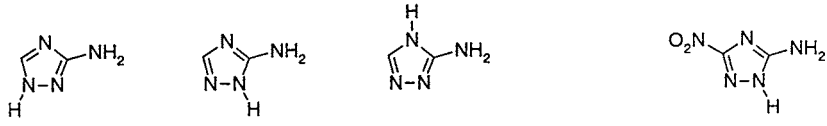
IV. Five-Membered Rings with More Than Two Heteroatoms

A. TRIAZOLES

Since HF calculations have a tendency to underestimate the N—N and the C—N bond lengths in triazoles [98JPC(A)620, 98JPC(A)10348], the structural parameters should be computed at least at the DFT or MP2 levels. This is particularly true if electron-donating substituents are attached to the ring. Nitrogen NMR shielding tensors were computed for a set of methylated triazoles and tetrazoles but will be discussed in the context of tetrazoles (cf. Section IV,B).

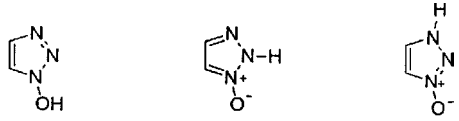
The relative stabilities of substituted triazoles were investigated for the 1*H* (**54a**), 2*H* (**54b**), and 4*H* (**54c**) tautomers of 3-amino-1,2,4-triazole [92JCS(P2)1681] and 3-amino-5-nitro-1,2,4-triazole **55** (Scheme 36) [98JPC(A)10348]. The latter compounds qualify for computational studies because they constitute highly explosive material. In the gas phase the 1*H* tautomer of both compounds appears to be slightly more stable than the 2*H* isomer, while the 4*H* species is destabilized by about 7 kcal/mol. These results were obtained from CCSD/6-31G** and MP4/6-311+G(2d,2p) calculations. However, solvent simulations by an SCRF approach indicate that the order of the stability of the 1*H* and 2*H* tautomers is reversed in polar solvents. Vibrational spectra and normal mode analyses were performed for the tautomers of **55** [98JPC(A)10348], the parent triazoles, and the anions of 1,2,3- and 1,2,4-triazole [98JPC(A)620, 00JST183]. For the former compounds, significant band shifts were found for several vibrations, e.g., the C—NO_2 stretching mode. This allows one to distinguish the isomers readily from their IR spectra. The best agreement between the computed and experimental spectra of the triazole anions was found for the B3-LYP density functional.

MP2/6-31+G* calculations in the gas phase indicate that 2*H*-1,2,3-triazole is about −5 kcal/mol more stable than the 1*H* isomer [92JOC3698]. The energy differences between 1-hydroxy-1,2,3-triazole **56a** and its 2*H* (**56b**) and 3*H* (**56c**) tautomers were investigated up to the MP4(SDTQ)/6-31+G* level. The 1-hydroxy form **56a** is the preferred tautomer in the gas phase, but owing to the strong polarity of the *N*-oxide 3*H* tautomer **56c,** this is the most stable structure in solution (Scheme 37) [92JOC3698].



54a **54b** **54c** **55**

SCHEME 36



56a **56b** **56c**

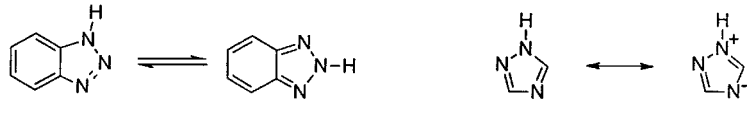
SCHEME 37

Because of low-level calculations, the relative stabilities of 1*H*- (**57**) and 2*H*-benzotriazole (**58**) led to a debate about the preferred tautomer (Scheme 38) [94CP27, 96CPL119, 96CPL689, 98JPC(A)3048]. It is now commonly acknowledged that in the gas phase **58** is slightly stabilized against **57.** However, energetic differences are very small and may by inverted under certain conditions. This underscores the importance of including electron correlation effects in calculations with adjacent heteroatoms. A comparison of MP2/6-311G** and B3-LYP/6-31G* computed vibrational frequencies with experimental data is provided [96CPL689, 98JPC(A)3048], allowing for a normal mode analysis of **58.** Rademacher *et al.* investigated the vertical ionization potentials of a series of 1-substituted 1*H*-benzotriazoles [99JST47b].

In 1*H*-1,2,4-triazole **59,** strong hydrogen bonding in the solid state hampers the comparison between experimental crystal data and computed geometric parameters. A model of the hydrogen bonding in the solid state shows that the intermolecular interactions affect not only the lengths of the N—H bond but also those of the adjacent C—N bonds [94STC1]. Consequently, in the solid state **59** is better represented by its zwitterionic resonance structure rather than its neutral form (Scheme 38).

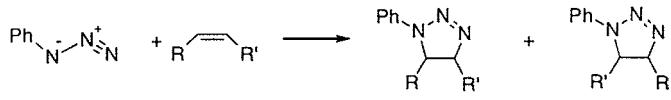
Friesner and coworkers investigated the 1,3-dipolar addition of phenyl azide **60** to carbon–carbon double bonds forming 1-phenyl-4,5-dihydro-1*H*-1,2,3-triazoles (**61** and **62**) (Scheme 39) [99JPC(A)1276].

For a set of 19 dipolarophiles, the activation energy scatters in the range between 18.5 and 24.5 kcal/mol at the B3-LYP/cc-pVTZ(f/d) level. In agreement with experimental data, they found that strong electron-withdrawing and -donating groups give only one product isomer, whereas aliphatic and aromatic substituents produce a mixture. The spontaneous 1,5-cyclization of iminodiazomethane **63** to 1*H*-1,2,3-triazole **64** was studied up to the MP4(SDTQ)/6-311+G** level (Scheme 40)



57 **58** **59**

SCHEME 38



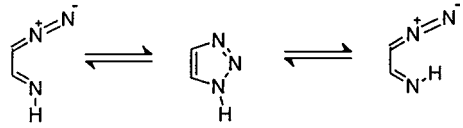
60 **61** **62**

SCHEME 39

[98JOC5801]. The transition state between **63a** and **64** was found to be planar and only 8.8 kcal/mol above the educt. This is in sharp contrast to the corresponding cyclization of **63b** with a nonplanar transition state and a much higher energy barrier of about 27.7 kcal/mol. This confirms the pseudopericyclic nature of the first reaction while the latter one must be considered a common electrocyclic process. The corresponding ring-opening reactions of different triazolium cations led to the conclusion that an acid-catalyzed N—N bond breaking mechanism in triazoles is preferred over the bond cleavage in the neutral species [00H291]. 1,2,4-Triazolium-5-ylidene and 1,2,4-triazole-3,5-diylidene were computed to be local minima on an RHF potential energy surface [00JOM112]. Since these carbenes have conjugated six-π-electron systems, they are both planar. For the ene reaction of 1,2,4-triazoline-2,5-dione with isobutene, a new mechanism via a biradical intermediate is proposed based on B3-LYP calculations [99JA11885]. For further work on triazoles, see Refs. [00JST143, 00MRC604].

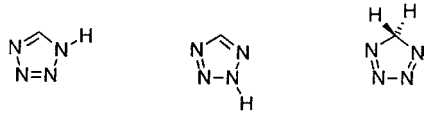
B. TETRAZOLES

The formation of 1*H*-tetrazole **65a** from HCN and HN_3 has been investigated at the MP2 and B3-LYP levels [00IJQ27]. The activation energy of the corresponding anionic reaction was found to be significantly lower in energy than for the neutral system. Formally, unsubstituted tetrazole allows for three protomers, namely 1*H*- (**65a**), 2*H*- (**65b**), and 5*H*-tetrazole (**65c**) (Scheme 41). Geometric parameters of these compounds cannot properly be described at the HF level, since the N—N distances appear to be very sensitive to electron correlation effects. This holds particularly true for **65c** [93JA2465], which fails to be accurately described



63a **64** **63b**

SCHEME 40



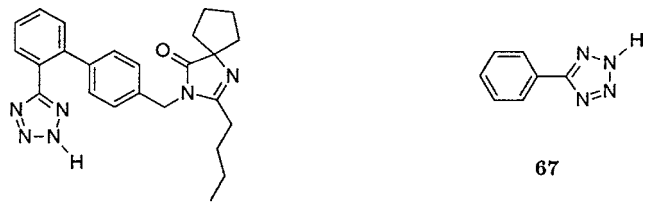
65a **65b** **65c**

SCHEME 41

even at the MP2 level. While **65a** is the only tautomer seen in the solid state, an equilibrium between **65a** and **65b** is observed in solution. Gas-phase QCISD(T)/6-311G+(2d,2p) calculations show that due to its nonaromatic character **65c** is about 20 kcal/mol higher in energy than the other two isomers. High-level *ab initio* calculations up to G2 and QCISD(T)/6-311+G(2d,2p) level show that **65b** is about −1.9 kcal/mol lower in energy than **65a.** However, in polar solvents the equilibrium is reversed. Isomerization from **65a** to **65b** was computed to have an energy barrier of about 49.4 kcal/mol in the gas phase. Tunneling corrections were not estimated. The temperature dependence of the tautomerization has been studied by computing thermodynamic properties of the isomers. The agreement with experimental data is excellent [98JST65, 99JST167]. Recent studies showed that the barrier for isomerization is much lower in the case of water or base assistance (about 16 kcal/mol). This value is consistent with experimental data for *irbesartan* **66** (Scheme 42).

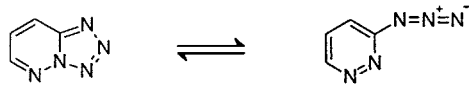
The barrier of rotation in 5-phenyl-2*H*-tetrazole **67** was computed at the DFT level to be 20.8 kcal/mol and 27.3 kcal/mol for the analogous rotation of the anion of **67** [98JCS(P2)2671]. Heats of formation were computed from isodesmic and isogyric reactions for a set of 49 substituted tetrazoles [99JPC(A)8062]. As found for the unsubstituted parent compounds, in most cases the 2*H* isomers are more stable than the 1*H* isomers, whereas the order is reversed for the corresponding anions. Vibrational spectra and activation energies of the thermal decomposition process were computed for a series of substituted tetrazoles [99JST249, 00IJQ350].

The nitrogen NMR shieldings in methylated triazoles and tetrazoles were computed at the GIAO/HF/6-31++G** level and more recently using multireference



66 **67**

SCHEME 42



69 **68**

SCHEME 43

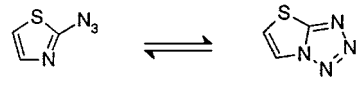
wavefunctions and density functionals [98MR54, 00JPC(A)1466, 00JPC(A)9600]. A nice correlation of the computed values with the experimental ones obtained from measurements in cyclohexane is observed. Using a linear relationship of

$$\sigma_{\text{exp}} = 0.8804\sigma_{\text{calc}} + 112.56 \tag{3}$$

for the RHF results, a standard deviation of 5.76 ppm was found, which amounts to about 2% of the range of the shieldings concerned. Solvent effects may shift particular shielding constants by up to 12 ppm in very polar solvents. Shielding constants for the methyl-substituted nitrogen atoms decrease with increasing dielectric constant while the shielding constants of all other nitrogen atoms in the molecule increase. Moreover, GIAO calculations were used to decide about the azide form **68** or tetrazole form **69** of tetrazolopyridazine and nitrotetrazolo [1,5-*a*]pyridines (Scheme 43) [99JST165, 99MRC493].

Diels–Alder reactions of the three tetrazole tautomers with ethylene were studied up to MP4/6-31G* level [95JST9]. Except for **65c,** activation barriers were computed as being too high to permit observation of these cycloadditions under common conditions. The barrier for **65c** was computed to be 20.8 kcal/mol; but inasmuch as this isomer is about 20 kcal/mol higher in energy than the others, this reaction needs strong forces to be observed at all. The transformation of 2-azidothiazole **70** into thiazolo[3,2-*d*]tetrazole **71** has been studied as a prototype reaction for the generation of tetrazoles (Scheme 44) [98JA4723, 98JOC2354].

The free energy of activation at the QCISD(T)/6-311++G(d,p) level amounts to 21.1 kcal/mol. According to the authors, the large electron density redistribution arising upon cyclization makes it necessary to use extended basis sets and high-order electron correlation methods to describe the gas-phase thermodynamics, which indicates clearly the gas-phase preference of the azido species. However, the equilibrium is shifted toward the tetrazole as the polarity of a solvent is increased. For instance, SCRF calculations ($\epsilon = 78.4$) yield a relative free energy of solvation with respect to the *cis*-azido isomer of -2.4 kcal/mol for the *trans*-azido compound and of -6.8 kcal/mol for the tetrazole isomer. At a much lower level, the



70 **71**

SCHEME 44

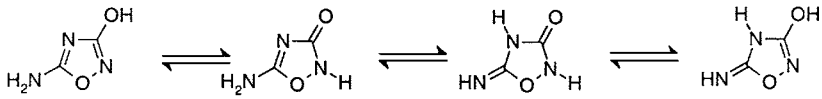
72 **73**

SCHEME 45

conversion of *N*-acetyltetrazole to 1,3,4-oxadiazole was investigated [94JST241]. Two mechanisms can be formulated for this reaction, one of them involving biradical transition states. However, in order to yield reliable quantitative data for this transformation, multireference *ab initio* studies are highly desirable.

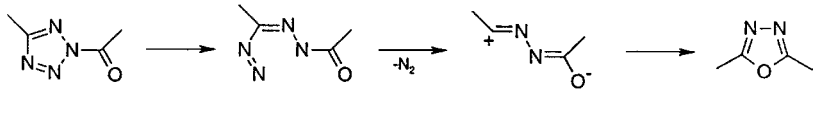
C. OXADIAZOLES

Recent computational studies focus mainly on the *N*-oxides of oxadiazoles rather than their parent compounds. Moreover, most investigations concern 1,2,5- (**72**) and 1,3,4-oxadiazoles (**73**) only (Scheme 45). Comparative MP2/6-31G** and B3-LYP/6-31G** calculations show that the DFT structure is in better agreement with experimental data [96SA(A)33]. This is also reflected in the vibrational force fields, which were computed for 1,2,5- and 1,3,4-oxadiazole and the corresponding [2-D] and [2,5-D_2] isotopomers. The same holds true for the calculated absorption intensities. Using a set of eight scaling factors within the SQM methodology, a rms error of 6 cm^{-1} was obtained [95SA(A)995, 96SA(A)33]. These calculations revealed possible misassignments in the IR spectrum of 1,3,4-oxadiazole. Computed nitrogen NMR shieldings of oxadiazoles and 3-methylsydnone show an excellent linear correlation with experimental results [00MRC580]. The nonlinear optical properties of donor–acceptor 2-dimethylamino-5-nitro-1,3,4-oxadiazoles were estimated by calculating their molecular hyperpolarizabilities using a sum-over-states approach. The results show that 1,3,4-oxadiazole exhibits much larger dipole moment changes upon excitation than furan [95JCS(P2)177]. MP4(SDQ)/6-31G* calculations were used to decide about the relative stabilities of the four different 5-amino-2,3-dihydro-1,2,4-oxadiazol-3-one tautomers **74** (Scheme 46) [99JCS(P2)81]. In agreement with experimental results, the most stable structure was found to be the keto-amino tautomer **74b.**



74a **74b** **74c** **74d**

SCHEME 46



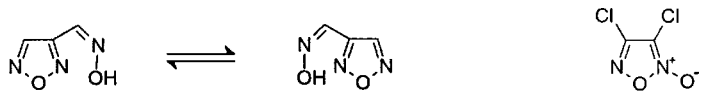
76 **75**

SCHEME 47

For the generation of 2,5-dimethyl-1,3,4-oxadiazole **75** from 1-(5-methyltetrazol-2-yl)ethanone **76,** two different mechanisms are proposed. According to quantum chemical calculation, the one depicted in Scheme 47 is the preferred one [94JST241]. Most likely, the elimination of the nitrogen molecule proceeds via a synchronous mechanism. MP2/6-31G* calculations on the activation barriers of the Diels–Alder reactions of **75** with five different dienophiles (ethylene, acrylonitrile, maleonitrile, fumaronitrile, and 1,1-dicyanotheylene) indicate that the most reactive dienophile is ethylene [94JPO634]. This result is in contrast to the corresponding reaction of cyclopentadiene. However, a comparison with MP3 results reveals that the activation barriers require a better representation of electron correlation effects than obtained by MP2 calculations. In general, cycloadditions with **75** are not favorable. In order to allow these reactions, strong electron-withdrawing substituents must be introduced [98JST153]. Computational studies on the monocyclic Boulton–Katritzky rearrangement of 3-hydroxyiminomethyl-1,2,5-oxadiazole **77** reveal a concerted and synchronous mechanism with a symmetric transition state (Scheme 48) [98JST67]. At the MP2/6-31++G** level, an activation barrier of 20.6 kcal/mol has been computed.

The computation of furoxans (1,2,5-oxadiazole-2-oxides) is very demanding. Very strong electron correlation effects hamper a proper treatment of this class of molecules. With respect to the geometric parameters, it is the endocyclic N—O bond that can be treated reliably either at the B3-LYP or at the MP4(SDQ) level [99MI1]. Table II demonstrates the problems associated with the exact determination of this bond length.

Pasinszki and Westwood investigated the dimerization of chloronitrile oxide ClCNO to 3,4-dichloro-1,2,5-oxadiazole-2-oxide **78** (Scheme 48) [98JPC(A) 4939]. From B3-LYP/6-31G* calculations, they conclude that the reaction path can be characterized as a typical Firestone-type cycloaddition, a two-step mechanism with a C—C bond forming characterizing the first reaction step. The activation



77 **77** **78**

SCHEME 48

TABLE II
THE ENDOCYCLIC N^+—O BOND LENGTH (Å) IN FUROXAN DEPENDING ON THE COMPUTATIONAL LEVEL[a]

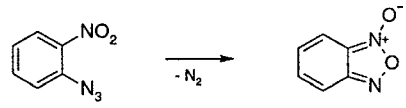
Method	Distance
RHF	1.336
BH&H-LYP	1.382
B3-LYP	1.477
MP2	1.578
MP4(SDQ)	1.442
QCISD	1.442
Exp.	1.441

[a]All values refer to a cc-pVDZ basis.

barrier was found to be 4.3 kcal/mol at this level of theory. A normal mode analysis of **78** permitted the assignment of all fundamentals.

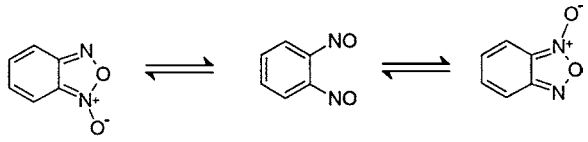
Benzofuroxan **79** can be generated from 2-nitrophenyl azide **80** (Scheme 49). Neighboring-group assistance within the pyrolysis leads to a one-step mechanism with an activation barrier of 24.6 kcal/mol at the CCSD(T)/6-311G(2d,p) level [99JPC(A)9086]. This value closely resembles the experimental one of 25.5 kcal/mol. Based on the *ab initio* results for this reaction, rate constants were computed using variational transition state theory.

Intermediates involved in the tautomerization of furoxans gave rise to speculations about their structure. Systematic calculations on possible intermediates being involved in the reaction of furoxan [92JCC177] and benzofuroxan **79** showed that dinitrosoethylene and dinitrosobenzene **81** are the most likely ones (Scheme 50) [94JOC6431, 94JPC12933].



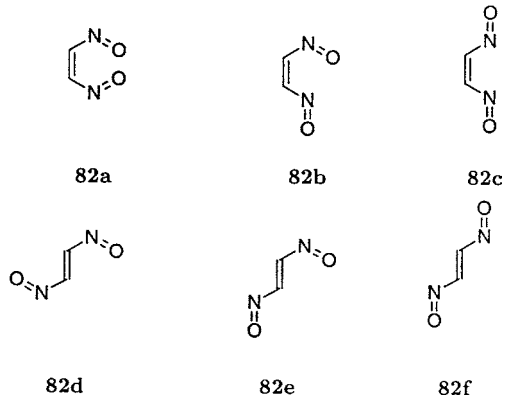
80 **79**

SCHEME 49



79 **81** **79**

SCHEME 50

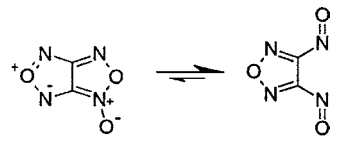


82a **82b** **82c**

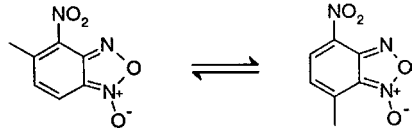
82d **82e** **82f**

SCHEME 51

This result is in agreement with experimental observations and was proven for benzofuroxan by a comparison of computationally and experimentally obtained IR spectra [97JCC489]. However, a quantitative description of the tautomerizations requires calculations up to the coupled-cluster level in combination with a triple-ζ basis [99MI1]. Calculations at the DFT level indicate the second reaction step of the tautomerization, i.e., the rotation of the nitroso groups, to be the rate-determining step [96JCC1848]. In contrast to that, more accurate coupled-cluster calculations predict the first reaction step—the ring opening—to be rate-determining [99JA6700, 99MI1]. The related tautomerism of 1,2,5-oxadiazole-2-oxide is even more intricate, since six conformers for the intermediate dinitrosoethylene **82** can be formulated in principle (Scheme 51) [00UPI]. MRCI and (R)CCSD(T) calculations reveal that **82b** is not a stable intermediate and that the structure of **82a** describes a transition state rather than an intermediate. Low-lying triplet states allow for alternative reaction mechanisms via spin–orbit coupling, but the reaction path on the ground-state potential energy surface appears to be the preferred one. The singlet–triplet gap of all species involved in this reaction can be reliably described neither at the B3-LYP nor at the CASPT2 levels. In a series of papers, Friedrichsen and coworkers [95JCR(S)120, 95JST23, 96T743, 98JST263] investigated the ring–chain tautomerism for nonclassical furoxans and furoxans fused to five-membered heterocycles. In contrast to the species discussed above for nonclassical furoxans (e.g., Scheme 52), the open-chain 1,2-dinitroso isomers are lower in energy at the B3-LYP level.



SCHEME 52

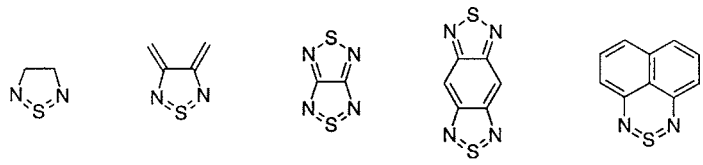


SCHEME 53

For 4-nitrobenzofuroxans, the tautomerization described above competes with the bicyclic Boulton–Katritzky rearrangement (Scheme 53). The direction of this rearrangement sensitively depends on the substituent in the 5 or 7 position, respectively. Geometric parameters for a series of 5- and 7-substituted 4-nitrobenzofuroxans obtained from B3-LYP/6-31G* calculations are provided [00MI1]. Coupled-cluster calculations with a perturbational treatment of triple excitations, CCSD(T), indicate that the bicyclic Boulton–Katritzky rearrangement proceeds via a pseudopericyclic one-step mechanism [98JA13478]. After correction for the zero-point vibrational energy, the activation barrier was computed to be 28 kcal/mol. Most substituents in the 5 position accelerate the reaction by lowering the activation barrier and exothermicity in a range between −3.0 and −7.0 kcal/mol [99JA6700]. An energy partitioning identifies the dominant driving forces for the Boulton–Katritzky rearrangement of 5-methyl-4-nitrobenzofuroxan to be strain effects of the six-membered ring and electronic effects due to the out-of-plane torsion of the nitro group.

D. THIADIAZOLES

There are comparatively few computational studies on thiadiazoles. Geometric parameters were obtained at the RHF, DFT, and MP2 levels. Strassner and Fabian studied a series of cyclic sulfur diimides with a representative selection shown in Scheme 54 [97JPO33]. According to DFT population analyses, the sulfur *d*-orbitals are hardly occupied and the electronic charge distributions indicate an ylidic structure with —N=N^+—N^-— and —N^-=S^+—N— structural motifs. Moreover, the authors conclude that strong S—N bond charge separations of organyl sulfur diimides are accompanied by short S—N bond lengths, narrow S_0–T_1 gaps, and first absorption bands at long wavelengths.



SCHEME 54

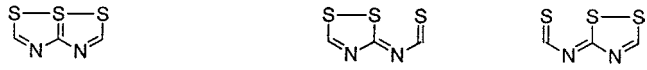
83 **84**

SCHEME 55

As found for most sulfur-containing molecules, the S—C and S—N bond lengths in thiadiazoles show larger deviations from experimental results at the DFT level than at *ab initio* levels [95SA(A)995, 96SA(A)33]. This phenomenon has been studied systematically by Altmann *et al.* [97MP339]. Consequently, geometries obtained from MP2 calculations are in better agreement with experimental data. On the contrary, within the SQM approach, B3-LYP/6-31G** vibrational force fields reproduce experimental IR spectra of thiadiazoles much better than the corresponding MP2 calculations. Although one would expect better force fields from the more accurate MP2 geometries, the SQM approach compensates for the deficiencies of the exchange-correlation functionals through specific scaling factors for the C—S and C—N internal coordinates. Normal mode analyses were performed for 1,2,5- (**83**) and 1,3,4-thiadiazole (**84**) and were compared with results for the corresponding oxadiazoles (Scheme 55) [96SA(A)33]. An analysis of the charge distribution in **83** and **84** reveals that **83** is more sensitive to nucleophilic and electrophilic attack than **84,** although both isomers have a high degree of polarity [95JST385]. In agreement with experimental results, nucleophilic additions to thiadiazoles will take place at the sulfur atoms. Ionization potentials and nitrogen nuclear quadrupole coupling constants of benzothiadiazole were compared with the corresponding data for benzoxadiazole and benzoselenadiazole [92JCS(F2)2641].

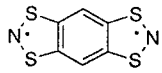
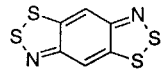
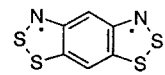
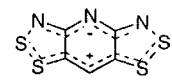
E. DITHIAZOLES

The molecular geometry and electronic structure of 3,4-diaza-1,6,6aλ^4-trithiapentalene **85a** has been studied and compared with the nitrogen-free 1,6,6aλ^4-trithiapentalene [98PS35]. Whereas Hartree–Fock calculations predict **85b** and **85c** to be valence isomers, DFT and MP2 calculations predict the minimum to be of C_{2v} symmetry corresponding to **85a** (Scheme 56).



85a **85b** **85c**

SCHEME 56

86 **87** **88** **89**

SCHEME 57

Consequently, structures **85b** and **85c** must be considered resonance structures rather than valence isomers. Hyperfine coupling constants were computed for a series of dithiazolyl radicals and related compounds [96MRC913]. An absolute mean deviation of 0.12 mT with respect to experimental data is reported for 10 sulfur hyperfine coupling constants obtained from UB3-LYP/TZVP calculations.

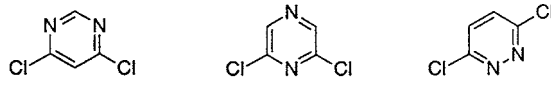
B3-LYP/6-31G(df,p) calculations of the ^{1}H, ^{13}C, ^{14}N, and ^{33}S hyperfine tensor components of the 1,3,2-dithiazol-2-yl radical show that modern density functionals are capable of reliably reproducing not only the anisotropic hyperfine tensor components but also the isotropic ones (Fermi contact terms) [99CPL545]. The formation of the corresponding 1,3,2-dithiazolium cation via a 1,3-dipolar cycloaddition of acetylene with SNS^{+} has been investigated at the MP2/6-31G* level [99JST25]. At this level the reaction was found to be exothermic by −60.2 kcal/mol with an activation barrier of 7.0 kcal/mol. While benzobis(1,3,2-dithiazole) **86** is biradical, the isomeric benzobis(1,2,3-dithiazole) **87** exhibits a quinoidal rather than a biradical ground state (Scheme 57) [97JA2633, 97JA12136, 00JA7602].

According to B3-LYP/6-31G** calculations, the triplet state of **88** is −5.1 kcal/mol lower in energy than the zwitterionic singlet state. The order is reversed for the pyridine-bridged **89.** Likewise, for 1,1′,2,2′,3,3′-tetrathiadiazafulvalene, the $^{1}A_{g}$ state was found to be more stable than the $^{3}B_{u}$ state [99JA6657]. However, one should keep in mind that B3-LYP calculations often lead to an exaggerated stabilization of triplet states.

V. Six-Membered Rings with Two Heteroatoms

A. DIAZINES

Comparative studies on the different diazines focus on their vibrational spectra, polarizabilities, homolytic bond dissociation energies, their interaction energies with water, and the rearrangement of their corresponding peroxy radicals [98JST145, 98JST225, 99JA491, 00JPC(A)6088]. Geometries and scaled MP2/6-31G* computed vibrational frequencies are provided for all three parent compounds [98JST225] and are compared with experimental results. Martin and van Alsenoy [96JPC6973] used the azabenzenes (i.e., diazines, triazines, and tetrazines) as a benchmark system to test the reliability of the B3-LYP functional for heterocyclic systems. They came to the conclusion that computed harmonic



90 **91** **92**

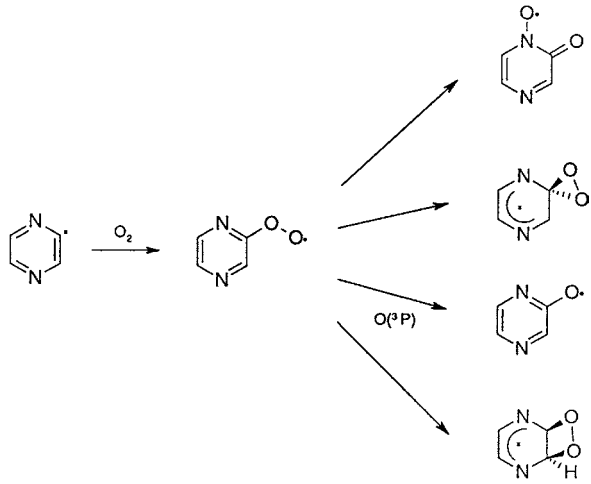
SCHEME 58

frequencies are in very good to excellent agreement with the available experimental data. Moreover, since the errors of the B3-LYP functional in predicting geometric parameters are fairly systematic, they provide correction schemes for B3-LYP computed geometries. Likewise, the same series of molecules was taken as a benchmark for testing the quality of vertical excitation energies of EOM-CCSD(T) and related methods [97JCP6051, 99SA(A)539]. Consequently, very accurate computational results are available for the diazines. The average error for the $\pi \rightarrow \pi^*$ transitions is reported to be 0.11 eV and 0.15 eV for $n \rightarrow \pi^*$ transitions. Interaction energies of all three diazines with one water molecule were determined at the MP2 level of theory [98JST145] while static polarizabilities and hyperpolarizabilities were studied using DFT methods [00JCP6301]. For both properties, the order pyrazine > pyridazine > pyrimidine was observed, which can be understood from resonances between the nitrogen atoms. This effect is more pronounced for hyperpolarizabilities than for the static mean polarizabilities. A comprehensive study on homolytic bond dissociation energies of the C—H bonds in the azabenzenes showed that, due to the delocalization of the unpaired electrons, C—H bonds adjacent to the nitrogens are about 7 kcal/mol weaker than the corresponding bonds in benzene [99JA491]. Furthermore, geometric parameters of 4,6-dichloropyrimidine **90,** 2,6-dichloropyrazine **91,** and 3,6-dichloropyridazine **92** are obtained from MP2/6-311G** calculations (Scheme 58) [97JCS(P2)857].

The reactions of the diazine radicals with O_2 were studied at the B3-LYP/6-311+ G** level (Scheme 59) [00JPC(A)6088]. Formation of dioxiranyl radical intermediates was found to be the most important pathway from the peroxy precursor. DFT-derived geometric parameters of pyrimidiniumolate are in good agreement with experimental data obtained for 1,2,3,5-tetraphenylpyrimidiniumolate [97MI1].

1. *Pyrazines*

The singlet and triplet valence excited states of pyrazine **93** have been investigated in detail (Scheme 60) [99JPC(A)9821, 99JPC(A)9830, 00CPL197, 00JCP7669]. A comparative study of 33 computational methods reveals that the highest quality of vertical excitation energies is obtained from CASPT2 and EOM-CCSD(T) calculations and from time-dependent B3-LYP density functional calculations [99JPC(A)9821]. Transition energies for six triplet states and eight singlet states are reported. Vibronically active modes of the $T_1(^3B_{3u})$ state are assigned



SCHEME 59

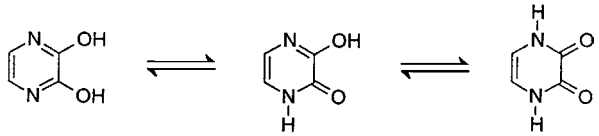
by a variety of methods [99JPC(A)9830, 00CPL197]. Moreover, vibrational frequencies of the $D_0(^2B_{3u})$ and $D_1(^2A_u)$ pyrazine anion were compared with experimental results [00JCP7669]. Further computational studies at the Hartree–Fock level concern electronic effects in chloropyrazines [99CH695], the relative stability of intermediates in the bromination of 5,8-dihydro-5,8-methanoquinoxaline derivatives [98BCJ1443], the rotational barriers in 2,6-dimethylpyrazine [98CP1], and the vibrational frequencies of solvated **93** [99JST201].

DFT and post-Hartree–Fock *ab initio* studies on the different tautomers and rotamers of 2-hydroxy- (**94**) and 2,3-dihydroxypyrazine (**95**) indicate that the former species is stabilized by about −3 kcal/mol with respect to its keto tautomer in the gas phase [99JST229]. In solution the opposite appears to be true. For **95,** the hydroxyoxo **95b** and diketo tautomers **95c** are most stable in the gas phase (Scheme 61).

Since **93** is a popular ligand in organometallic chemistry, a considerable number of studies deal with the ligand properties of this heterocycle [98IC2033, 98JCP8583, 98JCS(D)601, 99CPL130, 99IC3030]. Moreover, its occurrence in the Creutz–Taube ion **96** [99JA11418, 99JCP10926] initiated computational studies which primarily focus on the electronic properties of this ruthenium complex (Scheme 62).

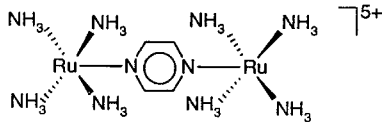
93 **94**

SCHEME 60



95a **95b** **95c**

SCHEME 61



96

SCHEME 62

The potential energy surface along the symmetric and the antisymmetric Ru–pyrazine–Ru stretching mode were computed at the DFT level with subsequent analyses of the vibronic coupling. Geometric parameters of the ion are provided [99JA11418]. Solvent simulations on $[Ru(NH_3)_5\text{-pyrazine}]^{m+}$ ($m = 2, 3$) complexes show that donor solvents increase the electron density at the ruthenium atoms [98JCP8583]. Likewise, the basicity of the complexes was investigated in the gas phase and in aqueous solution by self-consistent reaction field approaches [98IC2033]. DFT calculations on the electron affinities and polarizabilities of **93** and the effective charges at the Ru atom and the ligands of this complex showed that the π^*-accepting ability of the ligands in the transition metal complexes is mainly determined by their electron affinity [99CPL130]. Another popular ligand in organometallics is the quinoxaline-2,3-dithiolate dianion **97** (Scheme 63). The nature of its HOMO and its charge distribution were studied with respect to its donating ability in Mo complexes [00IC2273]. The IR spectrum of the parent quinoxaline-2,3-dithiol has been studied by a combined experimental and computational approach [99JPC(B)6509].

2,3-Didehydropyrazine is believed to be an intermediate in the pyrolysis of pyrazine-2,3-dicarboxylic anhydride. According to DFT calculations, this molecule has a triplet ground state with a singlet state about 10 kcal/mol higher in

97 **98**

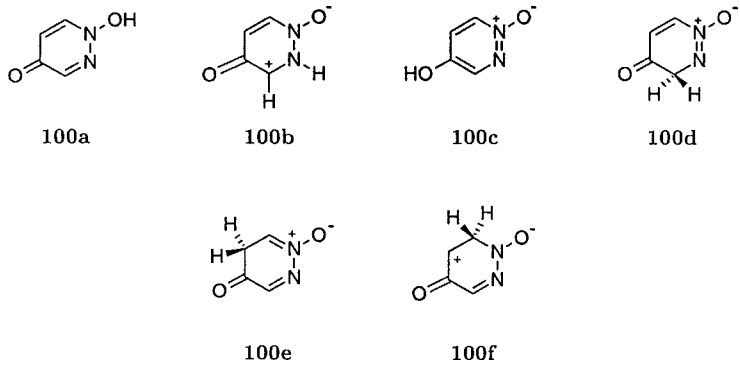
SCHEME 63

energy [99OM1774]. Its structure and the corresponding geometric parameters of Fe^+–2,3-didehydropyrazine **98** were determined for different electronic states (Scheme 63). The computed bond dissociation energy of about 87 ± 10 kcal/mol is slightly higher than for the Fe^+–*o*-benzyne complex. For further work on pyrazines see [99IC692].

2. *Pyridazines*

Heats of formation for pyridazine **99** were obtained from isodesmic equations [97JST99]. Among the 24 different density functionals tested in this study, the popular B3-LYP functional yielded results in a very good agreement with experimental data. The first singlet–singlet and singlet–triplet band systems of the absorption spectrum of **99** are analyzed by *ab initio* and vibronic coupling calculations [00CP1]. The major source of vibronic perturbation in the singlet–singlet absorption is attributed to coupling between near-resonant $^1A_2$ and $^1B_1$ states. Solvent shifts of the absorption bands of these states are also provided [96JPC9561]. Further computational studies on the properties of pyridazine concern its core excitation spectrum [99JCP5600].

Tautomers of hydroxypyridazine *N*-oxides **100** were studied with modified G2 and G2(MP2) theories (Scheme 64) [97JST97]. The calculated properties are generally in good agreement with existing experimental data. Within the series shown in Scheme 64, tautomers **100a** and **100c** are very close in energy. Consequently, the equilibrium is dominated by both species. In the case of 6-hydroxypyridazine 1-oxide, it is the 1-hydroxy tautomer that predominates both in the gas phase and in solution. Hydroxy-*N*-oxide tautomers predominate in 3- and 5-hydroxypyridazine 1-oxides. Calculations up to the CCSD(T)/6-311G** level were used to study the geometries of pyridazine, 3,6-dichloropyridazine, and 3,4,5-trichloropyridazine and the corresponding vibrational spectra at an appropriate lower level of theory



100a **100b** **100c** **100d**

100e **100f**

SCHEME 64

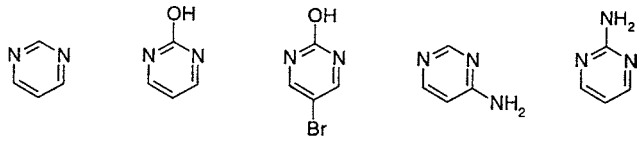
(B3LYP, MP2) [00JPC(A)2599]. On the basis of these calculations, complete assignment of the vibrational spectra is provided.

Moreover, **99** has been used as a catalyst ligand within the dihydroxylation of styrene [99JA1317]. Combined semiempirical and Hartree–Fock studies are presented for the formation of substituted pyridazines and some heterobetaines [99JOC9001, 00H1065].

3. *Pyrimidines*

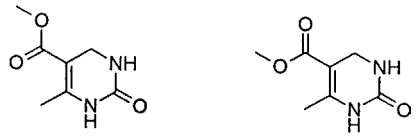
Vibrational assignments for pyrimidine **101** and five of its deuterated analogs are provided based on a comparison of experimental results and MP2/6-31G* calculations [99JPC(A)5833, 99SA(A)179]. The complexes of 2-hydroxypyrimidine **102** and its 5-bromo derivative **103** with water were investigated in a combined FT-IR and *ab initio* study [98JPC(A)8157]. Both compounds occur dominantly in their hydroxy tautomeric forms (Scheme 65). The estimated K_T (*h*/*o*) values of **102** and **103** are 60 and 184, respectively. Adding further water molecules to the complexes shifts the equilibria toward the oxo forms. A normal mode analysis is provided for the isolated tautomers. Calculations concerning the hydrogen bond between **101** and a water molecule indicate that only high-level calculations are able to account for the coplanarity of the water molecule with the pyrimidine ring [98JA11504].

4-Aminopyrimidine **104** and a series of isomeric 4-aminopyrimidinium radicals were studied by approximate QCISD(T)/6-311+G(2d,p) calculations [99JPC(A) 1905]. The latter can be obtained from hydrogen addition to the parent **104.** The preferred site of the hydrogen attack is the C_5 atom. While additions to all ring positions are exothermic, the addition to the amino group is endothermic. Šponer and Hobza investigated the stacking properties of **101, 104,** and 2-aminopyrimidine **105** up to the CCSD(T) level in order to determine the errors introduced by the less demanding MP2 approximation and by restrictions to the basis set [97CPL263]. They conclude that the inclusion of higher angular momentum functions is mandatory for describing the correlation interaction energy properly. Hydrogen-bonded and stacked dimers of **101** and pyrimidine/quinone complexes were studied by McCarthy *et al.* [97JPC(A)7208, 97MP513]. A comparison of computed and experimentally obtained shifts of the vibrational frequencies in these complexes with



101 **102** **103** **104** **105**

SCHEME 65



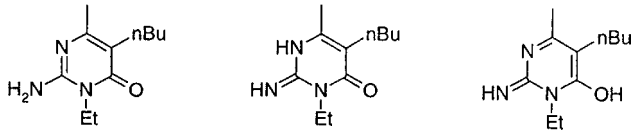
106a **106b**

SCHEME 66

respect to the monomers indicates that the planar hydrogen-bonded complexes are the preferred species in low-temperature Ar matrices. BSSE effects were found to be of significant importance. Moreover, ^{1}H NMR chemical shifts of **104, 105,** and higher amino-substituted pyrimidines were studied at the RHF/GIAO and DFT/GIAO levels [97JA8699]. Differences between the DFT and RHF computed chemical shifts show that electron correlation effects increase monotonically with the number of NH_2 substituents.

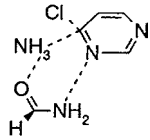
MP2/6-31+G** calculations on the two rotamers of dihydropyrimidine-5-carboxylate **106** yield a slight preference of the *cis* rotamer **106a** (Scheme 66) [98JST219a]. However, it could not be decided with certainty whether the dihydropyrimidine ring is planar or not, and thus calculations at higher theoretical levels are desirable. While the experimental data indicate an almost planar ring, the *ab initio* and density functional calculations do not. The tautomers of 2-amino-5-*n*-butyl-3-ethyl-6-methyl-4(3*H*)-pyrimidinone **107** were investigated by Craciun *et al.* (Scheme 67) [98M735]. In agreement with experimental results, the amino-oxo tautomer **107a** was found to be the most stable form.

DFT calculations were used to study the effects of hydrogen bonding on the aminolysis of 6-chloropyrimidine **108** [00JA5384]. The barrier of the reaction of **108** with NH_3 has been determined to be 32.9 kcal/mol. Addition of hydrogen-bond–forming species (i.e., formaldehyde or formamide) lowers the barrier considerably. When formamide is added, hydrogen bonds are formed to the incoming NH_3 moiety and to the pyrimidine ring nitrogen adjacent to the carbon at which the substitution occurs. These hydrogen bonds lower the barrier to just 22.7 kcal/mol. The structure of the transition state is sketched in Scheme 68. For further work on pyrimidines, see Ref. [96T5475].



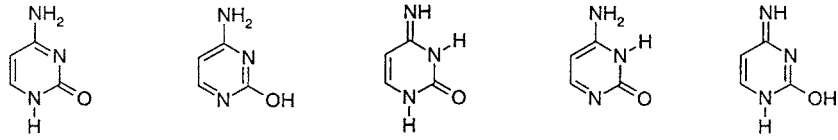
107a **107b** **107c**

SCHEME 67



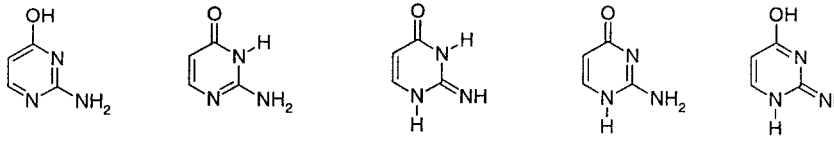
SCHEME 68

a. *Cytosine.* Because of its importance in biochemistry and its occurrence in DNA, this nucleobase has been extensively studied by many groups. The success of these studies strongly depends on the level of theory used and the problem to be solved. For instance, the stability of the different tautomers of cytosine **109** and isocytosine **110** is quite sensitive with respect to the basis set and the post-Hartree–Fock level (Scheme 69). In the gas phase the most stable tautomer at the MP4(SDQ)/6-31G(d,p)//MP2/6-31G(d) level is **109a,** while a different order is obtained at the MP2 level [96JA6811, 99JST47a]. DFT calculations were found to be less reliable with respect to the stability of these tautomers than high-level *ab initio* calculations. The sequence of relative stabilities obtained at the MP4 level is **109a** $\approx$ **109b** $\geq$ **109c** $\gg$ **109d** $\gg$ **109e.** Since the $-$OH and $=$NH groups allow two rotamers, there are four more local minima than shown in Scheme 69. The corresponding isomers of isocytosine **110** are shown in Scheme 70. At the MP4(SDQ) level the stability sequence in the gas phase is **110a** > **110b** $\gg$ **110c** > **110d** $\gg$ **110e.** Solvation effects change these sequences, initiating a series of studies that use self-consistent reaction field approaches [96JA6811, 96JPC5578, 99JST47a, 00CPL437], Monte Carlo methods [96JA6811, 00PCCP1281], or supermolecular calculations [99JST47a, 00JST1] with one or more water molecules



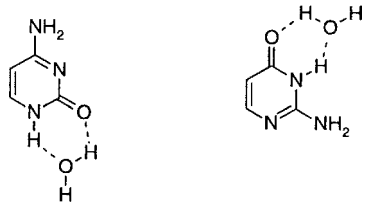
109a **109b** **109c** **109d** **109e**

SCHEME 69



110a **110b** **110c** **110d** **110e**

SCHEME 70



SCHEME 71

attached to the different cytosine tautomers. The most stable complexes of **109** and **110** with one water molecule are shown in Scheme 71. Moreover, diffusion Monte Carlo simulations indicate that zero-point vibrational effects play an important role in determining the structures of hydrated clusters [00PCCP1281]. A stretching of the intermolecular bond length by 0.2 Å was found. The effect is larger for the $O\cdots H_{water}$ than for the $H\cdots O_{water}$ hydrogen bonds. A correlation between the $O\cdots H$ hydrogen bond length and the proton affinities (PA) and deprotonation enthalpies (DE) was determined for cytosine and the other two pyrimidine nucleobases.

$$r(H\cdots O) = 2.542e^{-0.00812(PA-0.35DE)} \qquad \text{with} \qquad r = 0.9962 \qquad (4)$$

The hydration of **109** has been investigated systematically by adding up to 13 water molecules and additionally by applying an SCRF approach for bulk effects [99CP151, 99CPL461]. The water molecules in the larger clusters need to be classified: those that bind directly to the cytosine (six to seven) and those that are hydrogen-bonded only to other water molecules [99CP151, 00JPC(B)5357]. A computational B3LYP/6-31G* study of cytosine with 14 water molecules showed that the intermolecular interactions lead to significant changes of the gas-phase structure [00JPC(B)5357]. The structure in solution is best approximated by a superposition of the oxoamino and zwitterionic hydroxoimino resonance structures **109g,** as shown in Scheme 72 and Table III.

Frequency shifts of more than 200 cm^{-1} due to water complexation were computed for the N—H stretching mode [00JST1]. In a combined theoretical/experimental study, Smets *et al.* found smaller shifts for different H-bonded complexes of the amino-oxo tautomer of 1-methylcytosine with water [96JPC6434].

109c **109f** **109g**

SCHEME 72

TABLE III
SELECTED STRUCTURAL PARAMETERS (Å) OF **109c** AND **109f** IN THE GAS PHASE AND IN SOLUTION (**109g**)[a]

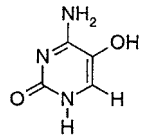
	Gas Phase		Solvated
Bond	**109c**	**109f**	**109g**
N_1–C_2	1.430	1.372	1.377
C_2–N_3	1.373	1.281	1.339
N_3–C_4	1.319	1.412	1.358
C_4–C_5	1.441	1.475	1.436
C_5–C_6	1.359	1.346	1.354
C_6–C_1	1.355	1.387	1.365
C_2–O_7	1.220	1.349	1.281
C_4–N_8	1.366	1.286	1.329

[a]Reprinted in part with permission from Shishkin *et al.* [00JPC(B)5357]. Copyright 2000 American Chemical Society.

The proton transfer in these clusters via the water bridge was found to be about three times as fast as a nonassisted transfer, underscoring the importance of the solvent for the reaction mechanism [98IJQ855]. In addition to the relative stabilities of the cytosine tautomers, the structures and properties of some cytosine derivatives have been investigated, mainly those of 5-hydroxycytosine **111** and 5,6-dihydroxycytosine **112** (Scheme 73) [99JST1, 99JST49].

For a long time it was assumed that isolated nucleobases are planar, but recent studies show that the amino groups in cytosine and isocytosine may adopt a nonplanar trigonal-pyramidal geometry. Calculations confirm that the ring systems in these molecules are not conformationally rigid and changes in the relevant torsional angles of more than 20 degrees cause energy changes of about 1.5 kcal/mol only [98JST1]. This finding is supported by low frequencies for the ring torsions in cytosines [96JPC6434].

Owing to the increasing efficiency of computational methods, it has become possible to investigate base pairs in the gas phase and solution simulated by supermolecular approaches with up to six water molecules [98IJQ37, 98JPC(A)10374, 98JPC(B)9109, 99JST107]. In the cytosine–isocytosine Watson–Crick base pair,



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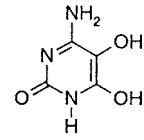
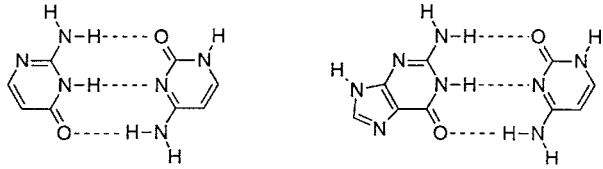


112

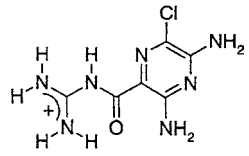
SCHEME 73



113 **114**

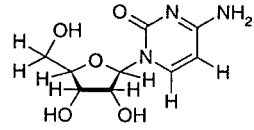
SCHEME 74

the isocytosine acts as a double proton donor to and a single proton acceptor from the cytosine molecule due to the formation of three relatively parallel H-bonds. In the case of six water molecules, the base pair becomes strongly nonplanar, while a smaller number of water molecules causes the molecule to deviate only slightly from its planar conformation [98IJQ37, 98JPC(B)9109]. These findings show that the water molecules in the first coordination sphere play an important role in determining the base pair structure. Strong similarities are found between the cytosine–isocytosine base pair **113** and the guanine–cytosine base pair **114** (Scheme 74) [98JPC(A)10374, 99JST107]. The intramolecular flexibility of **114** is manifested by very low out-of-plane modes of both molecules [99JST15]. The hydrogen bonds in Watson–Crick and Hoogsteen base pairs were investigated by chemical shift calculations and scalar coupling constants at the DFT level [99JA6019]. Correlations between the bond lengths and the computed shifts allow study of the hydrogen bonds by experimental NMR techniques. Studies on complexes of 5,6-dihydroxycytosine with standard nucleobases show that only a few of these systems have a potential mispairing character [99JST69]. An unconventional hydrogen bond between an amino group as proton donor and a benzene ring as proton acceptor was found in the cytosine–methylbenzene complex [99MI3]. Interaction energies for stacked systems consisting of cytosine and other molecules were studied by several groups [99CPL693, 00IJQ677, 00JPC(B)815]. For a complex of amiloride **115** with cytosine (Scheme 75) the calculations indicate that electrostatic interactions contribute up to a third of the interaction energy whereas the complexes with other nucleobases are significantly more dispersion-controlled [00JPC(B)815].



115

SCHEME 75

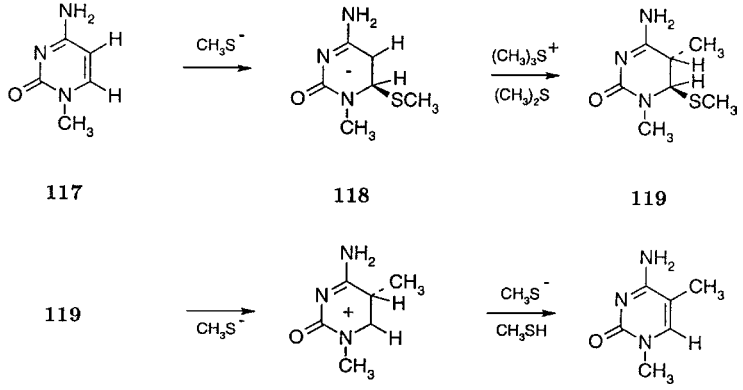


116

SCHEME 76

The vibrational spectra of cytosine and various protonated cytosines were investigated by SQM/B3-LYP/6-31G* calculations [96JPC5578]. Conformational studies and vibrational normal mode analyses of cytidine **116** and related compounds were performed at the MP2 and DFT levels (Scheme 76) [98JPC(B)7484, 99JPC(A)8716, 99JPC(B)10934, 99JPC(B)10955, 00JCS(P2)255]. The most stable structure of **116** was computed to be the C'_3-endo/anti conformer. This result is confirmed by a comparison of calculated neutron-inelastic scattering (NIS) spectra with experimental NIS and FT-IR results: The computed C_3-endo/anti spectra are in significantly better agreement with the experimental results than those of the C'_2-endo/anti conformer. Based on the rotational profile of a model compound of **116** (i.e., cytosine linked to tetrahydrofuran), Foloppe and MacKerell suggest that cytosine may destabilize the TA form of DNA [99JPC(B)10955]. Further computational studies concern the properties of the cytosine moiety in cytidine [99MI4, 00JPC(B)4560].

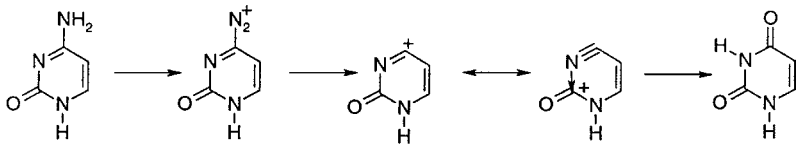
The reaction mechanism of the DNA (cytosine-5)-methyltransferase-catalyzed cytosine methylation was investigated at the MP2 and DFT levels [98JA12895]. This system has been modeled by 1-methylcytosine **117,** methylthiolate, and trimethylsulfonium. The cytosine methylation is initiated by an attack of the anionic methylthiolate at C_6 of the cytosine ring (Scheme 77). The formation of the methylthiolate adduct **118** of the neutral **117** was found to be endothermic in the gas phase and in solution. However, the MP2 and DFT results differ



117 **118** **119**

119

SCHEME 77



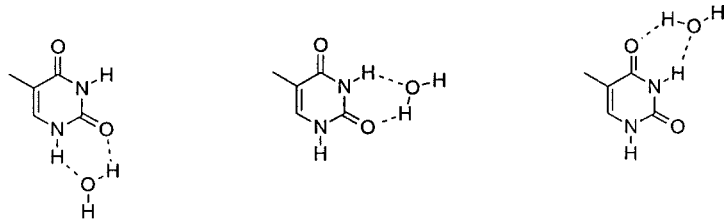
120 **121** **121**

SCHEME 78

significantly. In the case of protonated cytosine, the formation of the corresponding complex is strongly exothermic in the gas phase. Energetic considerations of the transition states and intermediates of subsequent steps, i.e., the methyl transfer to C_5 and the elimination of the C_5 proton and C_6 thiolate, led to the conclusion that the methylthiolate elimination has a high reaction barrier in the gas phase.

The deamination of cytosine to uracil is a well known mutagenic process. The mechanistic hypotheses invoke diazonium ions as the reactive species in DNA base deamination (Scheme 78). A computational study up to the MP3 level showed that two structures can be found for the diazonium ion **120,** the first one with a classical C—N bond of 1.58 Å and the second with a much longer bond of about 2.75 Å [99JA6108]. Therefore, the second structure must be considered a van der Waals complex between a nitrogen molecule and the remaining cation, which was found to be more stable than the classical diazonium ion. Dediazonization of **120** leads to an extreme shortening of the C_4—N_3 bond (1.188 Å) and extreme elongation of about 0.6 Å of the C_2—N_3 bond. Therefore, **121** might well be described as a C_5-cyano acylium cation, as indicated by the resonance forms in Scheme 78.

b. *Thymine.* The studies concerning thymine **122** closely resemble those performed for uracil and the other nucleobases (see Section V,A,3,c). A comparison of the DFT geometric parameters of the monomer, dimer, and trimer of **122** with experimental X-ray data is provided by Portalone *et al.* [99ACSA57, 99JPC(B)11205]. The S_1 and S_2 excited states of **122** show local minima while uracil appears to be dissociative in the S_2 state [99CP319]. Structural parameters and selected vibrational frequencies of the excited-state geometries differ significantly with respect to the ground state. Moreover, a rearrangement of the charge distribution is more pronounced for $n \rightarrow \pi^*$ excitations than for $\pi \rightarrow \pi^*$ excitations [98JCI678]. The geometries, harmonic vibrational frequencies, and the energies of four cyclic thymine–water complexes were studied at the MP2 [00PCCP1281] and density functional levels [98JPC(A)6010]. The strongest hydrogen bond is formed between the oxygen with the smallest proton affinity and the NH moiety with the highest acidity (Scheme 79) [00JST1]. The N_3H proton of thymine has a higher deprotonation enthalpy than the N_1H proton [99JPC(A)8853].

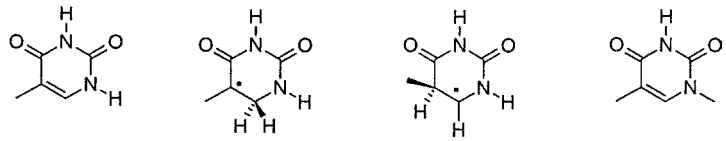


SCHEME 79

At the DFT level the preferred protonation site was found to be O_4 with a proton affinity of 208.8 kcal/mol at 298 K [98JCC989]. This value agrees nicely with the experimental value of 209.0 kcal/mol.

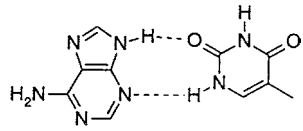
The radiation-induced addition of a hydrogen atom to the 5,6-double bond of **122** leads to the 5,6-dihydro-5-thymyl **123** and 5,6-dihydro-6-thymyl **124** radicals. Calculations at different theoretical levels indicate that **123** is more stable than **124** [98JA1864, 98JPC(B)5369, 99CPL255]. Solvation effects increase the exothermicity of the reaction toward **123** (Scheme 80). In contrast to **124, 123** is almost planar. This planarity leads to an equivalence of the two β-hydrogens of the methylene group. Consequently, the isotropic hyperfine coupling constants of both hydrogens are identical. According to the energetics and a comparison of experimental and theoretical hyperfine coupling constants, 1-methylthymine **125** loses a hydrogen from the methyl group in the 5 position upon irridation. As found for **122,** hydrogen addition most likely occurs in the 6 position. Studies on the relative stability of the tautomers of **125** in the gas phase and in solution indicate that the N_3H tautomer is the preferred isomer [98JPC(B)5228]. The influence of the additional methyl group in **125** on the dipole-bound electron affinity reduces the formation of the corresponding anions [99JCP11876]. A more detailed discussion of this subject is provided in Section V,A,3,c.

As found for other stacked base pairs, in the stacked thymine–thymine pair changes in the interaction energy upon rotation of one thymine unit are almost completely compensated for by solvation effects [99JPC(B)884]. The adenine–thymine (A–T) base pair, which possesses a significant degree of conformational



122 **123** **124** **125**

SCHEME 80

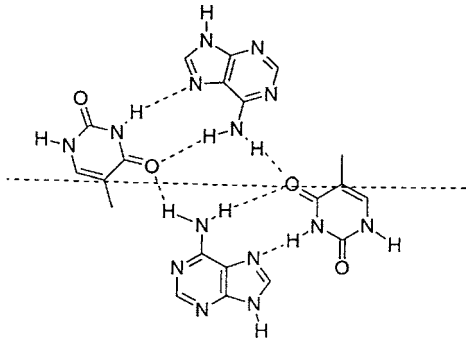


126

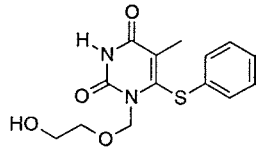
SCHEME 81

flexibility [99JST15], was studied in particular detail [98IJQ351, 98JA8159, 99JPC (A)6251, 99JPC(B)11415, 99PCCP1531, 00JA3495, 00JPC(A)1898, 00JPC(A) 2994]. Twenty-six energy minima were characterized as follows: 9 H-bonded structures, 8 T-shaped dimers, and 9 stacked conformers [00JA3495]. Hydrogen-bonded structures are the most stable while stacked and T-shaped structures are destabilized by at least 4 kcal/mol. The most stable complex **126** is neither a Watson–Crick nor a Hoogsteen base pair and cannot be observed in nucleic acids (Scheme 81).

In the A–T radical cation the double proton transfer appears to be less favorable than the single one, in contrast to the neutral system [98JA8159]. In the latter system the double proton transfer takes place in a concerted way, whereas a two-step mechanism has been obtained for the guanine–cytosine (G–C) pair [99JPC(A)6251]. However, this process, which leads to an unstable rare tautomer, is highly endothermic, allowing for the conclusion that the double proton transfer in the electronic ground state cannot account for mutagenic processes. However, in the low-lying π–π^* excited singlet state, the reaction barrier is considerably lower and the rare tautomer becomes relatively stable. The electronic excitation is localized in one of the two tautomers. A–T tetrads were found to be folded along a line between the two C_5 atoms of the thymine units (Scheme 82) [00JPC(A)1898]. The angle between the two A–T units is about 138°, the Hoogsteen tetrad being more stable than the Watson–Crick one. In the covalent A–T



SCHEME 82



127

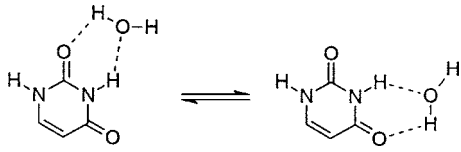
SCHEME 83

base pair anion, the excess electron is located at the thymine molecule; however, calculations predict a negative adiabatic detachment energy, indicating that the A–T pair does not trap excess electrons [00JPC(A)2994].

The conformations of the HIV-1 reverse transcriptase inhibitor 1-[(2-hydroxyethoxy)methyl]-6-(phenylthio)thymine **127** were studied at the Hartree–Fock and the B3-LYP/6-31G** levels (Scheme 83) [99BC265]. Two minima were found to be very close in energy ($\Delta E \sim 0.5$ kcal/mol). The fragmentation reaction mechanism of the thymine dimer radical cation has been studied at the CASSCF level [97JA12274]. The calculations support a stepwise mechanism. After an initial cleavage of the C_6—C_6' bond, the C_5—C_5' bond is broken to form a thymine monomer and a radical cation. The calculations show that the fragmentation proceeds very easily once an electron has been removed from the dimer. However, the enzymatic reaction most likely proceeds via the radical-anion pathway [00CEJ62]. The corresponding fragmentation of the uracil dimer is described in more detail below (see Scheme 87). Further computational studies concern the conformational features of *cis*-5-hydroperoxy-6-hydroxy-5,6-dihydrothymine [98JST143], the pairing properties of thymine glycol [99PCCP1531], and chemical shift calculations for anhydrodeoxythymidines [99JPC(A)4089]. In the latter study, rms deviations of about 5–6 ppm between different computational approaches and experimental ^{13}C chemical shifts and of 0.2–0.3 ppm for ^{1}H chemical shifts are reported.

c. *Uracil.* As for the other nucleobases, the relative stabilities of the uracil **128** tautomers and related derivatives have been investigated by many different computational methods [98JPC(B)5228, 99CP217, 99JST1]. Geometric parameters are provided for the isolated molecules, hydrated molecules, a uracil unit in the solid state simulated by a uracil hexamer [99ACSA57], and the $S_1(n–\pi^*)$ state of uracil [99CP319]. The 1-methyl and 5-bromo derivatives of **128** were computed up to the QCISD(T)/6-311+G** level. The authors conclude that the canonical oxo form is the main, if not exclusive, form in the gas phase.

Since hydration of biomolecules is of particular importance in molecular biology, uracil – water (U–W) complexes have been studied by many groups [98JCS(F) 1277, 98JST307, 99JPC(A)1611, 00PCCP1281]. In the cyclic U–W complex the most stable hydrogen bond is formed at the site characterized by the lowest proton



SCHEME 84

affinity and the highest acidity (cf. Section V,A,3,b) [98JCS(F)1277]. By calculating the transition states between the global minimum and an adjoining local minimum of the U–W complex, the barrier was found to be as high as 5.5 kcal/mol, while the barrier height between the most stable local minima is only 2.4 kcal/mol (MP2) (Scheme 84) [99JPC(A)1611]. The transition states show only one hydrogen bond. BSSE effects decrease the hydrogen bond lengths in the minima by about 0.1 Å.

Solvation effects on the molecular vibrations of **128** were studied by SCRF methods and by supermolecular approaches of **128** with one water molecule [97JPC(B)10923, 98JPC(A)6010]. Correlations between the N—H (uracil) and O—H (water) bond elongations and the corresponding frequency shifts of the stretching vibrations are reported as

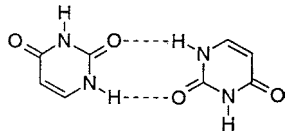
$$\Delta\nu(\mathrm{NH}) = 0.47 - 17.8 \times 10^3 \Delta_r(\mathrm{NH}) \qquad \text{with} \qquad r = 0.9995 \qquad (5)$$

$$\Delta\nu(\mathrm{OH}) = 19.0 - 10.0 \times 10^3 \Delta_r(\mathrm{OH}) \qquad \text{with} \qquad r = 0.9987 \qquad (6)$$

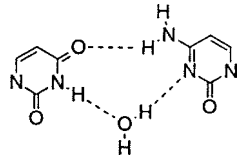
In the uracil dihydrate the harmonic N_1H and N_3H stretching modes are shifted by more than 200 cm^{-1} [97JST323, 98JST307]. The influence of halogen substituents on selected vibrations has been investigated for 5-halogenouracils [98JST115].

Uracil dimers were studied at the MP2 level using the 6-31G* basis with modified polarization functions. Eleven low-energy minima were located: Seven of them are H-bonded, one is T-shaped, and three correspond to various stacked arrangements. The most stable structure was found to be the H-bonded dimer with two $N_1—H\cdots O_2—H$ bonds (Scheme 85) [98JPC(A)6921].

Although it is now well known that the pyrimidine rings are not conformationally rigid [98JST1], one would not necessarily expect distortions in the stacked dimers. However, MP2 studies showed that the monomer rings in the stacked dimers strongly deviate from planarity, which holds particularly true for uracil and thiouracil [98CPL7]. Because the ring deformation permits formation of intermolecular H-bonds, the ring–ring distance is significantly shorter for the dimer



SCHEME 85

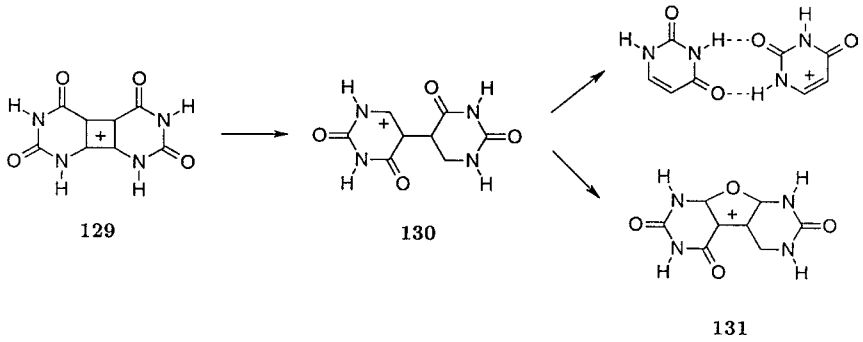


SCHEME 86

with distorted rings than that with rigid planar rings. The H-bond energies of the Watson–Crick adenine–uracil and the wobble guanine–uracil base pairs were found to be almost identical [00H1047]. Complexes with nucleobases other than uracil are also reported for 5,6-dihydroxyuracil and 5-formyluracil [99JST69, 99PCCP1531]. Water-mediated base pairs (as shown in Scheme 86 for the uracil–cytosine base pair) were found to have interaction energies ranging from -13.2 to -20.2 kcal/mol at the MP2/6-31G** level [99JA2605, 00JPC(A)11177]. The corresponding values of the related direct base pairs are -8.7 and -15.7 kcal/mol. The water-mediated uracil–cytosine, uracil–uracil, and guanine–adenine base pairs can be considered structurally autonomous building blocks, while the water-mediated uracil–guanine and guanine–guanine base pairs may not.

Since pyrimidine dimers are among the most common photoproducts in genetic material that has been exposed to UV radiation, the uracil dimer and its charged radicals have been studied as model compounds [97JPC(A)8335, 98JPC(A)7168, 99JST163a, 00CEJ62]. For the radical anion the currently accepted cleavage scenario includes the donation of an electron into the π^*-orbital of the $C_4{=}O$ double bond and subsequent delocalization of electron density into the $C_5{-}C_5'$ σ^*-bond orbital, which reduces the activation energy for the bond cleavage. This has been confirmed by computing the bond orders of the neutral and the anionic dimer [00CEJ62]. Although Hartree–Fock calculations still predict an activation barrier of 6 kcal/mol, this barrier entirely vanishes upon inclusion of dynamic correlation effects via the MP2 approach [97JPC(A)8335]. The intermediate formed by the $C_5{-}C_5'$ bond splitting in the dimer anion radical is found to be energetically favored over both the parent dimer and the product monomers. The corresponding pathway of the radical cation **129** is schematically shown in Scheme 87. Besides intermediate **130,** in which the uracil fragments are connected by a $C_5{-}C_5'$ bond, another tricyclic intermediate **131** was found [98JPC(A)7168, 99JST163a]. The transformation of the first intermediate into the latter was computed to occur activation-less.

In a debate about the existence of covalent-bound and dipole-bound uracil radical anions [97JPC(A)8123, 97JPC(A)9152, 98JPC(A)1274, 99CPL220, 99JPC(A) 4309, 99JPC(A)5784, 99JPC(A)7912], two minima were found, an ^2A dipole-bound state and an ^2A covalent-bound state. Energies were computed up to the UCCSD(T)/6-31++G** level. The vertical electron detachment energy (VEDE)



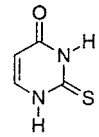
129 130 131

SCHEME 87

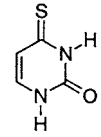
of the dipole-bound state is in good agreement with experimental data. Uracil dipole-bound anions are stabilized upon hydration. The corresponding minima of several neutral uracil–water complexes and uracil–anion complexes were studied in detail [99JPC(A)7912]. The VEDEs of all anions lie between 0.3 and 0.9 eV and the VEDE of the most stable anionic complex coincides with the experimentally observed maximum. For all complexes the anionic uracil ring is not planar. An investigation of the uracil anion with three water molecules reveals that a rearrangement of the H-bonds in the neutral complex occurs when an excess electron is attached. The positively charged hydrogens of the water molecules move out of the plane and dip into the π-density of the excess electron, providing additional stabilization to the anion [97JPC(A)9152]. Since the electron affinity increases upon N,N-dimethylation of uracil, the influence of the methyl groups on the attachment of excess electrons into diffuse dipole-bound states has been studied [97JPC(A)8123]. Moreover, three H-bonded conformers of the uracil dimer can form stable dipole-bound anions, while one covalent-bound uracil dimer anion was found. In the latter the excess electron is localized on one of the uracil molecules, which are almost perpendicular to each other [99JPC(A)5784]. Similar results were obtained for the anion of the H-bonded uracil–thymine base pair. However, two minima were found: The anion, where the excess electron is located at the uracil anion, is 1.4 kcal/mol more stable than the form in which the excess electron is located at the thymine molecule [99JPC(A)4309].

Further quantum chemical studies involving uracil derivatives concern the conformations and properties of uridines [98CEJ621, 98JA5488, 98JOC1033, 00JCS (P2)677], the nucleophilic attack in pseudouridine synthases [99JA9928], and the aza analogs of uracil [99JST349].

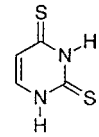
d. *Thiouracil.* The prototropic equilibria of 2-thiouracil **132,** 4-thiouracil **133,** and 2,4-dithiouracil **134** were studied by means of MP4(SDQ) and G2(MP2) theories (Scheme 88) [98JPC(A)2194, 00JPC(A)5122].



132



133



134

SCHEME 88

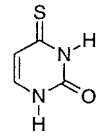
The stability order of **133** in the gas phase and in aqueous solution is given by

Gas phase: **133a** > **133b** > **133c** > **133d** > **133e** > **133f**

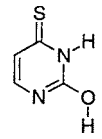
Aqueous solution: **133a** > **133b** > **133d** > **133c** > **133f** > **133e**

In aqueous solution **133d** is more stable than **133c** and **133f** is more stable than **133e** (Scheme 89). In both cases the 2-keto-4-thio **133a** form is the most stable tautomer. Thiouracils **132–134** behave as moderate bases in the gas phase, **134** being the most basic one.

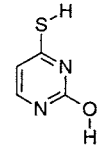
In all three molecules, protonation occurs at the heteroatom attached to position 4. As must be expected, a unimolecular proton transfer that transforms the different tautomers into each other is very unlikely, but can be achieved easily by building dimers [00JPC(A)5122]. A comparison of experimental and computed IR spectra reveals that the photoproduct of 2,4-dithiouracil **134** is 2,4-pyrimidinethiol [98SA(A)685]. Deprotonation of **132** and subsequent association with $[(C_2H_5)_3PAu]^+$ **135** leads to the formation of **136a** (Scheme 90) [97JPC(A)5368].



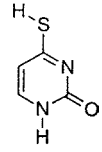
133a



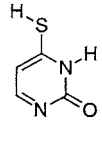
133b



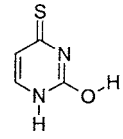
133c



133d

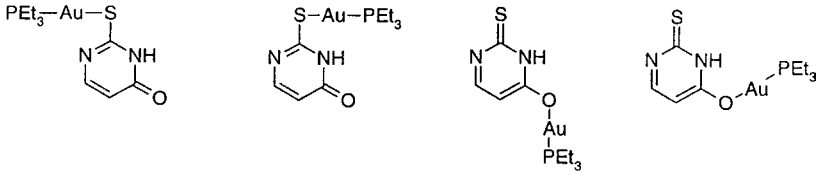


133e



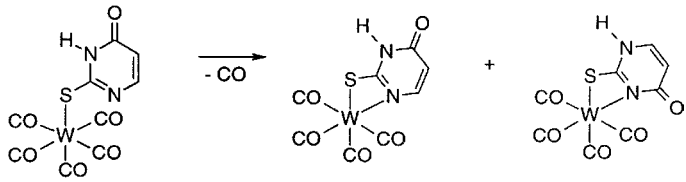
133f

SCHEME 89



136a **136b** **136c** **136d**

SCHEME 90



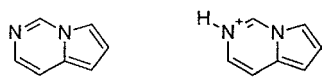
137 **138**

SCHEME 91

The deprotonation of **132** is favored at N_1 and the coordination of **135** occurs preferentially at S_2. A second entity of **135** coordinates at N_3. A computational study of thiouracil derivatives of the tungsten(0) hexacarbonyl shows that the sulfur-bound thiouracil is serving as a π-donor during the CO dissociation (Scheme 91) [99IC4715]. DFT calculations show that **137** is significantly stabilized with respect to the alternative reaction product **138.**

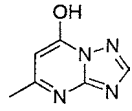
4. *Fused Pyrimidines*

The structures of pyrrolo[1,2-*c*]pyrimidine **139** and its N-protonated form **140** were obtained from MP2/6-31G* calculations (Scheme 92) [99JOC7788]. Proton affinities computed at the same level reveal that N-protonation is slightly preferred over protonation at the C_7 position. The most stable tautomers of 2-substituted 5-methyl-7-hydroxy-1,2,4-triazolo[1,5-*a*]pyrimidine **141** were



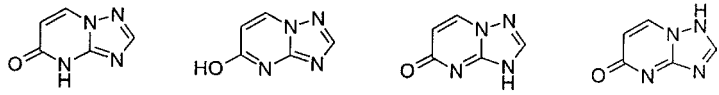
139 **140**

SCHEME 92



141

SCHEME 93



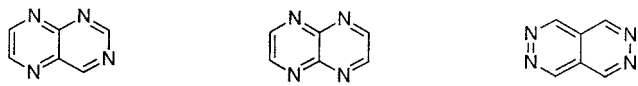
142a **142b** **142c** **142d**

SCHEME 94

determined by *ab initio* calculations in the gas phase and in DMSO solution (Scheme 93) [97JST65]. Comparison of experimental and computed ^{13}C and ^{15}N chemical shifts is provided for all isomers. Relative stabilities were computed for a series of 5-oxo-1,2,4-triazolo[1,5-*a*]pyrimidines **142** and related compounds (Scheme 94) [00JCS(P2)1675]. According to B3-LYP/6-311+G** calculations, **142a** is the most stable isomer.

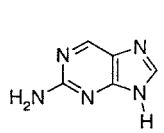
Hurst and colleagues investigated the vibrational and electronic spectra of pteridine (1,3,5,8-tetraazanaphthalene) **143** and other tetraazanaphthalenes (TAN), namely those of 1,4,5,8-TAN **144,** and 2,3,6,7-TAN **145** (Scheme 95) [99CP229, 99JPC(A)3089, 00JPC(A)7386]. They found that B3-LYP/6-31G*-computed IR spectra of these species are in better agreement than the corresponding MP2 spectra. Bis-μ-(5,7-dimethyl[1,2,4]triazolo[1,5-*a*]pyrimidine and the anion of 1,3,4,6,7,8-hexahydro-2*H*-pyrimido-[1,2-*a*]pyrimidine serve as ligands in metal complexes with short Ag—Ag and Cu—Cu contacts [98IC4066, 98JPC(A)2443]. Further work covers computational studies on alloxazines [00IC4052].

a. *Purines.* Although most computational investigations of purines focus on the nucleobases, there are several studies that cover other substances. In most cases,

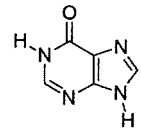


143 **144** **145**

SCHEME 95



146



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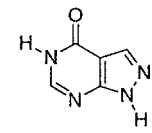


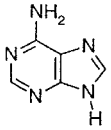
148

SCHEME 96

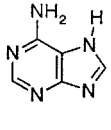
however, there is a strong relation to one of the bases, allowing for instructive comparisons.

In a combined experimental/computational study, the vibrational spectra of the N_9H and N_7H tautomers of the parent purine have been investigated [99SA(A) 2329]. Solvent effects were estimated by SCRF calculations. Vertical transitions, transition dipole moments, and permanent dipole moments of several low-lying valence states of 2-aminopurine **146** were computed using the CIS and CASSCF methods [98JPC(A)526, 00JPC(A)1930]. While the first excited state of adenine is characterized by an $n \rightarrow \pi^*$ transition, it is the $\pi \rightarrow \pi^*$ transition for **146.** The N_9H tautomer is the preferred molecule in the ground state and the N_7H tautomer in the S_1 state. In a series of papers Costas and coworkers investigated the tautomers of the neutral, protonated, and deprotonated forms of hypoxanthine **147** and the isomeric allopurinol **148** (Scheme 96) [97JPC(A)8309, 99JCC200, 99JST39, 99JST73, 00JST71, 00JST105]. For **147** they found a descending sequence of the relative basicity for the electron-donor sites: $N_1 > N_9 \approx N_7 > N_3 >$ O. The two N_1H keto tautomers of **147** are energetically most stable. Gas-phase tautomeric equilibrium constants and IR spectra were computed using density functional theory. The tautomerism of xanthine was studied by Cysewski and Jeziorek [98JST219b].

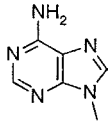
b. *Adenine.* The most important tautomers of adenine **149** are the N_9H **149a** and the N_7H **149b** forms, and consequently most studies focus on these two isomers (Scheme 97). A comparison of B3-LYP/6-31G**-calculated IR spectra of these molecules with a matrix isolation spectrum of **149** indicates that only



149a



149b



150

SCHEME 97

149a can be found in low-temperature matrices [96JPC3527]. Similar conclusions were drawn from a theoretical investigation of the UV/Vis absorption spectra. CASPT2 calculations using an ANO basis set allow an interpretation of the observed electronic spectrum based solely on transitions belonging to **149a,** although contributions from **149b** cannot be discarded completely [97JA6168]. The lowest weak transition observed in the spectrum at 4.6 eV can be assigned to the $2^1A'$ state of **149a,** but both the $2^1A'$ and the $3^1A'$ states of **149b** can contribute to the intensity in solution. Therefore, the participation of **149b** cannot be ruled out entirely.

A study of the electronic spectra of 7-methyladenine and 9-methyladenine **150** based on CIS/6-31G* and CASPT2 calculations indicates that the electronic transition moments of the 9-substituted adenine chromophore are essentially the same in a polar and a nonpolar solvent [97JA12240]. The IR spectrum of **150** and its deuterated derivatives were analyzed by an SQM/B3-LYP approach [00IJQ686]. The mean deviation between the computed and the experimental matrix-isolation IR spectra was determined to 6.4 cm^{-1}. A theoretical investigation of the vibrational spectrum of 9-β-arabinofuranosyladenine allowed an interpretation of the observed spectrum [98JPC(B)4233]. A standard deviation of 6.2 cm^{-1} is reported. Quite recently, the proton affinities (PA) of adenine and related nucleobases were investigated and were correlated to the H-bond energies computed for the corresponding complexes with water [99JPC(A)8853]. The resulting exponential expression

$$E_{HB} = 5347e^{-0.00401[1.5PA-DE]} \tag{7}$$

yields a correlation coefficient of 0.9929 (E_{HB} is provided in kJ/mol). DE denotes the deprotonation enthalpy in kilojoules per mole. ^{15}N chemical shift calculations are reported for adenine, cytosine, guanine, and thymine [98JA9863]. The authors conclude that the ^{15}N chemical shifts in all nucleobases are very sensitive with respect to small changes in the molecular geometry and the environment.

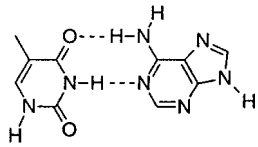
Gu and Leszczynski studied the intramolecular proton transfer in adenine **149** at the DFT level [99JPC(A)2744]. They found that the imino tautomers of **149a** and **149b** are destabilized relative to the amino form by 12.5 and 17.3 kcal/mol, respectively. Solvation effects lower the destabilization by about 2–3 kcal/mol. As found for related systems, the assistance of a water molecule in the proton transfer process reduces the activation barrier significantly. While a classical barrier of $\Delta G_{298} = 45.2$ kcal/mol was computed for the reaction of **149a** without water assistance, a value of 18.0 kcal/mol was found for the water-assisted process. The structures of the corresponding transition state are schematically depicted in Scheme 98. However, these values are not corrected for tunneling effects which may lead to a speedup of the related rate constants by a factor 10^{10}. Therefore, the classical values merely serve as an upper limit of the exact barrier and as an indicator of the preferred mechanism.

SCHEME 98

Most studies with respect to **149** concern the proton transfer between **149** and a second nucleobase. Shishkin and coworkers showed for the adenine–thymine (A–T) base pair **151** that it is intrinsically nonplanar. This nonplanarity increases with rising temperature [99JST15]. Although the double proton transfer reaction is preferred for the neutral **151,** it is the single proton transfer for the A–T radical cation (Scheme 99) [98JA8159]. While the classical barrier for the double proton transfer of the neutral A–T base pair **151** is still very high and endothermic, the situation alters completely for low-lying π–π^* excited singlet states: While the whole process is also concerted, the energy barrier is considerably lower and the product becomes quite stable. Therefore, radiation is a potential source of rare tautomers, which may be responsible for mutagenesis. The distance-dependent H-bond potentials of the Watson–Crick and Hoogsteen A–T base pairs were investigated at the local MP2 level, which effectively eliminates most of the basis set superposition error [97JPC(B)4851].

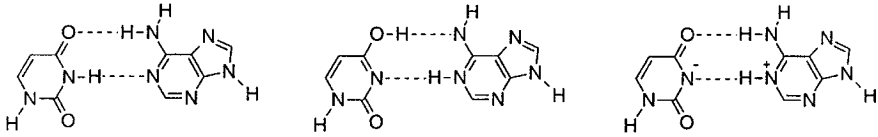
The substituent effects on the H-bonding in an adenine–uracil (A–U) base pair were studied for a series of common functional groups [99JPC(A)8516]. Substitutions in the 5 position of uracil are of particular importance because they are located toward the major groove and can easily be introduced by several chemical methods. Based on DFT calculation with a basis set including diffuse functions, variations of about 1 kcal/mol were found for the two H-bonds. The solvent effects on three different Watson–Crick A–U base pairs (Scheme 100) have been modeled by seven water molecules creating the first solvation shell [98JPC(A)6167].

MP2/6-31G* calculations were performed for bonded and stacked structures of adenine–2,4-difluorotoluene complexes **152** [99CPL393] and for adenine with guanine or thymine [97JPC(B)3846]. Classical base pair structures of **152**

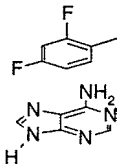


151

SCHEME 99



SCHEME 100

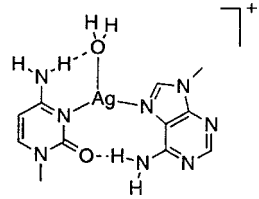


SCHEME 101

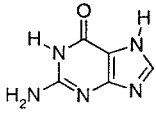
(i.e., Watson–Crick, reversed Watson–Crick, Hoogsteen, and reversed Hoogsteen) were found to be considerably less stable than the stacked structures (Scheme 101).

Pairing properties of 2-hydroxyadenine and 8-oxoadenine with four standard DNA bases were studied at the Hartree–Fock level [99JST59] and adenine–hydrogen peroxide complexes at the MP2 and DFT levels [99JPC(A)4755].

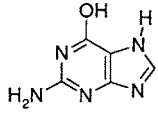
Metal-modified base pairs—i.e., those in which a proton of a hydrogen bond of the base pair is replaced by a metal—are dominated by the metal–base interactions (Scheme 102) [97JCS(D)3971, 99JBIC537, 99JPC(B)2528]. Calculations on Cu^+, Ag^+, and Au^+ complexes show that the metal-modified base pairs exhibit a large conformational flexibility toward out-of-plane motions. Interaction energies computed at the MP2 level are lowest for the silver complexes. The influence of hydrated group IIa metal cations (Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}) on the adenine–adenine and adenine–thymine base pairs was studied at the same level. Binding of the cations to N_7 of adenine does not enhance the strength of the base pairing [99JPC(B)2528]. This is in contrast to results obtained for the guanine–guanine and the guanine–cytosine base pairs. Moreover, the surrounding water molecules interact via H-bonding with the exocyclic amino group of the adenine. Calculations



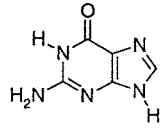
SCHEME 102



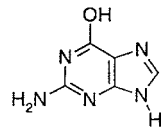
153a



153b



153c



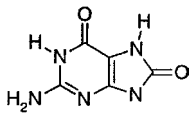
153d

SCHEME 103

on adenine deoxyribonucleotide monophosphate interacting with a pentahydrated Mg^{2+} metal cation indicated that the highly polarized water molecules of the hydration shell form very strong H-bond bridges between the cation and the anionic phosphate-group oxygens [00JPC(B)7535]. The cation binding to the N_7 of adenosine monophosphate forces the adenine amino group to be highly pyramidal and rotated.

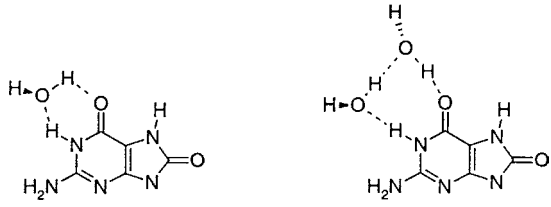
Further computational studies on adenines and adenosines concern the reaction mechanism of ribonuclease A with cytidyl-3,5′-adenosine [99BP697] and the molecular recognition of modified adenine nucleotides [99JMC5338].

c. *Guanine.* Owing to the different NH and OH prototropies in guanine **153,** this molecule allows for 15 tautomeric forms in principle. Seven of these different forms have been investigated up to the MP4(SDTQ) level [98JPC(A)2357]. Basis set effects appear to have a strong influence on the relative stability of these tautomers. The tautomers preferred in the gas phase are shown in Scheme 103. The most stable isomer in the gas phase depends strongly on the computational level: While it is **153a** or **153d** at the MP2/6-311++G(df,pd) level, it is **153a** or **153c** at the MP4(SDQ) level. In IR matrix experiments of isolated **153,** at least three different tautomers are observed. Given the large differences of the dipole moments of these tautomers, **153c** is predicted to be the most stable species in polar solvents. DFT and MP2 calculations on 42 tautomers and rotamers of 8-oxoguanine **154** indicate that the 6,8-diketo form **154a** is most stable (Scheme 104) [98JST219b]. The relative stability of the tautomers remains the same when solvation effects are included via an SCRF approach. Systematic studies suggest that **154** may form stable dimers with all four possible DNA bases



154a

SCHEME 104

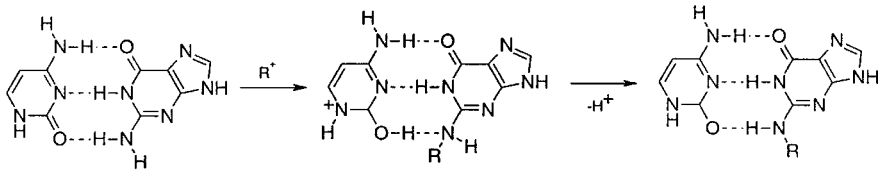


SCHEME 105

[98JCS(F)3117]. MP4/6-311++G(d,p) and B3-LYP/6-311++G(d,p) calculations suggest that the preferred protonation site in guanine **153** is N_7 followed by O_6 [98JCC989]. The calculated gas-phase proton affinities are in good agreement with the most recent experimental data. The absorption spectra of **153** and the other nucleobases were computed at the CIS and CASPT2 levels [97JPC(A)3589]. A new interpretation is proposed for the $\pi \rightarrow \pi^*$ absorption spectrum of guanine due to solvent effects and tautomerism.

Vibrational spectra were investigated for methylated guanines [98JST201, 99JST505]. Agreement between the experimental and calculated frequencies appears to be satisfactory at the HF level but improves at the B3-LYP level, especially when the SQM procedure is used. The amino-oxo form of 1,2-dimethylguanine is by far the most stable tautomer, as obtained from different computational approaches. Moreover, IR frequencies are reported for the oxo-amino tautomer of guanine and its mono- and dihydrated complexes [97IJQ759]. The addition of the second water molecule results in noticeable changes of the complex. All H-bonds become more linear compared to those in the monohydrated complexes (Scheme 105).

As for the other nucleic acid bases, most investigations concern the inter- and intramolecular proton transfer in guanines [98JA5024, 98JA8159, 99JPC(A)577, 00JCP566]. Post-Hartree–Fock *ab initio* calculations predict the height of the intramolecular proton transfer barrier for monohydrated guanine to be approximately two times lower for the oxo–hydroxo reactions and approximately three times lower for the reverse hydroxo–oxo reactions compared with non–water-assisted processes (98JA5024). However, owing to noticeable tunneling contributions to the barrier height, the computed activation energies cannot be used for estimating rate constants. Collective proton transfer is fast and efficient if the H-bonds are equivalent or nearly so. In that case, the transfer will lead to a minimal rearrangement of heavy nuclei and the protons will be able to move synchronously. Using a direct dynamics approach, the rate constant for the water-assisted proton transfer in guanine was computed to $0.45 \times 10^8\ s^{-1}$ [00JCP566]. The intramolecular proton transfer in **154** has been compared with the analogous reaction in **153** [99JPC(A)577].

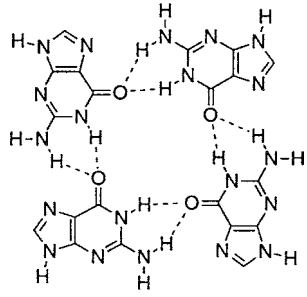


155

SCHEME 106

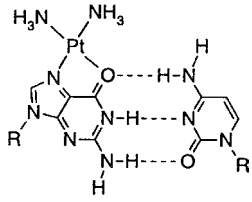
A comparison of single versus double proton transfer reactions in Watson–Crick base pair radical cations was performed at the DFT level [98JA8159]. The single proton transfer appears to be favorable in both the guanine–adenine and the adenine–thymine radical cations. This result is in contrast to the neutral systems, in which the double proton transfer reaction is preferred. The alkylation mechanism of the exocyclic nitrogen of guanine in a guanine–cytosine base pair **155** has been studied at the DFT level (Scheme 106) [00JA2062]. The calculations indicate that the reaction is facilitated by a temporary proton transfer from the guanine amino group to the cytosine oxygen. Thus, the basicity of the cytosine is utilized prior to the alkylation of the guanine. The guanine–cytosine base pair radical cation was studied at the UB3-LYP level [96JA7574]. The structures of several base triplets involving guanine were studied by Venkateswarlu and Leszczynski [99JPC(A)3489]. A computational study of a Hoogsteen-bonded guanine tetrad **156** shows that the structure differs from the traditional picture in the sense that bifurcated H bonds are responsible for the formation of the internal G–G pairs (Scheme 107) [99CPL209].

The geometry of a platinated guanine–guanine–cytosine triplet was computed at the Hartree–Fock level [99IC1481]. The mechanism of cisplatin antitumor activity



156

SCHEME 107

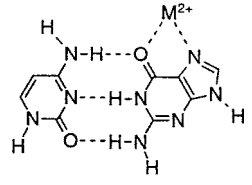


SCHEME 108

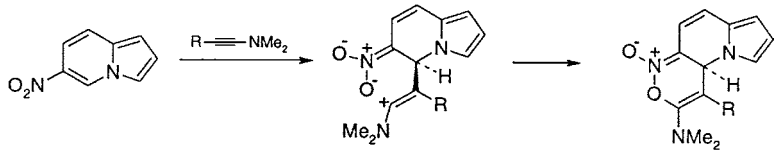
has been considered in terms of the mutagenic property of a Pt(II)–amino complex with guanine and the guanine–cytosine (G–C) pair [97JST73, 98JPC(B)1659, 99CPL496]. The *cis*-$Pt(NH_3)_2^{2+}$ coordination results in breaking of the (cytosine) N_4—H· · ·O_6 (guanine) H bond and a substantial nonplanarity of the G–C moiety (Scheme 108).

Complexes of pentahydrated Zn^{2+} with guanine and the G–C base pair showed that Zn^{2+} binds mainly to the N_7 position due to 3*d*-electron–lone pair interactions [99JPC(B)11415]. Moreover, the calculations demonstrate a significant flexibility in the binding of Zn^{2+} to nucleobases. As a consequence the cation can adopt coordination numbers between 4 and 6 while the binding energies vary only slightly. A 6-fold coordinated Zn^{2+} cation bound to guanines N_7 was found to be the most stable complex. The interaction of the Watson–Crick G–C and A–T base pairs with various metal cations (Mg^{2+}, . . ., Hg^{2+}) has been studied in detail [97JPC(B)9670, 98JPC(A)5951]. MP2 calculations show that the disruption of the base pairs is energetically more demanding in the presence of a metal cation than for the isolated base pairs (Scheme 109). However, solvation of the cation reduces this effect considerably. All transition metals and the Mg^{2+} cation are tightly bound to the nitrogen in the 7 position of guanine, while the Ca^{2+}, Sr^{2+}, and Ba^{2+} cations are also coordinated to O_6.

The influence of stacking properties on the ionization potential of guanine were studied in detail [96JA7063, 98JA845, 98JA12686, 99JA8712]. The main conclusion from these studies is that guanine residues located 5′ to a second guanine are the most easily oxidized. If electron transfer along DNA is facile, G–G stacks can act as thermodynamic sinks, and the hole caused by an oxidizing agent would eventually migrate to this location. With respect to 5′-$TG_1G_2G_3T$-3′ sequences, the G_2



SCHEME 109



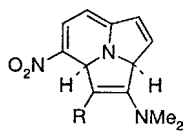
157 158

SCHEME 110

is more reactive toward photoinduced one-electron oxidation than G_1 [99JA8712]. Base-stacking and H-bonding properties of thioguanine and other bases were studied at post-Hartree–Fock levels [97JPC(A)9489, 99JPC(B)884]. The thio group increases the polarizability of the monomers and their dipole moments. Consequently, in stacked complexes of thiobases, both dispersion attraction and electrostatic interactions are enhanced. The antiparallel undisplaced (6-thioguanine)$_2$ is much more stable than the stacked guanine dimer. For further work on guanines, see Refs. [99B16443, 00JST93].

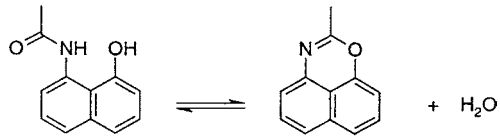
B. OXAZINES

Only a few computational studies concern the properties and reactivity of oxazines [96LA1615, 98JCS(P2)635, 99JOC9057, 00JPC(A)6301]. The reaction between 6-nitroindolizine **157** and *N*,*N*-dimethylaminoacetylenes has been investigated at the Hartree–Fock level (Scheme 110). According to these calculations [99JOC9057], a zwitterionic intermediate with a remarkable dipole moment of 17 D is the precursor of the 1,2-oxazine **158.** However, rotation of the amino acetylene fragment may allow for a cyclization toward **159** (Scheme 111). The cyclazine **159** was found to be more stable than the isomeric **158,** but the activation barrier of this reaction path was computed to be higher than for the formation of **158.** At the same computational level, the condensation of 1-hydroxy-8-(acetylamino)naphthalene **160** toward 2-methyl naphtho[1,8-*d*,*e*]-1,3-oxazine **161** was studied (Scheme 112) [98JCS(P2)635].



159

SCHEME 111



160 161

SCHEME 112

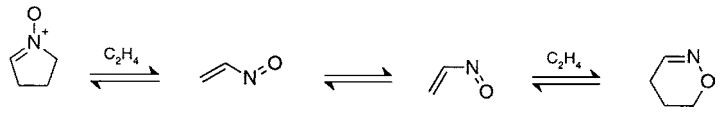
The energy and enthalpy changes accompanying the cyclization are strongly unfavorable, but large entropy changes yield Gibbs energies that enable this reaction in the gas phase and in solution. However, this result is still in contrast to experimental findings, and thus calculations at higher levels are desirable. QCISD/6-31G* calculations on the [4+2]-cycloaddition of nitrosoethylene **162** with ethene show that this reaction is preferred over the formation of 2*H*-pyrrole-1-oxide **163** via a [3+2]-cycloaddition (Scheme 113) [96LA1615]. Analogous results were obtained for the formation of the corresponding thiazines.

A few computational studies focus on the saturated analog of 4*H*-1,4-oxazine, i.e., morpholine [98JCS(P2)1223, 00JCS(P2)1619, 00TL5077]. These cover the structure of lithium morpholide, cycloaddition reactions, and molecular complexes with genistein.

C. DIOXINS

The vibrational spectrum of 1,4-dioxin was studied at the MP2 and B3-LYP levels in combination with the 6-31G* basis set [98JST265]. The DFT results tend to be more accurate than those obtained by the perturbational approach. The half-chair conformation of 4*H*-1,3-dioxin **164** was found to be more stable than the corresponding conformations of 3,4-dihydro-1,2-dioxin **165,** 3,6-dihydro-1,2-dioxin **166,** and of 2,3-dihydro-1,4-dioxin **167** (Scheme 114) [98JCC1064, 00JST145]. The calculations indicate that hyperconjugative orbital interactions contribute to its stability.

Owing to their extreme toxicity, polychlorinated dibenzo-*p*-dioxins are of particular interest [99CPL355, 99JA2561, 99JPC(A)7686]. Okamoto suggested a new



163 162 162

SCHEME 113

decomposition pathway for the most toxic 2,3,7,8-tetrachlorodibenzo-*p*-dioxin **168** [99CPL355]. The process is characterized by selective abstractions of chlorine atoms and a proton-assisted decomposition of the dioxin ring using hydrogen radicals. The formation of **168** via condensation of 2,4,5-trichlorophenol **169** is favored with respect to radicaloid pathways (Scheme 115) [99JPC(A)7686]. Moreover, **168** is expected to be the only product of the proposed mechanism. The vibrational spectra of **168** and other benzodioxins were studied at the SQM/B3-LYP level [95JA4167]. All fundamentals, including the infrared inactive ones, are predicted and assigned.

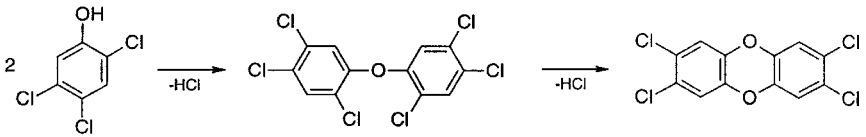
D. DITHIINS

Structure determinations are reported for 1,2-dithiin **170,** its radical cation, 3,6-diamino-1,2-dithiin, 3,6-dicyano-1,2-dithiin, and 3,6-dimethyl-1,2-dithiin [95JST51, 00JA5052]. For the S—S bond length, an MP2/6-31+G* value of 2.07 Å has been computed, in good agreement with an experimental value of 2.05 Å. The thermal ring opening of **170** and a subsequent formation of 2,6-dithiabicyclo[3.1.0]hexane **171** has been investigated in detail at the DFT and CASSCF levels (Scheme 116) [98CPL391, 00JCP10085].

The results are critically dependent on the level of theory. However, a stepwise mechanism with closed shell structures along the reaction path was found to be lower in energy than a concerted reaction. An all-*cis* conformer of **172** is reported to be a transition state rather than an intermediate. Similarities of the conformational isomers of the intermediate 2-butenedithial **172** with the dinitrosoethylenes discussed in Section IV,c are evident. 3,6-Diamino-substituted dithiins are predicted to be more stable in the open-chain bisthioamide structure [95JST51]. The

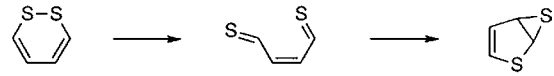
164 **165** **166** **167**

SCHEME 114



169 **168**

SCHEME 115



170 **172** **171**

SCHEME 116

dication of **170** was confirmed to be aromatic by NICS calculations [96JA6317, 99CC777]. A triplet state (C_{2h}) of $\mathbf{170}^{2+}$ was determined to be much higher in energy than the singlet ground state (D_{2h}). Similar results were obtained for the thianthrene dication.

Whereas 1,4-dioxin is planar, 1,4-dithiin **173** and 1,4-oxathiin are significantly distorted from planarity [98JST11]. For **173** a planar nonequilibrium structure was computed to be destabilized by about 2.5 kcal/mol with respect to the boat conformer. The half-chair and boat conformations of 3,4-dihydro-1,2-dithiin, 3,6-dihydro-1,2-dithiin, 4*H*-1,3-dithiin, and 2,3-dihydro-1,4-dithiin **174** were investigated at the MP2/6-31G* level [98JCC1064] (see the structures of the corresponding dioxines in Scheme 114). The half-chair conformers are stabilized with respect to the corresponding boat conformers, and the most stable structure was found to be the half-chair conformer of **174.**

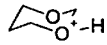
VI. Saturated Six-Membered Rings with Two Heteroatoms

A. DIAZANES

Conformational studies have been performed for 1,3-diazanes **175** and 1,3,5,7-tetraazadecalins **176** [98JOC8850, 99JPC(A)932]. At the MP2/6-31+G* level the equatorial–axial conformer of **175** is stabilized with respect to the diaxial conformer by −0.14 kcal/mol. Interestingly, the *eq,ax,eq,ax-cis* conformer of **176** (i.e., **176b**) was found to be 2.4 kcal/mol less stable than the *ax,eq,ax,eq-cis* conformer **176a** (Scheme 117). Anomeric, steric, and hydrogen-bonding effects are used to explain this effect. In the case of the *trans* conformers of **176,** energetic differences were found to be less than 0.1 kcal/mol for several conformers. Higher correlation

176a **176b**

SCHEME 117

	178a	**178b**
Proton affinity [kcal/mol]	194.8	192.7

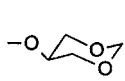
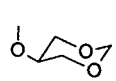
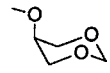
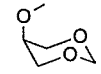
SCHEME 118

levels and larger basis sets are mandatory to establish a conclusive energetic order. Further work on diazanes includes conformational studies on substituted piperazines [00JA5856, 00JST161]. The C_2 boat conformation of diketopiperazine is a true minimum on the potential energy surface while the chair C_i conformer is a transition state.

B. DIOXANES

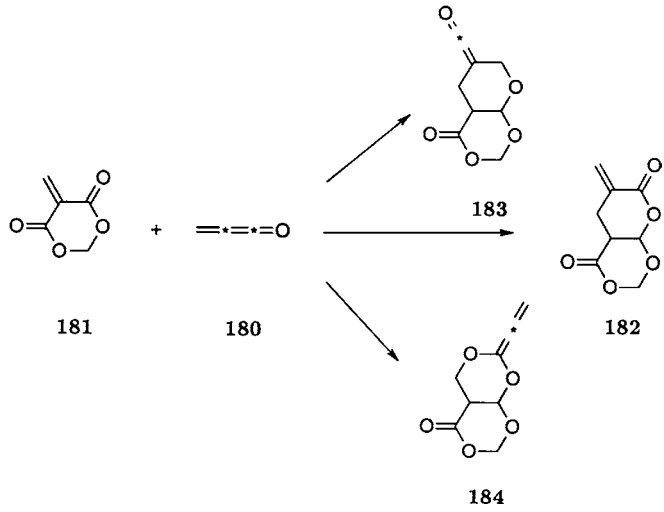
MP2/6-31+G* calculations of neutral 1,3-dioxane **177** and protonated 1,3-dioxane **178** reveal that the preferred protonation site of **177** is axial, since the equatorial lone pair is delocalized due to hyperconjugation (Scheme 118) [97JOC8892]. Based on systematic studies of 1,3-dioxa systems, quantum chemical calculations confirm the general rule that molecules with the OCO structural motif are weaker bases than the corresponding ethers or alcohols. Of particular interest in **177** is the normal and the reversed Perlin effect; i.e., the axial C—H bond coupling constant $^1J_{C-H_{ax}}$ is slightly smaller than $^1J_{C-H_{eq}}$ (normal Perlin effect). DFT calculations of NMR chemical shifts, $^1J_{C-H}$ coupling constants and detailed natural bond orbitals analyses were used to investigate the impact of hyperconjugative effects [97JST231, 99JPC(A)932, 00JOC3910]. Comparisons with 1,3-oxathiane and 1,3-dithian are provided. A conformational study on 5-methoxy-1,3-dioxane **179** indicates that the equatorial structure **179a** is slightly preferred over all others (Scheme 119) [98CPL480]. This finding is in a good agreement with NMR vicinal coupling constant measurements.

The cycloaddition of methyleneketene **180** with 5-methylene-1,3-dioxane-4,6-dione **181** in principle allows all three double bonds of **180** to react with **181** (Scheme 120) [99JST187].

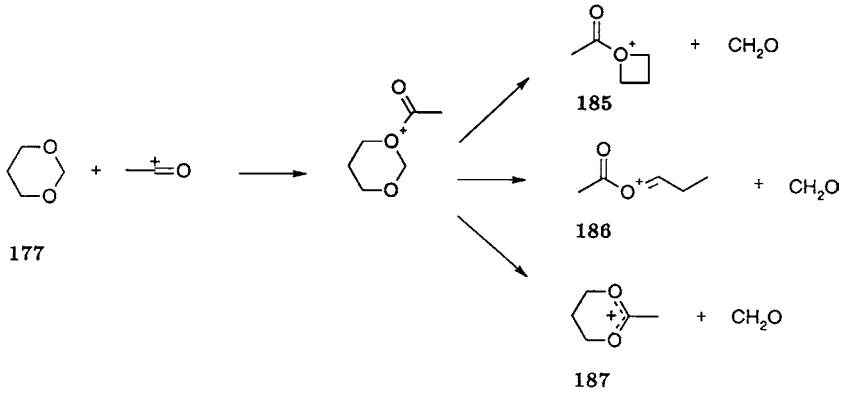
179a **179b** **179d** **179d**

SCHEME 119



SCHEME 120

The activation energies were computed to 3.0 (toward **183**), 0.3 (toward **182**), and 21.8 kcal/mol (toward **184**) at the B3-LYP/6-31G* level, and thus the mechanism leading to **182** is the preferred one. The transition states of all three reactions belong to concerted but asynchronous reaction paths. The transacetalization of **177** with acylium cations results in the formation of the thermodynamically stabilized **187** (Scheme 121) [97JCS(P2)2105]. **186** is less stable than **187,** and **185** is destabilized by 32.5 kcal/mol. Moreover, transacetalization of **177** with sulfinyl cations is not a general reaction. Further computational studies on dioxanes cover electrophilic additions to methylenedioxanes [98JCS(P2)1129] and the influence



SCHEME 121

189a **189b**

SCHEME 122

of **177** on the vibrational spectrum of 2-pyridone **188** [99JCP8397]. In the latter study a shift of -226 cm^{-1} of the ν_{NH} stretching frequency of **188** has been observed.

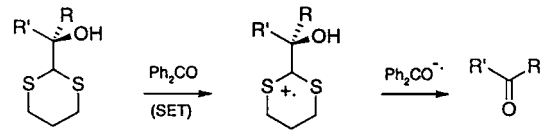
C. DITHIANES

Most computational studies on dithianes focus on stereoelectronic interactions and consequently provide comparisons with dioxanes, oxathianes, and diazanes [97JST231, 99JPC(A)932, 00JOC3910]. Two conformers of 1,4-dithiane **189** were studied at the MP2 and B3-LYP/6-31G* levels. The C_{2h} chair conformer **189a** is about -4.7 kcal/mol more stable than the twisted D_2 conformer **189b** (Scheme 122). Excellent agreement between an experimental IR spectrum and corrected DFT results has been obtained for **189a** [99SA(A)121]. The enthalpies of formation $\Delta_f H_m^\circ$ of **189** and 1,3-dithiane **190** were computed up to G2(MP2) and G3 levels and were compared with calorimetric measurements [99JOC9328]. Within this comparison, a correlation coefficient of $r = 0.9998$ and a standard deviation of 0.7 kcal/mol have been obtained for a series of 10 molecules.

DFT ^{1}H NMR chemical shifts for **190** and the related dioxanes and oxathianes quantitatively reproduce the experimental shifts; consequently, the shielding of the C_2 axial hydrogen in **190** was found to be smaller than for the equatorial hydrogen [97JST231]. Moreover, the observed reverse Perlin effect of the C_5 hydrogens in **190** can be reproduced by DFT calculations [99JPC(A)932]. Calculations on 1,3-dithianes with substituents in the 2 position were used to discuss an enthalpic anomeric effect [97JCS(P2)1835, 99T359, 00JA692]. However, hydrogen bonds are also important in these systems and thus determine the relative energetic order of the conformers (Scheme 123).

A comparison of **190** with 1,3-dioxane **177** shows that the anomeric interactions in **177** are much stronger than in **190.** Moreover, the balance of the computed hyperconjugative interactions successfully accounts for the relative C—H_{ax} and C—H_{eq}

SCHEME 123



SCHEME 124

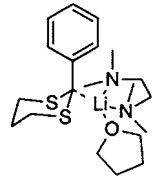
bond lengths [00JOC3910]. The dissociation of 1,3-dithiane–aldehyde/ketone adducts upon irradiation in the presence of benzophenone was investigated by means of UHF and UMP2 theory (Scheme 124) [98JOC9924]. The results indicate that the actual mechanism of the fragmentation involves a benzophenone anion radical which accelerates the bond cleavage via deprotonation of the hydroxy group. Moreover, the mechanism of an electrophilic addition of CO_2 to 2-lithio-2-phenyl-1,3-dithianetetrahydrofuran tetramethylethylendiamine **191** was investigated at the B3-LYP/6-311+G* level (Scheme 125) [00JOC1193].

The overall reaction is exothermic by −18.8 kcal/mol and proceeds via precomplexation of the CO_2. For further computational studies on dithianes, see Refs. [97BCJ2571, 99T5027].

VII. Six-Membered Rings with More Than Two Heteroatoms

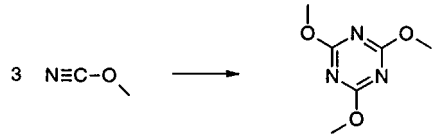
A. TRIAZINES

Although triazine allows for several isomeric structures, most computational studies focus on 1,3,5-triazine **192,** since this structure has only three degrees of freedom and can thus be computed at very high levels of theory. Geometry optimizations of this molecule up to the CCSD(T)/6-311G** level were carried out [97JPC(A)10029]. The best computational estimates of the bond lengths are 1.338 Å for the C—N bonds and 1.084 Å for the C—H bonds. The vibrational frequencies were studied at various levels of theory and most of them are in excellent agreement with experimental results [97JPC(A)10029, 98P(B)247,



191

SCHEME 125

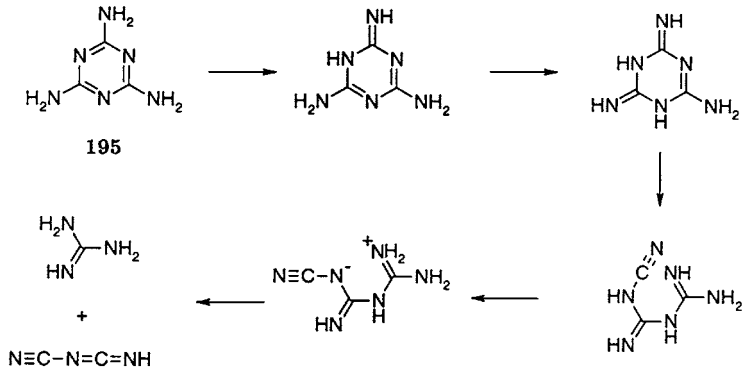


194 **193**

SCHEME 126

99SA(A)1011]. Static dipole polarizabilities were computed up to the MP4(SDQ) level [94MP557]. A study of the electronic structure of the 2^+ and 3^+ states of **192** showed that inclusion of dynamic electron correlation effects is very important [98JPC(A)8021]. The multiplicity of the 1,3,5-triazine dication is predicted to be a high-spin triplet while the trication is most likely a doublet. In hexahydro-1,3,5-triazine the situation is more complicated; the low- and high-spin states are almost degenerate in both the dicationic and the tricationic states. The decomposition mechanism of **192** has been studied by DFT and QCISD(T) calculations. A concerted pathway yielding three HCN molecules is energetically preferred over a stepwise decomposition via an intermediate dimer species [96JPC5681, 96JPC15368]. The best estimates for the activation barrier and the reaction energy are 81.2 kcal/mol and 35.5 kcal/mol, respectively. The formation of 2,4,6-trimethoxy-1,3,5-triazine **193** from methyl cyanate **194** was investigated at the B3-LYP/6-311+G(2d,p) and lower levels (Scheme 126) [99JOC4742]. Although a transition state of a C_{3h} concerted reaction path was found, this mechanism appears to be very unlikely. The addition of catalysts (zinc formate) gives rise to a stepwise mechanism being significantly lower in energy. A reaction in the opposite direction, i.e., the fragmentation of melamine **195** (2,4,6-triamino-1,3,5-triazine), allows for several reaction paths [99JPC(B)582]. The energetically most favorable dissociation mechanism involves a series of hydrogen shifts from the exocyclic amino groups to the nitrogen atoms of the ring system, which finally lead to the ring opening and subsequently to the fragmentation (Scheme 127). Two alternative reaction mechanisms were found to be at least 10 kcal/mol higher in energy. Further computational studies concern the structures of tris(2-cyanophenyl)-1,3,5-triazine **196** [99ACSA602], of 2,4,6-tri[1-[4-(dimethylamino)pyridinium]]-1,3,5-triazine trichloride **197** and related molecules (Scheme 128) [98CM1984].

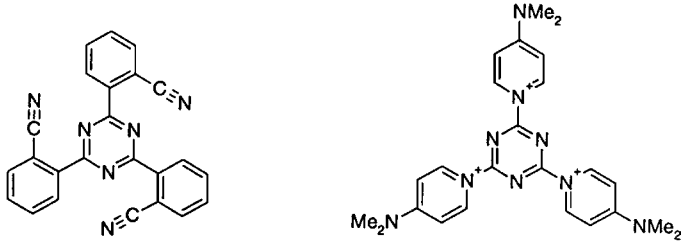
Of particular interest is the well known explosive hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) [97JA6583, 97JPC(A)8675, 97JPC(A)8720, 98JPC(A)8386, 00JPC(A)2261]. Geometry optimizations and normal-mode analyses of five RDX conformers were performed at the DFT and MP2 levels [97JA6583, 97JPC(A) 8720]. Conformers with two nitro groups in axial positions are very close in energy to the conformer with all three nitro groups in the axial positions. Consequently,



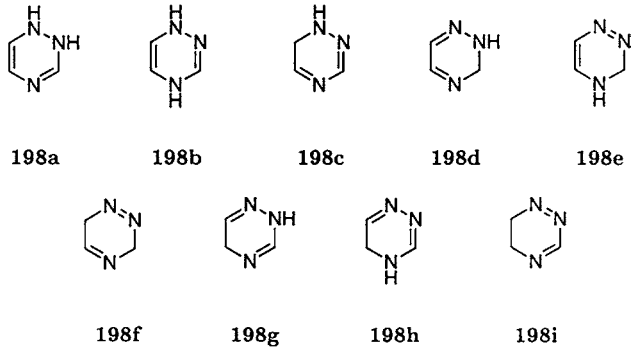
SCHEME 127

the molecule should exist as a mixture of chair, twist, and boat conformers. RDX N—NO_2 and C—H bond dissociation energies were estimated to be 42 and 85 kcal/mol, respectively. Three reaction paths are discussed for the unimolecular decomposition of RDX: (1) a concerted ring fission forming three H_2C=C—N—NO_2 molecules, (2) a homolytic cleavage of an N—NO_2 bond, and (3) a successive HONO elimination to form 3-HONO plus stable 1,3,5-triazine [97JPC(A)8675, 00JPC(A)2261]. The consecutive HONO elimination was identified as the energetically most favorable decomposition pathway. The concerted reaction, which is of importance for 1,3,5-triazine, can be neglected in this case.

Only a few computational studies focus on 1,2,4-triazines [98JOC5824, 98JSP331, 99JSP77, 00CPL459]. The vibrational spectrum of 1,2,4-triazine has been investigated by combined *ab initio* and experimental approaches [98JSP331, 99JSP77]. Bis-1,2,4-triazines were explored as potential ground-state triplet molecules [00CPL459]. The most comprehensive study of 1,2,4-triazines focuses on the relative stabilities of dihydro-1,2,4-triazines **198** and related dihydrotriazinium cations (Scheme 129) [98JOC5824, 00PCCP2187].



SCHEME 128



198a **198b** **198c** **198d** **198e**

198f **198g** **198h** **198i**

SCHEME 129

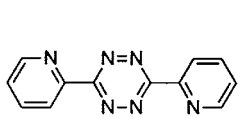
The isomer lowest in energy is predicted to be the 2,5-dihydro-1,2,4-triazine **198g.** The most stable structures always show two C=N double bonds. Moreover, in polar solvents, **198h** should also be a dominant species [00PCCP2187]. The valence and Rydberg excited states of 1,2,3-triazine have been studied by multireference methods (MRD-CI) and the results are compared with experimental spectra [98CP39].

B. TETRAZINES

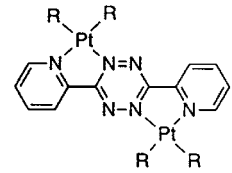
Most computational studies deal with 1,2,4,5-tetrazines (*s*-tetrazine) **199** rather than 1,2,3,4-tetrazines (*v*-tetrazine) **200** (Scheme 130). Of particular interest is the electronic spectrum of *s*-tetrazine [96JCP9859, 99MP603, 99MP859]. Time-dependent DFT calculations and CASPT2 calculations were used to assign 47 electronic states. The spectrum is rather complex, with a large number of low-lying excited states. The complexity arises from high-lying lone-pair orbitals in combination with low-lying virtual π-orbitals. The lowest doubly excited state ($n,n\rightarrow\pi^*,\pi^*$) was found at 4.37 eV [99MP603]. A comparison with experimental data led to some new assignments. Harmonic vibrational frequencies are provided for the ground state and the first excited singlet state [96JCP9859]. A comparison of TD-DFT results with experimental data for the electronic transitions in 3,6-bis(2-pyridyl)-*s*-tetrazine **201** and related compounds led to a consistent assignment of the first 20 states (Scheme 131).

199 **200**

SCHEME 130



201

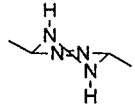


202

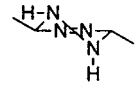
SCHEME 131

For all studied systems the first transition is a symmetry-allowed n–π^* transition. One-electron reduction of the corresponding platinum complex **202** (Scheme 131) leads to a radical anion, showing that, according to DFT calculations, the singly occupied molecular orbital is mainly of ligand π^* character with small contributions from metal valence orbitals [98JCS(F)2979]. DFT-computed polarizabilities of **199** are in excellent quantitative agreement with experimental data [00JCP6301]. The mean polarizability of **199** is smaller than those of triazines or diazines, which can be rationalized by the lower atomic polarizability of the nitrogen atom. Further computational studies of the parent compound concern its basicity [98CH111].

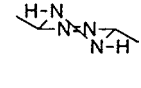
While **200** is planar, tetrahydrotetrazines possess two low-energy conformations [97JST157]. However, their relative stability depends on the computational level, and the barrier between the two minima is very low. DFT calculation favor the boat conformation. For tetrahydro-*s*-tetrazine **203,** three conformers were found (Scheme 132). The diaxial conformer **203c** is significantly higher in energy than the diequatorial **203a** or the axial/equatorial conformer **203b.** The barrier between the latter two minima is much higher than for the ν-tetrazines. Calculations on the thermolysis of 1,2,3,6-tetrahydro-3,6-dimethyl-1,2,4,5-tetrazine resulted in the elimination of N_2 via a transition state for a [2+2+2]-cycloreversion that leads to the corresponding imines [98JST189]. The reaction of dichlorobenzaldazine with sodium azide and 1-propanethiol (PrSH) allows for three pathways in principle (Scheme 133). However, the only reaction observed leads to the triazine ylide **204.** Computational results suggest that the formation of the ylide involves an intramolecular cyclization of a nitrile imine [00JA2087]. The authors note that



203a

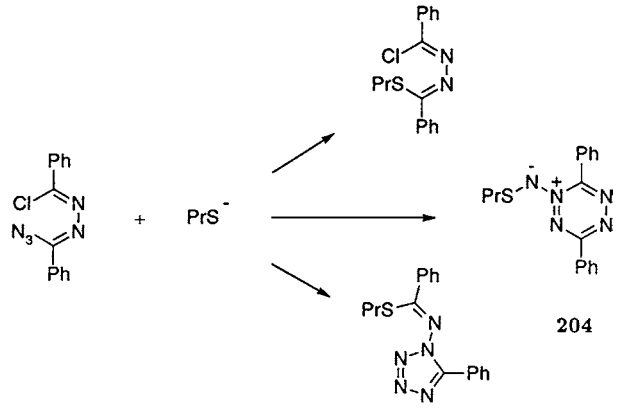


203b



203c

SCHEME 132

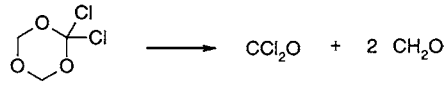


SCHEME 133

the ylide **204** is a remarkable structure that can be described as an intramolecular donor–acceptor adduct in a linear conjugated chain rather than a tetrazine derivative.

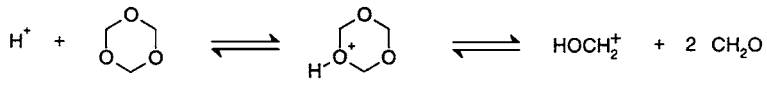
C. TRIOXANES AND TETROXANES

Only a few computational studies focus on trioxanes and related systems, and some of the molecules under investigation even have not been synthesized [97CPL234, 97JA7218, 98CC583, 99JA8544, 99JST103]. The thermal decomposition of 1,3,5-trioxane **205** and some of its derivatives (polychlorinated compounds and *N*-methyl-1,3,5,2-trioxazinane **206**) has been studied by DFT methods and high level *ab initio* approaches (Scheme 134) [98CC583, 99JA8544]. The activation barrier for the concerted ring opening of **206** is about 10 kcal/mol lower in energy than for **205.** Moreover, it is found that DFT calculations significantly underestimate the reaction barrier and that the 6-31G* basis set is inadequate for yielding quantitatively correct energies [99JA8544]. The unknown 2,2-dichlorotrioxane **207** is predicted to be thermodynamically stable and may be useful as a source of phosgene.



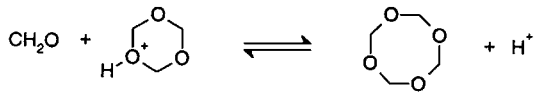
207

SCHEME 134



205 **208**

SCHEME 135



208 **209**

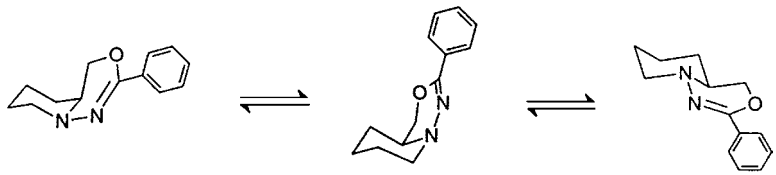
SCHEME 136

DFT molecular dynamics simulations were used to investigate the kinetics of the chemical reactions that occur during the induction phase of acid-catalyzed polymerization of **205** [97JA7218]. These calculations support the experimental finding that the induction phase is characterized by the protolysis of **205** followed by a rapid decomposition into two formaldehyde molecules plus a methylenic carbocation (Scheme 135). For the second phase of the polymerization process, a reaction of the protonated 1,3,5-trioxane **208** with formaldehyde yielding 1,3,5,7-tetroxane **209** is discussed (Scheme 136).

1,2,4-Trioxane **210** has been used as a model system by Gu and coworkers to study the antimalarial drug artemisinin **211** (Scheme 137) [97CPL234, 99JST103]. It is the boat/twist form rather than the chair conformer of **210** that describes the subunit in **211.** Moreover, geometric parameters and vibrational frequencies can only reliably be computed at the DFT level and by post-Hartree–Fock methods. B3-LYP/6-31G* calculations on the conformers of 3,3,6,6-tetramethyl-1,2,4,5-tetroxane show that the chair conformer is stabilized with respect to the twisted conformer by about −2.8 kcal/mol [00JST85]. No corresponding boat conformer was found.

210 **211**

SCHEME 137



212a **212b** **212c**

SCHEME 138

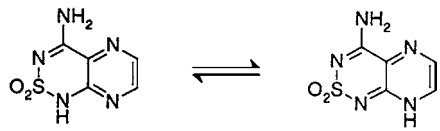
D. OXADIAZINES

Hexahydropyrido[1,2-*d*]-1,3,4-oxadiazines **212** may formally exist in three conformers (Scheme 138) [99ACSA213]. However, according to simple Hartree–Fock calculations, the *trans* conformer **212c** is the energetically preferred structure.

E. THIADIAZINES

The tautomerism of 4-amino-1*H*-pyrazino[2,3-*c*]-1,2,6-thiadiazine 2,2-dioxides **213** has been investigated in the gas phase and in solution by different solvent simulations (Scheme 139) [98JCS(P2)1889].

While the N_1H **213a** tautomer is the only relevant isomer in the gas phase and in solvents with low dielectric constants, the N_8H tautomer **213b** also becomes important in aqueous solutions. Supermolecular approaches with one and two water molecules show that the second water molecule still has significant impact on the $N_1H \rightleftharpoons N_8H$ equilibrium. Likewise, the tautomerism of the structurally similiar **214** has been studied by Campillo and colleagues (Scheme 140) [98H1833]. Calculations in the gas phase and SCRF studies show that **214a** is the preferred tautomer. The reaction path of the ring expansion of 1,2,4-thiadiazole upon quaternization toward 2*H*-1,3,5-thiadiazine has been studied by Butler and coworkers [99JCS(P2)1709]. The investigation of two different pathways showed that the reaction is characterized by the ring opening of **215** and a subsequent 1,6-heteroelectrocyclization (Scheme 141).



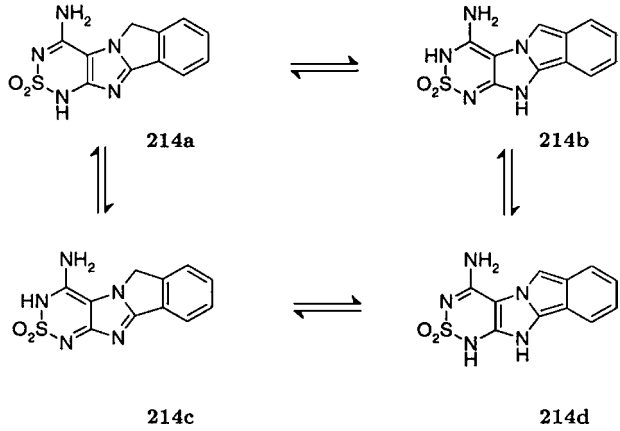
213a **213b**

SCHEME 139

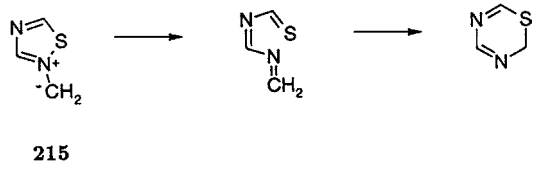
Rotational barriers and intramolecular S···O interactions were studied for acyliminothiadiazolines at the Hartree–Fock level [98JA3104].

VIII. Summary

Recent developments in computer technology and the increasing efficiency and accuracy of current *ab initio* and density functional programs allow the investigation of increasingly complex systems. Molecules that could be treated only at the semiempirical level ten years ago can now be computed at the density functional or the MP2 level with basis sets of double-ζ quality. Very often, these calculations are accurate enough to explain experimental findings, and consequently many experimental studies are augmented by quantum chemical calculations. However, in many cases just a few kilocalories per mole may decide between different reaction mechanisms, different explanations of physical effects, or even a preferred tautomer or conformer. Since the inherent errors of MP2 and DFT calculations are still significantly larger than chemical accuracy, high-level calculations are mandatory for many problems. This holds particularly true for the investigation of reaction



SCHEME 140



SCHEME 141

barriers involving bond-breaking processes. Although these problems have been recognized by many investigators, a substantial number of papers lack sufficient accuracy. This accuracy problem appears to be more severe for heteroatom-rich species than for other systems, in particular for systems with adjacent heteroatoms. However, DFT calculations were found to cope surprisingly well with the geometric parameters of most of these systems.

As is common in heterocyclic chemistry, many studies concern tautomeric equilibria. While quantum chemical calculations are straightforward for the question of the most stable isomer, experiments are sometimes very demanding. Therefore, quantum chemistry can easily provide answers that may require substantial experimental effort. Comparatively few studies concern the investigation of entire reaction paths. This is much more demanding than computing a limited number of tautomers, of course, but usually provides a very detailed picture of the reaction mechanism. In certain cases, it was only possible to judge the nature of a chemical reaction on the basis of quantum chemical calculations.

Most studies concerning pyrimidines originate from biochemical questions. Since these systems are dominated by hydrogen-bonding and/or dispersion contributions, methods beyond the Hartree–Fock level are mandatory. The success of quantum chemical studies in this field is impressive and many effects could be explained on the basis of these theoretical investigations.

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ADVANCES IN HETEROCYCLIC CHEMISTRY, VOL. 81

The Chemistry of 2(5*H*)-Furanones

AHMED HASHEM

Department of Chemistry, Ain Shams University, Abassia, Cairo, Egypt

ERICH KLEINPETER

Institut für Organische Chemie und Strukturanalytik, Universität Potsdam, D-14415 Potsdam, Germany

I. Introduction

Furanones, previously named butenolides, are classified into three main types: the 2(3*H*)- **1,** 2(5*H*)- **2,** and the 3(2*H*)-furanones **3** (76CRV625).

Of these, the 2(5*H*)-furanones **2** are perhaps the compounds having the most interesting synthetic and biological importance. The synthesis and properties of compounds **2** have recently attracted much attention. The 2(5*H*)-furanone fragment is present in a wide variety of biologically active natural products (84MI1); moreover these furanones possess utility as valuable synthetic intermediates (86T3715).

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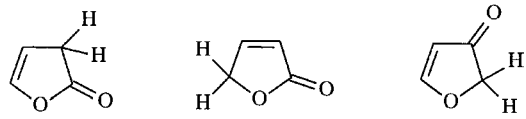


1 **2** **3**

SCHEME 1A

Several reviews deal with the chemistry of these unsaturated lactones (64CRV-353; 68RCR254; 76CRV625; 77UK1250; 82CSR75). Synthetic approaches to these compounds have recently been reviewed (94COS287; 95COS133).

In the present review we emphasize (1) the recent developments in the synthesis of 2(5*H*)-furanones, covering the last six years (1995–2000), and (2) reactions of these compounds, as reported in the period from 1980–2000.

II. Synthesis

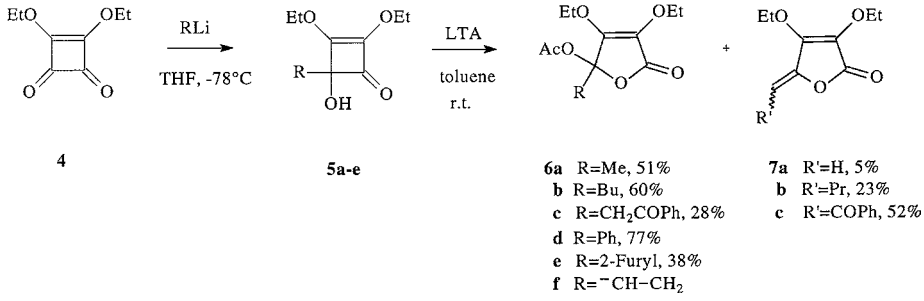
Owing to their frequent occurrence in natural products and their synthetic utility, 2(5*H*)-furanones are important synthetic targets and intermediates. In considering the methods for the preparation of these compounds, we will emphasize the recent developments in this area.

A. From Cyclobutenone Derivatives

Cycloalkoxy radical intermediates are readily generated from a parent alcohol by various methods (e.g., nitrite ester photolysis, hypohalite thermolysis, lead tetraacetate oxidation) (83MI1). Once formed, reactive cycloalkoxy radicals undergo β-scission to produce a carbonyl compound and a new carbon-centered radical.

A number of hydroxycyclobutenones **5,** obtained from the diethoxy diketone **4** and organolithium reagents (88JOC2477; 88JOC2482), were subjected to oxidation with lead tetraacetate (95JA9653). Ring enlargement occurred to give a mixture of 5-acetoxy- and 5-methylene-2(5*H*)-furanones **6** and **7** (Scheme 1).

A possible mechanism for the formation of the furanones **6** and **7** is illustrated in Scheme 2. The initial alkoxy radical generated from the alcohol **5** and lead tetraacetate (LTA) undergoes β-scission to produce the acyl radical intermediate **9.** Subsequent cyclization to **10** proceeds through attack of the radical at the carbonyl oxygen. The resulting Pb(IV) intermediate **11** finally collapses via the reductive

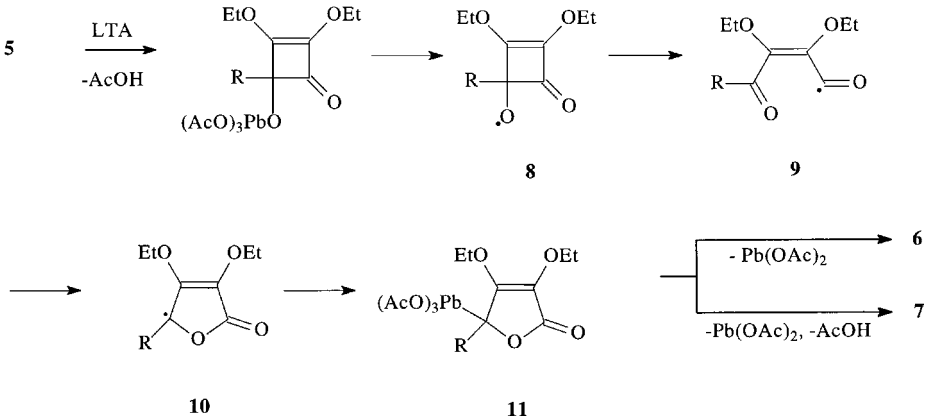


SCHEME 1

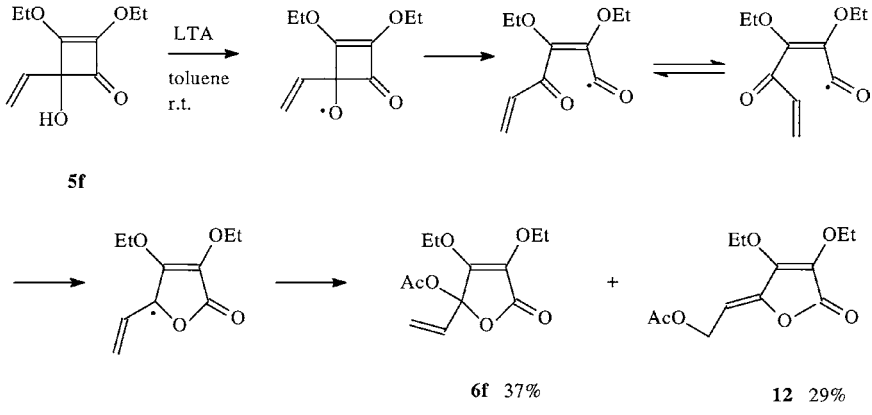
elimination of Pb(II) acetate to give the acetoxyfuranone **6,** which can further eliminate acetic acid to give the 5-ylidenefuranone **7.**

In the mechanism just described, the ring-opened acyl radical intermediate reacts intramolecularly with the carbonyl double bond, although for **5d** it is possible that the phenyl group participates in 6-*exo*-trig cyclization (91MI1). To obtain further insight into the process, another typical mode of cyclization, 5-*exo*-trig, was examined using the 4-vinyl derivative **5f.** As depicted in Scheme 3, no cyclopentenediones, which are the 5-*exo*-trig cyclization products, were obtained. This selectivity implies that 5-*endo* cyclization involving the carbonyl terminus is a favorable process.

Recently, the ring enlargement of 4-hydroxy-2-cyclobutenones **5** was promoted by $PhI(OAc)_2$, a popular and accessible hypervalent iodine reagent (99JOC8995). Thus, when **5a–c** (R = Me, Bu, Ph) were treated with a slight excess of $PhI(OAc)_2$ in dichloromethane at room temperature, the 5-acetoxy-3,4-diethoxyfuranones **13**



SCHEME 2



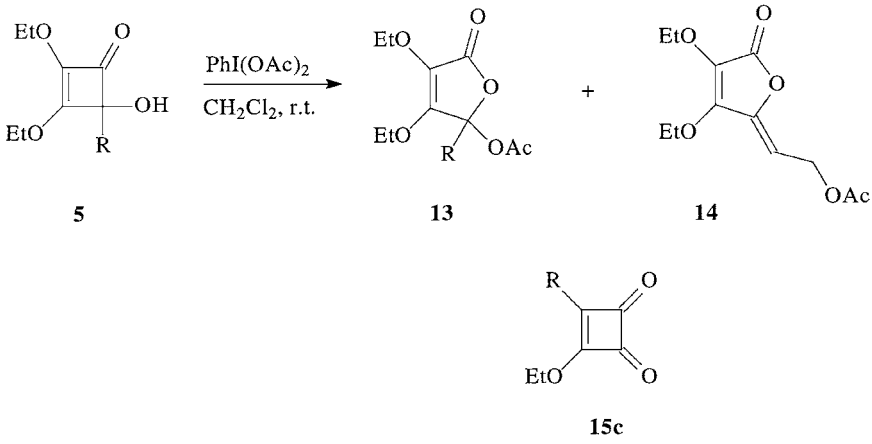
SCHEME 3

were obtained (99JOC8995). The vinyl derivative **5d** (R = CH=CH_2) gave, in addition to the 5-vinylfuranone **13d,** another product which was proved to be (*Z*)-5-ethylidenefuranone **14.** In the phenyl-substituted case, 4-ethoxy-3-phenyl-3-cyclobutene-1,2-dione **15c** was obtained as a byproduct (Scheme 4) (99JOC8995).

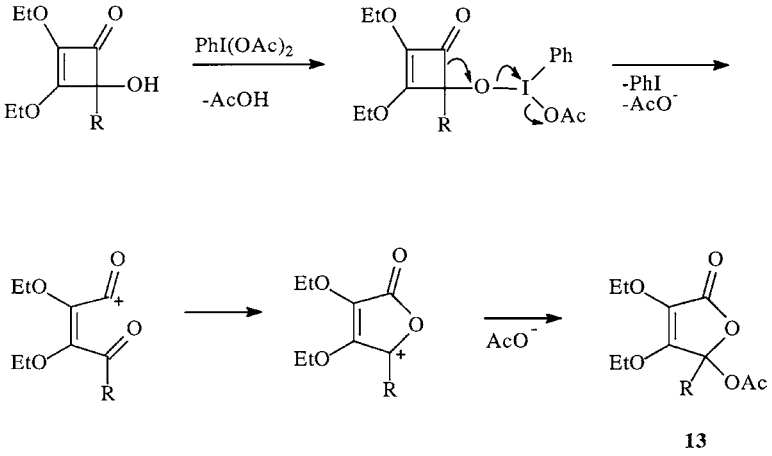
A plausible mechanism for the formation of **13** is illustrated in Scheme 5.

B. From Acetylenic Compounds

Winterfeldt reported a triphenylphosphine-catalyzed lactone formation from benzaldehyde and dimethylacetylenedicarboxylate in less than 20% yield



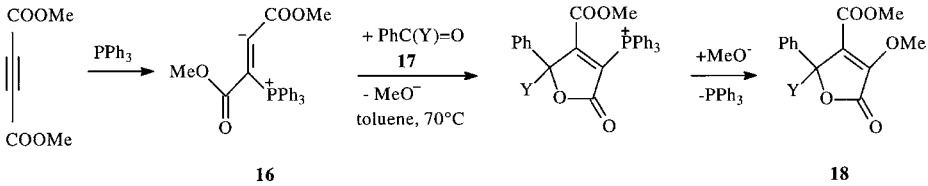
SCHEME 4



SCHEME 5

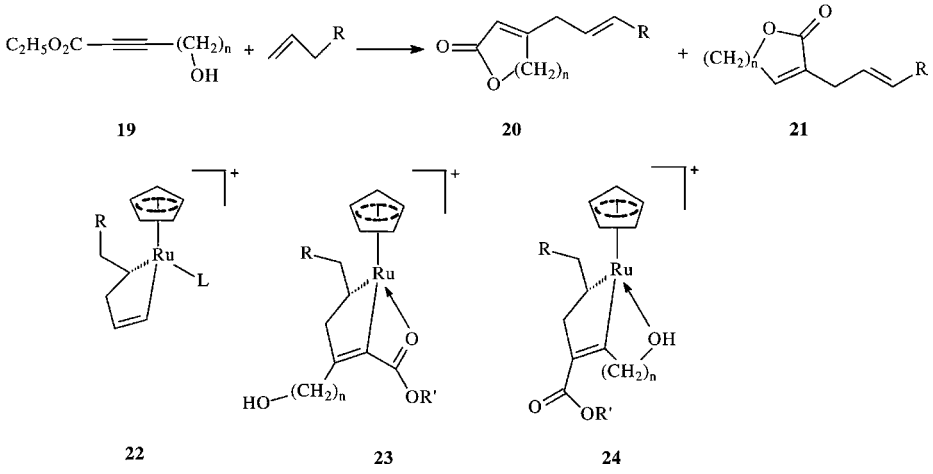
(66CB1558). The proposed mechanism includes a zwitterionic intermediate **16** (Scheme 6). Other investigators (96JOC4516) used activated carbonyl compounds, e.g., α-keto esters, α-keto nitriles, and α,α,α-trifluoroacetophenone, as trapping agents for this zwitterionic intermediate **16.** Thus, treatment of the activated carbonyl compounds **17** with dimethylacetylenedicarboxylate and triphenylphosphine afforded the corresponding 2(5*H*)-furanones **18** (Scheme 6) (96JOC4516).

The formation of **18** was also shown to involve the intermediate formation of the zwitterion **16,** which further undergoes a nucleophilic attack on the strongly electrophilic carbonyl compound (96JOC4516). The addition of alkenes to hydroxy-2-alkynoates **19** in an Alder ene-type mode in the presence of ruthenium catalysts produced the furanones **20** and **21** (Scheme 7) (95JA1888). Among various ruthenium complex catalysts, CpRu(COD)Cl appears to be the most effective for this reaction. The Ru-catalyzed reaction of terminal alkenes and simple acetylenes is believed to involve a metallocycle such as **22.** If L is a weakly coordinated ligand, its displacement by either the carbonyl oxygen as in **23** or hydroxy oxygen as in



Y = COOMe, CN, CF_3

SCHEME 6



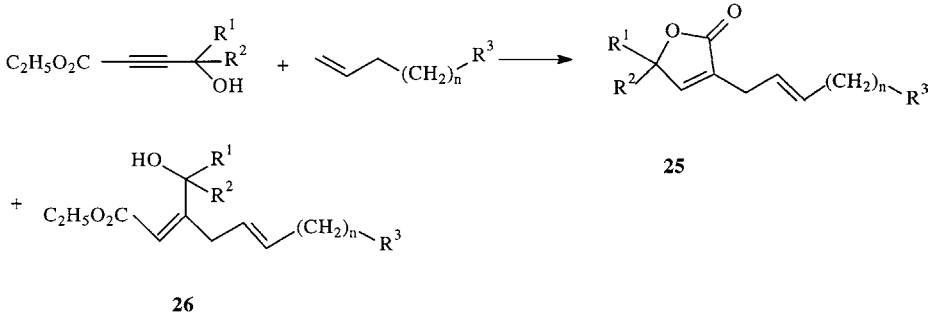
SCHEME 7

24 of the hydroxyalkynoate substrate **19** may be expected to play a significant role in determining the regioselectivity (95JA1888).

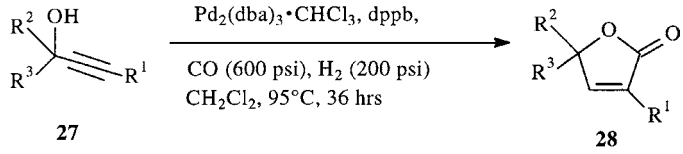
The generality of this protocol was established with a variety of terminal alkenes and alkynes (Scheme 8) (95JA1888). The initial α-alkylation product always spontaneously lactonizes to **25,** whereas the β-alkylation product **26** was always isolated uncyclized.

In 1991, El-Ali and Alper reported the cyclocarbonylation reaction of terminal propargyl alcohols with formation of 5,5-disubstituted 2(5*H*)-furanones using $Pd(dba)_2$ and 1,4-bis(diphenylphosphino)butane (dppb) (91JOC4099). However, this reaction was not applicable to internal alkynols.

Recently, a modified procedure for this reaction was reported, extending its utility to internal alkynols with alkyl, phenyl, and vinyl units (R^1 = H, alkyl, Ph,



SCHEME 8



27 **28**

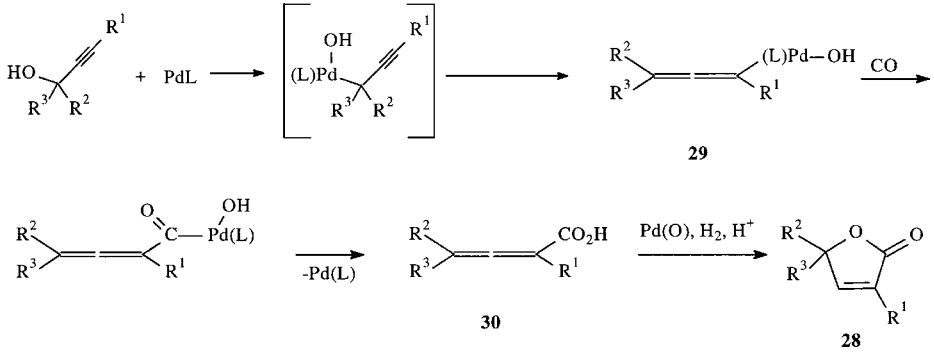
SCHEME 9

vinyl; R^2, R^3 = H or alkyl) attached to one propargylic carbon atom (Scheme 9) (97JOC5684).

The proposed mechanism for this cyclocarbonylation was shown to involve the insertion of Pd(0) species into the C—O bond of the substrate followed by rearrangement to the allenylpalladium intermediate **29** (as proposed for alkyl systems). Insertion of CO and subsequent reductive elimination may lead to the 2,3-dienoic acid **30,** which undergoes cyclization, catalyzed by trace quantities of an acid present in the solvent, to the 2(5*H*)-furanone **28** (Scheme 10) (93JOC1538).

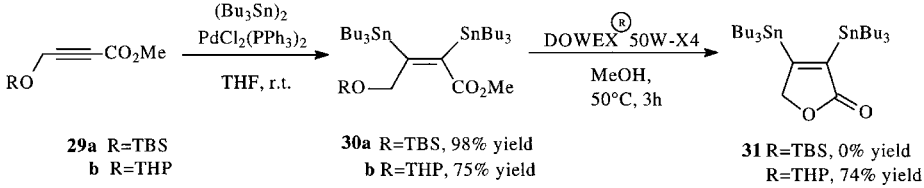
Butynoate **29a** reacted with hexabutylditin in the presence of $PdCl_2(PPh_3)_2$ to give the 2,3-bis(tributylstannyl)acrylate **30a** in nearly quantitative yield. But **30a** could not be converted to the 3,4-bis(tributylstannyl)-2(5*H*)-furanone **31.** However, the analogous THP-protected bis(stannate) **30b** prepared by a similar procedure reacted with acidic ion-exchange resin in methanolic solution; the hydroxylic group of **30b** was deprotected and cyclization occurred to furnish the furanone **31** (Scheme 11) (99JOC328).

The same authors were also able to prepare mixed stannylsilylfuranones. Thus, the ester **29b** reacted with (tributylstannyl)trimethylsilane in the presence of $PdCl_2$-$(PPh_3)_2$ to give a mixture of the acrylates **32a** (X = $SnBu_3$, Y = $SiMe_3$) and **32b** (X = $SiMe_3$, Y = $SnBu_3$) which were inseparable using routine purification



29 **30** **28**

SCHEME 10



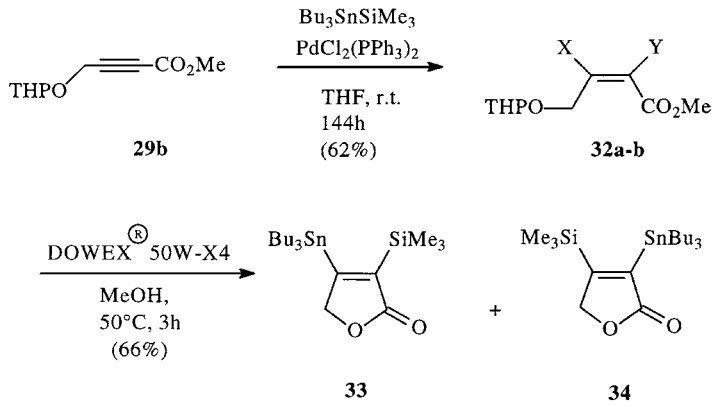
SCHEME 11

methods. This mixture was deprotected and cyclized to the 2(5*H*)-furanones **33** and **34** (Scheme 12) (99JOC328).

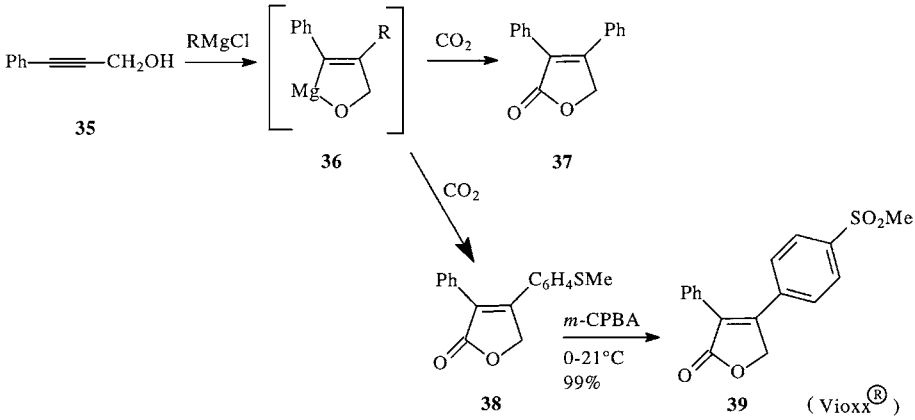
Recently, Forgione and coworkers reported the synthesis of some 2(5*H*)-furanones of medicinal interest by the magnesium-mediated carbometallation of phenylpropargyl alcohol **35** (00TL17). Thus, the alcohol **35** reacted with phenylmagnesium chloride to form a chelate **36** (R = Ph) which, on exposure to carbon dioxide, gave the 3,4-diphenylfuranone **37.** Modification of this protocol in which the propargyl alcohol **36** reacted directly with 4-methylthiophenylmagnesium chloride (R = $MeSC_6H_4$) and further with carbon dioxide afforded the furanone **38.** The latter, on oxidation with *m*-chloroperbenzoic acid, gave the sulfone **39,** the new Merck antiinflammatory drug (Vioxx^R)(Scheme 13) (00TL17).

C. FROM CARBONYL COMPOUNDS

3-Functionalized 5-alkoxymethyl- and 5-phenoxymethyl-2(5*H*)-furanones **44**–**46** were obtained starting from 3-alkoxy- and 3-phenoxy-2-hydroxy ketones **40** (98T1801). Condensation of the hydroxy ketones **40** with a slight excess of diethyl malonate **41** (Z = COOMe; R^3 = Me), ethyl cyanoacetate **42** (Z = CN; R^3 = Me),



SCHEME 12

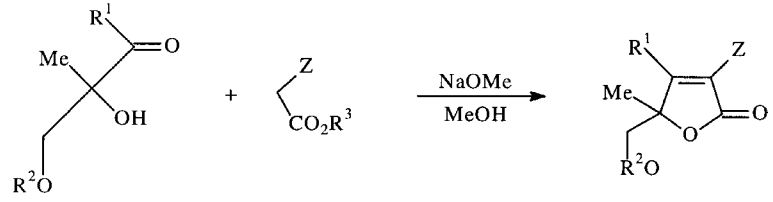


SCHEME 13

or ethyl acetoacetate **43** (Z = COMe; R^3 = Et) in the presence of sodium methoxide in methanol afforded 3-functionalized 5-alkoxymethyl- and 5-phenoxymethyl-2(5*H*)-furanones **44–46** (Scheme 14) (98T1801).

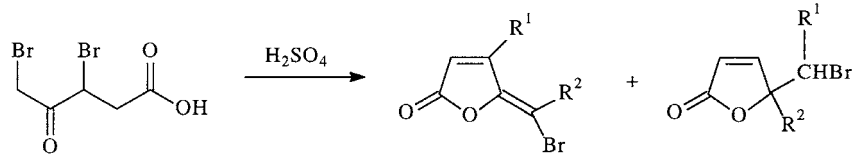
It has been reported that concentrated H_2SO_4 (98%) promotes conversion of 3,5-dibromolevulinic acid **47** into 4-bromo-5-(bromomethylene)-2(5*H*)-furanones **48** (R^1 = Br; R^2 = H) along with minor products, while similar treatment using 20% oleum gives the isomeric 5-(dibromomethylene)-2(5*H*)-furanone **49** (R^1 = H; R^2 = Br) as the major product (63AJC165). Spectroscopic data and chemical structures were not provided for the minor substances, but the formation of the major product was explained on the basis of the enol-lactonization process followed by oxidation (63AJC165).

This reaction was reinvestigated by Manny and coworkers, who stated that treatment of 3,5-dibromolevulinic acid **47** with concentrated H_2SO_4 (98%) gives a mixture of 4-bromo-5-(bromomethylene)-2(5*H*)-furanone **48** (54%), 5-(dibromomethylene)-2(5*H*)-furanone **49** (8%), and 5-(bromomethylene)-2(5*H*)-furanone **50** (R^1 = H; R^2 = Br; 2%) along with small amounts of the beckerelide derivatives **51**



40 **41-43** **44-46**

SCHEME 14



47 **48-50** **51-53**

SCHEME 15

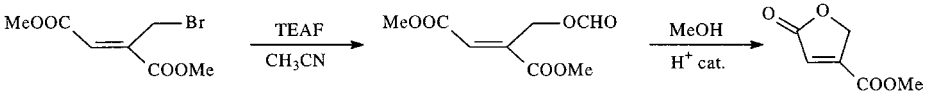
($R^1 = H$; $R^2 = OH$), **52** ($R^1 = Br$; $R^2 = OH$), and **53** ($R^1 = H$; $R^2 = Br$), so called because of their similarity to natural beckerelides (Scheme 15) (97T15813).

The 4-methoxycarbonyl-2(5*H*)-furanone **56** was obtained using a simple two-step synthesis (97TL813) consisting of the formylation of dimethyl-2-(bromomethyl)furmarate **54** followed by the acid-catalyzed transesterification in methanol. The formylation was realized with two molar equivalents of the triethylammonium formate reagent (TEAF) with the composition of $2(Et_3N)_2$, 5(HCOOH) to afford the corresponding allylic formate **55** in 80% yield. The latter undergoes transesterification in methanol in the presence of concentrated HCl, affording finally the furanone **56** (Scheme 16) (97TL813).

D. FROM OTHER HETEROCYCLES

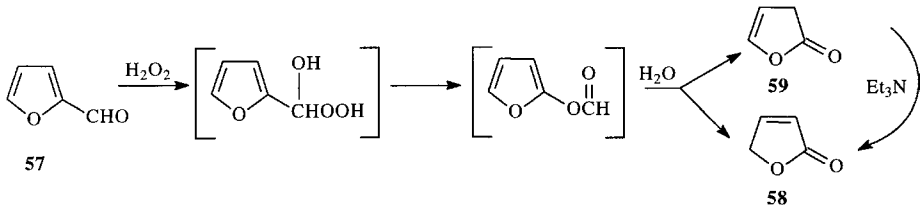
The 2(5*H*)-furanone **58** has been prepared by oxidation of furfural **57** with hydrogen peroxide in the presence of formic acid (78KG1314; 85S786), thiourea (89GEP274333), or cobaltous oxide (75SUP470516). Although these methods are one-pot reactions, they are deficient in some respects: The reagents are expensive, the handling is inconvenient, and, perhaps most importantly, the yield is low (96OPP215). A more convenient modified method was described which involved refluxing furfural and hydrogen peroxide in dichloroethane and sodium sulfate. This oxidation afforded a mixture of the 2(5*H*)-furanone **58** and 2(3*H*)-furanone **59** which were separated by distillation. Isomerization of **59** with triethylamine afforded the 2(5*H*) isomer **58** in high yield (Scheme 17) (96OPP215).

Casuscelli and colleagues (95T8605) reported the conversion of the 3-carboxybutyl-substituted isoxazolidines **60** (R^1 = alkyl, CH_2OH; $R^2 = H$, Me) into 3-methylamino-2(5*H*)-furanones **61** by the activity of sodium hydride in tetrahydrofuran



54 **55** **56**

SCHEME 16

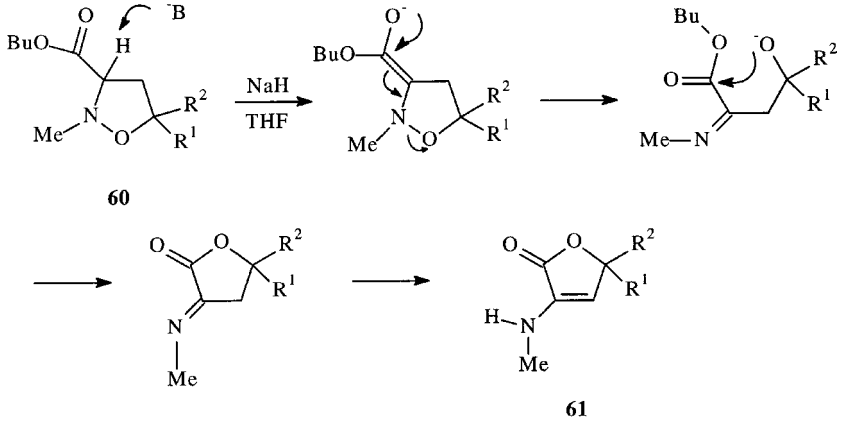


SCHEME 17

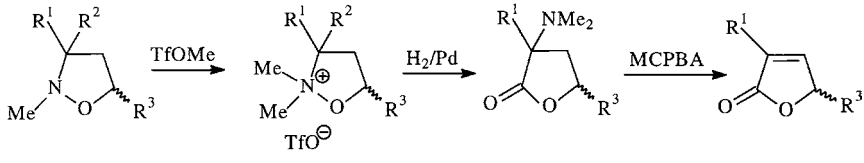
(THF) at room temperature (Scheme 18) (95T8605). The proposed mechanism for this conversion involves the abstraction of H3 by basic attack of NaH to give an enolate anion, which, via ring opening, affords the 2(5*H*)-furanone **61** by a straightforward intramolecular nucleophilic acyl substitution (Scheme 18) (95T8605).

The conversion of the isoxazolidines **62** (R^1 = alkyl; R^2 = COOEt; R^3 = Me, CH_2OH, CH_2CH_2Ph) into the 2(5*H*)-furanones **65** was performed by a three-step sequence (Scheme 19) (98T5695): (1) treatment with methyl trifluoromethanesulfonate in carbon tetrachloride to give the epimeric isoxazolidinium salts **63;** (2) subsequent hydrogenolysis with 10% palladium on activated carbon yielding the epimeric α-amino-γ-lactones **64;** (3) formation of the 3,4-double bond via the Cope elimination of the transient *N*-oxides obtained by treatment of **64** with *m*-chloroperbenzoic acid (MCPBA) in dry dichloromethane. The Cope elimination occurred regioselectively to give the furanones **65;** the regioisomeric γ-methylene lactones were not formed.

In an alternative route, the isoxazolidine **62a** (R^1 = *n*-pentyl; R^2 = COOEt; R^3 = Me) was directly cleaved by hydrogenolysis to the α-methylaminolactone, which by subsequent treatment with CH_3I and Hofmann elimination afforded



SCHEME 18

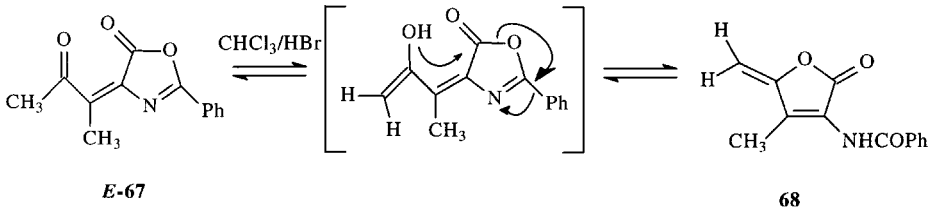


SCHEME 19

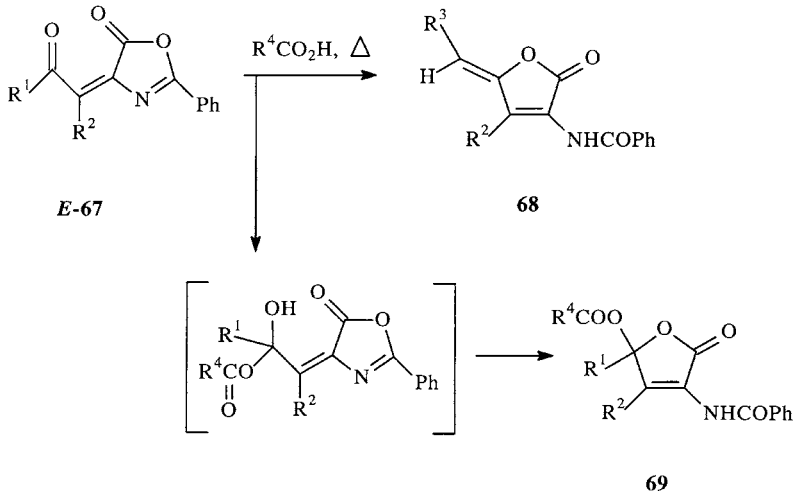
the furanone **65a** (98T5695); however, the yield was found to be poorer than in the previous case (98T5695). Oxazolones are known to be ideal synthons to obtain heterocycles containing an α-amino-substituted lactone moiety (86MI1). The transformation of the azlactones **67** into the furanones **68** was achieved both with acid and base catalysis (97T1843). Thus, for example, when the azlactone **67** reacted with anhydrous HBr in chloroform, the 3-benzylamino-5-alkylidene-2(5*H*)-furanone **68** was obtained in satisfactory yields. The formation of **68** was explained on the basis of the initial acid-catalyzed enolization of the keto group of the azlactone to give an enol intermediate, which, through a translactonization reaction, is transformed into the final products (Scheme 20) (97T1843).

When the translactonization reaction of **67** (R^1, $R^2 = Me$, Et) was conducted in acetic acid ($R^4 = Me$) as a reaction solvent, at the boiling point, somewhat different results were obtained: A mixture of products identified as the furanones **68** and the 4-benzoylamino-5-oxo-2,5-dihydrofuran-2-yl acetates **69** were obtained (Scheme 21) (97T1843).

Refluxing the oxazolone **67a** (R^1, $R^2 = Me$) in propionic acid ($R^4 = Et$) gave, in addition to **68a,** the propionate **69d,** confirming that the acyl group originates from the acid used as a reaction solvent. If the reaction was started with the isomer *Z*-**67a,** the same products were obtained but in lower yields. This behavior was ascribed to the unfavorable stereochemistry of the double bond in the starting material (97T1843). Different results were obtained starting from the azlactone *E*-**67b** ($R^1 = R^2 = Et$) under basic conditions (97T1843); only the furanone *Z*-**68b** was isolated. The formation of this compound was explained on the basis of translactonization reaction of the enolate **70b** which is in equilibrium with the primary deprotonation product **70a.** The existence of this equilibrium was confirmed both

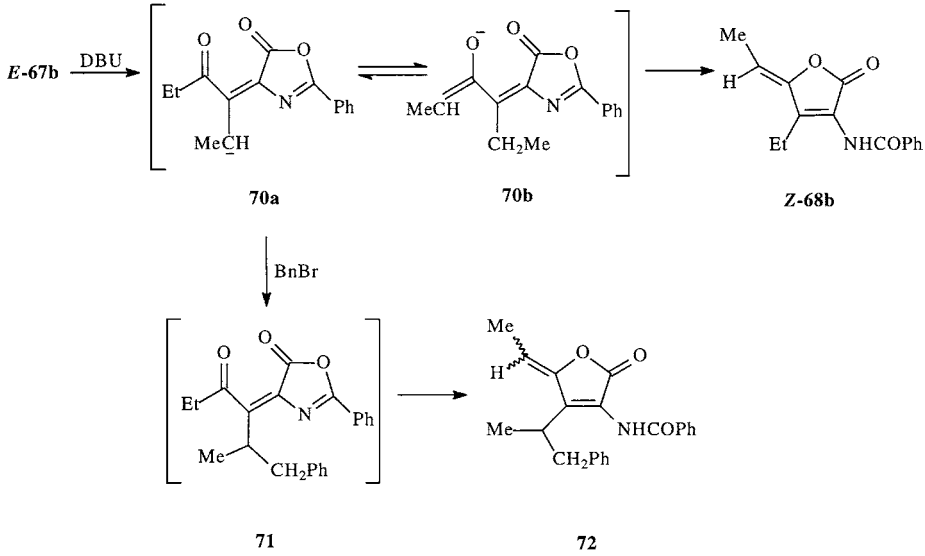


SCHEME 20



SCHEME 21

by the red color of the reaction mixture after addition of 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU) and by the addition of benzyl bromide. The latter reagent acted as an alkylating agent and afforded directly a 2 : 1 mixture of *E* - and *Z*-furanones **72,** which were formed by translactonization reaction of the azlactone intermediate **71,** alkylated at the allylic carbon (Scheme 22) (97T1843).



SCHEME 22

E. Biologically Active 2(5*H*)-Furanones

Several chlorinated 5-hydroxy-4-methyl-2(5*H*)-furanones **73** (HMFs) and mucochloric acid 3,4-dichloro-5-hydroxy-2(5*H*)-furanone **74** (MCA) have been identified as byproducts of the chlorine disinfection of drinking water and of chlorine bleaching of pulp [93EST(27)1811]. These compounds have been shown to generate mutagenicity in the *Salmonella typhinurium* assay; 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5*H*)-furanone **75** (MX) proved to be an extremely potent bacterial mutagen [90MR(240)109].

Franzen and Kronberg (95TL3905) reported an efficient synthesis of **75** (MX) and other chlorinated HMFs. This procedure also allowed the synthesis of ^{13}C- and ^{14}C-labeled HMFs and MCA. The corresponding starting material **76** (* indicating the labeled carbon atom) was prepared from bromoacetic acid, bromoacetic acid-2-^{13}C, and bromoacetic acid-2-^{14}C according to Fieser and Fieser (67MI1). The steps involved in these syntheses are illustrated in Scheme 23 (95TL3905).

The fimbrolide **83,** isolated in 1977 from the red marine algae *Delisea fimbriata,* is a halogenated 2(5*H*)-furanone with interesting antifungal and antimicrobial properties (77TL37; 77TL41). It has been synthesized from methyl-2-butyl-2,3-pentadienoate **82** as starting material according to the steps illustrated in Scheme 24 (95JOC1814).

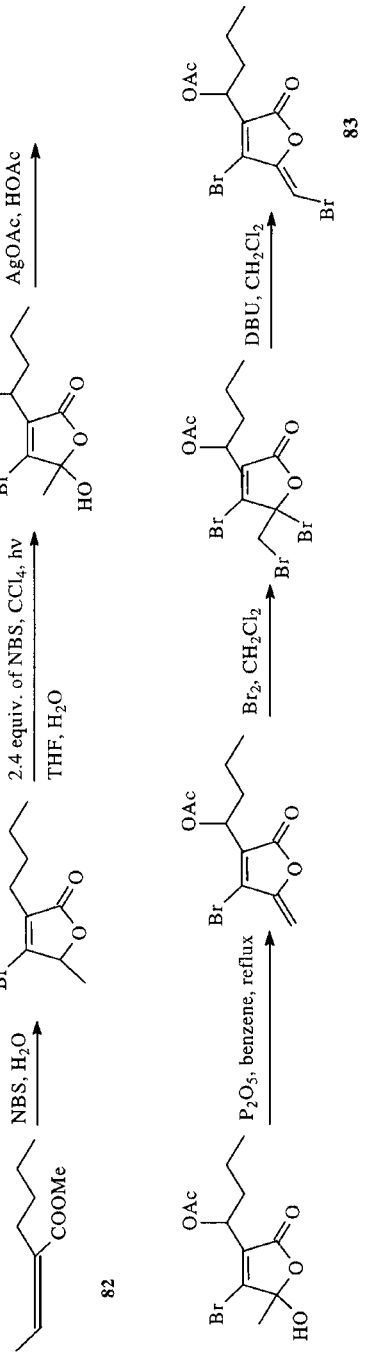
The 2(5*H*)-furanone (*R*)-(+)-umbelactone **89** has been isolated from the alcoholic extracts of *Memycelon umbelatum Brum* (78P1663). The crude extracts of this plant have shown antiviral, antiamphetamine, and spasmolytic activity (68IJEB241); consequently, the synthesis of **89** has been the subject of synthetic interest. This umbelactone was synthesized in five steps starting from the (*S*)-acid **84** (96TA1281), which was converted into the amide **85** by reaction with *N,O*-dimethylhydroxyamine hydrochloride in pyridine. Subsequent reaction of the amide **85** with excess methylmagnesium chloride in THF afforded the (*S*)-ketone **86** in 86% yield. Treatment of the latter ketone with bis(2,2,2-trifluoroethyl)-(methoxycarbonylmethyl)phosphonate and potassium bis(trimethylsilyl)amide in the presence of 18-crown-6 gave a mixture of the *Z*- and *E*-esters **87** and **88.** Finally, the removal of the isopropylidene protecting group and lactonization of the *Z*-ester **88** by stirring in an ethanol solution in the presence of an acidic ion exchange resin (Amberlyst XN-1010) afforded, directly, the *R*-(+)-umbelactone **89** (Scheme 25) (96TA1281).

The 4-aryl-2(5*H*)-furanone unit proved to be present in many naturally occurring (91JOC6275) and medicinally important compounds (93JHC1581). Examples are the potent antibiotics rubrolide A–F **90a–f,** isolated by Miao and Andersen from the colonial tunicate *Ritterela rubra* (Scheme 26) (91JOC6275).

The more utilitarian means for installing an aryl substituent in position 4 onto the 2(5*H*)-furanone ring, the Suzuki-type cross-coupling of arylboronic acid with

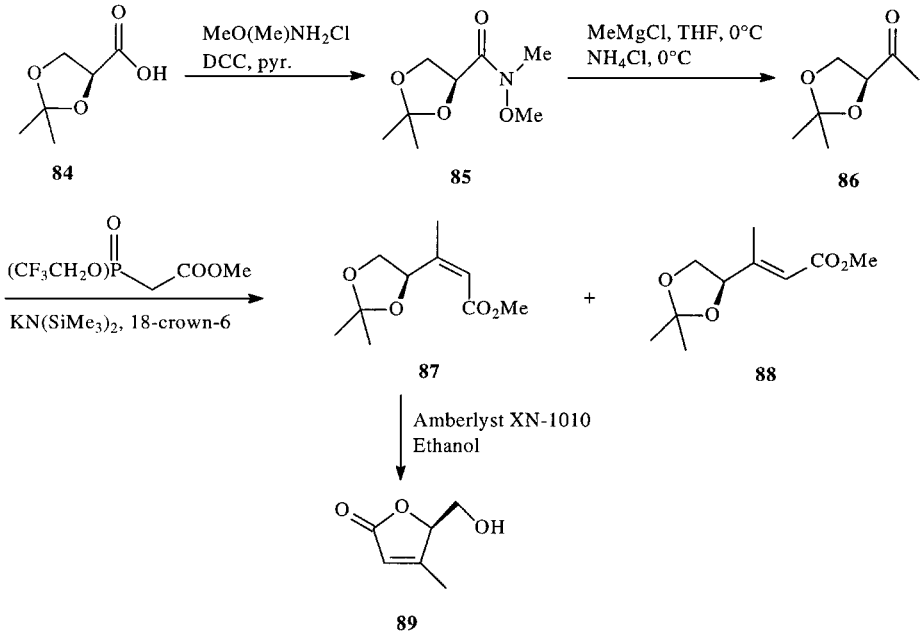
Ph3P=CHCOOMe + Cl2CH-C-R
THF
50-70%
76
77
77a R=H
b R=CH3
c R=CH2Cl
d R=CHCl2
(a) Cl2/CCl4/AlCl3 b) Cl2/CCl4/AlCl3
UV 1-2 h UV 1-2 h
NEt3/CH2Cl2 70%
77a
77b-d
(b) Cl2/CCl4/AlCl3
UV 1-2h
70%
78
NEt3/CH2Cl2
70-90%
79
HCOOH/H2SO4/H2O
60-80%
R=Cl 74 (MCA)
R=CH3 80 (MCF)
R=CH2Cl 81 (CMCF)
R=CHCl2 75 (MX)

SCHEME 23



82 83

SCHEME 24

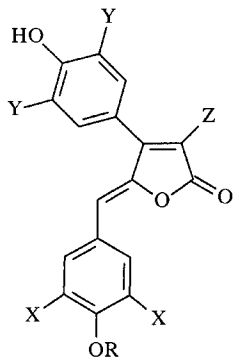


84 **85** **86** **87** **88** **89**

SCHEME 25

suitably activated furanones seems to be the most convenient synthesis of a wide variety of 4-aryl-2(5*H*)-furanones **92** (Scheme 27) (81SC513).

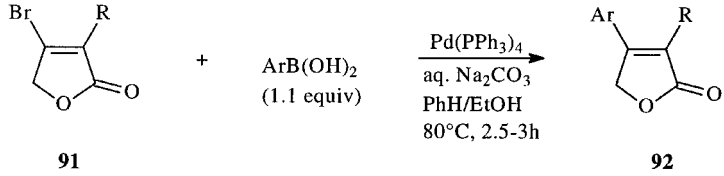
Recently, this methodology was used for the straightforward synthesis of the rubrolides **90c** and **90e :** The furanone **92b** (Ar = C_6H_4—OMe) was treated with the appropriate aldehyde **93** or **95** in the presence of diisopropylamine, followed *in situ*



90

90a R=Z=H, X=Y=Br
b R=H, X=Y=Br, Z=Cl
c R=Y=Z=H, X=Br
d R=X=Z=H, Y=Br
e R=X=Y=Z=H
f R=Me, X=Y=Z=H

SCHEME 26



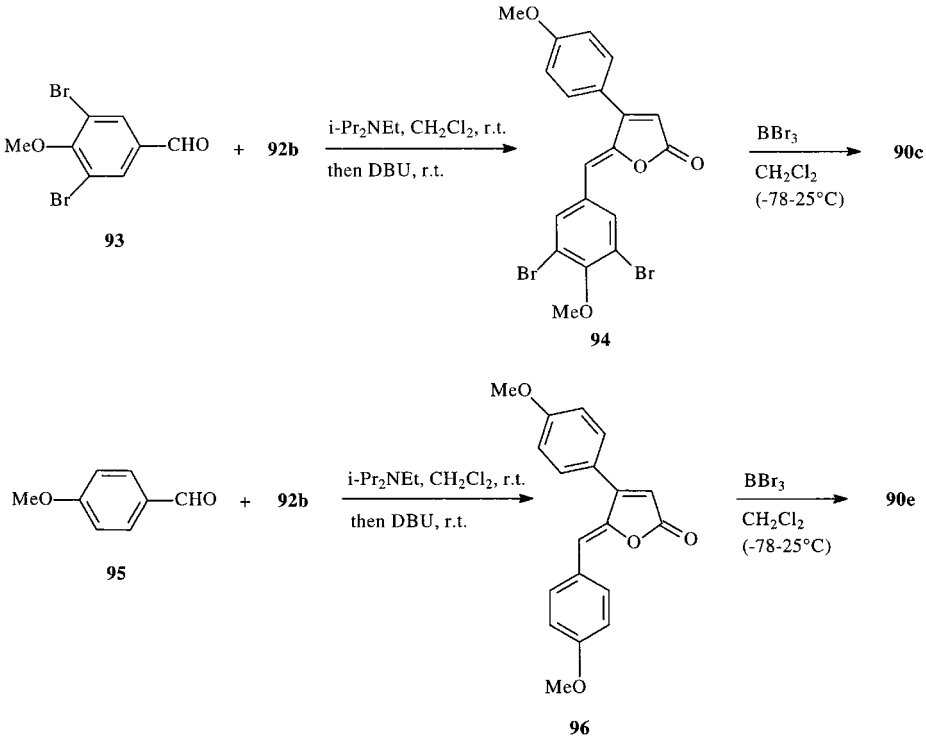
91 **92**

R= H, Ar = Ph, 4-MeOC$_6$H$_4$, 3-ClC$_6$H$_4$, 4-BrC$_6$H$_4$, 1-naphthyl, 2-thienyl, 3-thienyl
R= Me, Ar = Ph, 4-BrC$_6$H$_4$

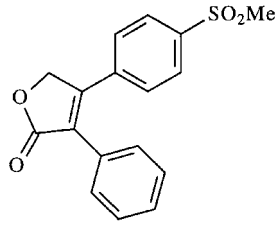
SCHEME 27

by DBU-mediated β-elimination to give the corresponding *Z*-arylmethylenefuranone **94** or **96** (Scheme 28) (98TL7665). Exposure of **94** to boron trifluoride in dichloromethane afforded the rubrolide **90c** and demethylation of **96** gave the rubrolide **90e.**

Cyclooxygenase is known to exist in two distinct isoforms: COX-1 and COX-2 (92JBC21438). The constitutive isoform COX-1 is present in a variety of tissues and is thought to be important in maintaining normal physiological functions such



SCHEME 28

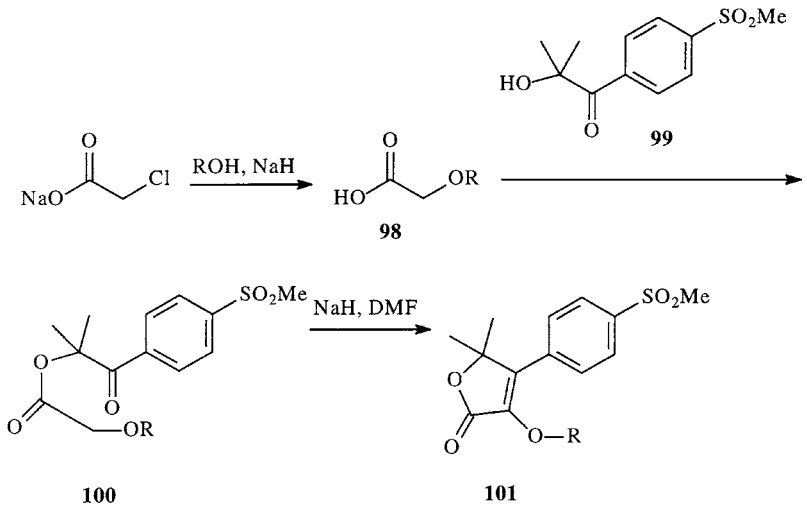


97

SCHEME 29

as gastric cytoprotection. COX-2 is the inducible isoform that appears to play a major role in the inflammation cascade through the production of inflammatory prostaglandins (93BBR494). It is well accepted that a selective COX-2 inhibitor will have the therapeutic effects of NSAIDs without the side effects associated with nonselective COX inhibitors. It was shown that the 2(5*H*)-furanone **97** (rofecoxib in Scheme 29) is a potent COX-2 inhibitor (99BMC1773). This compound showed good efficacy in animal models of inflammation and effective clinical efficacy in both dental pain and osteoarthritis studies (99JCT336).

It has been thought that when an oxygen atom is inserted between the phenyl group and the furanone moiety, the activity may be enhanced. A series of alkoxy-lactones **101** were synthesized according to the procedure described by Scheme 30 (99BMC2207). Alcohols are condensed with sodium chloracetate to provide the

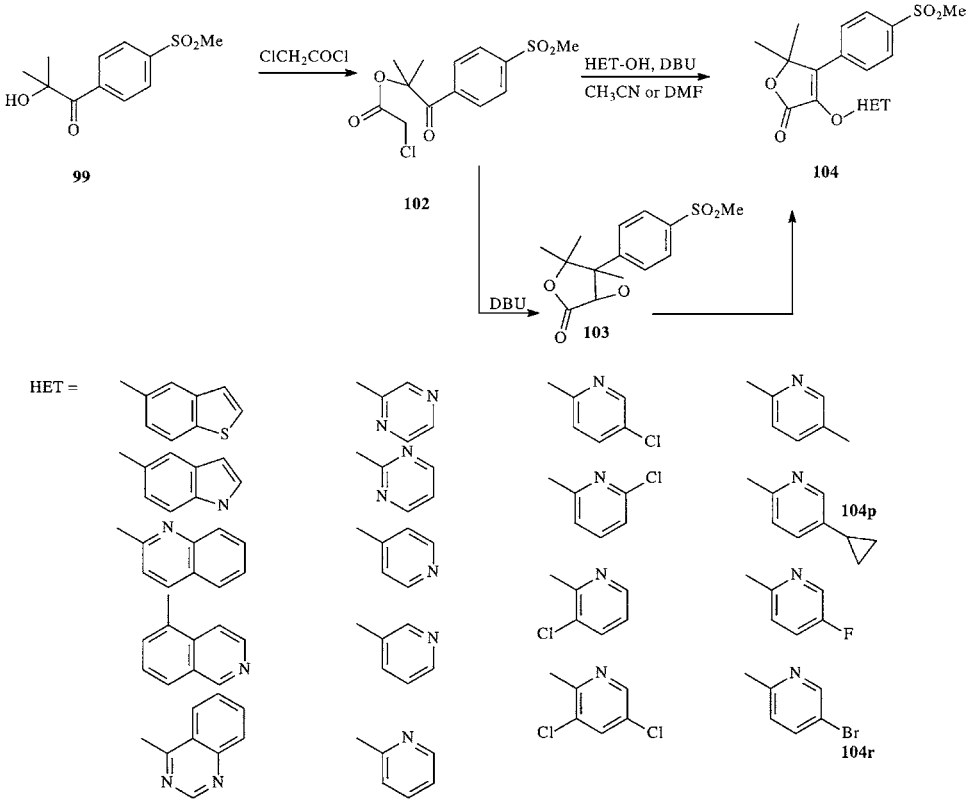


R= cyclohexyl; cyclopentyl; cyclobutyl; cyclopropyl; isoamyl; Me; Et; isopropyl

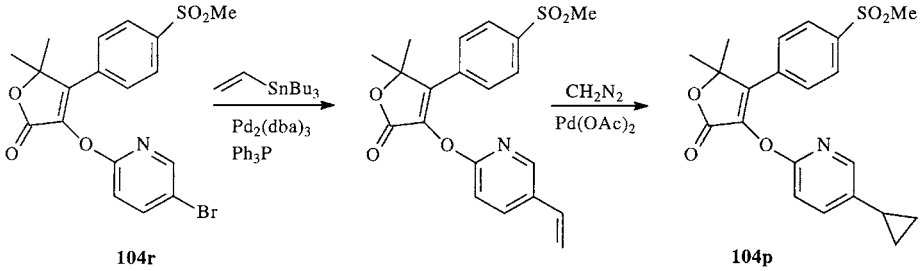
SCHEME 30

alkoxy acid **98** which is coupled with the tertiary alcohol **99** to give the ester **100.** The latter ester was treated with NaH in DMF or DBU in CH_3CN to provide the furanones **101.**

Of the above furanones, 5,5-dimethyl-3-(2-propoxy)-4-(4-methanesulfonylphenyl)-2(5*H*)-furanone **101** (R = isopropyl-DFP) was shown to have excellent pharamacokinetic properties. It was considered one of the most selective COX-2 inhibitors reported. Its high selectivity makes this compound potentially very useful in chronic dosing situations (99BMC2207). As a diversification of the furanone template, a number of compounds **104,** containing various oxygen-linked heterocycles at position 3, were synthesized according to the steps outlined in Scheme 31 (99BMC3187). The tertiary alcohol **99** was coupled with chloroacetyl chloride to give compound **102.** Treatment of **102** with DBU gives the epoxide **103.** Displacement of the chloride **102** or the epoxide **103** with the appropriate hydroxyheteroaryls followed by *in situ* cyclization and dehydration in the



SCHEME 31



SCHEME 32

presence of DBU in acetonitrile or DMF gave the furanones **104** (Scheme 31) (99BMC3187).

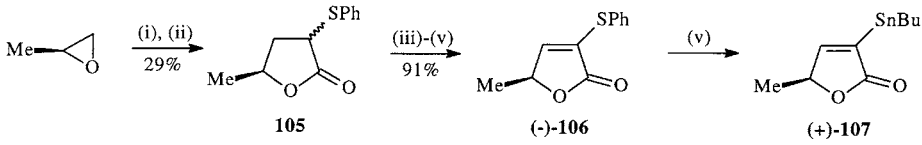
The above procedure was used for the preparation of all compounds except **104p,** which was obtained from **104r** by palladium-catalyzed coupling with tributylvinylstannane followed by palladium-catalyzed cyclopropanation of the resulting vinyl intermediate with diazomethane (Scheme 32) (99BMC3187).

The different furanones **104** were tested for their potency as inhibitors of PGE_2 production both in transfected Chinese hamster ovarian (CHO) cells expressing human COX-2 and in human whole blood. Compound **104r** proved to be an orally active and selective COX-2 inhibitor that is devoid of the ulcerogenic effect at >100 times the dose for antiinflammatory, analgesic, and antipyretic effects (99BMC3187).

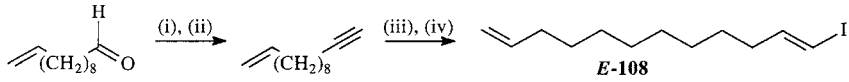
Recently, Richecoeur and Sweeney reported the total synthesis of Hamabiwalactone B **109,** a naturally occurring 2(5*H*)-furanone isolated from the roots of *Litsea japonica,* which grows in the southern part of Japan. The absolute stereochemistry of the single asymmetric center of (+)-hamabiwalactone B **109** was postulated as 5*S* (00T389). Two coupling partners were required to accomplish the total synthesis of **109:** (5*S*)-methyl-3-tributylstannyl 2(5*H*)-furanone **107** and the (E)-iodo-1,11-dodecadiene **108.** The steps followed for obtaining these two partners and hence the synthesis of **109** are outlined in Scheme 33 (00T389).

III. Chemical Reactions

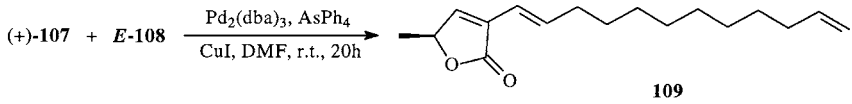
(5*H*)-Furanones are useful building blocks in the synthesis of a variety of organic compounds. In addition, they often serve as valuable synthetic intermediates in the stereoselective construction of substituted γ-butyrolactones via conjugated addition to the α,β-unsaturated carbonyl moiety or catalytic hydrogenation of the double bond (88JOC1560).



Conditions: (i) $PhSCH(Li)CO_2Li$, THF, 0°C; (ii) Benzene, *p*-TSA, Dean-Stark, 3h;
(iii) SO_2Cl_2, CCl_4, 0°C; (iv) LiBr, Li_2CO_3,THF, reflux; (v) Bu_3SnH, VAZO®-88, $PhCH_3$, reflux



Conditions: (i) CBr_4, PPh_3, Zn, CH_2Cl_2, 0°C; (ii) 2BuLi, THF, -78°C to r.t.;
(iii) DIBAL-H, toluene, 60°C; (iv) I_2, -78°C THF

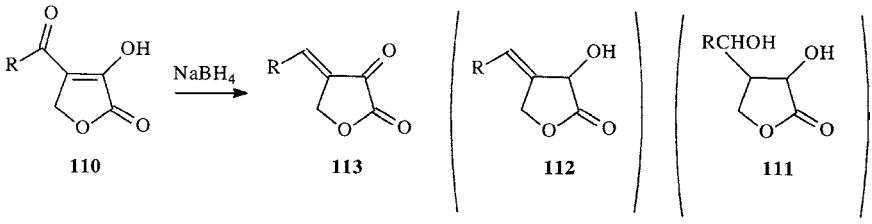


SCHEME 33

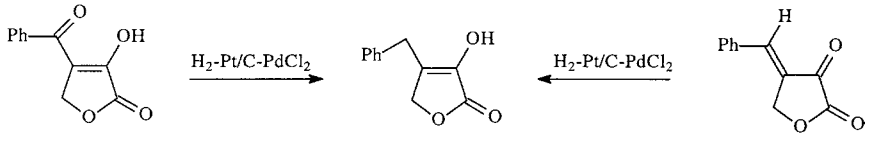
A. REDUCTIONS

When the furanones **110** (R = Ph, *p*-$MeOC_6H_4$, *p*-Cl—C_6H_4) were subjected to reduction using sodium borohydride, neither the glycols **111** nor the allyl alcohols **112** were formed. Instead, the corresponding 4-(arylmethylene)-2,3-(4*H*,5*H*)-furandiones **113** were obtained (Scheme 34) (86JHC199).

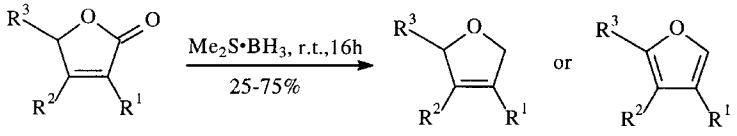
Two isomeric structures can be obtained for these products (*E*-**113** and/or *Z*-**113**). The stereochemistry was conveniently elucidated on the basis of NMR data which showed coupling constant values ^3J(H,CO) consistent with the *E*-isomers only. The formation of **113** was explained to occur via the enolate salts (86JHC199). Catalytic



SCHEME 34



SCHEME 35



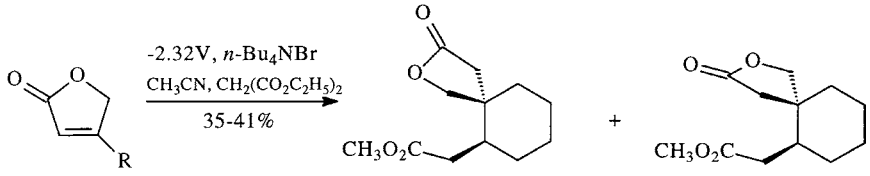
115 **116** **117**

SCHEME 36

hydrogenation of **110a** using platinum on charcoal supported by palladium chloride as a catalyst afforded 4-benzyl-3-hydroxy-2(5*H*)-furanone **114.** The latter product was also obtained from the reduction of **113a** using the same catalyst (Scheme 35) (86JHC199).

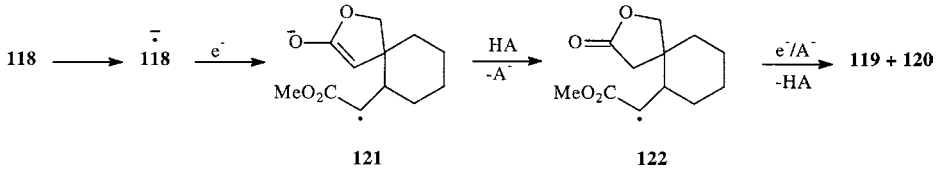
Reduction of 3,5,5-tris-aryl-2(5*H*)-furanones **115** (R^1, R^2, R^3 = aryl) with dimethyl sulfide–borane led to the formation of the 2,5-dihydrofurans **116** in high yields. However, in the case of 3,4-diaryl-2(5*H*)-furanones **115** (R^1, R^2 = aryl; R^3 = H or R^1 = H; R^2, R^3 = aryl), the reduction led to a complicated mixture of products of which only the diarylfurans **117** could be characterized (Scheme 36) (88S68). It was concluded that the smooth conversion of the tris-aryl-2(5*H*)-furanones to the corresponding furan derivatives with the dimethylsulfide–borane complex in high yields could be due to the presence of bulky aryl substituents which prevent addition reaction across the double bond (88S68).

The electroreductive cyclization of the furanone **118** (R = *E*-$(CH_2)_4$CH=CH–COOMe; Scheme 36) using a mercury pool cathode, a platinum anode, a saturated calomel reference electrode, and a degassed solution of dry CH_3CN containing *n*-Bu_4NBr as the electrolyte, gave the spirocyclic lactones **119** and **120** in a ratio 1.0 : 1.1 (Scheme 37) (91T383).



118 **119** **120**

SCHEME 37



121 **122**

SCHEME 38

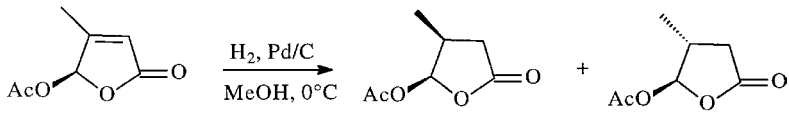
The proposed mechanism for the conversion of the furanone **118** to the spirocyclic lactones **119** and **120** involves electron transfer to the α,β-unsaturated methyl ester electrophore to generate an anion radical **118** which cyclizes on the β-carbon of the furanone. The resulting radical anion **121** acquires a proton, giving rise to the neutral radical **122,** which undergoes successive electron transfer and protonation to afford the lactones **119** and **120** (Scheme 38) (91T383).

Along with the total synthesis of (−)-acetomycin, a highly functionalized γ-lactone with antitumor activity, Kinderman and Feringa (98TA1215) described the stereoselective hydrogenation of the enantiomerically pure (+)-(*S*)-5-acetoxy-2(5*H*)-furanone **123** in methanol at 0°C and in the presence of palladium on carbon: (−)-*cis*-**124** was obtained together with the *trans* product in a total yield of 99% (Scheme 39) (98TA1215).

B. HALOGENATION

2(5*H*)-Furanones containing one or more bromine atoms are found as structural moieties in several known natural or designed products (77TL37). Hoffmann and coworkers, during the synthesis of aflatoxins M_1 and M_2, described the conversion of O-alkylated tetronic acids **125** [R = Me, CH_2=$CHCH_2CH_2$, CH≡CCH_2CH_2, $Me_3SiCH_2CH_2$, $CH_3(CH_2)_4$, $(CH_3)_2CH$, $(CH_3CH_2CH_2CH_2)_2CH$] into the 5-bromo derivatives **126** using *N*-bromosuccinimide/azo-bis-isobutyronitrile in carbon tetrachloride (Scheme 40) (89T6113).

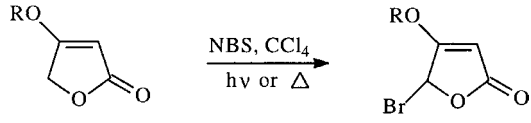
Polar impurities, including moisture and traces of acids, had to be excluded because they tend to promote ionic reactions. Previous work by Reffstrup and



123 **(-)-*cis*-124** ***trans*-124**

ratio 9 : 1

SCHEME 39



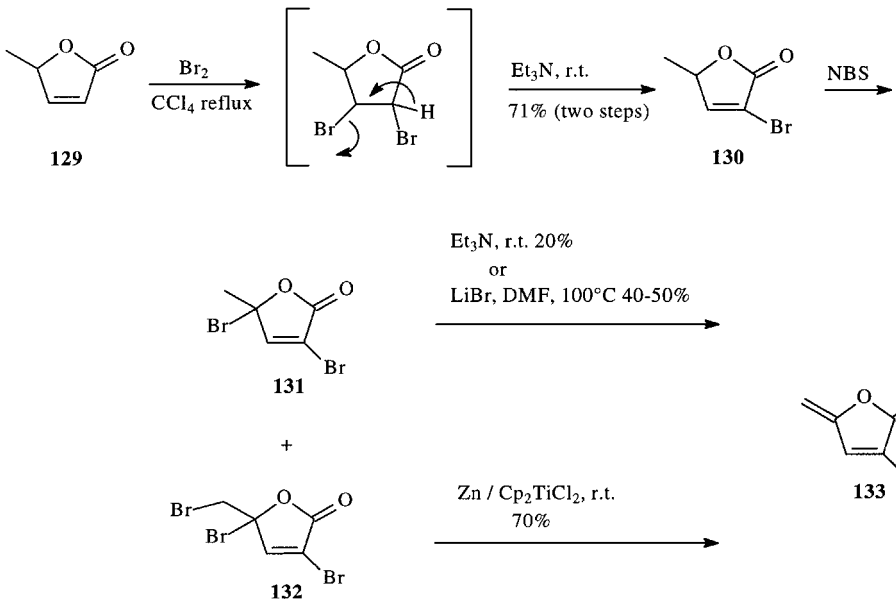
125 **126**

SCHEME 40

Boll (79P325) showed that the bromination of **125a** (R = Me) with NBS in CCl_4 afforded three products: the 3-bromo **127,** 5-bromo **126,** and 3,5-dibromo **128** derivatives (79P325). But Hoffmann and colleagues found that when excluding moisture and using anhydrous NBS under controlled free radical conditions, the reaction occurred regioselectively at C5, giving the bromofuranones **126a** (R = Me) (89T6113).

3-Bromo-5-methylene-2(5*H*)-furanone **133** was obtained from the β-angelica lactone **129** by using mild simple methods that combine bromination and dehydrobromination or debromination processes accomplished in a convenient order, as illustrated in Scheme 41 (94T12457).

Hollingworth and coworkers (94SC755) described a facile method for the preparation of 4-X-2(5*H*)-furanones **135** (X = Cl; 60%), **136** (X = Br; 80%), and **137** (X = I; 59%) from 4-tributylstannyl-2(5*H*)-furanone **134.** The latter compound



129 **130** **131** **132** **133**

SCHEME 41

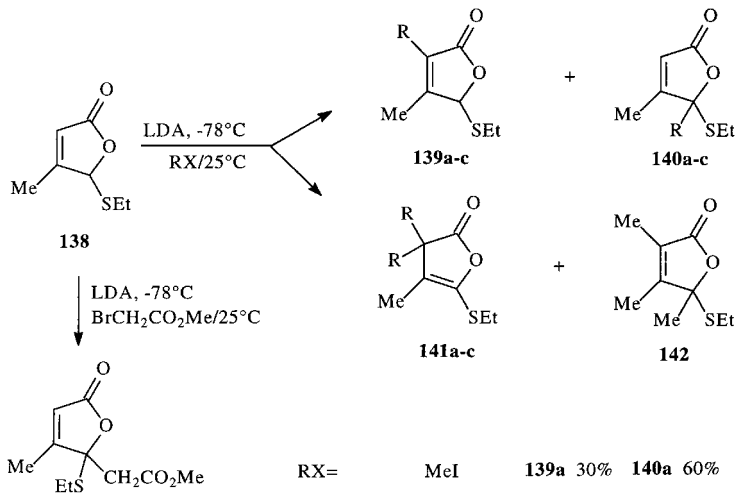
reacted with elemental chlorine, bromine, or iodine in methylene chloride to give the corresponding halofuranones.

C. Alkylation and Arylation

The regioselective alkylation of 2(5*H*)-furanones could afford biologically interesting compounds such as pheromones, beckerelides, and tetronic acid derivatives. The tridentate anion (in which the negative charge is spread over three atoms) generated from 5-ethylthio-4-methyl-2(5*H*)-furanone **138** with lithium diisopropylamide (LDA) was alkylated with methyl iodide, allyl bromide, benzyl bromide, and methyl bromoacetate (96SC2573). The results obtained (Scheme 42) revealed that the regioselectivity depends on the alkylating agent.

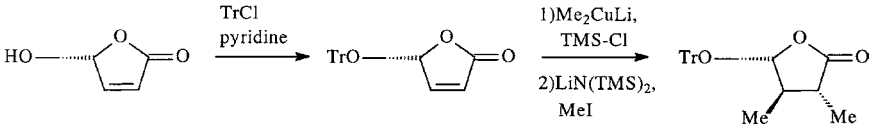
The stereoselective introduction of two methyl groups into *R*-(+)-5-hydroxymethyl-2(5*H*)-furanone **143** was effected by tritylation followed by the conjugated addition (87JOC1170) of Me_2CuLi (TMSCl/Et_2O, −78°C) and, finally, treatment with $LiN(TMS)_2$/MeI (Scheme 43) (97TL1439).

The allylation reaction of the optically active tetronic acid derivatives **146** was shown to give a variety of isomers depending on the reaction conditions (temperature and reaction time) (Scheme 44 and Table I) (99H1321). The reaction is carried out by treating **146** with allyl bromide in DMF and in the presence of K_2CO_3.



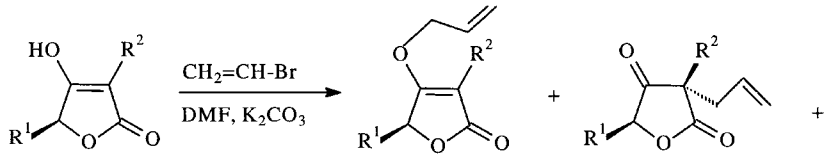
RX=				
MeI	**139a** 30%	**140a** 60%	-	**142a** 10%
AllylBr	**139b** 12%	**140b** 50%	**141b** 38%	-
BnBr	**139c** 70%	**140c** 18%	**141c** 12%	-
$BrCH_2CO_2Me$	-	**140d** 100%	-	-

SCHEME 42

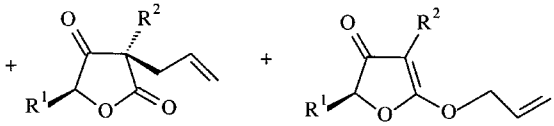


143 **144** **145**

SCHEME 43



146 **147** **148**



149 **150**

SCHEME 44

TABLE I

ALLYLATION REACTION OF TETRONIC ACID DERIVATIVES

R^1	R^2	Temperature (°C)	Time (h)	Yield(%)				Diastereomeric excess (% de)
Me	Me(**146a**)	80	4	31(**147a**)	22(**148a**)	18(**149a**)	—	10
Me	Me(**146a**)	10	8	42(**147a**)	29(**148a**)	8(**149a**)	2.5(**150a**)	56
Bn	Me(**146b**)	80	4	28(**147b**)	33(**148b**)	16(**149b**)	—	35
Bn	Me(**146b**)	10	8	39(**147b**)	30(**148b**)	5(**149b**)	2.4(**150a**)	70
i-Pr	Me(**146c**)	80	4	26(**147c**)	39(**148c**)	13(**149c**)	—	50
i-Pr	Me(**146c**)	30	11	29(**147c**)	61(**148c**)	3(**149c**)	—	90
i-Pr	Me(**146c**)	−15	48	25(**147c**)	73(**148c**)	1(**149c**)	—	96
i-Pr	Me(**146c**)	10	8	39(**147c**)	42(**148c**)	2(**149c**)	1.3(**150c**)	90
i-Pr	Ph(**146d**)	30	15	14(**147d**)	77(**148d**)	2(**149d**)	—	94
i-Pr	Ph(**146d**)	−5	184	12(**147d**)	73(**148d**)	1(**149d**)	—	96
i-Pr	*p*-$MeOC_6H_4$(**146e**)	30	24	16(**147e**)	78(**148e**)	3(**149e**)	—	93
i-Pr	*p*-$MeOC_6H_4$(**146e**)	−15	240	11(**147e**)	85(**148e**)	1(**149e**)	—	98

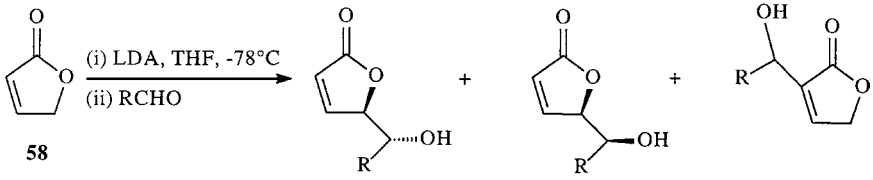
The 3- and 4-arylfuran-2(5*H*)-ones **152** and **153** (Ar = Ph, 2-Me−COO−C_6H_4, 3-CF_3−C_6H_4, 2-Me−C_6H_4, 2-thienyl) were conveniently obtained by coupling of 3- and 4-stannylfuranones **151** and **134** with aryl iodides using dichloro-bis(triphenylphosphine)Pd(II) as catalyst and toluene as the solvent [96JCS(P1)1913].

D. Aldol-Type Condensation

The lithium enolate of the 2(5*H*)-furanone **58** reacted with aldehydes to give a mixture of the γ-adducts **154** and **155** together with the α-adduct **156,** typically in a 1 : 1 : 6 ratio (Scheme 45); however, no significant selectivity was achieved (87TL985).

The furanone **157** is readily converted to its tridentate anion **158** by removal of the acidic proton at position 5 by means of a suitable base such as LDA. This anion was treated with an equimolecular amount of propionaldehyde and the 3-substituted furanone **161** was obtained in a regioselective manner. This regioselectivity was rationalized in terms of the hard–soft nature of the reactive sites of the anion, favoring the initial attack at C3 of the anion, which proved to be harder than carbon C5 of the same compound (88JOC3330). When the reaction of the anion was effected with 2.2 molar equivalents of the aldehyde, the sole product **162** was obtained, which originated from the reaction with two propionaldehyde molecules at the 3 and 5 positions of the furanone ring system. The reaction presumably involves the initial formation of the 3-substituted anion **159** which, on subsequent isomerization to the carbanionic intermediate **160,** enables the reaction with the second aldehyde molecule to give the 3,5-disubstituted furanone **162** (Scheme 46) (88JOC3330).

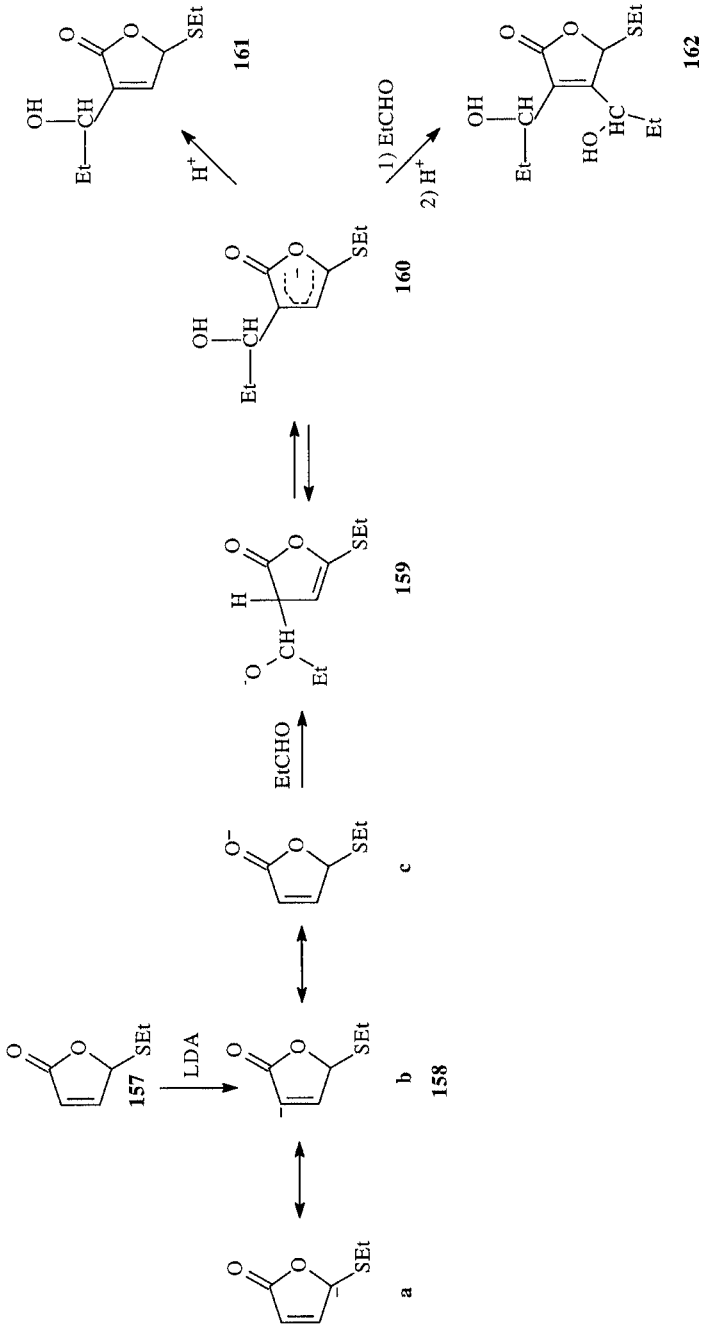
Ancos and colleagues studied the behavior of 5-methoxy- **163a** and (5-ethylthio)-4-pyrrolidin-1-yl-2(5*H*)-furanones **163b** (Y = OMe, SEt) toward aldehydes (91T3171). First, the lithium enolates **164** from these furanones, generated by



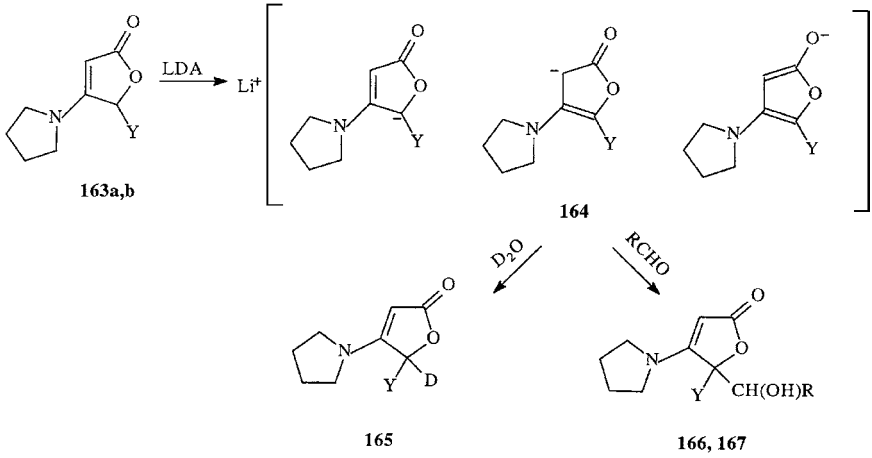
58 **154** **155** **156**

R = Me; Et; i-Pr; $PhCH_2$; $C_{10}H_{21}$

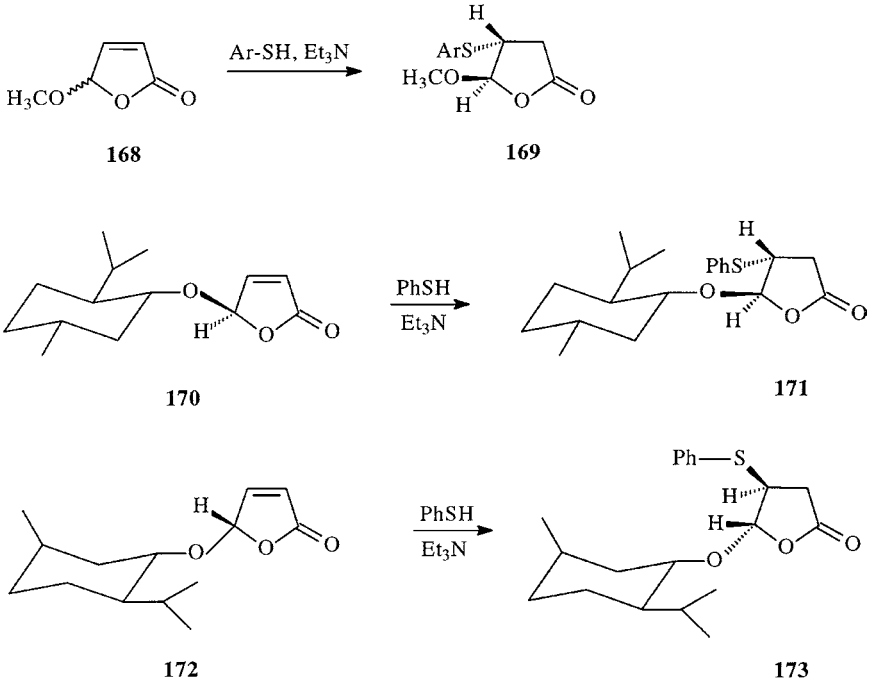
Scheme 45


157
LDA
158
a
b
c
EtCHO
159
160
161
162
1) EtCHO
2) H+
H+
SEt
OH
Et
CH
HO
HC

SCHEME 46



SCHEME 47



SCHEME 48

treatment with LDA, were quenched with D_2O: Only the 5-deutero derivatives **165** were detected, and no products arising from C3 substitution were obtained. This behavior led the authors to conclude that the reactions of these anions with electrophiles, such as aldehydes, occur exclusively at the 5 position (Scheme 47) (91T3171).

These results were confirmed by later studies, which proved that the lithium enolate, generated from the reaction of **163b** with LDA, reacted with 2-chlorobenzaldehyde to give the corresponding 5-hydroxyfuranone **167** ($R = o\text{-}Cl{-}C_6H_4$) (96H191).

E. Michael Additions

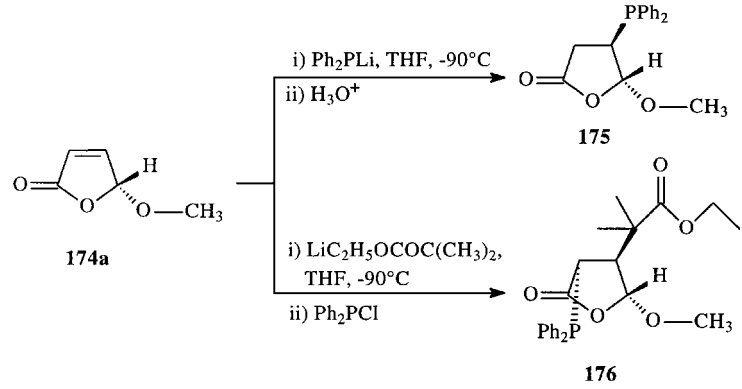
When having an α,β-unsaturated carbonyl moiety, 2(5*H*)-furanones are capable of undergoing 1,4-Michael–type additions. It was found that 1,4-addition reactions of thiophenols to the furanones **168, 170,** and **172** take place at room temperature in the presence of triethylamine to give a quantitative yield of the adducts **169, 171,** and **173.** Complete diastereoselective Michael-type addition occurred in all cases (Scheme 48) (88T7213).

The trans relationship between the alkoxy and thiophenoxy substituents was deduced from ^{1}H NMR coupling constants between the hydrogen atoms at the asymmetric centers in the lactone ring. The addition of lithiodiphenylphosphide to the γ-alkoxyfuranones **174a,b** was also found to be a trans diastereoselective process, producing the corresponding 1,4-adducts **175** and **177,** respectively. The lactone enolate, formed by an initial diastereoselective Michael addition to the furanone **174a,** was quenched stereoselectively with diphenylphosphine chloride to furnish **176** (Scheme 49) (90TA719).

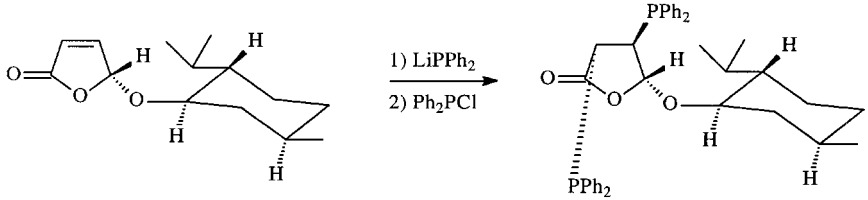
Addition of *p-tert*-butylthiophenol **178** to the racemic furanone **168** in dry toluene, and in the presence of quinidine as a chiral catalyst, provided (*R*)-**168** together with the Michael adduct **179.** The enantiomeric excess of the recovered furanone (*R*)-**168** was determined via the addition of (*l*)-α-methylbenzylamine: This amine addition showed complete diastereofacial control to give the adduct **180** in quantitative yield (Scheme 50) (94T4775).

The reactions of the anions generated (by the action of lithium diisopropylamide) from 5-ethylthio- and 5-phenylthio-2(5*H*)-furanones **157, 181a,** and the corresponding sulfones **181b,c** ($Z = SO_2Et$, SO_2Ph) with the naphthoquinone monoketals **182** ($R^1 = H$, OMe) and **183** (R^1, $R^2 = H$, H; H, OMe) were studied. It was found that the reaction occurs regiospecifically at position 5 of the furanone to give the corresponding Michael adducts **184** and **185** (Scheme 51) (97T1823).

This annelation reaction was also investigated for the 4-bromo-5-ethylthio- and 4-bromo-5-phenylthio-2(5*H*)-furanones **186** in which the presence of the halogen atom in position 4 of the furanone ring could favor the formation of anthraquinone derivatives (Scheme 52) (97T1823). Actually, the reaction of the

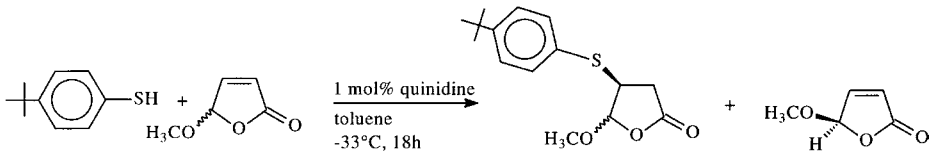


174a 175 176

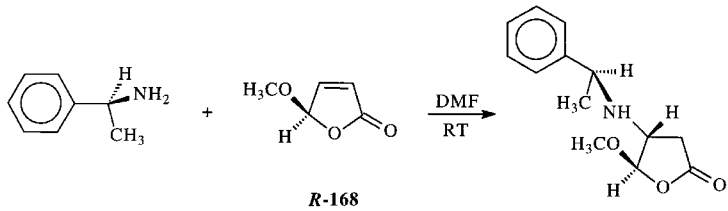


174b 177

SCHEME 49

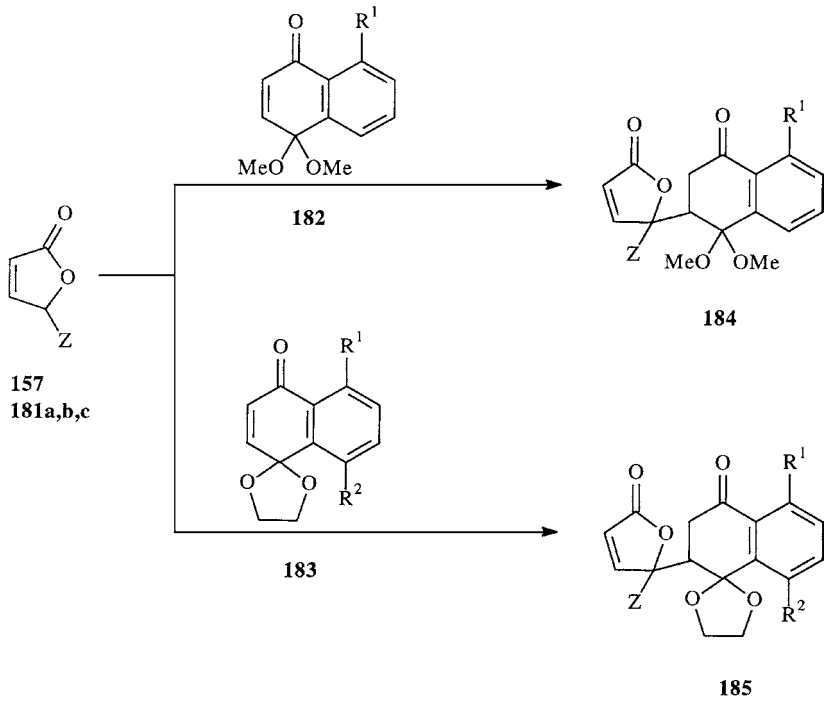


178 168 179 *R*-168

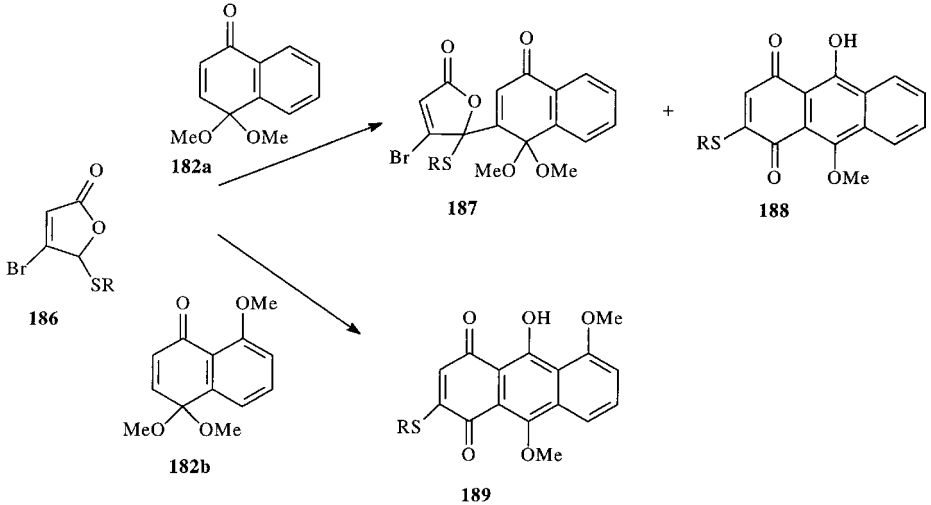


R-168 180

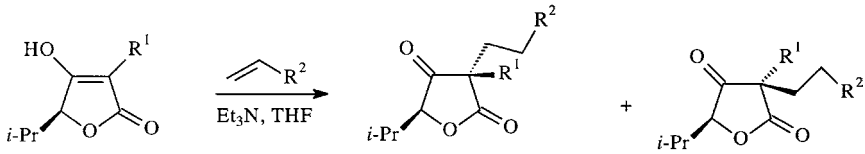
SCHEME 50



SCHEME 51



SCHEME 52



146c,e **190** **191**

SCHEME 53

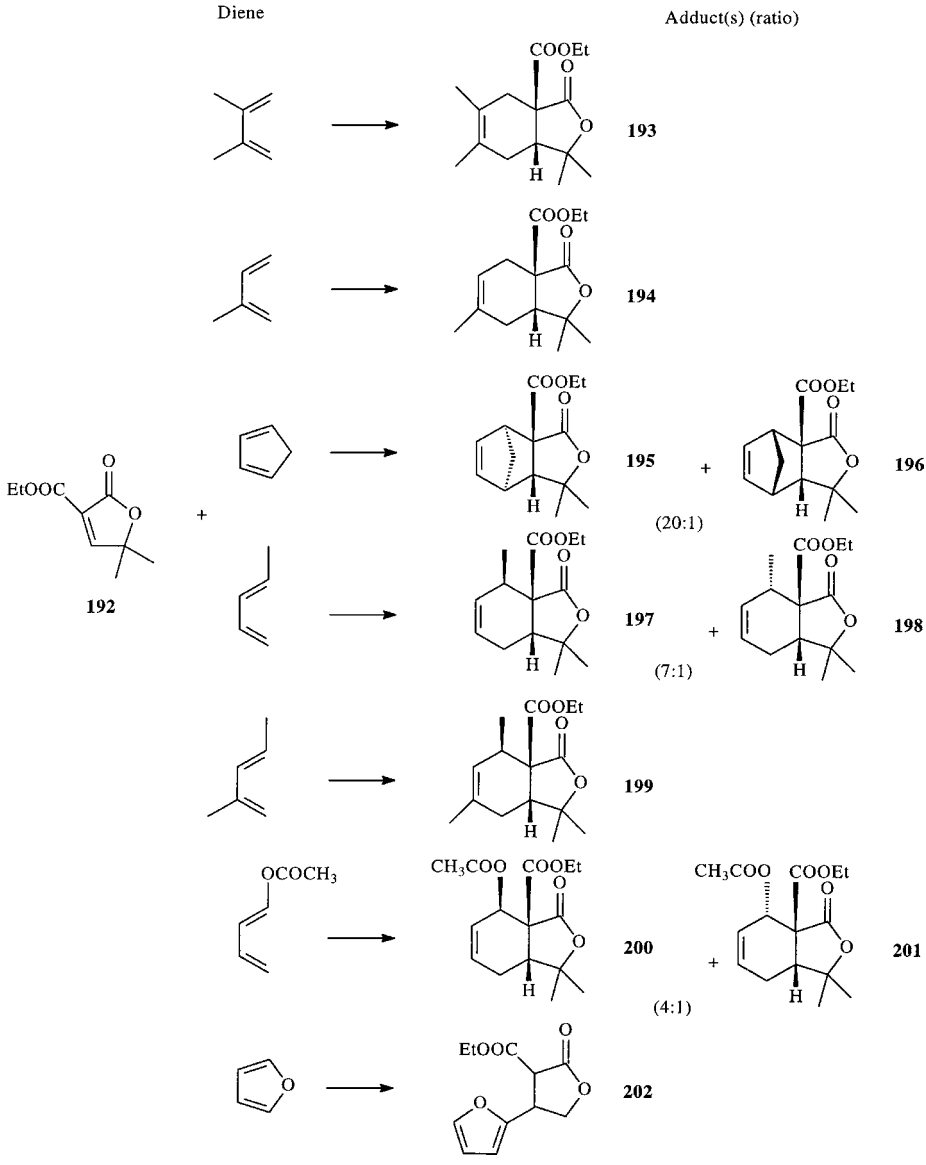
anion generated from **186** with the monoketal **182a** afforded as the main product the 1,4-anthraquinone **188** in a 55 : 45 mixture with the diastereomeric Michael adducts **187;** however, the annelation reaction with **183b** leads exclusively to the 1,4-anthraquinone derivative **189.**

Recently, the Michael addition of the optically active α,γ-disubstituted tetronic acids **146c,e** with a variety of α,β-unsaturated aldehydes, ketones, esters, and nitriles was studied (Scheme 53) (99H1321).

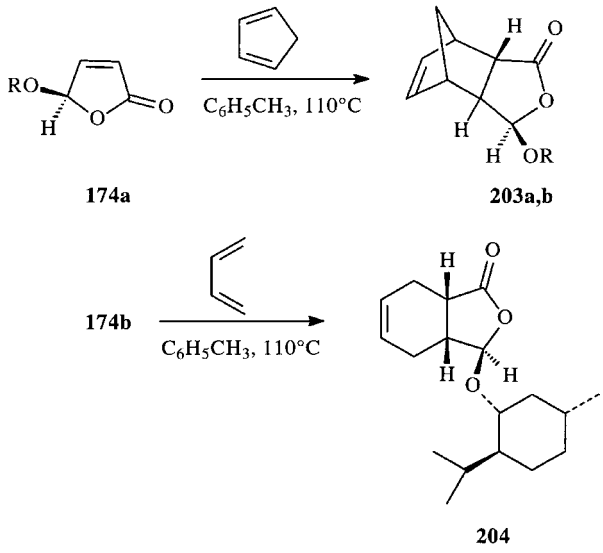
The ratio of the two diastereomeric products **190** and **191** was found to depend on the reaction temperature and reaction time. The addition of acrolein or methyl vinyl ketone proceeded smoothly, but in the case of methylacrylate or acrylonitrile the reaction did not proceed under the same conditions (Et_3N; THF; 30°C). An accompanying AM1 calculation of these α,β-unsaturated compounds [LUMOs for acrolein, −0.13877; for methyl vinyl ketone, −0.06805 (*s-trans*); for methyl acrylate, −0.01413 (*s-trans*); for acrylonitrile, 0.04971] suggested the low reactivity of methyl acrylate and acrylonitrile toward the Michael reaction (99H1321).

F. DIELS–ALDER REACTION

α,β-Unsaturated esters and carboxylic acids have been characterized as reactive dienophiles and widely used as such in organic synthesis; however, the Diels–Alder reaction of the corresponding lactones has not been extensively studied in spite of its potential utility as a more direct approach to useful intermediates. Possibly, this is due to the expectation of a low level of reactivity for such compounds (82CJC921). However, it was found that the lactone ester **192** reacted efficiently with a variety of dienes under stannic chloride catalysis in ether at room temperature to give the corresponding adducts in good yields (Scheme 54) (82CJC921); furan produced only the addition product **202.** With unsymmetrically substituted dienes, the adducts were found to be those predicted on the basis of the normal rules governing the orientation of Diels–Alder addition, corroborated by the results of an accompanying NMR study.


Diene
Adduct(s) (ratio)
EtOOC
192
COOEt
193
194
195
196
(20:1)
197
198
(7:1)
199
OCOCH3
CH3COO
200
201
(4:1)
202

SCHEME 54

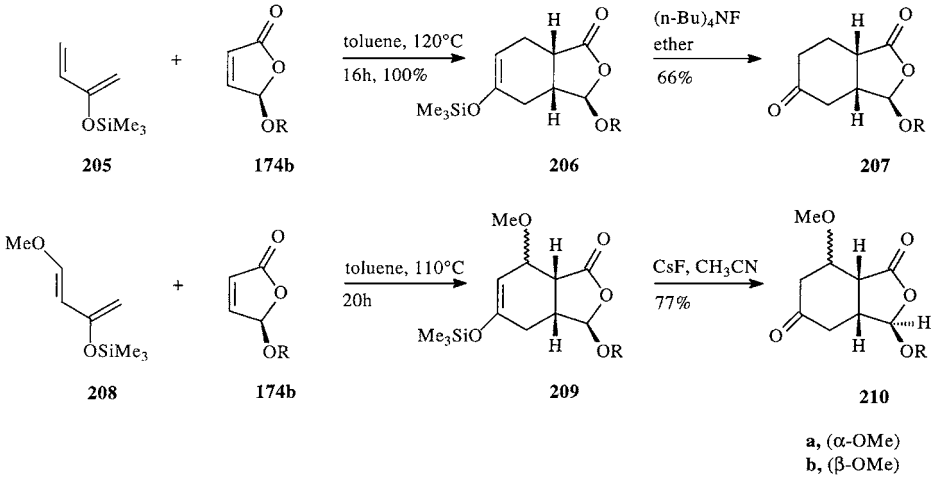


SCHEME 55

A versatile synthetic route to enantiomerically pure Diels–Alder adducts was deduced and found dependent on the application of enantiomerically pure 5-methoxy- **174a** (R = Me) and 5-(1-menthyloxy)-2(5*H*)-furanones **174b** (R = menthyl), which were expected to undergo π-face-selective cycloaddition with dienes. The reaction was effected by heating; no Lewis acid catalysts were required (Scheme 55) (88JOC1127).

An essential feature of the chiral furanone **174b** is the directing group at C5 which shields one of the π faces of the molecule from being attacked; re-face addition is expected with the *S*-furanone. In this sense, the stereogenic center at C5 is responsible for the diastereoselectivity exerted during the cycloaddition reaction at the α,β-unsaturated moiety of the furanone present (91TA1247). Also (5*R*)-5-(1-menthyloxy)-2(5*H*)-furanone **174b** (R = menthyl) and 2-trimethylsilyloxy-1,3-butadiene **205** readily react at 120°C in dry toluene; after treating the resulting silyl enol ether **206** with tetrabutylammonium fluoride, the 3,4-disubstituted cyclohexanone **207** was obtained as the only isomer. This again indicates that the addition of the diene component takes place with complete π-face selectivity *trans* to the menthyloxy substituent. On the other hand, the reaction of **174b** with the diene **208** (Danishefsky's diene) afforded two diastereomeric adducts **210a** and **210b** (Scheme 56) (91TA1247).

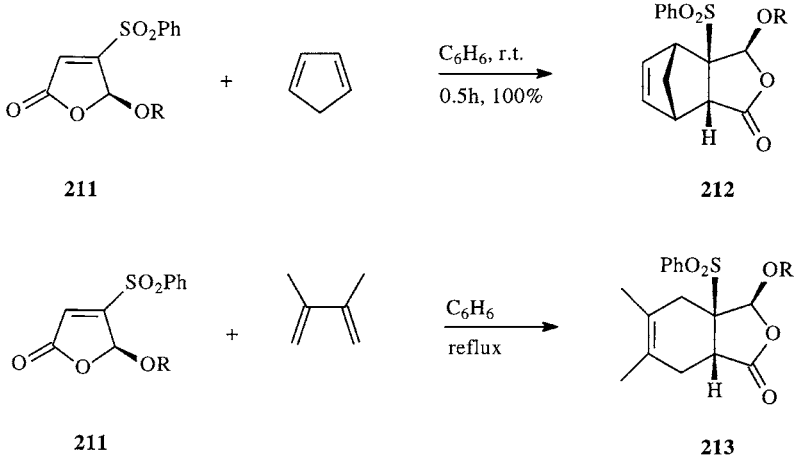
The two diastereomers **210a,b** are epimeric at the carbon bearing the methoxy group; i.e., they are the result of the concurrent *endo*- and *exo*-addition of the diene **208** to the 5-menthyloxy-2(5*H*)-furanone (91TA1247).



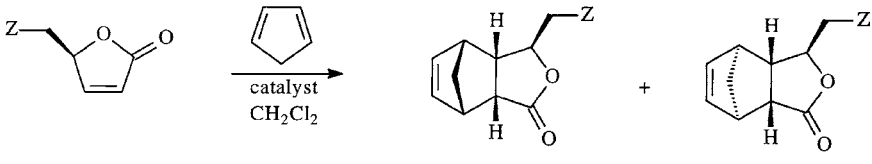
SCHEME 56

It was found that the introduction of a sulfonyl substituent considerably enhances the furanone reactivity in Diels–Alder reaction. Thus, (5*S*)-5-(*d*-menthyloxy)-4-(phenylsulfonyl)-2(5*H*)-furanone **211** (R = menthyl) reacted with cyclopentadiene at room temperature in benzene with complete conversion to the adduct **212.** Also, the reaction of **211** with 2,3-dimethyl-1,3-butadiene was readily performed in refluxing benzene to give the adduct **213** in 98% yield (Scheme 57) (91TL7751).

The reaction between the chiral furanones (*R*)-β-angelica lactone **129** (Z = H) and 5-hydroxymethyl-2(5*H*)-furanone **143** (Z = OH) with cyclopentadiene was



SCHEME 57



anti-endo *anti-exo*

129, 143 **214** **215**

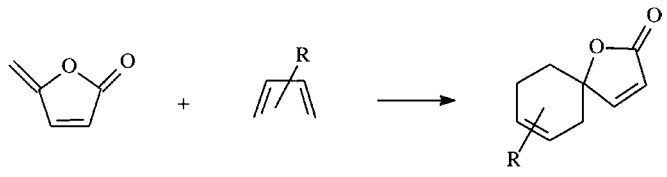
SCHEME 58

carried out using $EtAlCl_2$ and zinc halides as catalysts. It was observed that the use of Lewis acid catalysts in such cycloadditions improves the *endo/exo* stereoselectivity. Thus, in the reaction mixture of the *endo*- and *exo*-adducts **214** and **215,** the *endo* isomers proved to be the major products (Scheme 58) (94TA371).

The 5-methylene-2(5*H*)-furanone **216** was found to be a good dienophile in Diels–Alder reactions with acyclic dienes (R = H, 2-Me, 2,3-di-Me, 1-Me, 1,3-di-Me). The reaction took place specifically at the *exo*-cyclic double bond to give the corresponding spiro adducts **217** in good yields (Scheme 59) (90JOC3060).

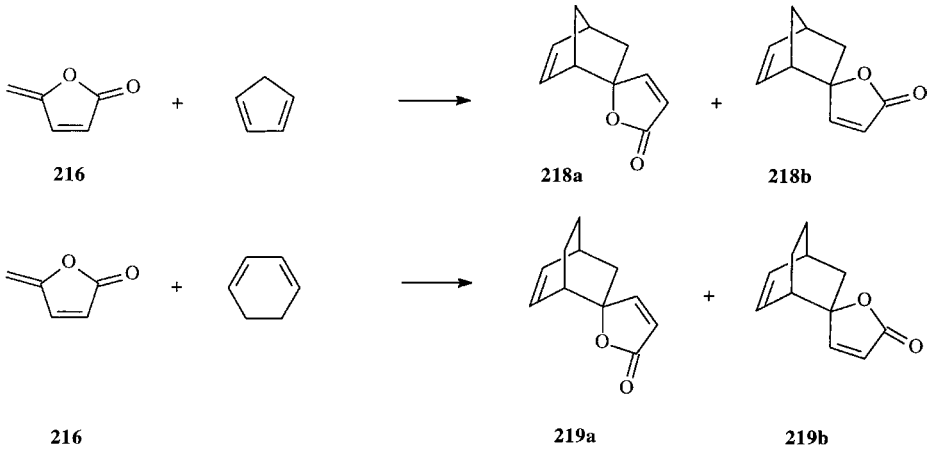
The reaction of the *exo*-methylenefuranone **216** with cyclopentadiene and cyclohexadiene was conducted in dichloromethane as a solvent at temperatures ranging from 60 to 160°C (90T4371). The tricyclic stereoisomeric adducts **218a,b** and **219a,b,** respectively, were obtained (Scheme 60) (90T4371). It was found that the ratios of the isomers **a/b** are temperature-dependent; the proportion of **b** is increasing moderate at higher reaction temperatures.

Thermal cycloadditions of butadiene to 3-bromo- **133** and 3-methoxy-5-methylene-2(5*H*)-furanones **220** were studied (95TL749). These systems contain substituents at C3 capable of stabilizing also a possible radical intermediate, influencing hereby the rate and/or the course of the reaction. Thus, the reaction of **133** and **220,** respectively, with butadiene at 155°C afforded mixtures of the expected 1,4-cycloadducts **221** and **222,** respectively, and of the cyclobutane derivatives



216 **217**

SCHEME 59



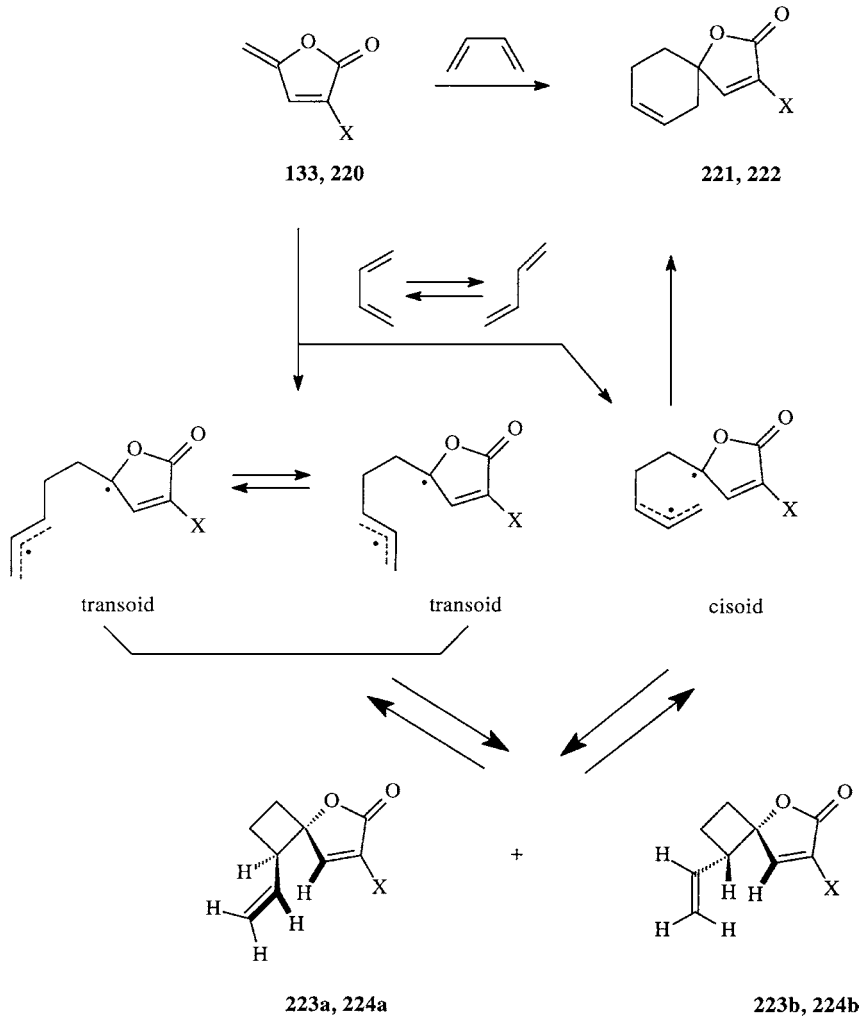
SCHEME 60

223 and **224.** The synthesis of the cyclobutane derivatives under these thermal conditions was explained on the basis of the formation of biradical intermediates, as depicted in Scheme 61 (95TL749).

G. 1,3-DIPOLAR CYCLOADDITIONS

1,3-Dipolar cycloaddition reactions are a valuable method for the construction of five-membered heterocyclic rings (84MI2). While the cycloadditions to substituted alkenes and alkynes have been intensively investigated (84MI2), the use of furanones as dipolarophiles has been limited to just a few reports. It was found that 1,3-dipolar cycloadditions of nitrile oxides to 2(5*H*)-furanone **58** occur regioselectively, affording head-to-tail cycloadducts **225** (Scheme 62) (86MI2). The 1,3-dipolar cycloaddition of arylnitrile oxides to 5-alkoxy-2(5*H*)-furanones **174** (R = Me, Et) was shown to give exclusively 3-aryl-4-oxo-6-alkoxy-3a,4,6,6a-tetrahydrofuro[3,4-*d*]isoxazoles **226a** with the substituent at C6 in *exo* configuration. In principle, the reaction could lead to two regioisomeric pairs of *exo*- and *endo*-diastereomers **226a** and **226b,** but the *endo* isomers were not detected (Scheme 62) (87CCC1315).

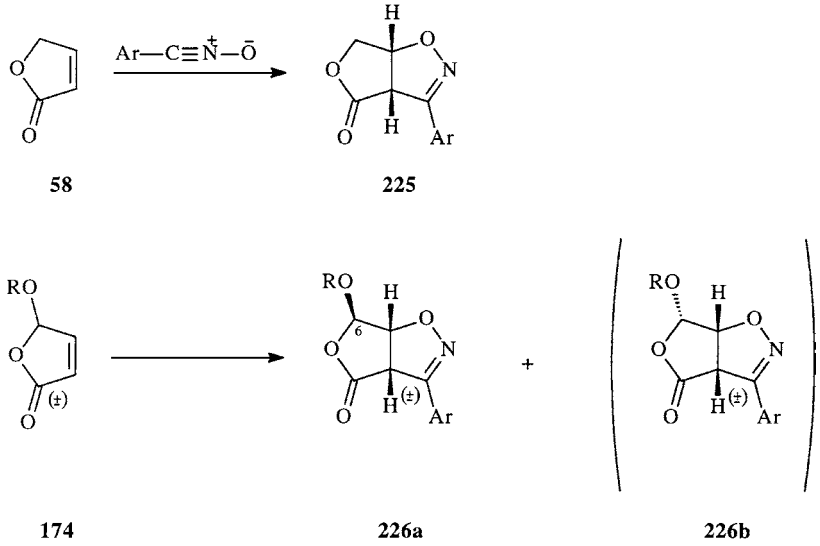
The use of chiral dipolarophiles, such as the nitrile oxide additions to chiral furanones, have received much interest. The cycloaddition of various 1,3-dipolar reagents to the enantiomerically pure furanones **170** and **227** showed excellent diastereofacial control by the menthyloxy substituent, especially in nitrone and nitrile oxide additions (cf. Table II) (88TL5317).



SCHEME 61

The results obtained showed that carbon, oxygen, or nitrogen functionalities are readily introduced into the α,β positions of the lactone moiety. In this way, useful precursors for natural product synthesis are accessible (88TL5317).

It was found that the reaction of 5-acetoxy- and 5-benzoyloxy-2(5*H*)-furanones **174** with aryl nitrile oxides afforded only one cycloadduct, the condensed isoxazoline **233** (88TL5317). In principle, there are four possible cycloadducts: **233** and **234** resulting from the *anti* approach of the 1,3-dipolarophile to the acetoxy group (with *exo* configuration of the acetoxy substituent), and two further isomers



58 **225**

174 **226a** **226b**

SCHEME 62

235 and **236** corresponding to the *syn*-face attack (with *endo* configuration of the acetoxy substituent). This cycloaddition to the furanones **174** is therefore regio- and stereospecific. The isolated products **233** result from the addition to the less hindered face of the furanone with an antiperiplanar relationship between the new C—C bond and the acetoxy or benzoyloxy substituent (Scheme 63) (91M165).

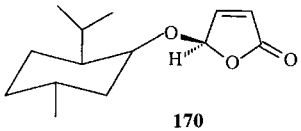
Cid and colleagues reported that the 1,3-dipolar cycloaddition of 3,4,5,6-tetrahydropyridine-1-oxide to the 2(5*H*)-furanones **58** (R = H), **129** (R = Me), and **237** ($R = CH_2CH_2OCH_2Ph$) gives a mixture of three products: **238, 239,** and **240** (Scheme 64) (92TL667). The reaction was conducted in chloroform under mild temperature conditions to ensure kinetic control with a high degree of diastereoselectivity.

The 1,3-dipolar cycloaddition of a variety of nitrile oxides, nitrones, ethyl diazoacetate, and azomethine ylide to the chiral furanone **174a** was studied with respect to the present regio- and diastereoselectivity (93T8899). In the case of the azomethine ylide addition, three stereoisomeric adducts were obtained. However, in the case of the other dipoles only two stereoisomeric adducts were isolated; the major product proved to be the *anti*-facial isomer. In this way, a number of multifunctional (lactone-annulated) isoxazolines **241** and **242,** isoxazolidines **243** and **244,** pyrazolines **245a,b,** and pyrrolidines **248a,b,c** could be synthesized (Scheme 65) (93T8899).

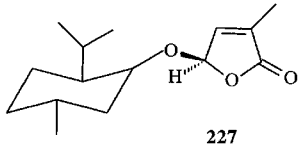
The 1,3-dipolar cycloaddition of nitrile oxides to 2(5*H*)-furanones substituted at C5 by sulfur-bearing groups were also studied with respect to the regio- and stereoselectivity of the reaction (96T3457). Benzonitrile oxide (R = Ph), for

TABLE II

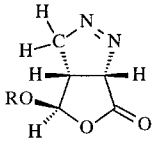
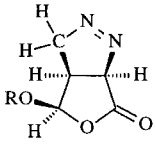
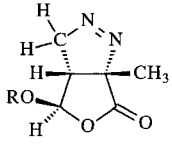
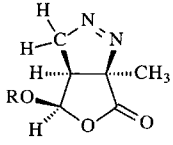
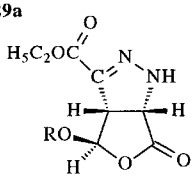
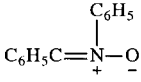
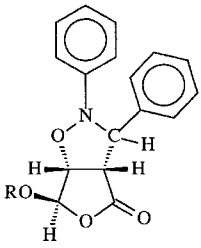
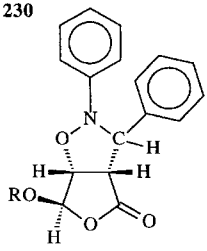
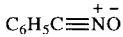
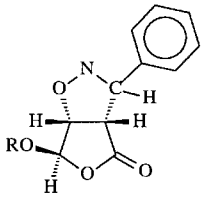
1,3-DIPOLAR CYCLOADDITION OF VARIOUS REAGENTS TO THE ENANTIOMERICALLY PURE FURANONES **170** AND **227**

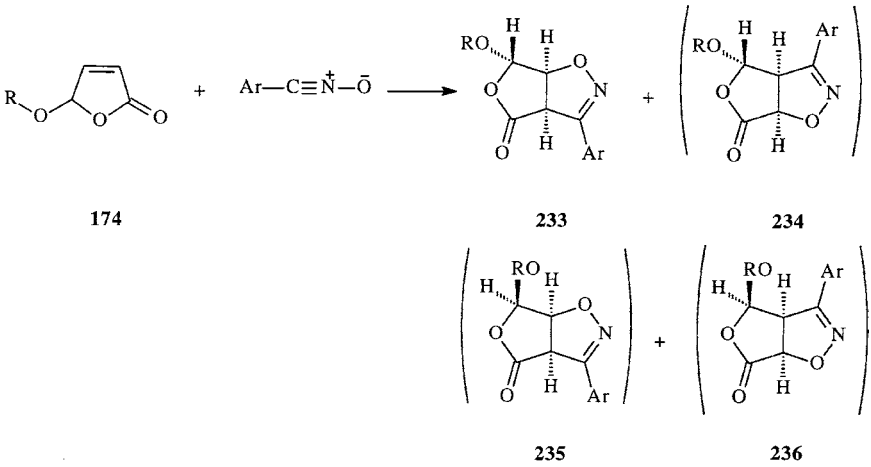


170



227

Furanone	1,3-Dipolar Reagent	Reaction Conditions	Product(s)
170	CH_2N_2	Et_2O r.t., 12 h	 **228a**  **228b**
227	CH_2N_2	Et_2O r.t., 144 h	 **229a**  **229b**
170	$H_5C_2O_2CCHN_2$	Dioxane 95°C, 12 h	 **230**
170		Toluene 110°C, 2 h	 **231a**  **231b**
170		Et_2O r.t., 12 h	 **232**

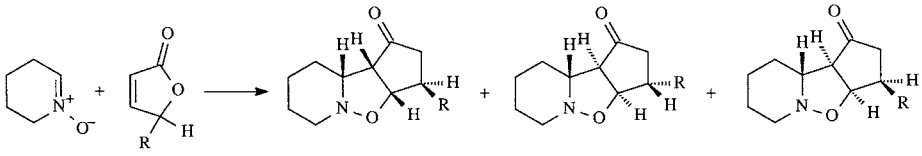


174 **233** **234** **235** **236**

SCHEME 63

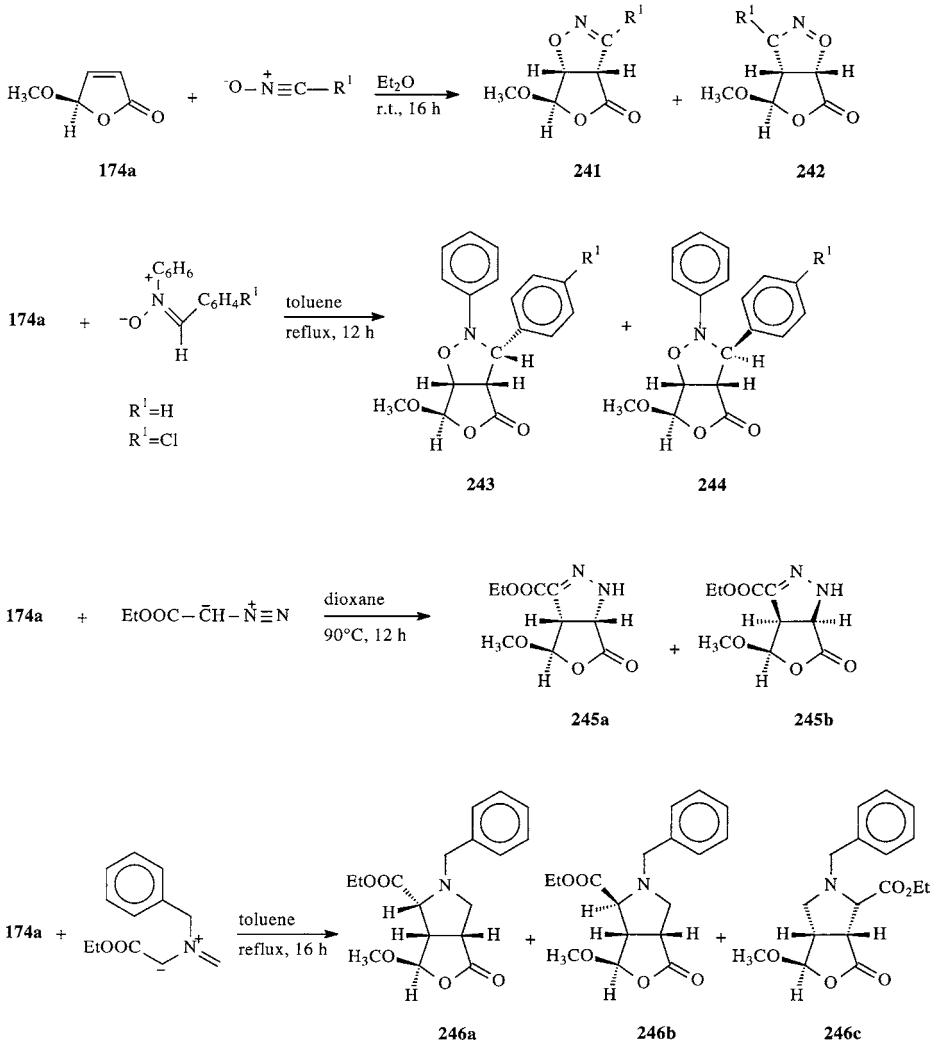
instance, reacted with the furanones **157** (Z = SEt) and **181a–c** (Z = SPh, SO_2Et, SO_2Ph), affording the regioisomeric adducts **247a,b** (orientation A) and **248** (orientation B). The products according to orientation A proved predominant in accordance with the regiochemistry reported for cycloadditions of dipolarophiles to 2(5*H*)-furanones (87CCC1315; 88TL5317). The reactions led to a mixture of isoxazolines in which the major products are those in which the sulfur-containing group is in the *exo* arrangement. This fact suggests that the attack of the dipolarophile occurs preferentially at the face opposite to the substituent Z in position 5, i.e., with face-selectivity (Scheme 66) (96T3457).

The same mixture of epimeric furoisoxazolines **249** (R = Me), **250** (R = Br), and **251** (R = Br) was found along with the reaction of acetonitrile oxide (R = Me) (96T3457) and bromonitrile oxide (R = Br) (96T3457), respectively, with the furanone **157.** The *cis* or *trans* relationship between H6 and H6a, and hence the face selectivity of cycloaddition, was established from ^{1}H NMR of the two epimers by comparing their coupling constants. The furanones **157** and **181a** react with bromonitrile oxide to give the corresponding regioisomeric adducts of type A and B, the predominant orientation being the same as in the previous additions



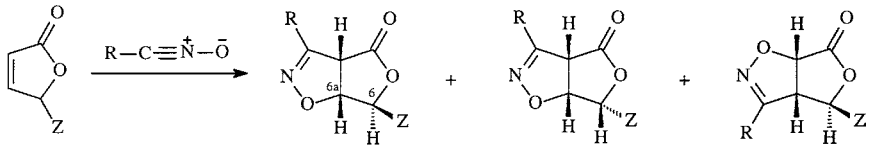
58,129,237 **238** **239** **240**

SCHEME 64



SCHEME 65

(96T3457). In a more recent publication, the same authors studied the behavior of the 2(5*H*)-furanones **157** and **181a–c** toward the 1,3-dienophiles diazomethane and ethyl diazoacetate in order to gather information on the influence of the 5 substituent upon the regio- and stereoselectivity of the corresponding cycloaddition (99T229). The exclusive formation of the pyrazolines **252** and **253** with the sulfur-containing group in *exo* arrangement confirmed that the attack of diazo compounds occurs preferentially at the face opposite to the 5 substituent



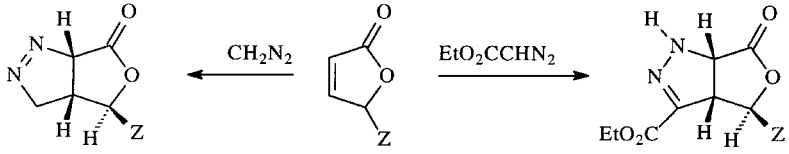
157,181a-c **247a,249a,250a** **247b, 249b,250b** **248,251**

SCHEME 66

(Scheme 67) (99T229). This result suggests that the nature of the substituents at position 5 of the furanone ring plays a significant role in controlling the regio- and stereoselectivity of the cycloaddition.

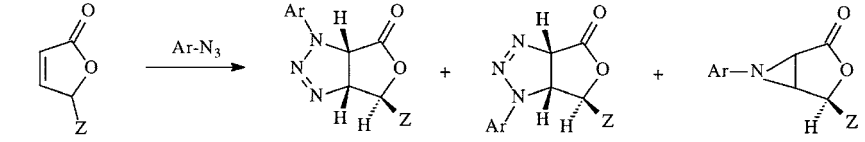
The behavior of the 2(5*H*)-furanones **168** (Z = OMe), **157** (Z = SEt), and **181a** (Z = SPh) toward azides has been recently investigated, in particular with respect to the present regio- and stereoselectivity (00H237). The cycloaddition of *p*-methoxyphenyl azide, for example, was conducted without solvent at 60°C. Starting from the 5-methoxyfuranone **168,** a mixture of the regioisomeric cycloadducts **254** (Z = OMe), **255** (Z = OMe), and the aziridine **256** (Z = OMe) was obtained. In contrast, the cycloaddition reaction of the thioethers **157** and **181a** proceeded in a regiospecific manner to afford only the corresponding triazolines **257** (Z = SEt) and **258** (Z = SPh) as the single regioisomers. However, during the purification of the latter products by flash column chromatography, the corresponding aziridines **259** (Z = SEt) and **260** (Z = SPh) were isolated (Scheme 68) (00H237). The predominant orientation A is in accord with the regiochemistry reported for the cycloaddition of *N*-aryl azides to α,β-unsaturated lactones (94AQ473). The formation of the aziridines along this reaction was explained on the basis of the partial decomposition of the primary cycloadducts by ring cleavage with nitrogen expulsion (85AHC217).

The reaction of *p*-nitrophenyl azide with the furanones **168, 157,** and **181a** under the same reaction conditions was also studied (00H237). This dipolarophile reacted in a nonregiospecific manner with 5-methoxyfuranone **168** to give a mixture of the epimeric triazolines **261a** and **261b.** After flash chromatography, a diazo compound **262** and an enamine **263** were also isolated in poor yield (6 and 4%,



252 **157, 181a-c** **253**

SCHEME 67

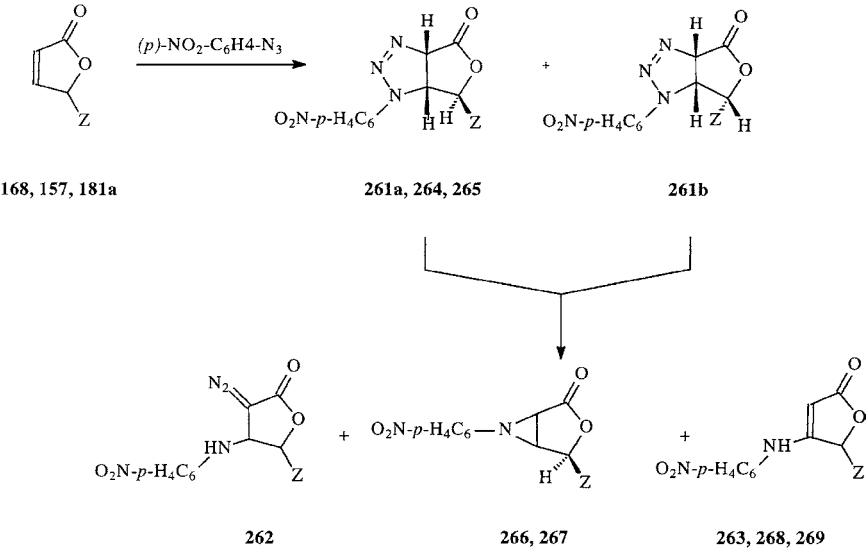


SCHEME 68

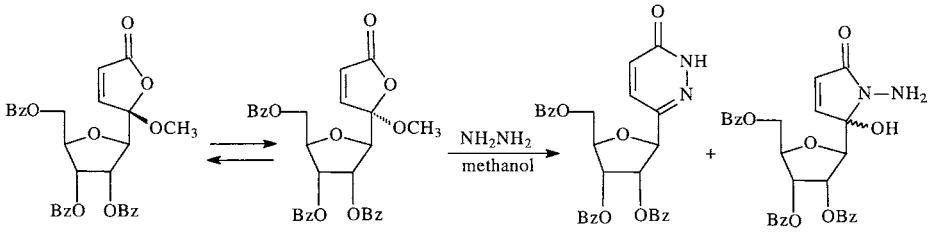
respectively). In contrast, the reaction with the thioethers **157** and **181a** occurred in a regiospecific manner and afforded the corresponding triazolines **264** (Z = SEt) and **265** (Z = SPh) as single isomers. But the aziridines **266** (Z = SEt) and **267** (Z = Sph) as well as the enamines **268** (Z = SEt) and **269** (Z = Sph) could also be isolated from the crude reaction mixture (Scheme 69) (00H237).

H. REACTIONS WITH NITROGEN NUCLEOPHILES

γ-Butyrolactones are structural subunits in a wide variety of natural products with diverse biological activities (89MI1), and are frequently used as intermediates for the synthesis of biologically active compounds (96TA3209). The synthesis of enantiopure γ-butyrolactones is therefore an area of growing interest. One of the most effective approaches to obtain enantiopure γ-butyrolactones is asymmetric conjugated addition of nucleophiles to chiral furanones (92MI1).



SCHEME 69



270 **271** **272** **273**

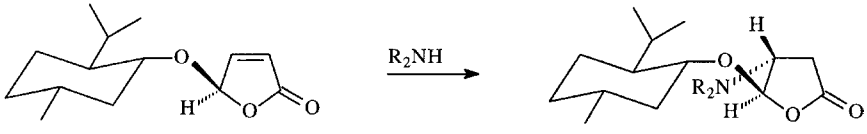
SCHEME 70

It was found that the reaction of the lactone glycosides (5*R*)- and (5*S*)-5-methoxy-5-(2,3,5-tris-*O*-benzoyl-β-D-ribofuranosyl)-2(5*H*)-furanone **270** and **271** with hydrazine hydrate in methanol gave two products: the pyridazinone **272** and a mixture of diastereomeric *N*-aminopyrrolinones **273,** which could not be separated, in yields of 26 and 71%, respectively (Scheme 70) (87JOC4521).

De Lange and colleagues reported a facile synthetic strategy leading to enantiomerically pure β-amino lactones based on the conjugated addition of amines to the enantiomerically pure 5-menthyloxy-2(5*H*)-furanone **170** (89T6799). In line with the observed diastereofacial Diels–Alder reaction of this 2(5*H*)-furanone derivative (88JOC1127), it was expected that the amine addition to **170** would proceed preferentially *anti* to the C5 menthyloxy substituent. Various primary and secondary amines were indeed found to undergo a diasteroselective addition to furanone **170,** yielding the diastereomerically and enantiomerically pure β-amino lactones **274** (Scheme 71) (89T6799).

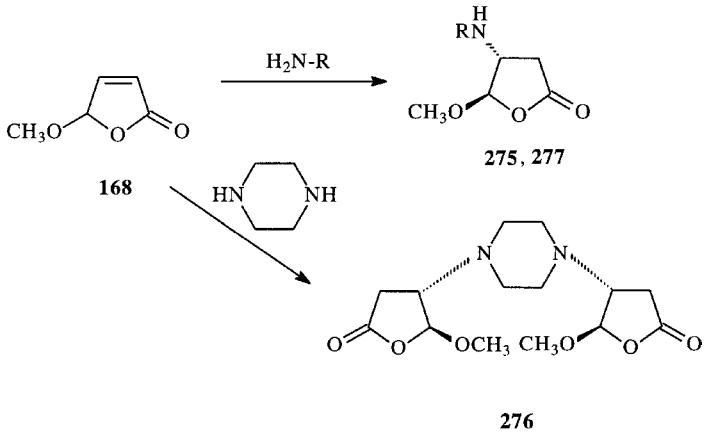
The reaction of 5-methoxy-2(5*H*)-furanone **168** with amines was also studied (89T6799). The conjugated addition of ethanolamine to the furanone **168** gave the racemic amino lactone **275** (R = CH_2CH_2OH). Similarly, piperazine reacted with two equivalents of **168** to provide the diadduct **276** as a single diastereomer (no traces of the other isomer were detected). With tryptamine, the reaction was nearly quantitative with the the formation the *trans*-adduct **277** (R = tryptophanyl) (Scheme 72) (89T6799).

The enantioselective synthesis of the *N*-benzyl-substituted β-lactam **274a** (NR_2 = $PhCH_2NH$), a precursor for carbapenem antibiotics, was described starting from the chiral synthon 5(*R*)-menthyloxy-2(5*H*)-furanone **170** (Scheme 71)



170 **274**

SCHEME 71



SCHEME 72

(95TL7133). The reaction proceeded with high diastereoselectivity *trans* with respect to the menthyloxy substituent.

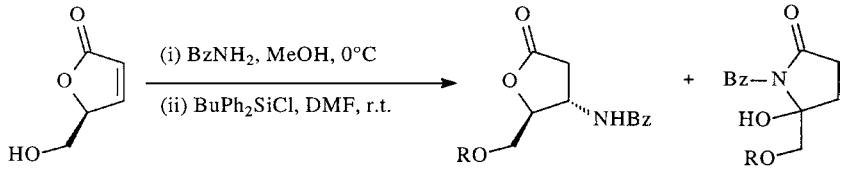
The chiral 5-hydroxymethyl-2(5*H*)-furanone **143** reacted with benzylamine to give the amino lactone **278a** (R = H), which was difficult to purify but could be directly silylated using *t*-butyldiphenylsilyl chloride, affording **278b** (R = TBDPS). Another byproduct **279** was isolated arising from the corresponding 1,2-addition (Scheme 73) (95TL7133).

Recently, it was found that the addition of benzylamine to 2-(5*H*)-furano-3-ylmethanesulfonate **280** (X = O−SO_2Me) in methanol afforded a 7 : 1 mixture of the *trans*- and *cis*-methyl-*N*-benzyl-2-hydroxymethylaziridine-2-carboxylates **281** and **282,** respectively (00TL3061). Treatment of **281** with benzyl alcohol in the presence of $BF_3 \cdot OEt_2$ furnished, after hydrolysis, *rac-cis*-amino-α-hydroxy-β-butyrolactone **284** (Scheme 74).

The formation of the *trans*-aziridine **281** as the major product of the conjugated addition of benzylamine to the furanone **280** was rationalized in terms of selective facial protonation of the initially formed enol **284** (Scheme 75) (00TL3061).

I. REARRANGEMENTS

Few reports are available dealing with the rearrangements of 2(5*H*)-furanones. It was found that when 4-arylsulfonyl-3-diphenylmethoxy-2,5-dihydro-2-furanones **285** (Ar = Ph, 4-Br−C_6H_4) are maintained at 170–175°C for 20–30 min, they undergo rearrangement to 4-arylsulfonyl-4-diphenylmethyl tetrahydrofuran-2,3-diones **286** (Scheme 76) (85CHE1178). Mack and coworkers reported the rearrangement of the 2(5*H*)-furanones **287** [R^1 = Ph, 3-NO_2−C_6H_4, 2-MeO−C_6H_4,



143 **278a, b** **279**

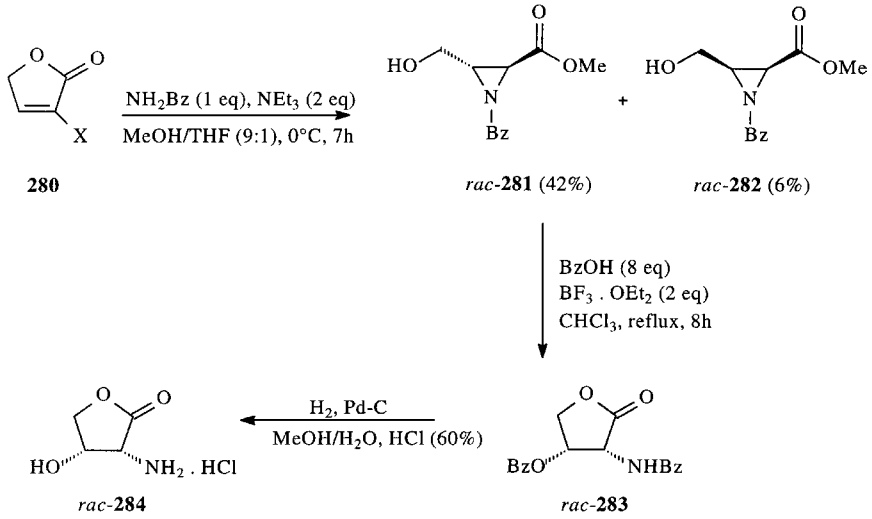
SCHEME 73

4-Br−C_6H_4, *trans*-2-Ph-cyclopropyl; R^2 = H, Me, Et; R^3 = Ph, 4-Cl−C_6H_4, 3-$CF_3C_6H_4$, Et, $CH_3(CH_2)_{13}$] into the 3(2*H*)-furanones **288** by refluxing in aqueous ethanolic solution and in the presence of excess KOH (Scheme 76) (88HCA783).

Two mechanisms were presented to explain this base-catalyzed rearrangement (Scheme 77). Both of these two proposed mechanisms involve nucleophilic attack by the base which leads to ring opening to generate the amine alcohol intermediate. Subsequent ring closure with concomitant loss of the amine followed by tautomerization completed the rearrangement.

J. PHOTOCHEMICAL REACTIONS

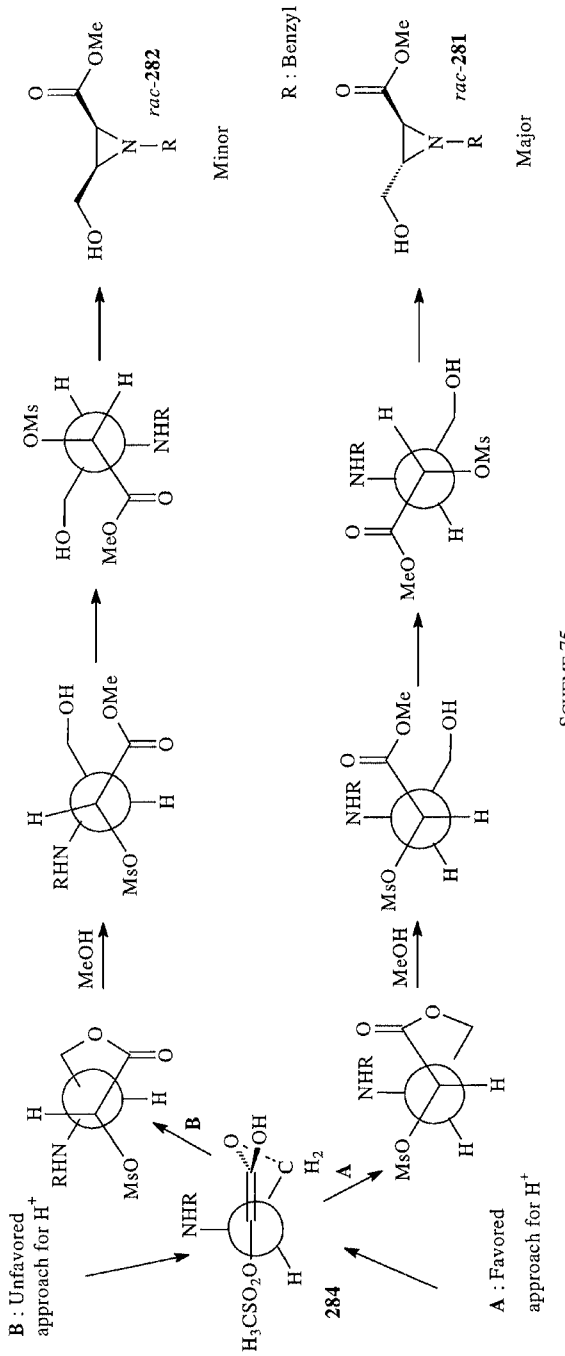
Photochemical transformations of 2(5*H*)-furanones have been recently reviewed by one of us (98OPP401). So, in this part, the more recent developments are



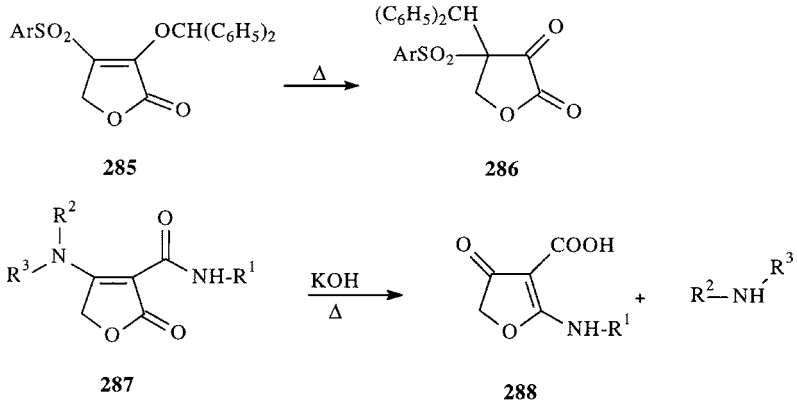
280 *rac*-**281** (42%) *rac*-**282** (6%)

rac-**284** *rac*-**283**

SCHEME 74


B : Unfavored approach for H+
A : Favored approach for H+
284
MeOH
MeOH
Minor
Major
R : Benzyl
rac-282
rac-281

SCHEME 75



SCHEME 76

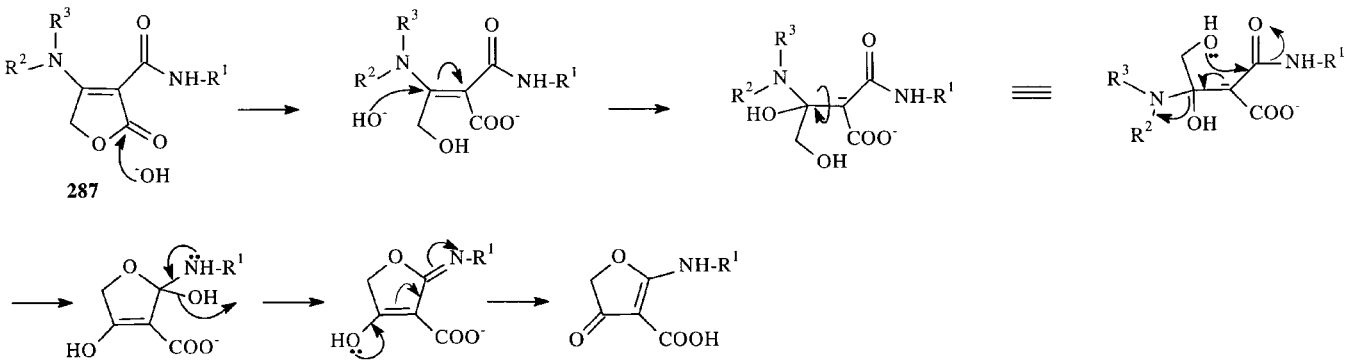
emphasized. The [2 + 2]-photocycloadditions of 2(5*H*)-furanones have been successfully used for the construction of cyclobutane derivatives which are widely spread in many natural products. The photoreactivity of 4-methyl-5-cinnamyloxy-2(5*H*)-furanone **289** was studied by irradiation (mercury high-pressure lamp) at different temperatures in acetone as the solvent (97T14701). It was shown that a photostationary equilibrium between the *cis/trans* isomers **289** and **290** is rapidly established. Then the cyclobutane derivatives **291** and **292** are generated by a slow reaction, **291** being the major product. This isomerization was believed to proceed via the intermediate **293** (Scheme 78) (97T14701).

Irradiation of cyclopentenone (at $\lambda = 366$ nm) in acetonitrile in the presence of (5*R*)-5-menthyloxy-2(5*H*)-furanone **174b** afforded four stereoisomeric cycloadducts **294a–d** (Scheme 79) (98T4873). The isolated products were formed under kinetic control (irreversible reaction). No facial stereoselectivity [(**294a** + **294c**): (**294b** + **294d**) = 1 : 1] was obtained. The absence of facial selectivity in the approach of cyclopentenone to the chiral furanone indicated that an energy transfer between the $^3\pi\pi^*$ excited state of cyclopentenone to the chiral furanone **174a** was involved (98T4873).

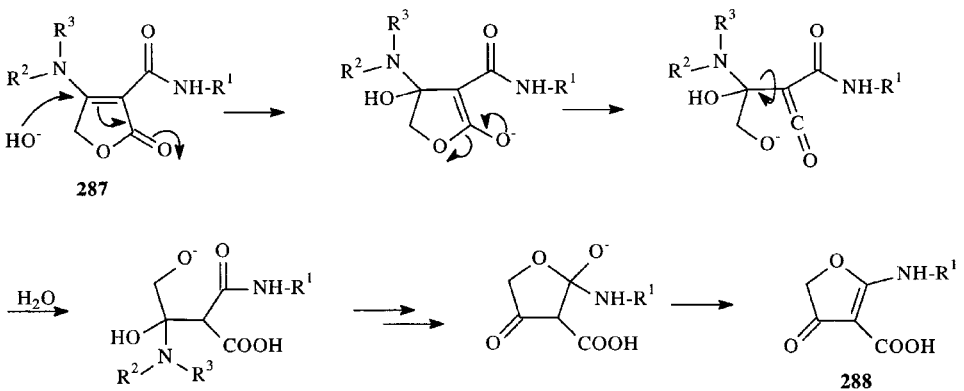
The [2 + 2]-photocycloadditions of the homochiral 2(5*H*)-furanones **129** ($R^1 = R^2 = H$), **174a** ($R^1 = OCOCH_3$, $R^2 = H$), **174b** ($R^1 = OCOPh$, $R^2 = H$), **295** [$R^1 = OCO(CH_3)_3$, $R^2 = H$] and **296** [$R^1 = OSiPh_2C(CH_3)_3$, $R^2 = H$] to vinylene carbonate were studied in order to enhance the induced facial diastereoselectivity created by a new stereogenic center. The enantiopure products **297** and **298** were obtained in good yield (Scheme 80) (98TL6961). The stereochemistry of the products was established by NOE experiments and *trans* vicinal H,H-coupling constants.

It was found out that when the bisfuranones **299** (R = H, Me, CMe_3, TMS) were irradiated in a solution of acetone saturated with ethylene (medium pressure, 125 W, mercury lamp at −78°C), the biscyclobutane adducts **300, 301,** and **302**

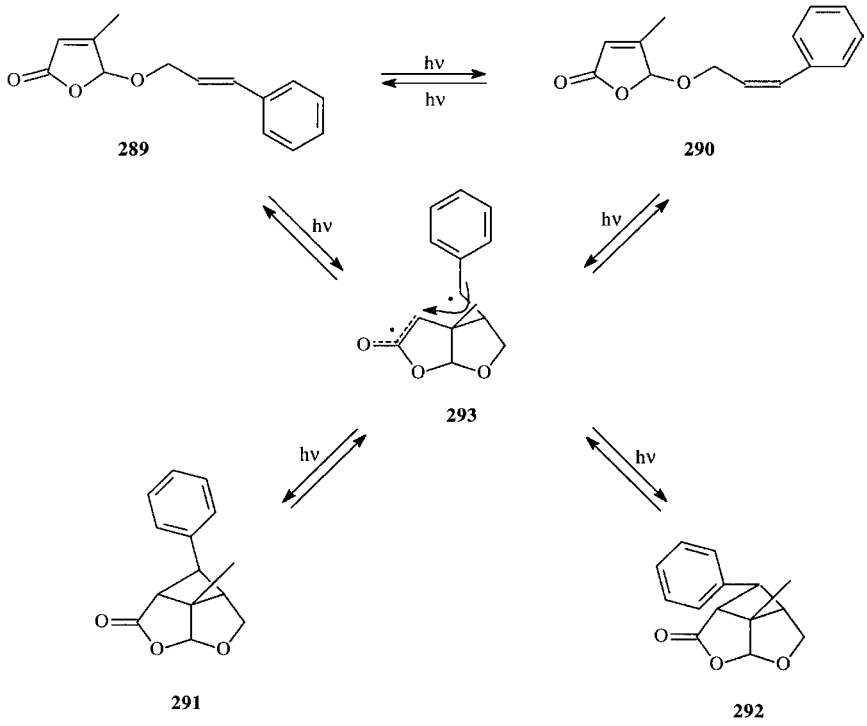
mechanism 1:



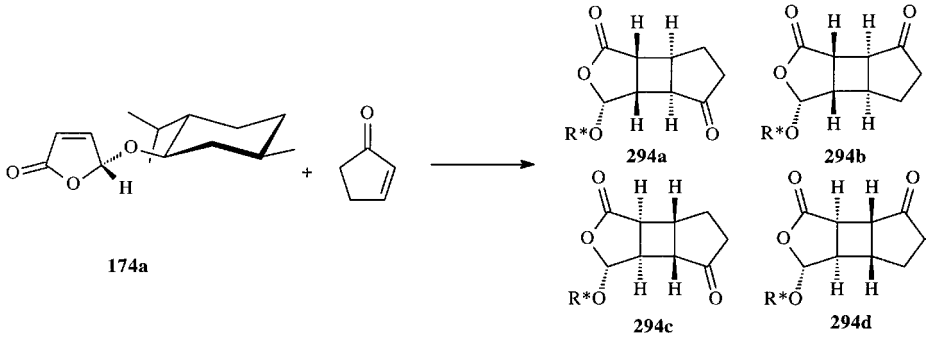
mechanism 2:



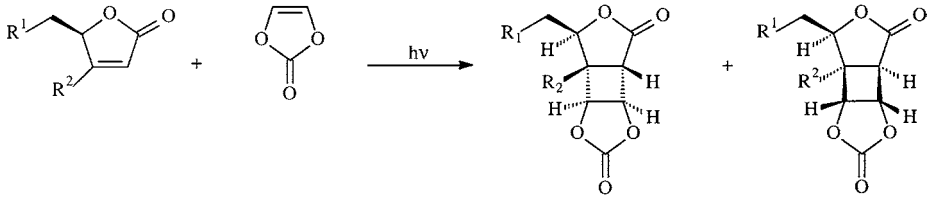
SCHEME 77



SCHEME 78



SCHEME 79



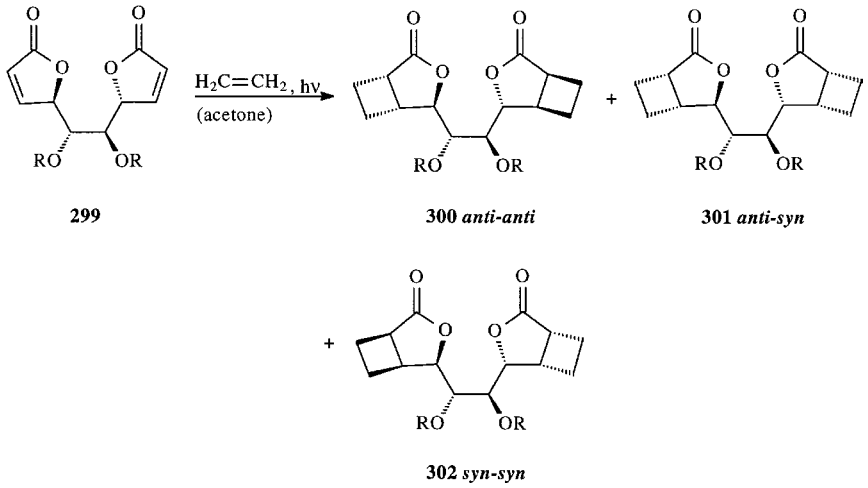
129, 174a, 174b, 295, 296 **297** **298**

SCHEME 80

were obtained in very good yields (Scheme 81) (99TL2205). The conversion was followed quantitatively by ^{1}H NMR analysis of aliquot samples. Other protecting groups for the central diol system (R^1 = Me, Et, CH_2Ph), during the [2 + 2]-photocycloaddition had been tested, albeit with less success: Very complex reaction crudes were obtained.

It was stated that tertiary amines **304** derived from pyrrolidines [R = alkyl, benzyl, $SiMe_3$, Si(*t*-Bu)$_2$Me] add very efficiently (yields up to 94%) to (5*R*)-5-menthyloxy-2(5*H*)-furanone **170** under photosensitized conditions to give the isomeric adducts **305** and **306** (Scheme 82) (99TL3169).

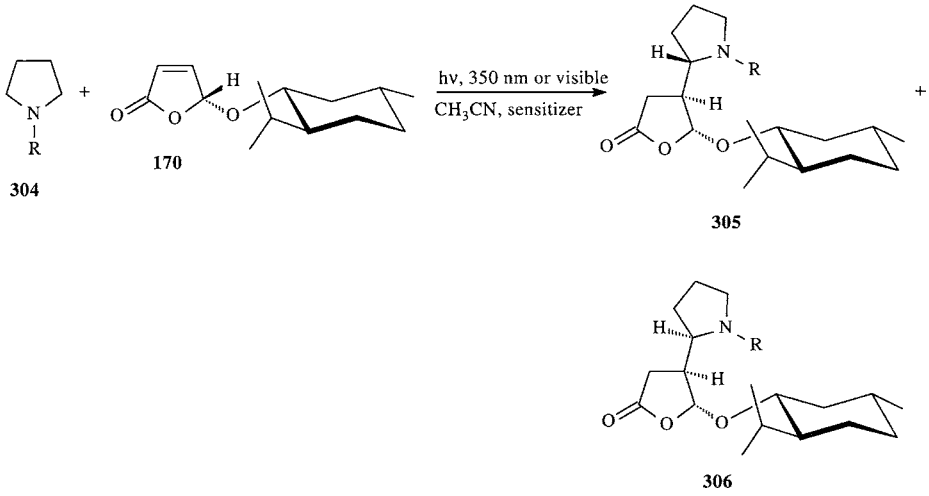
The addition followed a radical chain mechanism initiated by photoinitiated electron transfer from the tertiary amine to the excited aromatic ketone and occurred with complete facial selectivity on the furanone ring (99TL3169). The yields increased and best results were obtained with sensitizers (4-methoxyacetophenone,



299 **300** ***anti-anti*** **301** ***anti-syn***

302 ***syn-syn***

SCHEME 81



SCHEME 82

4,4′-dimethoxyacetophenone, 4,4′-dimethylaminoacetophenone) possessing an alkoxy or dimethylamino substituent in the *para* position.

IV. Conclusions

The 2(5*H*)-furanone ring system is widely spread in many biologically active natural products. They are synthesized from a variety of compounds, including cyclobutenone derivatives, acetylenic compounds, carbonyl compounds, acids, and esters, as well as from other heterocycles. Synthesis of biologically active 2(5*H*)-furanones has received great attention, especially in the last few years. 2(5*H*)-Furanones exhibit high reactivity toward different reagents due to the presence of the α,β-unsaturated carbonyl moiety. The reactions of homochiral furanones are a field of extensive study owing to the regio- and diastereoselectivity observed in most of these reactions.

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ADVANCES IN HETEROCYCLIC CHEMISTRY, VOL. 81

Organometallic Complexes of Pyrazolylborates and Related Ligands

ALEXANDER P. SADIMENKO

Department of Chemistry, University of Fort Hare, Baysville, East London 5241, Republic of South Africa

I. Introduction

In a continuation of our review of the organometallic chemistry of heterocycles [01AHC(78)1, 01AHC(79)115, 01AHC(80)157], particularly that of pyrazoles and chelating ligands containing pyrazol-1-yl groups, we now devote special attention to pyrazol-1-yl borates, gallates, methanes, and silanes, R_xEpz_{4-x} ($x = 0$–2, E = B, Ga; $x = 1, 2$, E = C, Si). The work done on the coordination and organometallic chemistry of these ligands is enormous, as is reflected in numerous reviews on the subject [71ACR17, 72CRV497, 77JOM(L)157, 83CSR331, 86PIC115,

Abbreviations: aapy, 2-acetamidopyridine; Alk, alkyl; AN, acetonitrile; Ar, aryl; Bu, butyl; cod, 1,5-cyclooctadiene; COE, cyclooctene; COT, cyclooctatetraene; Cp, cyclopentadienyl; Cp*, pentamethylcyclopentadienyl; Cy, cyclohexyl; DME, 1,2-dimethoxyethane; DMF, dimethylformamide; DMSO, dimethyl sulfoxide; dmpe, dimethylphosphinoethane; dppe, diphenylphosphinoethane; dppm, diphenylphosphinomethane; dppp, diphenylphosphinopropane; Et, ethyl; Fc, ferrocenyl; ind, indazolyl; Me, methyl; Mes, mesitylene; nb, norbornene or bicyclo[2.2.1]heptene; nbd, 2,5-norbornadiene; OTf, triflate; Ph, phenyl; PPN, bis(triphenylphosphoranylidene)ammonium; Pr, propyl; py, pyridine; pz, pyrazolate; pz′, substituted pyrazolate; pz*, 3,5-dimethylpyrazolate; quin, quinolin-8-olate; solv, solvent; tfb, tetrafluorobenzobarrelene; THF, tetrahydrofuran; THT, tetrahydrothiophene; tmeda, tetramethylethylenediamine; Tol, tolyl; Tp, $HB(C_3H_3N_2)_3$; Tp*, $HB(3,5\text{-}Me_2C_3HN_2)_3$; Tp′, substituted hydrotris(pyrazol-1-yl)borate; Ts, tosyl; tz, 1,2,4-triazolate; Vin, vinyl.

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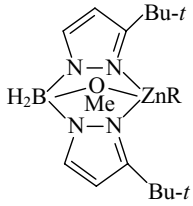
86TCC1, 87MI1, 92MI1, 93CRV943, 94CRV737, 95AIC291, 95NJC551, 95PIC419, 96CCR(147)571, 96CCR(156)201, 99ACR589, 99MI1, 99MI2]. So far, these ligands have been considered in general. However, organometallic complexes have never previously been singled out and treated systematically. Such an attempt is made herein.

Hydrotris(pyrazol-1-yl)borate ligands are similar in electronic and steric properties to their cyclopentadienyl counterparts [80IC1582, 81CSR1, 83IC2689, 83OM936, 83OM1475, 96IC1006, 97OM4071, 97OM4121, 98JCS(CC)973, 99JCS(CC)417], although differences in electrochemical, spectral, and structural properties, as well as in reactivity pattern, are often profound [84ICA(94)50, 89JCS(D)1393, 00CRV1205, 00OM2428]. This also follows from some theoretical modeling (94IC4376, 95IC3928, 96JA1703). In this respect, ligands with sterically bulky groups at the pyrazol-1-yl rings merit special concern (95JA11745, 96JA1703, 97CEJ1668). In the great majority of such complexes, hydrotris(pyrazol-1-yl)borates exhibit η^3- or η^2-coordination modes, where three or two pyrazol-1-yl frameworks are involved in coordination, respectively [85JCS(D)669, 86JA1550, 87IC1507, 89IC4392, 90IC2452, 90IC4429, 90JA3662, 90JA8190, 90JA8192, 90JCS(D)3329, 90JCS(D)3577, 91IC778, 91IC2582, 91IC2795, 91IC 4098, 91JCS(CC)717, 91JCS(D)1835, 91OM1010, 92JCS(D)1429, 94IC6050, 94OM1851]. Sometimes, the η^3-coordination situation is accompanied by the B—H $\cdots$ M agostic interaction, and quite often both coordination modes are in dynamic equilibrium in solution. Some special cases exist, including the η^2-coordination of tris- and bis(pyrazol-1-yl)borates with two nonequivalent metal–nitrogen bonds, one normal and one weak [81JCS(D)956, 87AJC1609], and pure η^1-coordination [92JCS(D)2651]. Thus, in spite of the fact that in a majority of cases pyrazol-1-ylborates play the role of spectator ligands and the further transformations refer to the metal center or the rest of the inner coordination sphere, changes of the coordination mode and other considerations make them noninnocent ligands. Dihydrobis(pyrazol-1-ylborates) resemble in properties the acetylacetonate ligand. Catalytic activity of binuclear species based on pyrazol-1-ylborates has also been reviewed (99CRV3379, 00CRV1169).

II. Complexes of Non-transition and Late Transition Metals

Thallium tris(3-*tert*-butylpyrazol-1-yl)borate with MgR_2 (R = Me, Et, *i*-Pr, *t*-Bu, CH_2SiMe_3, CH=CH_2, Ph) gives [(η^3-Tp′)MgR] (R = Me, Et, *i*-Pr, *t*-Bu, CH_2SiMe_3, CH=CH_2, Ph) (89JA7276, 90JA3662, 90POL1775, 91OM1010, 96IC 1429, 96MI1, 97POL1255). [(η^3-Tp′)BeMe] is also known (93IC4968). The products with R = *i*-Pr and *t*-Bu react with oxygen to yield the peroxo species [(η^3-Tp′)Mg(OOR)] (R = *i*-Pr, *t*-Bu) (90JA3662), while the one with R = CH_2SiMe_3 gives [(η^3-Tp′)MgOSiMe$_3$] in these circumstances (90POL1775, 90POL2655).

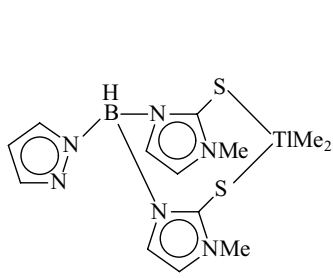
With HX, complexes [(η^3-Tp′)MgX] (X = SH, SMe, OEt, OPr-*i*, OBu-*t*, Cl, Br, I, NHPh, NCO, NCS, Ph, $Me_3SiC{\equiv}C$) result, and with acetone, the enolate [(η^3-Tp′)MgOC(Me)=CH_2] is the product (92JA748). Species [(η^3-Tp*)MgR] (R = Me, Et, *i*-Pr, *n*-Bu, *t*-Bu, Ph, Vin) are much less stable with respect to ligand redistribution and readily form [(η^3-Tp*)$_2$Mg] [90JOM(393)C43]. Trimethyl aluminum in a similar starting reaction with thallium tris(3-*tert*-butylpyrazol-1-yl)borate gives the η^2-coordinated derivative [(η^2-Tp′)$AlMe_2$], where one of the pyrazolates does not participate in coordination, while ZnR_2 (R = Me, Et) behave similarly to Grignard reagents [90JCS(CC)220]. Thus, species [(η^3-Tp′)ZnR] (Tp′ = tris(3-*tert*-butylpyrazol-1-yl)borate; R = Me, Et) are formed in an analogous reaction, and they are isomorphous to the relevant magnesium compounds [90JCS(CC)220, 91JA8414, 95OM274]. These species as well as tris(3-phenylpyrazol-1-yl)borate and tris(3-*p*-tolylpyrazol-1-yl)borate analogs (90AGE898, 93CB685) are characterized by their stability to air oxidation and hydrolysis to bis(ligand) L_2Zn. TlTp* with $CdMe_2$ gives [(η^3-Tp*)CdMe] (93OM2600). The derivative based on tris(3-methyl-5-*tert*-butylpyrazol-1-yl)borate was prepared in a similar fashion (94IC1158). Thallium phenyltris(3-*tert*-butylpyrazol-1-yl)borate with R_2Mg (R = Me, Et) or Me_2Zn gives [(η^3-Tp′)MR] (M = Mg, R = Me, Et; M = Zn, R = Me) [00JOM(596)22]. In the reaction with thallium dihydrobis(3-*tert*-butylpyrazol-1-yl)borate, ZnR_2 (R = Me, Et, *t*-Bu) give rise to [(η^2-H_2B(3-*t*-Bupz)$_2$ZnR] (R = Me, Et, *t*-Bu) (90JA4068). In reactions of the latter in acetone, the products **1** (R = Me, Et, *t*-Bu) are formed.



1

Triethyl aluminum complexes of hydrotris(3,5-di-*tert*-butylpyrazol-1-yl)borate and hydrotris(3-*tert*-butylpyrazol-1-yl)borate are characterized by the η^2-bidentate coordination (96IC445). The potassium salts of R_2Bpz_2 (R = Et, Ph, pz) react with Et_2MCl (M = Al, Ga) to yield [(η^2-R_2Bpz_2)MEt_2] (M = Al, R = Et; M = Ga, R = Et, Ph, pz) (91IC4799). [(η^2-$H_2Bpz'_2$)$AlMe_2$] (pz′ is 3,5-di-*tert*-butylpyrazol-1-yl) is known (90POL265). [(η^1-H_2Bpz_2)$_2$GaMe] and [(η^1-H_2Bpz_2)GaMeCl] follow from $MeGaCl_2$. [(η^1-R_2Bpz_2)$GaMe_2$] (R = Me, Et, Ph) are also known [90CJC59, 90OM2218, 97CCR(163)107, 98MI1]. Species [(η^2-H_2Bpz_2)$GaMe_2$] and [(η^2-Me_2Bpz_2)$GaMe_2$] can be prepared by metathesis of $Me_2GaCl(OEt_2)$ with the corresponding potassium bis(pyrazol-1-ylborato) salts. Similarly, [(η^1-H_2Bpz_2)$lnMe_2$], [(η^1-H_2Bpz_2)ln(Cl)Me], and [(η^2-H_2Bpz_2)ln(O_2CMe)]

(90OM2581), as well as [(η^2-Me_2Bpz_2)lnMe$_2$] [96JOM(512)91] can be synthesized. Thallium bis(3-*tert*-butyl-5-methylpyrazol-1-yl)borate with trimethylaluminum and -gallium gives [(η^2-$H_2Bpz'_2$)MMe$_2$] (M = Al, Ga) (99POL3567). [(η^2-Bpz$_4$)TlR$_2$] (R = Et, *n*-Bu) are known and result from sodium tetrakis (pyrazol-1-yl)borate and dialkylthallium bromide (80BCJ1459). Lithium hydrobis (2-mercapto-1-methylimidazol-3-yl)(pyrazol-1-yl)borate with dimethyl thallium chloride gives complex **2** [00JCS(D)1267]. The same starting salt enters the lithium/thallium exchange with thallium acetate and gives the thallium salt of this anionic ligand. The latter appeared to be a convenient precursor for the methylzinc derivative **3** with a coordination mode different from that prepared using dimethylzinc. The methylzinc derivative containing hydrotris(2-mercapto-1-methylimidazol-3-yl)borate is also known [00JCS(D)891].



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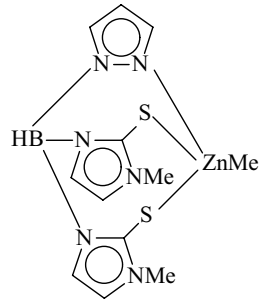


3

Potassium hydrotris(pyrazol-1-yl)borate with methyltin chlorides gives [(η^3-Tp)SnMe$_n$Cl$_{3-n}$] (*n* = 0–3) [84JOM(265)153, 86JOM(309)257, 89JOM(378)139]. Numerous analogs of these species exist [88JCR(S)410, 89JOM(387)139, 90JOM(391)155, 91IC3249, 91JOM(403)317, 92JOM(440)27], among them [(η^3-HB(4,5-$Me_3pz)_3$)SnMeCl$_2$] [95JOM(485)45] and [(η^3-HB(4-Mepz)$_3$)SnMeCl$_2$] [96JCS(D)2475]. If $Cl_3Sn(CH_2)_2COOMe$ is taken, the result is [(η^3-Tp)SnCl$_2$ $(CH_2)_2$COOMe]. The latter with potassium thiocyanate gives [(η^3-Tp)Sn(NCS)$_2$ $(CH_2)_2$COOMe] [90JOM(399)235]. Complexes [(η^3-tetrakis(nitroindazol-1-yl) borate)SnR$_3$] (R = Me, *n*-Bu, Ph) are also known [86IJC(A)863]. KBpz$_4$ and R_2SnCl_2 (R = Me, Et, *n*-Bu) give [(η^2-Bpz$_4$)SnR$_2$] (R = Me, Et, *n*-Bu) (91IC3249). The same product (R = Me) follows from KBpz$_4$ and Me_3SnCl. Solutions of these complexes show a high degree of fluxionality, and it was difficult to determine the coordination mode of the tetrakis(pyrazol-1-yl)borate ligand. HCpz$_3$ or HC(4-Mepz)$_3$ and $RSnCl_3$ react and give [(η^3-HC(4-R′pz_3))$SnCl_2R]_2$($RSnCl_5$) (R′ = H, Me; R = Me, *n*-Bu, Ph) (99IC5777). The 1 : 1 complexes are prepared from HCpz′$_3$ and $RSnCl_3$, and the products are [(η^3-HCpz′$_3$)$SnCl_2$R]($RSnCl_4$)

(pz′ = pz*, 3,4,5-Me_3pz; R = Me, *n*-Bu, Ph). Among the dihydrobis(pyrazol-1-yl)methane derivatives of tin are the species [(η^2-H_2C(4-Mepz)$_2$)$SnMe_2Cl_2$] [95JOM(496)69] and [(η^2-H_2Cpz*$_2$)$SnPh_2Cl_2$] (95MI1). An organoarsenic species [(η^3-Tp)$AsMe_2$] is known [86JCS(D)645].

III. Complexes of the Titanium and Vanadium Groups

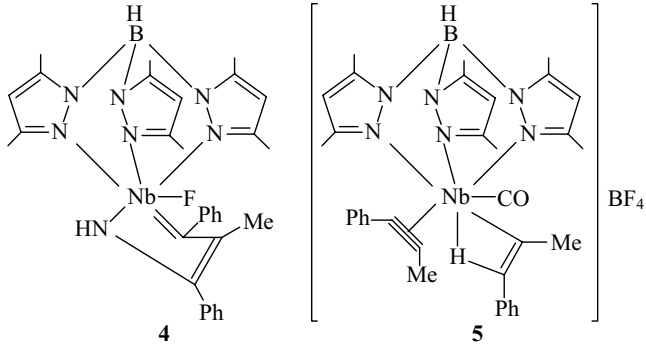
Compounds [(η^3-Tp*)Ti(OR)Cl_2], [(η^3-Tp*)Ti(OR)$_2$Cl], and [(η^3-Tp*)Ti(OR)$_3$] (R = Me, Et) with MeMgl and Me_3SiCH_2MgCl give [(η^3-Tp*)Ti(OR)$_2$R′] (R′ = Me, Me_3SiCH_2) [92JOM(426)59]. Tetraethylammonium hydrotris(pyrazol-1-yl)borate enters the ligand substitution with [Ti(CO)$_5$(dmpe)] to yield the titanium(0) species (NEt_4)[(η^3-Tp)Ti(CO)$_4$] (88JA163).

[(η^5-Cp)MCl_2] (M = Zr, Hf) and the protonated form of Tp^- give [(η^5- Cp)M(η^3-Tp)Cl_2] (M = Zr, Hf) [86IC2046, 90POL2185, 91JCS(D)603]. Further reaction of the zirconium species with phenols HOC_6H_4R (R = H, 4-OMe, 4-NO_2, 2-Ph) in the presence of triethylamine yields the bis(phenoxide) species [(η^5-Cp)Zr(η^3-Tp)(OC_6H_4R)$_2$] (R = H, 4-OMe, 4-NO_2, 2-Ph), and that of the hafnium species with HOC_6H_4R (R = 4-F, 4-OMe) affords [(η^5-Cp)Hf(η^3-Tp)(OC_6H_4R)$_2$] (R = 4-F, 4-OMe). However, the hafnium phenoxide species could not be isolated and their structures follow from the spectral data. The coordination environment of the zirconium site in [(η^2-H_2Bpz$_2$)Zr(Cp)$_2$] is formed by the two nitrogen heteroatoms and the B—H framework (86IC2046). Complex [(η^2-H_2Bpz$_2$)Ti(η^5-Cp)$_2$] is known [75JOM(102)167].

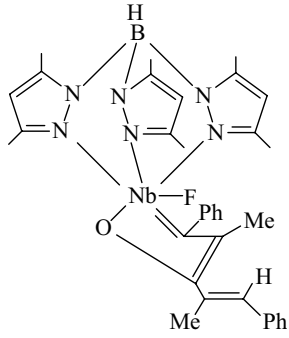
Complexes [(η^2-L)$TaMe_3Cl$] (L = Tp, Tp*, Bpz_4) are characterized by the η^2 mode which excludes one of the two pyrazol-1-yl groups of the coordination unit (84IC349). Complexes [(η^3-Tp)$NbCl_2$(η^2-RC≡CR′)] (R = Ph, R′ = Me; R = R′ = Me, Et, $SiMe_3$, Ph) (91OM3801, 96OM1106, 96OM4597, 98OM3015) are prepared from $NbCl_3$(DME)(RC≡CR′) and the corresponding potassium pyrazol-1-ylborate salt. Species [(η^3-Tp*)$NbCl_2$(η^2-RC≡CR′)] (R = R′ = Me, Ph; R = Ph, R′ = Me, Et, *n*-Pr, Ph, $SiMe_3$) are known as well (93OM4010, 97JA3218). [(η^3-Tp)$NbCl_2$(η^2-PhC≡CMe)] with the DME solvate of sodium cyclopentadienyl gives [(η^3-Tp)(η^5-Cp)NbCl(η^2-PhC≡CMe)]. [(η^3-Tp*)Nb(CO)$_2$(η^2-PhC≡CMe)] (96AQIE88) with nitriles RC≡N gives [(η^3-Tp*)Nb(CO)(η^2-PhC≡CMe)(η^2-RC≡N)] (R = Me, Et, Ph, $PhCH_2$, 4-$MeOC_6H_4$, 4-$CF_3C_6H_4$) (96OM1090, 99OM3075). The product with R = Ph enters the ligand substitution reactions with methylphenylacetylene to give [(η^3-Tp*)Nb(CO)(η^2-PhC≡CMe)$_2$] and with dimethylphenylphosphine to afford [(η^3-Tp*)Nb(CO)(η^2-PhC≡CMe)(PMe_2Ph)].

Protonation of [(η^3-Tp*)Nb(CO)(η^2-PhC≡CMe)(η^2-PhC≡N)] with tetrafluoroboric acid proceeds differently depending on conditions. At relatively low temperatures the product is [(η^3-Tp*)Nb(CO)(η^2-HN=CPh)(η^2-PhC≡CMe)]BF_4, while at

higher temperatures or in a broad range of temperatures but in methylene chloride medium, **4** is formed. Protonation of [(η^3-Tp*)Nb(CO)(η^2-PhC≡CMe)$_2$] gives **5** at low temperatures and **6** at higher temperatures or at any temperature if the reaction is conducted in methylene chloride.



4 **5**



6

[(η^2-H$_2$Bpz*$_2$)TaMe$_3$Cl] is characterized by a less common coordination mode when not only two nitrogen atoms but also the B—H group bridge the tantalum site (83JA5343). Species [(η^2-H$_2$Bpz$_2$)$_2$TaMe$_3$] is also known [74JOM(77)C25, 76JCS(D)807]. Bis(pyrazol-1-yl)methanes (L), including those with pyrazol-1-yl as well as with 3,5-dimethyl- and 3-trimethylsilylpyrazol-1-yl fragments, with NbCl$_3$(DME) form the dimers [(η^2-L)NbCl$_3$]$_2$ that react with diphenylacetylene to yield [(η^2-L)NbCl$_3$(η^2-PhC≡CPh)] [95JCS(D)1015]. A wider variety of such complexes follows from [NbCl$_3$(DME)(η^2-RC≡CR)] and the aforementioned ligands giving [(η^2-L)NbCl$_3$(η^2-RC≡CR)] (R = Ph, COOMe, Me). Tris(pyrazol1-yl) methane and tris(3,5-dimethylpyrazol-1-yl)methane (L) with [NbCl$_3$(DME)

(η^2-RC≡CR)] and silver tetrafluoroborate in turn give [(η^3-L)$NbCl_2$(η^2-RC≡CR)] (BF_4) (R = Ph, Me). Lithium hydrate of bis(3,5-dimethylpyrazol-1-yl)acetate also reacts with [$NbCl_3$(DME)(RC≡CR′)] to give [(η^3-HCpz*$_2$COO)$NbCl_2$(η^2-RC≡CR′)] (R = R′ = Me, Et, Ph, $SiMe_3$; R = Ph, R′ = Me, Et, $SiMe_3$) [99JCS(D) 3537, 00JCS(D)2367]. 2,2′-Bis(3,5-dimethylpyrazol-1-yl)ethanol in the same circumstances gives a series of complexes [(η^3-HCpz*$_2$$CH_2O$)$NbCl_2$($\eta^2$-RC≡CR′)] (R = R′ = Me, Et, Ph; R = Ph, R′ = Me, Et, $SiMe_3$). Compound [(η^3-HCpz*$_2$ COO)$NbCl_2$(η^2-PhC≡CMe)] with lithium trimethylsilylcyclopentadienyl gives [(η^3-HCpz*$_2$COO)NbCl(η^5-$C_5H_4SiMe_3$)].

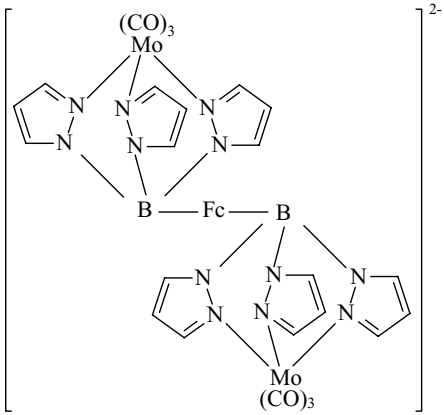
IV. Complexes of the Chromium Group

In [(η^3-Tp)$Mo(CO)_3$]$^-$, prepared from the tris(pyrazol-1-yl)borate anion and [$Mo(CO)_6$] or [$Mo(CO)_3$(η^6-toluene)] (86OM2529), hydrotris(pyrazol-1-yl)borate fragment donates one electron to the molybdenum site in a π fashion using appropriate combinations of the σ-orbitals of the pyridine-like nitrogen atoms, while cyclopentadienyl in [(η^5-Cp)$Mo(CO)_3$]$^-$ donates only 0.81e$^-$ (83OM936, 86JA3335). Under the action of oxidizing agents like Cp_2Fe^+, the complex anion turns into the paramagnetic radical. The 17-electron radical [(η^3-Tp)$Mo(CO)_3$]$^\bullet$ was isolated [88JOM(348)357]. It decarbonylates to give [(η^3-Tp)$_2Mo_2(CO)_4$] containing the Mo≡Mo bond (86JA3335). Complex (NEt_4)[(η^3-Tp*)$W(CO)_3$] is oxidized by ferrocenium to generate a stable 17-valence-electron radical W(I) species [(η^3-Tp*)$W(CO)_3$]$^\bullet$. The stability and monomeric character of this radical species and its analogs (molybdenum species, Tp derivatives of both tungsten and molybdenum) are well known [86JA3335, 88JOM(348)357, 91MI1, 92OM-2761, 93JA5077, 93JA5559]. Further oxidation leads to the cationic [(η^3-Tp*) $W(CO)_3$]$^+$, which adds various phosphines to give the seven-coordinate complexes [(η^3-Tp*)$W(CO)_3$L]$^+$ (L = PMe_3, PMe_2Ph, PPh_3, PEt_3) (92IC3825). Electrochemical study of the whole series [(η^3-Tp)$M(CO)_3$]$^-$ (M = Cr, Mo, W) is performed (90IC1736). The anion [(η^3-Tp*)$Mo(CO)_3$]$^-$ is also characterized by the η^3-coordination of the Tp* ligand [82JOM(226)57]. Both Tp and Tp* anionic species of the whole range of group VI metals may be protonated to yield [(η^3-Tp) $M(CO)_3H$] and [(η^3-Tp*)$M(CO)_3H$], respectively (93JA5077).

The tungsten species [(η^3-L)$W(CO)_3H$] (L = Tp, Tp*) are extensively described [69JA588, 76JCS(D)898, 83POL53, 89JA6477, 91OM2842, 92JA2951, 92OM-1295, 97OM370]. Potassium tris(3-*tert*-butylpyrazol-1-yl)borate with [$W(CO)_3$ $(EtCN)_3$] gives [(η^3-Tp′)$W(CO)_3$]$^-$ (91OM2842). The reaction of [$W(CO)_6$] with this ligand does not occur, although it takes place with hydrotris(3-phenylpyrazol-1-yl)borate, and the product is further protonated to yield [(η^3-Tp′)$W(CO)_3H$]. Lithium ferrocenyltris(pyrazol-1-yl)borate with $Mo(CO)_6$ gives Li[(η^3-FcBpz$_3$)

$Mo(CO)_3$] and analogous transmetallation of an appropriate dimeric ligand gives complex **7** (97IC2103). Both species with 3-bromo-2-methyl-1-propene give the η^3-methylallyl products of substitution of one carbonyl group. Similar complexes of hydrotris(3,5-dimethyl-1,2,4-triazol-1-yl)borate ligand are known, namely $[N(PPh_3)_2][(\eta^3\text{-}HBtz_3)Mo(CO)_3]$ [93JOM(453)211] and $(NEt_4)[(\eta^3\text{-}HBtz_3)Mo(CO)_3]$ [96JOM(506)301]. The latter is made from the corresponding potassium salt and $Mo(CO)_6$ followed by the subsequent metathesis with tetraethyl ammonium chloride. Oxidation of the product with molecular iodine gives $[(\eta^3\text{-}HBtz_3)Mo(CO)_3I]$. Methyltris(3,5-dimethylpyrazol-1-yl)silane reacts with $M(CO)_6$ (M = Mo, W), $[M(CO)_3(AN)_3]$ (M = Mo, W), or $[W(CO)_3(EtCN)_3]$ to yield $[(\eta^3\text{-}MeSipz^*_3)M(CO)_3]$ (M = Mo, W) (00IC1561). Oxidative bromination or iodination of $(NEt_4)[(\eta^3\text{-}Tp)Mo(CO)_3]$ gives $[(\eta^3\text{-}Tp)Mo(CO)_3X]$ (X = Br, I) (85IC1213, 86JA3335); iodination of $(NEt_4)[(\eta^3\text{-}Tp^*)W(CO)_3]$ gives $[(\eta^3\text{-}Tp^*)W(CO)_3I]$ (91OM3504, 98IC1299). The product and the starting reagent react to give $[(\eta^3\text{-}Tp^*)W(CO)_3]$. Addition of molecular iodine to the latter gives the iodo complex. The starting species containing hydrotris(3-isopropylpyrazol-1-yl)borate enters the same reactions. A complex of hydrobis(3-isopropylpyrazol-1-yl)(5-methylpyrazol-1-yl)borate is also known (95IC5950, 96IC5368). Oxidative bromination of $[(\eta^3\text{-}Tp^*)W(CO)_3]$ takes a more complicated route yielding a mixture of the expected $[(\eta^3\text{-}Tp^*)W(CO)_3Br]$ and new $[(\eta^3\text{-}(4\text{-}Brpz^*_3BH)W(CO)Br]$ products. In the latter species all three pyrazol-1-yl rings undergo bromination at position 4. This concurrent ring bromination (or chlorination) reaction is avoided when $(NEt_4)[(\eta^3\text{-}Tp^*)W(CO)_3]$ interacts with *N*-bromo- or *N*-chlorosuccinimide, the products being $[(\eta^3\text{-}Tp^*)W(CO)X]$ (X = Br, Cl).

At slightly elevated temperatures (reflux in AN or THF), $[(\eta^3\text{-}Tp^*)W(CO)_3X]$ (X = Cl, Br, I) and $[(\eta^3\text{-}(4\text{-}Brpz^*_3BH)W(CO)_3Br]$ give the corresponding *cis*-dicarbonyl complexes, the process being reversible. Prolonged reflux in acetonitrile leads to the formation of the products of CO/AN substitution, $[(\eta^3\text{-}Tp^*)W(CO)Br(AN)]$ and $[(\eta^3\text{-}(4\text{-}Brpz^*_3BH)W(CO)Br(AN)]$. These complexes are precursors for the acylimidotungsten(IV) species (98IC590). The complex $[(\eta^3\text{-}Tp^*)W(CO)_2I]$ (91OM3504, 92IC3825) is obtained by reflux of $[(\eta^3\text{-}Tp^*)W(CO)_3I]$ in toluene, contains 16 valence electrons, and is oxidized by moist air, yielding $[(\eta^3\text{-}Tp^*)WO(CO)I]$ (91IC2582). $[(\eta^3\text{-}Tp^*)W(CO)_2I]$ reacts with acetylenes to afford $[(\eta^3\text{-}Tp^*)W(CO)I(PhC{\equiv}CR)]$ (R = H, Me). With amines, $[(\eta^3\text{-}Tp^*)W(CO)_2I]$ gives amido complexes $[(\eta^3\text{-}Tp^*)W(CO)_2(NR_2)]$ (92JA7928, 92OM1433). Reaction between KTp^* and $[Mol_2(CO)_3(AN)_2]$ was reported to give $[(\eta^3\text{-}Tp^*)Mo(CO)_2I] \cdot 2AN$ (96POL1705). The product obtained was very unstable and rapidly transformed to the insoluble compound, which was tentatively regarded as a tetramer consisting of two dimeric units $[(\eta^3\text{-}Tp^*)Mo_2O_4(CO)_2(OH)]$. Attempts to isolate the iodine-containing product led to the degradation of the Tp^* ligand and isolation of $[Mo_4O_4(\mu_3\text{-}O)_2(\mu_2\text{-}OH)_2(Hpz^*)_6]I_2 \cdot 4AN$. However, these data were later disputed by Saleh *et al.* (97POL1391).



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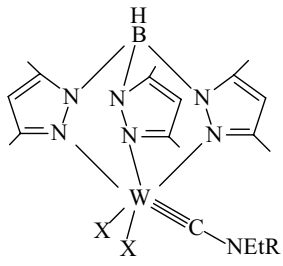
Ligand substitutions allowed preparation and study of [(η^3-Tp)Mo(NO)$(CO)_2$] [76ACSA(A)225], [(η^3-Tp*)Mo(NO)$(CO)_2$] [84IC2721, 85IS4, 85JCS(D)1249], [(η^3-Tp*)Mo(CO)(NO)(PPh_3)] and a number of derivatives [85ICA(96)L5], [(η^3-Bpz_4)Mo(CO)(NO)(PPh_3)] [77AX(B)2653], as well as mixed carbonyl–nitrosyl complexes of the derivatives of tris(pyrazol-1-yl)borate anion, [(η^3-Tp′)Mo$(CO)_2$(NO)], where Tp′ = tris(3-*p*-methoxyphenylpyrazol-1-yl)borate [92JCS(D)2435] and tris(4-benzyl-3,5-dimethylpyrazol-1-yl)borate [94JCS(D)2559]. Complexes [(η^3-Tp′)Mo$(CO)_2$(NO)] [Tp′ = tris(4-*R*-3,5-dimethylpyrazol-1-yl)borate, R = Me, Et, *n*-Pr, *n*-Bu, *n*-C_5H_{11}] are prepared from the corresponding pyrazol-1-ylborate salt and $Mo(CO)_6$ with subsequent nitrosylation using *p*-$TolSO_2NH(NO)$ (96POL27). Further interaction with iodine and benzyl chloride gives [(η^3-Tp′)$MoCl_2$(NO)] with R = Me and *n*-Bu.

Photolysis of [(η^3-Tp*)W$(CO)_3$H] with nitriles RC≡N (R = Me, Et) gives azavinylidenes [(η^3-Tp*)W$(CO)_2$(=N—CHR)] (94JA8613); with alkynes $RCH_2C{\equiv}CR'$ (R = Me, Et; R′ = H, Ph), mixtures of η^2-vinyl and η^3-allyl species result, which give the η^3-allyl derivatives [(η^3-Tp*)W$(CO)_2$(η^3-RHCCHCHR′)] on heating (97OM3737). Photolysis with PhC≡CR (R = H, Ph) gives only η^2-vinyl complexes [(η^3-Tp*)W$(CO)_2$(η^2-CPh=CHR)] (00OM1497). The same type of reaction run in the presence of methylacetylene gives the carbyne [(η^3-Tp*)W$(CO)_2$(≡CMe)]. With trimethylsilylacetylene, however, a mixture of η^2-vinyl, [(η^3-Tp*)W$(CO)_2$(η^2-C$(SiMe_3)$=CH_2)], and carbyne, [(η^3-Tp*)W$(CO)_2$(≡CCH_2SiMe_3)], results. *tert*-Butylacetylene gives the η^2-acyl species [(η^3-Tp*)W$(CO)_2$(trans-η^2-C(O)CH=CHBu-*t*)] as the major product together with minor amounts of the η^2-vinyl [(η^3-Tp*)W$(CO)_2$(η^2-C(*t*-Bu)=CH_2)] and carbyne [(η^3-Tp*)W$(CO)_2$(≡CCH_2Bu-*t*)].

With propyne or 1-hexyne, the mixture of the photolysis products consists of the η^2-vinyl species [(η^3-Tp*)W$(CO)_2$(η^2-C(R)=CH_2)] (R = Me, *n*-Bu) (00OM221,

00OM1497) and metallafuran [(η^3-Tp*)W(CO)$_2$(η^2(C,O)—CR=CHC(=O)CH=CHR)] (R = Me, *n*-Bu) (00OM1497). Finally, photolysis in the presence of $Me_3SiC{\equiv}CMe$ gives the allyl species [(η^3-Tp*)W(CO)$_2$(η^3-$CH_2CHCHSiMe_3$)]. Complexes **8** (R = Me, Et; X = CO) [92JOM(438)C15] on decarbonylation with molecular bromine or iodine produce monoaminocarbynes **8** (R = Me, Et; X = Br, I) [93JOM(459)233, 94POL353]. The seven-coordinate product of incomplete carbonylation, [(η^3-Tp*)Br_2(CO)W≡CNREt], is not stable [83CSR331, 87JA2938, 91OM693, 92JOM(438)C15]. Reductive dehalogenation by sodium amalgam in the presence of ethyl isonitrile gives **8** (R = Me, Et; X = EtNC) [93JOM(459)233]. The reagent Et_3OBF_4 causes ethylation of **8** (R = Me, Et; X = EtNC) to give **9** (R = Me, Et).



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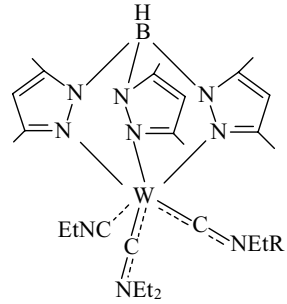

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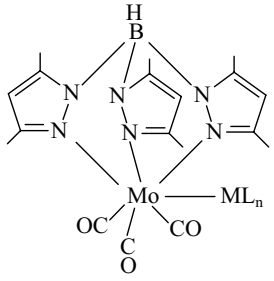
Complexes [(η^3-Tp)Mo(CO)$_3$]$^-$ and [(η^3-Tp*)Mo(CO)$_3$]$^-$ exhibit the ligating properties with respect to R_3SnCl (R = Me, Ph), Me_2SnCl_2, $[Cu(PPh_3)Cl]_4$, and [CuI(tmeda)] (88CJC1997), the products being represented by a general formula **10** [R′ = H, Me (R′ are not shown); M = Sn, L_n = Me_2Cl, Ph_2Cl; ML_n = Cu(PPh_3), Cu(tmeda)]. In this series, the species [(η^3-Tp)Mo(CO)$_3$Rh(PPh_3)$_2$] should be mentioned (86CJC373). Reaction of [(η^3-Tp*)Mo(CO)$_3$]$^-$ with copper(I) iodide and dppe gives the trinuclear product **11** (88CJC2194).

The nucleophilic attack by KHB(O^{i}Pr)$_3$ on the carbyne [(η^3-Tp*)W(CO)$_2$(≡$CPMe_3$)](PF_6) gives the carbene [(η^3-Tp*)W(CO)$_2$(=C(H)PMe_3)], and subsequent addition of methyl iodide leads to the hydrocarbyne [(η^3-Tp*)W(CO)$_2$(≡CH)] (87OM1350, 93MI1). The silylcarbynes [(η^3-Tp*)M(CO)$_2$(≡$CSiMe_2Ph$)] (M = Mo, W) can be attained starting from M(CO)$_6$ (M = Mo, W) by a consecutive reaction with dimethylphenylsilyllithium, $(F_3CCO)_2O$ and KTp* (91JA5057). Further interaction of these carbynes with tetra-*n*-butylammonium fluoride also leads to hydrocarbynes [(η^3-Tp*)M(CO)$_2$(≡CH)] (M = Mo, W). Dimerization of both these products gives species **12** (M = Mo, W). Complexes [(η^3-Tp)M(CO)$_2$(≡CR)] (R = H, Me, *p*-Tol; M = Mo, W) are well known for their remarkable



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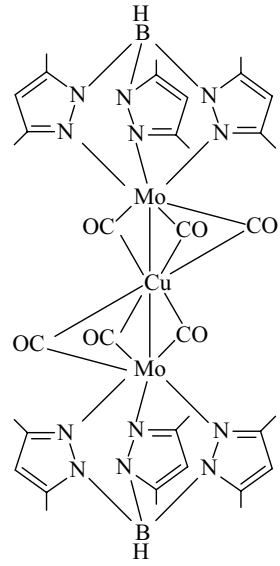

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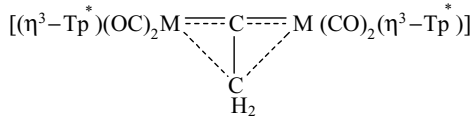
reactivity [82JOM(240)371, 82JOM(265)257, 86JCS(D)187, 86JCS(D)1697, 87JCS(D)1235, 89JOM(378)81, 89POL2265, 93MI2]. Potassium hydrotris (pyrazol-1-yl)borate with [M(≡CTol-*p*)Br(CO)$_4$] (M = Cr, Mo) gives [(η^3-Tp)M(≡CTol-*p*)(CO)$_2$] (M = Cr, Mo) [87JCS(D)1235]. The molybdenum and tungsten complexes react with $Fe_2(CO)_9$ and form two products, **13** (M = Mo) and **14** (M = Mo, W). Complexes **13** (M = Mo, W) give the products of the CO/PMe_3 monosubstitution. The molybdenum complex **13** reacts with sulfur to yield mainly **15** and a trace amount of **16.** The tungsten species [(η^3-Tp)W(≡CMe)(CO)$_2$] reacts with [$Mo_2(CO)_4(\eta^5$-Cp)$_2$] or [Mo(CO)$_3$(AN)$_2$] to give the trinuclear complexes **17** and **18.** Among the starting species for numerous cluster compounds is [(η^3-Tp)Mo(≡CC_6H_4OMe-2)(CO)$_2$] [88JCS(D)2467, 88JCS(D)3035]. Species [(η^3-Tp)W(≡CTol-*p*)(CO)$_2$] with [$Co_2(CO)_8$] gives [Co_2W(μ_3-CTol-*p*)(CO)$_8$(η^3-Tp)]; [(η^3-Tp)W(≡CMe)(CO)$_2$] with [Rh(CO)$_2$(η^5-indenyl)] affords [Rh_2W(η^3-Tp)(μ_3-CMe)(μ-CO)(CO)$_2$(η^5-C_9H_7)$_2$] [86JCS(D)187, 88JOM(347)115]; [(η^3-Tp)W(≡CTol-*p*)(CO)$_2$] with [$Fe_2(CO)_9$] yields [FeW(η^3-Tp)(μ_2-CTol-*p*)(CO)$_5$] and on carbonylation [FeW(η^3-Tp)(μ_2-CTol-*p*)(CO)$_6$] [84JCS(CC)1623, 86JCS(D)1697]. On heating with diphenylphosphine, the pentacarbonyl derivative [FeW(η^3-Tp)(μ_2-CMe)(CO)$_5$] gives [FeW(η^3-Tp)(μ_2-PPh_2)(CO)$_5$] [86JCS(D)-1709]. Reaction of [(η^3-Tp)W(CO)$_2$(≡CTol-*p*)] with [Ru(CO)$_4$(η^2-C_2H_4)] leads to the tetranuclear cluster [(η^3-Tp)W(≡CTol-*p*)Ru_3(CO)$_{11}$] [88JCS(D)3035]. Complex [(η^3-Tp′)W(CO)$_2$(≡CTol-*p*)] [Tp′ = hydrotris(3-phenylpyrazol-1-yl)borate] should be mentioned here as well (91POL215).



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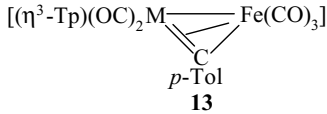

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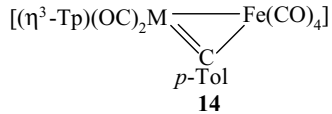

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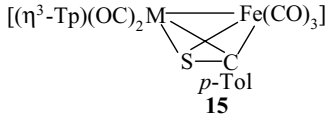

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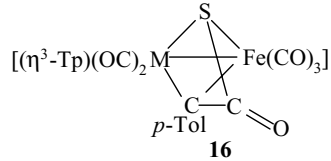

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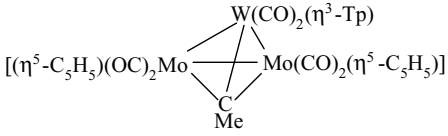

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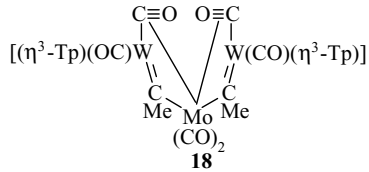


18

Cluster formation with $Co_2(CO)_8$ was also studied for [(η^3-Tp*)Mo(≡C—C≡CBu-*t*)$(CO)_2$] and [(η^3-Tp)W(≡C—C≡CBu-*t*)$(CO)_2$] [89JCS(D)2261], the products being [(η^3-Tp*)Mo(≡C—C≡CBu-*t*)$Co_2(CO)_8$] and [(η^3-Tp)W(≡C—C≡CBu-*t*)$Co_2(CO)_8$], respectively.

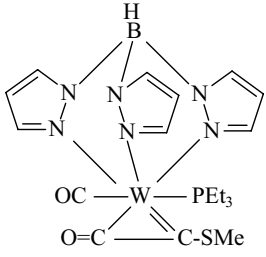
[(η^3-Tp)$W(CO)_2$(CS)]$^-$ has an interesting reactivity pattern (75JA1261, 81IC2983). Oxidative iodination gives [(η^3-Tp)$W(CO)_2$(CS)I] [80JOM(191)49]. It is alkylated at the sulfur atom to give [(η^3-Tp)$W(CO)_2$(CSR)] [89JOM(378)81]. The methylation product, [(η^3-Tp)$W(CO)_2$(≡CSMe)], with triethylphosphine gives the η^2-ketenyl **19,** which could be further methylated to **20.** [(η^3-Tp)$W(CO)_2$(C≡SMe)] can also be protonated to yield [(η^3-Tp)$W(CO)_2$(η^2-CSHMe)]$^+$. Addition of the phosphine ligands to the latter gives [(η^3-Tp)$W(CO)_2$(η^2-CSHMe)(PR_3)]$^+$ (R_3 = Ph_3, Ph_2H). When deprotonated, the product (R_3 = Ph_2H) gives **21** (86OM2481). [(η^3-Tp)$W(CO)_2$(CSMe)] enters nucleophilic addition reactions with the anions of mercaptans and ethylene malonate to afford [(η^3-Tp)$W(CO)_2$ (η^2-CSMe)X] [X = SMe, SEt, SPr-*i*, $CH(COOMe)_2$], and with the neutral 4-dimethylaminopyridine (L), [(η^3-Tp)$W(CO)_2$(η^2-CSMe)(L)]$^+$ is formed. Secondary amines, dimethyl- and diethylamine, give the products of the SMe substitution, [(η^3-Tp)$W(CO)_2$(≡CNR_2)] (R = Me, Et), and primary amines similarly give

[(η^3-Tp)W(CO)$_2$(≡CNHR)] (R = Me, Et, *i*-Pr, *t*-Bu, CH_2CH_2OH, *p*-Tol) which is in isomeric equilibrium with [(η^3-Tp)W(CO)$_2$(H)(CNR)] (86OM2489, 93MI1).

Species [(η^3-Tp)W(CO)$_2$(≡CSMe)] with the methylsulfide cation gives [(η^3-Tp)W(CO)$_2$(η^2-C(SMe)SMe)]$^+$, readily converting into [(η^3-Tp)W(CO)$_2$(η^2-C(SMe)(X)SMe)] (X = H, Me, SPh) [89JOM(375)73]. Thermolysis of **22** (R = Me, Et) gives the products of decarbonylation, cleavage of the C—S bond, and migration of the SR (R = Me, Et) moiety, **23** (R = R′ = Me; R = Me, Et, R′ = Et, Me) (90JA194). Species **22** (R = Ph, *p*-Tol) eliminate RSSMe (R = Ph, *p*-Tol) in these conditions and produce [(η^3-Tp)(OC)$_2$W(≡CSMe)]. The same reaction for **22** (R = Ph, *p*-Tol) but under photolytic conditions gives **23** (R = Ph, *p*-Tol; R = Me) (90JA194). The similar complex [(η^3-Tp*)(OC)$_2$Mo(≡CSC$_6$H$_4$—NO$_2$-4)] is also mentioned [84JCS(CC)75]. With ClAu(PR$_3$) (R = Me, Ph), [(η^3-Tp)W(CO)$_2$(CS)]$^-$ gives the products **24** where the gold atom adds to the tungsten site (84OM1124, 86JA5154). The tungsten–molybdenum (**25**) (89JA4995) and tungsten–platinum (**26**) (87OM50) complexes have similar arrangements.

Species [(η^3-Tp)Mo(CO)$_3$]$^-$ and [(η^3-Bpz)$_4$Mo(CO)$_3$]$^-$ with arenediazonium cations give **27** (R = H, pz; R′ = Ar) (66IC300, 69IC2675), while [(η^3-Tp*)Mo(CO)$_3$]$^-$ give the σ-arene **28** (R′ = Ar) with evolution of molecular nitrogen (71IC504). The other species of this nature are [(η^3-Tp)W(CO)$_2$(N=NPh)] [90JOM(381)213], [(η^3-Tp)Mo(CO)(N=NPh)(PPh$_3$)]BF$_4$ [90JOM(381)357], and [(η^3-Tp)M(CO)$_2$(N=NAr)] (M = Mo, W; Ar = *m*- and *p*-FC$_6$H$_4$) [74JCS(D)1837, 74JOM(67)C19]. Anions [(η^3-Tp*)M(CO)$_3$]$^-$ served as the starting materials for the numerous coordination compounds of molybdenum and tungsten not containing the metal–carbon bond, [e.g., 86IC3667, 86ICA(114)L7, 92IC593, 96OM2428, 98OM182]. The range of the Ar groups in complexes **28** embraces Ph, 4-O$_2$NC$_6$H$_4$, and 4-Me$_2$NC$_6$H$_4$. However, more recent structural studies permit rejection of structure **28** in favor of the isomer **29** containing the η^2-coordinated aroyl group.

The tungsten analog [(η^3-Tp*)W(CO)$_2$(η^2-COPh)] was prepared from [(η^3-Tp*)W(CO)$_3$]$^-$. The isomerization trend was confirmed by the theoretical computations of [(η^3-Tp)Mo(CO)$_3$Me] and [(η^3-Tp)Mo(CO)$_2$(η^2-COMe)] species



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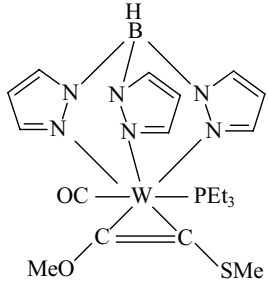

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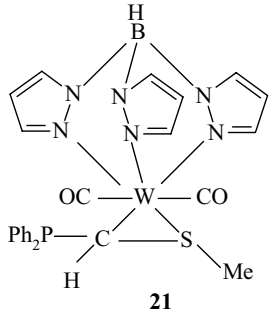

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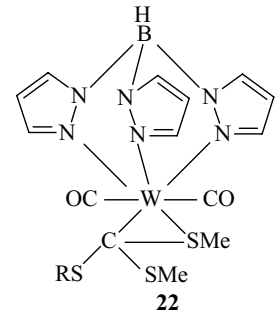

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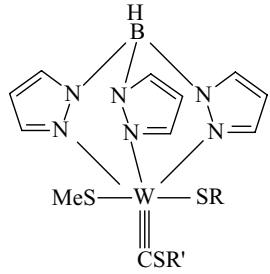

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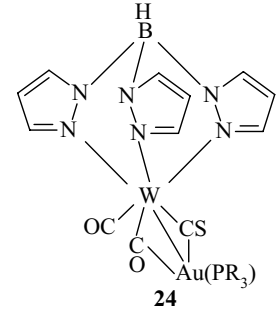

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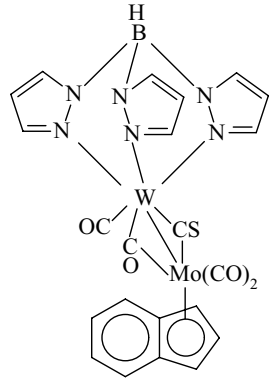

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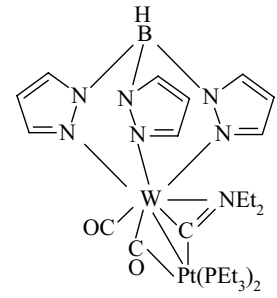

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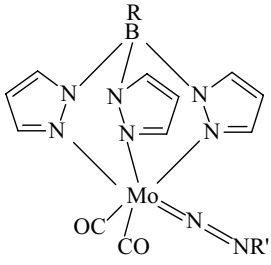
and by the fact that interaction of the parent anion with methyl iodide or OMe_3^+ leads exclusively to the η^2-COMe product (86JA1550, 86JA3335). All these reactions were conducted in DMF. 3-Methyl- [84JOM(277)91], 3,4,5-trimethyl-, and 3,5-dimethyl-4-chloropyrazol-1-yl [95JCS(D)1709] analogs react exclusively along the σ-aroyl route. If this type of transformation is run in mixtures of acetonitrile/cyclohexane or dichloromethane/cyclohexane, the product [(η^3-Tp*)



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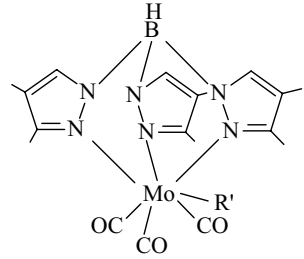

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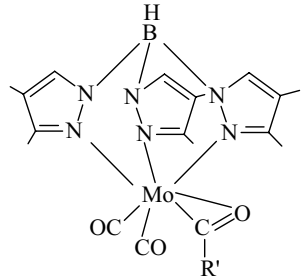

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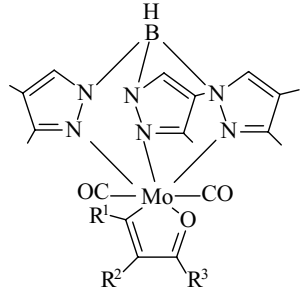
$Mo(CO)_2(\eta^2\text{-COCy})$] followed [83JCS(CC)55]. Oxidation of [$(\eta^3\text{-Tp}^*)Mo(CO)_3I$] with diphenyliodonium in methyl iodide gives [$(\eta^3\text{-Tp}^*)Mo(CO)_2(\eta^2\text{-COMe})$], and in THF this reaction becomes possible even in the absence of an oxidant (89JA2550, 89JCCS31).

Other reactions of similar nature are known (88JCCS187, 89JCCS25, 90OM669). Anion [$(\eta^3\text{-Tp}^*)Mo(CO)_3]^-$ is not directly oxidized by triphenylsulfonium cation. The first step of the process is salt formation leading to [SPh_3][$Mo(Tp^*)(CO)_3$]; then, on standing in visible light, the internal oxidation–reduction takes place to yield [$(\eta^3\text{-Tp}^*)Mo(\eta^2\text{-COPh})$] [95JCS(D)1709]. 4-Dimethylaminobenzenediazonium cation gives a mixture of the η^2-aroyl derivative and the product of direct substitution, [$(\eta^3\text{-Tp}^*)Mo(CO)_2(N_2C_6H_4NMe_2\text{-}4)$]. [$(\eta^3\text{-Tp})Mo(CO)_2(N_2Ph)$] is also known [71AX(B)725]. Reaction of [$(\eta^3\text{-Tp})Mo(CO)_3]^-$ with excess p-$TolN_2^+$ gives the neutral [$(\eta^3\text{-Tp})Mo(CO)_2(N_2Tol\text{-}p)$] [85JOM(282)75]. For the Tp* derivative, the fraction of the CO-substitution product increases.

Thallium hydrotris(pyrazol-1-yl)borate with [$(\eta^5\text{-Cp})Mo(N_2Tol\text{-}p)(PPh_3)$][$BF_4$] gives [$(\eta^3\text{-Tp})MoF(N_2Tol\text{-}p)$]. A mixture of the CO-substituted and η^2-aroyl products also follows from [$(\eta^3\text{-pz}'_4B)Mo(CO)_3]^-$ (pz′ is 4-p-tolylpyrazolate), [$(\eta^3\text{-Tp}')Mo(CO)_3]^-$ [Tp′ is hydrotris(4-tolyl)pyrazol-1-ylborato group], and the benzenediazonium cation or its 4-dimethylamino derivative. The CO-substituted products can be formed either through the stage of [$(\eta^3\text{-Tp}^*)Mo(CO)_2(N_2Ar)$]

(75CSR443, 88CRV765) or [(η^3-Tp*)Mo(CO)$_2$(C—O—N=N—Ar) intermediates (92NJC39). [(η^3-Tp)Mo(CO)$_2$(N$_2$Ar)] with excess triphenylphosphine gives the substitution product [(η^3-Tp)Mo(CO)(PPh$_3$)(N$_2$Ar)] (Ar = *p*-Tol, *p*-FC$_6$H$_4$) (82IC188). Anion [(η^3-Tp*)Mo(CO)$_3$]$^-$ with *p*-chlorobenzenesulfonyl chloride gives the product of substitution of the carbonyl ligand, [(η^3-Tp*)Mo(CO)$_2$ (η^1-SC$_6$H$_4$Cl-*p*)], when the arenethiolate ligand fulfills the terminal but not the expected bridging function owing to the steric constraints of the Tp* ligand (81IC3420). Di-*p*-tolylsulfide substitutes both carbonyl groups of the complex [(η^3-Tp)Mo(CO)$_2$(η^1-STol-*p*)] and gives [(η^3-Tp)Mo(STol-*p*)$_2$(N$_2$Ar)]. Complexes [(η^3-Bpz$_4$)Mo(CO)$_2$(η^2-CONMe$_2$)] [91AX(C)2651] and [(η^3-Bpz$_4$)Mo(CO)$_2$ (η^2-CSNMe$_2$)] [90JOM(381)C33] may also be mentioned at this stage. Some σ-alkyl derivatives are known, namely [(η^3-Tp)Mo(CO)$_3$(σ-CH$_2$CN)] (93OM4402) and [(η^3-MeGapz$_3$)Mo(CO)$_3$R] (R = Me, Et), although the methyl derivative undergoes isomerization to [(η^3-MeGapz$_3$)Mo(CO)$_2$(η^2-COMe)] quite easily (87CJC2464). This difference in behavior received profound analysis [83JCS(CC)55, 83JCS(CC)457, 95JCS(D)1709].

The η^2-coordinated COR species can be modified by a combination of deprotonation and alkylation. This sequence was applied, in particular, to [(η^3-Tp*)Mo(CO)$_2$(η^2-COMe)] and [(η^3-Tp*)Mo(CO)(P(OPh)$_3$)(η^2-COMe)]. The first step is achieved by treatment with *n*-butyllithium or potassium hydride and gives enolates. If *tert*-butyl iodide or benzyl bromide are then applied as the alkylating agents, the respective products [(η^3-Tp*)Mo(CO)$_2$(η^2-COBu-*t*)] and [(η^3-Tp*)Mo(CO)(P(OPh)$_3$)(η^2-COCHMePh)] follow (86JA4652). Insertion of acetylenes into the Mo—C bond of the η^2-COMe framework is also known; it leads to a series of products, e.g., **30** (R^1 = R^2 = R^3 = Et) (89JA2550). [(η^3-Tp*)Mo(CO)$_2$(η^2-COR)] (R = Me, Et, Ph) with sodium ethylate give the carbyne derivatives [Mo(η^3-Tp*)(CO)$_2$(≡CR)] (R = Me, Et, Ph). Deprotonation of the products with R = Me or Et gives the anionic vinylidenes, while irradiation of the product (R = Ph) in acetonitrile gives the corresponding η^2-ketenyl (89OM2786). The product with R = *t*-Bu was also described (99OM2262).



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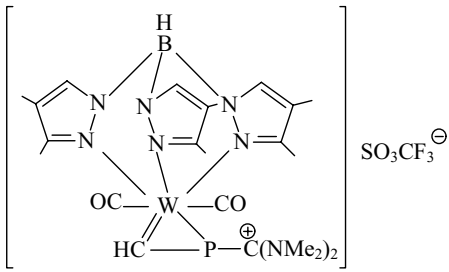
When methylene chloride was used as a solvent, it was found that **28** are obtained in minor amounts, while the dominating product is the η^1-coordinated chlorocarbyne species $[(\eta^3\text{-Tp}^*)\text{Mo(CO)}_2(\equiv\text{CCl})]$, whose yield increases abruptly with substitution in the pyrazol-1-yl fragments (3-methyl-, 3,4,5-trimethyl-, and 3,5-dimethyl-4-chloro derivatives) [90AX(C)59, 95JCS(D)1709]. The tungsten analog can be prepared similarly. The chlorocarbyne molybdenum complex follows also from the reaction of the parent anion with triphenylsulfonium cation but conducted in dichloromethane. The bromo- and iodocarbyne derivatives are made similarly.

With aryloxide anions, the substitution product $[(\eta^3\text{-Tp}^*)\text{Mo(CO)}_2(\equiv\text{COAr})]$ can be prepared, and the cationic species $[(\eta^3\text{-Tp}^*)\text{Mo(CO)}_2(\equiv\text{CPMe}_2\text{Ph})]^+$ follows from the reaction with dimethylphenylphosphine (91OM1954). Substitution of the chloride may be achieved using $R^1CH_2R^2$ ($R^1 = R^2 = $ CN, COOEt; $R^1 =$ CN, $R^2 =$ COOEt), the results being $[(\eta^3\text{-Tp}^*)\text{Mo(CO)}_2(\equiv\text{CCHR}^1\text{R}^2)]^-$ ($R^1 = R^2 =$ CN, COOEt; $R^1 =$ CN, $R^2 =$ COOEt). For the product with $R^1 =$ CN, $R^2 =$ COOEt, the transformation to **30** ($R^1 =$ H, $R^2 =$ CN, $R^3 =$ OEt) is known [85JCS(CC)68, 88JCS(CC)1606]. Another substitution reaction of $[(\eta^3\text{-Tp}^*)\text{Mo(CO)}_2(\equiv\text{CCl})]$ occurs with $[(\eta^5\text{-Cp})\text{Fe(CO)}_2]^-$ to give $[(\eta^3\text{-Tp}^*)\text{Mo(CO)}_2(\equiv\text{CFe}(\eta^5\text{-Cp}))(\text{CO})_2]$ (91JA2324).

The chlorocarbynes $[(\eta^3\text{-Tp}^*)\text{M(CO)}_2(\equiv\text{CCl})]$ (M = Mo, W) react with phosphaalkenes $Me_3SiP{=}C(NR_2)_2$ (R = Me, Et) to give $[(\eta^3\text{-Tp}^*)\text{M(CO)}_2(\equiv\text{C}{-}\text{P}{=}\text{C}(\text{NR}_2)_2)]$ (M = Mo, W; R = Me, Et) (97CB1305). Molecular oxygen oxidizes these products to the corresponding phosphinatocarbynes $[(\eta^3\text{-Tp}^*)\text{M(CO)}_2(\equiv\text{C}{-}\text{P(O)}_2\text{C}(\text{NR}_2)_2)]$ (M = Mo, W; R = Me, Et) (98EJIC579). Methyl triflate methylates the phosphaalkenyl carbynes to yield the cationic complexes $[(\eta^3\text{-Tp}^*)\text{M(CO)}_2(\equiv\text{C}{-}\text{P(Me)}{=}\text{C}(\text{NR}_2)_2)](\text{SO}_3\text{CF}_3)$ (M = Mo, W; R = Me, Et) (98OM5254). Protonation of the latter with triflic acid gives **31.** $[(\eta^3\text{-Tp}^*)\text{M(CO)}_2(\equiv\text{CCl})]$ (M = Mo, W) also react with $Me_3SiAs{=}C(NMe_2)_2$ and give $[(\eta^3\text{-Tp}^*)\text{M(CO)}_2(\equiv\text{C}{-}\text{As}{=}\text{C}(\text{NMe}_2)_2)]$ (M = Mo, W) (99OM4603). These are also methylated to $[(\eta^3\text{-Tp}^*)\text{M(CO)}_2(\equiv\text{C}{-}\text{As(Me)}{=}\text{C}(\text{NMe}_2)_2)](\text{SO}_3\text{CF}_3)$ (M = Mo, W). Species $[(\eta^3\text{-Tp}^*)\text{W(CO)}_2(\equiv\text{C}{-}\text{PMe}_2\text{Ph})]^+$ is also known (86AGE469, 87ZAAC73).



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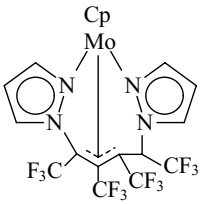
[(η^3-Tp*)M(≡CMe)(CO)$_2$] (M = Mo, W) enter the nucleophilic substitution of chloride with [(η^3-Tp*)Mo(≡CCl)(CO)$_2$] and give [(η^3-Tp*)(OC)$_2$M≡CCH$_2$C=Mo(CO)$_2$(η^3-Tp*)] (M = Mo, W) (96JA7418). The complex with M = W can be further deprotonated with *t*-BuOK to afford first the anionic [(η^3-Tp*)(OC)$_2$W≡CCHC≡Mo(CO)$_2$(η^3-Tp*)]$^-$ and then the dianionic [(η^3-Tp*)(OC)$_2$W=C=C=C=Mo(CO)$_2$(η^3-Tp*)]$^{2-}$. Both of these anions are methylated by methyl iodide to [(η^3-Tp*)(OC)$_2$W≡CCH(Me)C≡Mo(CO)$_2$(η^3-Tp*)] and [(η^3-Tp*)(OC)$_2$W≡CCMe$_2$C≡Mo(CO)$_2$(η^3-Tp*)], respectively. When exposed to potassium *tert*-butylate in air, [(η^3-Tp*)(OC)$_2$Mo≡CCH$_2$C≡Mo(CO)$_2$(η^3-Tp*)] gives the molybdenum(II)–molybdenum(VI) species [(η^3-Tp*)(OC)$_2$Mo≡CC≡CMo(=O)$_2$(η^3-Tp*)], while the tungsten–molybdenum analog under the same conditions gives a mixture of binuclear complexes, [(η^3-Tp*)(OC)$_2$W≡CC≡CMo(=O)$_2$(η^3-Tp*)] and [(η^3-Tp*)(=O)$_2$ WC≡CC≡Mo(CO)$_2$(η^3-Tp*)].

[(η^3-Tp*)W(CO)(PhC≡CPh)I], prepared from [(η^3-Tp*)W(CO)$_3$I] and diphenylacetylene, reacts with nucleophiles like LiMe$_2$Cu and yields [(η^3-Tp*)W(CO)(PhC≡CPh)Me] (94JA2878). Alkyne substitution of the iodide ligand in the complexes [(η^3-Tp*)W(CO)(PhC≡CR)I] (R = H, Me) in the presence of silver tetrafluoroborate gives [(η^3-Tp*)W(CO)(PhC≡CR)$_2$](BF$_4$) (R = H, Me) (92JA2951). Complex [(η^3-Tp*)W(CO)(PhC≡CH)$_2$](BF$_4$) reacts with LiBEt$_3$H to form the neutral η^1-vinyl species [(η^3-Tp*)(OC)W(η^3-PhC≡CH)(η^1-CPh=CH$_2$]. Protonation of the product with tetrafluoroboric acid gives [(η^3-Tp*)W(CO)(PhC≡CH)(η^2-CPh=CH$_2$)](BF$_4$). Deprotonation of [(η^3-Tp*)M(CO)$_2$(≡CMe)] (M = Mo, W) with potassium *tert*-butanolate gives the anionic complexes [(η^3-Tp*)M(CO)$_2$(=C=CH$_2$)]$^-$ (M = Mo, W) that enter numerous reactions with electrophiles (89OM2786, 96JA7418, 98OM1655). These complexes also enter the reaction with [(η^3-Tp)W(CO)(PhC≡CPh)I] and yield dinuclear species [(η^3-Tp*)(OC)$_2$M(≡CCH$_2$)W(η^3-Tp)(CO)(PhC≡CPh)] (M = Mo, W) (98JA9028). The tungsten product with one equivalent of potassium *tert*-butylate gives [(η^3-Tp*)(OC)$_2$W=C=CHW(η^3-Tp)(CO)(PhC≡CPh)]$^-$, while addition of the second equivalent of potassium *tert*-butylate followed by molecular iodine gives [(η^3-Tp*)(OC)$_2$W≡CC≡W(η^3-Tp)(CO)(PhC≡CPh)]. [(η^3-Tp*)W(CO)$_2$(PhC≡CMe)]$^+$ is known [94JOM(478)103].

KTp with [(η^5-Cp)MoCl(F$_3$C≡CF$_3$)$_2$] gives the species **32** [75JCS(CC)803, 77JCS(D)287]. Complex [(η^3-Tp*)W(CO)$_2$(PhC≡CH)](BF$_4$) with trimethyl phosphite gives [(η^3-Tp*)W(CO)$_2$(η^2-PhC=CHP(O)(OMe)$_2$)]. Protonation of the latter occurs at the phosphoryl oxygen, the product being [(η^3-Tp*)W(CO)$_2$(η^2-PhC=CHP(OH)(OMe)$_2$)](BF$_4$) (92OM2168). Species Li[(η^3-Tp*)W(CO)(I)(η^2-PhC=C=CHMe)] adds benzaldehyde to afford [(η^3-Tp*)W(CO)(I)(PhC≡CH)(MeCH(OH)Ph)] (89MI1, 92JA3771). [(η^3-Tp*)W(CO)(I)(PhC≡CMe)] is also known (92JA10097). Deprotonation of the latter with *n*-butyllithium leads to the η^2-allenyl anionic complex **33** (96CM93). Further reaction with *p*-anisaldehyde

followed by protonation by HCl gives **34** (R = OMe). The latter can be deprotonated with potassium *tert*-butylate to **35** (R = C_6H_4OMe-*p*, R′ = H). Similar reactions using 4-dimethylaminobenzaldehyde give **34** (R = NMe_2) and **35** (R = $C_6H_4NMe_2$-*p*, R′ = H). With *n*-butyllithium, followed by formylferrocene and dilute hydrochloric acid, only **35** (R = Fc, R′ = H) is formed. With *n*-butyllithium, acetylferrocene activated with $BF_3 \cdot Et_2O$, and dilute hydrochloric acid, the sole product is **35** (R = Fc, R′ = Me).



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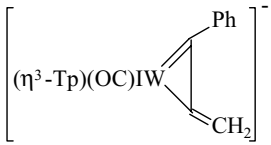

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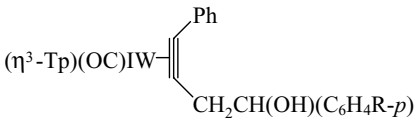

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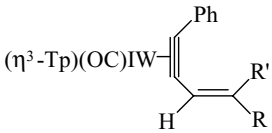
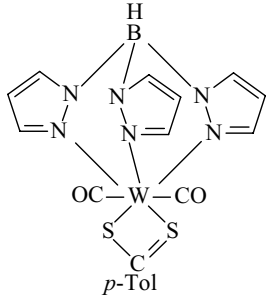


35

Anionic complex $[(\eta^3\text{-Tp}^*)W(CO)_3]^-$ with arenesulfonyl chlorides gives 16-electron monomers of composition $[(\eta^3\text{-Tp}^*)W(CO)_2(SR)]$ with a substantial role of the π-donation directed from thiolate to the metal (71IC504). The Tp* ligand has a remarkable capability to stabilize such reactive ligands as oxo (90IC1777), thio (87IC2925, 87JA2938), nitrido (90AJC1347), and S_2CNR_2 (92IC587). This leads to a stabilization of the enhanced oxidation state of a metal in organometallic complexes, e.g., $[(\eta^3\text{-Tp}^*)_2W^{IV}O(CO)(\mu\text{-O})W^{VI}O_2(\eta^3\text{-Tp}^*)]$ (90IC1777). Oxidative decarbonylation of $(NEt_4)[(\eta^3\text{-Tp}^*)Mo(CO)_3]$ by $(S_2CNR_2)_2$ (R = Me, Et) gives $[(\eta^3\text{-Tp}^*)Mo(\eta^1\text{-}S_2CNR_2)(\eta^2\text{-}S_2CNR_2)]$ (R = Me, Et) [86IC3667, 86ICA-(114)L7].

The tungsten analog (67JA6288, 69JA588) gives a wider diversity of products, $[(\eta^3\text{-Tp}^*)W(CO)_2(\eta^2\text{-}S_2CNEt_2)]$ (92IC3825), $[(\eta^3\text{-Tp}^*)W(CO)(\eta^2\text{-}S_2CNEt_2)_2]$, and the mixed-valence $[(\eta^3\text{-Tp}^*)W^{II}(CO)_2(\mu\text{-S})W^{IV}(\eta^2\text{-}S_2CNEt_2)_2(\eta^2\text{-SCNEt}_2)]$ (92IC587), as well as the products of complete decarbonylation (92IC593). Another illustration is the oxidation of $(NEt_4)[(\eta^3\text{-Tp}^*)W(CO)_3]$ by bromine or iodine to yield $[(\eta^3\text{-Tp}^*)W(CO)_3X]$ (X = Br, I) and subsequent oxidation of the latter by molecular oxygen to afford $[(\eta^3\text{-Tp}^*)W^{IV}O(CO)X]$ (X = Br, I) (91IC2582). The iodine derivative $[(\eta^3\text{-Tp}^*)WO(CO)I]$ with aniline produces the nitrene complex $[(\eta^3\text{-Tp}^*)W(NPh)(CO)I]$.

Metathesis of arene thiolates or sodium alkyl thiolates with $[(\eta^3\text{-Tp}^*W(CO)_2I]$ gives $[(\eta^3\text{-Tp}^*)W(CO)_2(SR)]$ (R = Me, Et, *i*-Pr, Ph, *p*-$NO_2C_6H_4$, $PhCH_2$) (93IC5437). $[(\eta^3\text{-Tp}^*)W(CO)_3]^-$ and $N_3S_3Cl_3$ yield the ditungsten(II) complex containing the μ-thio bridge, $[\{(\eta^3\text{-Tp}^*)W(CO)_2\}_2(\mu\text{-S})]$ (84IC2718). The related molybdenum complex is known (85IC1355). An alternative preparation of this complex is based on interaction of $[(\eta^3\text{-Tp}^*)W(CO)_2Br]$ or $[(\eta^3\text{-Tp}^*)W(CO)_3H]$ and propylene sulfide (94IC1416). The complex of hydrotris(3-isopropylpyrazol-1-yl)borate was also prepared using this technique. Interaction of potassium tris(pyrazol-1-yl)borate with $[W(\eta^2\text{-}S_2CTol\text{-}p)Br(CO)_4]$ gives **36** [97JCS(CC)955, 97JCS(D)2003]. With KH_2Bpz_2, however, species **37** results, the process also observed not only for the dithiocarboxylate but also for the acyl ligand (95OM14).



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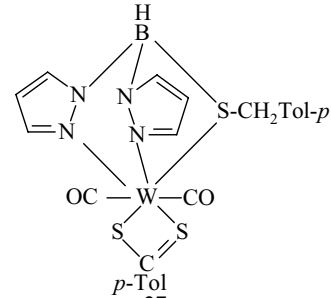
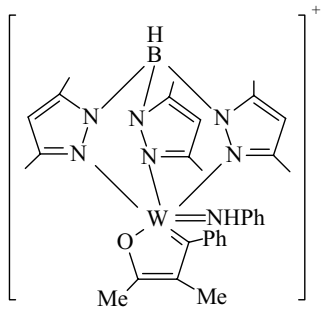


37

Amides $[(\eta^3\text{-Tp}^*)W(CO)_2(NHR)]$ (R = Ph, CH_2Ph, H) are starting materials for the anionic nitrenes $[(\eta^3\text{-Tp}^*)W(CO)_2(NR)]^-$ (R = Ph, $PhCH_2$, H) that can be made by deprotonation using *tert*-butyllithium or lithium diisopropylamide. Analogously, the amide species with R = H, *n*-Bu, *t*-Bu, Ph, Ts, CH_2Ph, CPh_3 can be used to prepare the corresponding cationic nitrenes $[(\eta^3\text{-Tp}^*)W(CO)_2(NR)]^+$ by oxidation with Ph_3CPF_6 (R = H, *n*-Bu, *t*-Bu, Ph, Ts, CH_2Ph, CPh_3) or molecular iodine (R = Ph, Ts) (90JA8190, 92JA7928, 92OM1433, 93OM261, 94OM1851). The cationic species with R = *t*-Bu, Ph, Ts could be converted back to amides using

lithium alumohydride. Oxidation of [(η^3-Tp*)W(CO)(PhC≡CMe)(NHPh)] with molecular iodine in the presence of triethylamine gives the cationic nitrene [(η^3-Tp*)W(CO)(PhC≡CMe)(≡NPh)]$^+$ (96OM5127, 97OM2547, 98AGE2093). If no Et_3N is added, nitrene is formed but in equimolar mixture with [(η^3-Tp*)W(CO)(PhC≡CMe)(NH_2Ph)]$^+$. On treatment with potassium borohydride, nitrene transforms to the starting amide (97OM2547). However, excess KBH_4 gives hydride species [(η^3-Tp*)WH(CO)(PhC≡CMe)(≡NPh)]. Nitrene also reacts with methyl magnesium bromide and affords the cationic species **38** containing the metallacycle. This process involves the protonation ascribed to traces of water. Phenyllithium with the cationic nitrene gives rise to the acyl derivative [(η^3-Tp*)W(COPh)(PhC≡CMe)(≡NPh)].



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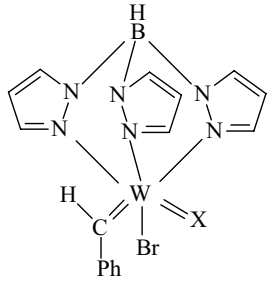
Another route to the amido complexes originates from [(η^3-Tp*)W(CO)(PhC≡CMe)(OTf)] and benzylamine and yields [(η^3-Tp*)W(CO)(PhC≡CMe)($NHCH_2$Ph)] (96JA6916). The latter can be protonated with tetrafluoroboric acid to give the amine derivative [(η^3-Tp*)W(CO)(PhC≡CMe)(NH_2CH_2Ph)](BF_4), and this process can be reversed by *n*-butyllithium. Hydride abstraction by silver tetrafluoroborate, molecular iodine, or Ph_3CPF_6 leads to the cationic imine derivatives [(η^3-Tp*)W(CO)(PhC≡CMe)(HN=CHPh)]$^+$. *n*-Butyllithium deprotonates the product and gives the neutral azavinylidene species [(η^3-Tp*)W(CO)(PhC≡CMe)(N=CHPh)]. The latter with silver tetrafluoroborate forms the cationic nitrile species [(η^3-Tp*)W(CO)(PhC≡CMe)(N≡CPh)](BF_4).

The Tp ligand has a feature of stabilizing the W(VI) and Mo(VI) oxidation states in the alkylidene complexes [91JA7066, 92JMC(76)229, 92OM2342, 93OM2814] that serve as efficient catalysts in various polymerization reactions (90MMC365, 91MM2649). Complex [W(≡CPh)Br($CO)_2$($py)_2$] interacts with KTp to yield [(η^3-Tp)W(≡CPh)($CO)_2$] (87OM50). Subsequent bromination leads to the substitution of the carbonyl ligands, [(η^3-Tp)W(≡CPh)Br_2] [93JOM(459)233, 94POL353]. Reaction of the product with primary amines or water gives a series of amido or oxo complexes **39** (X = NBu-*t*, *N*-adamantyl, N–$C_6H_3Me_2$-2,6, O)

(91JA7066, 93OM2814). Further bromination gives **40** (X = NBu-*t*, *N*-adamantyl, N—$C_6H_3Me_2$-2,6, O) [96JA7408, 00ICA(300)406], where the alkylidyne group inserts into one of the metal–nitrogen bonds and modifies the structure of the rigid metal–pyrazol-1-ylborate framework.



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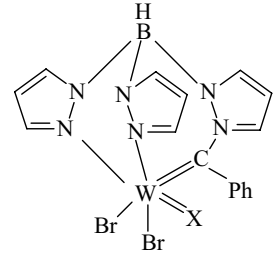

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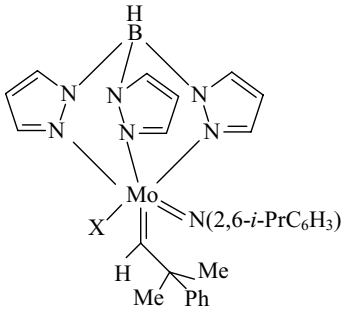
Compound **41** (X = OTf) [95JOM(485)37] is remarkable because of its enhanced reactivity (95OM1567). Alkylation of this compound with methyllithium gives **41** (X = Me), which can be reverted to **41** (X = OTf) using triflic acid. Parent **41** (X = OTf) also enters methanolysis to give **41** (X = OMe). However, with potassium methoxide, the alkylidyne complex **42** results. With the ether adduct of tetrakis(3,5-bis(trifluoromethyl)phenyl)boric acid, **41** (X = Me) gives rise to the unstable cationic alkylidene complex **43** [L = Et_2O, A = $B(3,5\text{-}C_6H_3(CF_3)_2)_4$] and methane; with trityl tetrakis(pentafluorophenyl)borate and acetonitrile, it gives **43** [L = AN, A = $B(C_6F_5)_4$]; and with $B(C_6F_5)_3$ and acetonitrile or tetrahydrofuran, it gives **43** [L = AN, A = $BMe(C_6F_5)_3$] or **43** [L = THF, A = $BMe(C_6F_5)_3$], respectively. Addition of trimethylphosphine to **41** (X = OTf) yields **43** (L = PMe_3, A = OTf). [(η^3-Tp*)MO_2Cl] (M = Mo, W) can be converted to [(η^3-Tp*)MO_2(Me)] using trimethylaluminum. Similar transformations of [(η^3-Tp*)WO_2Cl] to [(η^3-Tp*)$WO_2(CH_2R)$] [R = $SiMe_3$, *t*-Bu, CMe_2Ph, C(Me)=CH_2] were carried out using RCH_2MgCl [R = $SiMe_3$, *t*-Bu, CMe_2Ph, C(Me)=CH_2]. Exchange reaction of [(η^3-Tp*)WO_2Cl] with Me_3P=CH_2 gives [(η^3-Tp*)$WO_2(CHPMe_3)$] (93CB289).

[(η^3-C_3H_5)Mo$(CO)_2$(η^3-Tp)] [69JA588, 69JA3183, 72JA5677, 92JOM(431)-303, 92JOM(434)303], [(η^3-C_3H_5)Mo$(CO)_2$(η^3-Tp*)] [95JOM(485)C1], and [(η^3-C_4H_7)Mo$(CO)_2$(η^3-Tp)] [73JCS(D)2444] are known. A wider variety of allyl derivatives [(η^3-R^1R^2C=(R^3)C—CR^4H)Mo$(CO)_2$(η^3-Tp)] ($R^1 = R^2 = R^3 = R^4$ = H; $R^1 = R^3 = R^4$ = H, R^2 = Me, Et, *i*-Pr, *t*-Bu, Cy, Ph, *p*-Tol, *p*-$CF_3C_6H_4$, COOMe; R^1 = Me, Et, *i*-Pr, Cy, Ph, $R^2 = R^3 = R^4$ = H; $R^2 = R^3$ = H; $R^1 = R^4$ = Me, R^1 = Me, R^4 = Ph, $R^1 = R^4$ = Ph, $R^1 = R^4$ = *t*-Bu; $R^1 = R^3$ = H, $R^2 = R^4$ = Me, R^2 = Me, R^4 = Ph, $R^2 = R^4$ = Ph, $R^2 = R^4$ = *t*-Bu, R^2 = *t*-Bu, R^4 = Ph;



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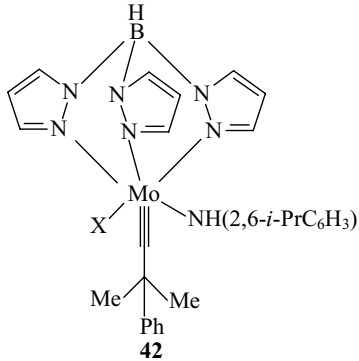

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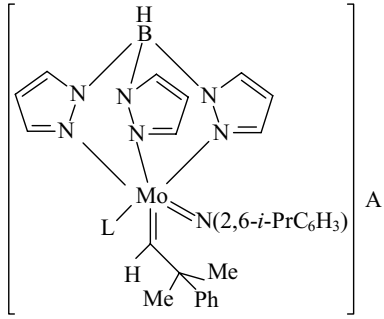

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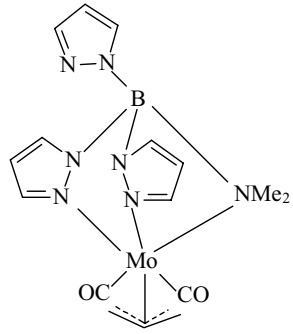
$R^1 = R^2 = Me$, $R^3 = H$, $R^4 = Me$; $R^1 = H$, $R^2 = R^3 = R^4 = Me$; $R^1 = R^3 = R^4 = Me$, $R^2 = H$) were prepared from $Mo(CO)_3(AN)_3$ or $Mo(CO)_3(DMF)_3$, allyl halides or acetates, and potassium hydrotris(pyrazol-1-yl)borate (95OM4132). Thallium hydrotris (3-mesitylpyrazolyl)borate with $[(AN)Mo(CO)_2(Cl)(\eta^3\text{-}C_4H_7)]$ gives $[(\eta^3\text{-}Tp')Mo(CO)_2(\eta^3\text{-}C_4H_7)]$ (93IC3471). Hydrotris(indazol-1-yl)borato ligands (L) form the η^2-coordinated complexes of composition $[Mo(L)(CO)_2(\eta^3\text{-}CH_2CMeCH_2)]$ (97IC5097). Potassium salt of hydrotris(3-neopentylpyrazol-1-yl)borate with $[Mo(CO)_2(\eta^3\text{-}C_4H_7)(AN)_2Cl]$ gives $[(\eta^3\text{-}Tp')Mo(CO)_2(\eta^3\text{-}C_4H_7)]$ (92IC4810). $[(\eta^3\text{-}Tp)Mo(CO)_2(\eta^3\text{-}C_3H_5)]$ reacts with NO to yield $[(\eta^3\text{-}Tp)Mo(CO)_2(NO)_2(NO_2)]$ along with allyl nitrite and 1-nitro-2-propene [78JMC(4)87]. The ligand Me_2NBpz_3 coordinates via its dimethylamino group and two pyrazolate ligands in **44** (85IC4222).

$[(\eta^2\text{-}Tp)Mo(\eta^5\text{-}Cp)(CO)_2]$ contains the bidentate pyrazol-1-ylborate ligand [67JA3904, 69JA588, 72JOM(37)127, 72JOM(38)105, 73JCS(D)1893]. $[(\eta^5\text{-}Cp)Mo(CO)_2(\eta^3\text{-}C_3H_5)]$ with tetrakis(pyrazol-1-yl)methane in the presence of tetrafluoroboric acid gives $[(\eta^5\text{-}Cp)Mo(CO)_2(\eta^2\text{-}Cpz_4)_2](BF_4)$ (98POL1091). With tetrakis(pyrazol-1-yl)borate, the binuclear species $[((\eta^5\text{-}Cp)Mo)_2(\mu\text{-}\eta^2\text{-}Bpz_4)](BF_4)$ is



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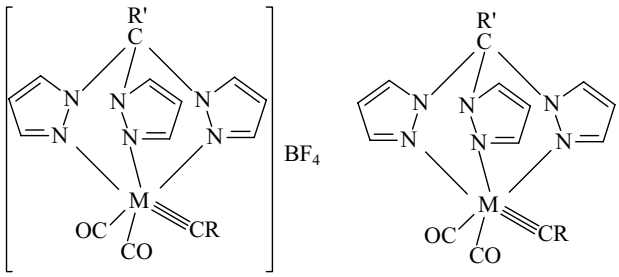
formed under these conditions. Reaction of the Cpz_4 complex with $ClReO_3$ gives the binuclear species $[(\eta^5\text{-Cp})(OC)_2Mo(\mu\text{-}\eta^2\text{-Cpz}_4)ReClO_3]$. Cyclopentadienone species $[(\eta^4\text{-}C_5H_4O)M(\eta^3\text{-Tp})(CO)_2](PF_6)$ (M = Mo, W) (96OM181) with a variety of nucleophiles, such as PR'_3 (R′ = *n*-Bu, Cy, Ph), KCN, MeMgBr, LiSPh, $NH_2Pr\text{-}i$, $HNEt_2$, py, 2-NH_2py, give the addition products of the following composition: $[(\eta^3\text{-}C_5H_4OR)M(\eta^3\text{-Tp})(CO)_2](PF_6)$ (R = $PBu_3\text{-}n$, PCy_3, M = Mo, W; R = PPh_3, py, M = Mo) and $[(\eta^3\text{-}C_5H_4OR)M(\eta^3\text{-Tp})(CO)_2]$ (R = CN, NEt_2, M = Mo, W; R = Me, SPh, NHPr-*i*, 2-NHpy, M = Mo) (96OM2954). Complex $[(\eta^4\text{-}C_5H_3O\text{-2-Me})Mo(\eta^3\text{-Tp})(CO)_2](PF_6)$ with such strong nucleophiles as methyllithium, diethylamine, or pyridine gives the products of deprotonation of the 2-methyl group, $[(\eta^3\text{-}C_5H_4O\text{-2-}CH_2)Mo(\eta^3\text{-Tp})(CO)_2]$.

Chromium alkyls $[(\eta^3\text{-(3-}t\text{-Bu-5-Mepz)}_3B)CrR]$ (R = Et, CH_2SiMe_3, Ph) follow from the corresponding homoleptic complexes and alkyllithium compounds (97CEJ1668).

Sodium methyl tris(pyrazol-1-yl)gallate with $Mo(CO)_6$ gives $[(\eta^3\text{-MeGapz}_3)Mo(CO)_3]^-$ (78CJC2099). Ligand substitution with allyl bromide yields $[(\eta^3\text{-MeGapz}_3)Mo(CO)_2(\eta^3\text{-}C_3H_5)]$ (78CJC2099, 79CJC1823). With isoamyl nitrite, $[(\eta^3\text{-MeGapz}_3)Mo(CO)_2(NO)]$ results, and the tungsten analog can be prepared similarly. The 3,5-dimethylpyrazol-1-yl analogs can be made in the same way (79CJC139). Reactions of $[(\eta^3\text{-MeGapz}_3)Mo(CO)_3]^-$ or $[(\eta^3\text{-Tp})Mo(CO)_3]^-$ with Wilkinson catalyst $Rh(PPh_3)_3Cl$ lead to the substitution of the chloride ligand, elimination of phosphine, and formation of the Mo—Rh bond (86CJC373). The product is formulated as $[(\eta^3\text{-MeGapz}_3)Mo(CO)(\mu\text{-}CO)_2Rh(PPh_3)_2]$ or $[(\eta^3\text{-Tp})Mo(CO)(\mu\text{-}CO)_2Rh(PPh_3)_2]$, respectively. With $[Cu(PPh_3)Cl]_4$, $[(\eta^3\text{-MeGapz}_3)Mo(CO)_3]^-$ forms $[(\eta^3\text{-MeGapz}_3)Mo(CO)_3Cu(PPh_3)]$ containing the Mo—Cu bond. $[(\eta^3\text{-MeGapz}_3)Mo(CO)_3]^-$ with R_3SnCl (R = Me, Ph) and Me_2SnCl_2 give products containing the Mo—Sn bond, $[(\eta^3\text{-MeGapz}_3)Mo(CO)_3(SnR_3)]$ (R_3 = Me_3, Ph_3, Me_2Cl) (86CJC321).

The tris(pyrazol-1-yl)methane derivatives **45** (M = W, R = Me, Tol-*p*, $C_6H_3Me_2$-2,6, R′ = H, Me; M = Mo, R = Tol-*p*, R′ = H, Me) and **46** (M = W, R = Me,

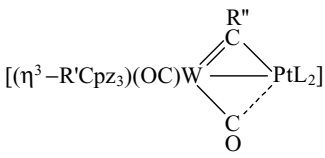
Tol-*p*, $C_6H_3Me_2$-2,6, R′ = AuC_6F_5; M = Mo, R = Tol-*p*, R′ = AuC_6F_5) are interesting ligands [90JCS(D)3701]. These and some other derivatives follow from [(η^3-R′Cpz$_3$)M(≡CR)(CO)$_2$] (M = Mo, W; R = *p*-Tol, $C_6H_3Me_2$-2,6; R′ = H, Me). The reaction of the latter with $Co_2(CO)_8$, [Pt(nb)$_3$], and [Pt(nb)($Me_2PhP)_2$] [90JCS(D)3499] affords mixed-metal complexes as described below. The transformation of **45** to **46** is achieved by treatment of **45** (R′ = H) with bases (sodium ethylate, methyl lithium, or *n*-butyllithium) with subsequent treatment with [Au(C_6F_5)(THT)]. Addition of $BF_3 \cdot Et_2O$ to some of the complexes **45** gives **46** (M = W; R = Me, C_6H_4Me-4; R′ = BF_3) [91JCS(D)93].



45 **46**

The ligating properties of different species **46** may be illustrated by their reactions with [Pt(η^2-nb)($PMe_2Ph)_2$] to give **47** (R′ = BF_3, AuC_6F_5, R″ = Me, L = PMe_2Ph). Complex **48** (R′ = AuC_6F_5, R″ = Me, M = Au, R = C_6F_5, L = PMe_2Ph) is obtained along with **47** (R′ = AuC_6F_5, R″ = Me, L = PMe_2Ph). A series of species **48** (R′ = BF_3, R″ = Me, M = Au, R = Cl, C_6F_5, L = PMe_2Ph; R′ = BF_3, R″ = Me, M = Cu, R = Cl; L = PMe_2Ph) was prepared by treatment of **47** (R′ = BF_3, R″ = Me, L = PMe_2Ph) with [AuR(THT)] (R = Cl, C_6F_5) or with CuCl. Another continuation is the interaction of **48** (R′ = BF_3, R″ = Me, M = Au, R = Cl, L = PMe_2Ph) with Na[Mn(CO)$_5$] that leads to **48** [R′ = BF_3, R″ = Me, M = Au, R = Mn(CO)$_5$, L = PMe_2Ph]. The coordination capacity of **46** (M = W, R = Me, C_6H_4Me-4; R′ = BF_3) is also realized in the presence of [Pt(η^4-cod)]$_2$ to yield a variety of compounds: **47** (R′ = BF_3, R″ = Me, C_6H_4Me-4, L$_2$ = cod), **48** (R = cod, R′ = BF_3, R″ = Me, C_6H_4Me-4; L$_2$ = cod, M = Pt), and **49** (R = Me, C_6H_4Me-4, R′ = BF_3). Complexes [$WPt_2(\mu$-CR)$_2$(CO)$_4$(η^3-Tp)$_2$] (R = Alk, Ar) should be mentioned as the Tp analogs of **49** [86JCS(D)2091, 87JCS(D)1229].

Complexes [(η^2-R$_2$B(3,5-R′$_2$pz)$_2$)Mo(CO)$_4$] with allyl halides give the 16-electron [(η^2-R$_2$B(3,5-R′$_2$pz)$_2$)Mo(CO)$_2$(η^3-C_3H_4R″)] (R = H, R′ = Me; R = Et, R″ = H; R″ = H, Me) (72CRV497). Species [(η^2-Et$_2$Bpz$_2$)Mo(CO)$_2$(η^3-C_3H_5)] is characterized by the agostic C—H···Mo interactions (89IC3210). In [(η^3-C_3H_5)Mo(CO)$_2$($pz^*_2BH_2$)] [68JA4754, 70IC2493, 71AX(B)1859, 71AX(B)2493]



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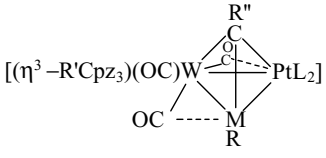

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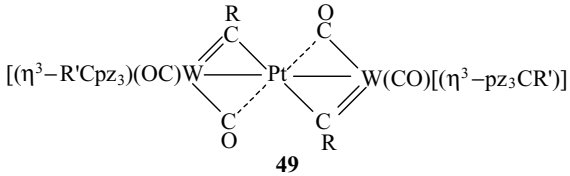
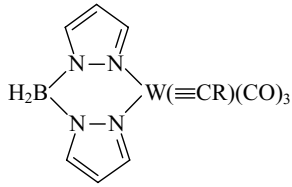


49

as well as in $[(\eta^3\text{-}C_7H_7)Mo(CO)_2(pz^*_2BH_2)]$ [72ICA(6)543, 72JCS(CC)777, 72JOM(42)419], the B—H group participates in bridging the molybdenum atom. $Na(H_2Bpz^*_2)$, $Mo(CO)_6$, and 1-bromocycloocta-2,4-diene give $[(\eta^2\text{-}H_2Bpz^*_2)Mo(\eta^3\text{-}C_8H_{12})(CO)_2]$ (97OM2618), where the role of Mo $\cdots$ H—B interaction is also pronounced. With benzaldehyde, this product gives $[(\eta^2\text{-}H_2Bpz^*_2)Mo(\eta^3\text{-}C_8H_{11})(CO)_2(OCH_2Ph)]$. $[(AN)_3Mo(CO)_3]$, PhCH=CHCH=CHCH$_2$Cl, and further $Na(H_2Bpz^*_2)$ give $[(\eta^2\text{-}H_2Bpz^*_2)Mo(\eta^3\text{-}PhCH{=}CHCH{=}CHCH_2)(CO)_2]$ with Mo $\cdots$ H—B interaction. The role of the B—H $\cdots$ Mo interactions is underscored in $[(Et_2Bpz_2)Mo(\eta^3\text{-}C_3H_5)(CO)_2]$ [68JA4754, 70IC2493, 74JA754, 74JA5074, 74JCS(CC)415]. Such agostic interactions become even more pronounced when cyclooctane-1,5-diylbis(pyrazol-1-yl)borate (L) is used as a ligand and $[(L)Mo(\eta^3\text{-}allyl)(CO)_2]$ results [89AGE205, 91ICA(183)203, 92IC974]. The agostic interaction can be eliminated by the adduct formation of the 18-valence-electron molybdenum species, e.g., $[(\eta^2\text{-}Et_2Bpz_2)Mo(\eta^3\text{-}C_3H_5)(CO)_2[Hpz)]$ (73ICA(7)503] and $[(\eta^2\text{-}Ph_2Bpz_2)Mo(\eta^3\text{-}C_7H_7)(CO)_2(Hpz)]$ [77ICA(22)75]. It is absent in $[(\eta^2\text{-}Ph_2Bpz_2)Mo(\eta^3\text{-}C_3H_5)(CO)_2]$ (75JA2118) for conformational reasons.

Potassium dihydrobis(pyrazol-1-yl)borate with $[W(\equiv CR)Br(CO)_4]$ (R = Me, *p*-Tol) gives species **50** (R = Me, *p*-Tol) [88JCS(D)1139]. On reaction with sulfur, the triple bond is cleaved and the dithiocarboxylate complexes **51** (R = Me, *p*-Tol) are formed. Products **50** have an interesting ligating potential. Thus, **50** (R = *p*-Tol) with $Co_2(CO)_8$ gives **52, 50** (R = Me) with $[RhL_2(\eta^5\text{-indenyl})]$ (L = CO, C_2H_4) gives **53,** and **50** (R = *p*-Tol) with $Fe_2(CO)_9$ gives **54.** The latter is the 32-valence-electron compound which on further interaction with dppm forms **55,** with alkynes RC≡CR (R = Me, Ph) gives **56** (R = Me, Ph), and with diazomethane yields **57.** Species **50** (R = *p*-Tol) also reacts with $[Pt(cod)_2]$ to form **58** (L_2 = cod), and with trimethylphosphine to afford **58** (L = PMe_3). The product **58** (L_2 = cod) with **50** (R = *p*-Tol) gives the trinuclear product **59** (M = Pt, R = *p*-Tol). An analog **59** (M = Pt, R = Me) may be prepared from **50**



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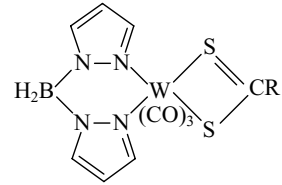

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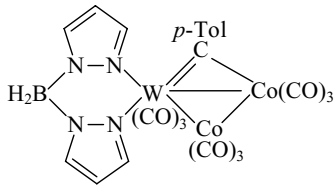

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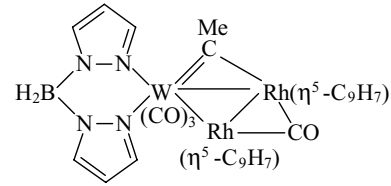

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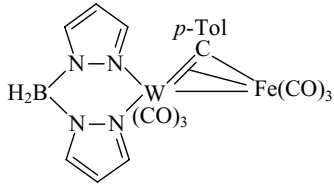

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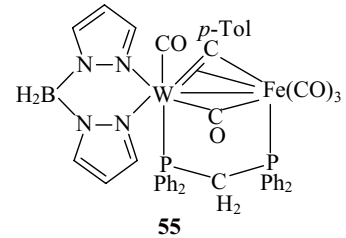

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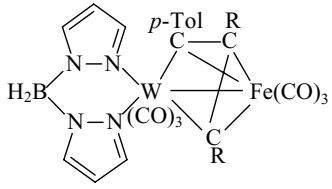

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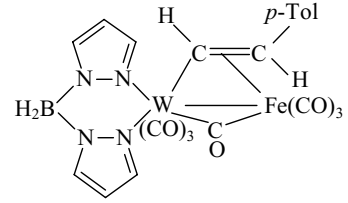

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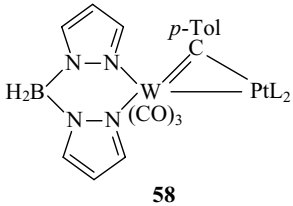

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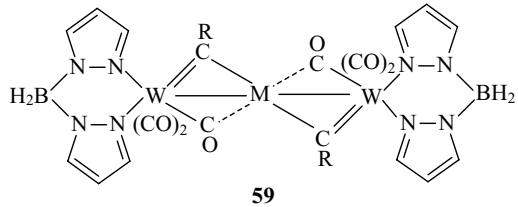
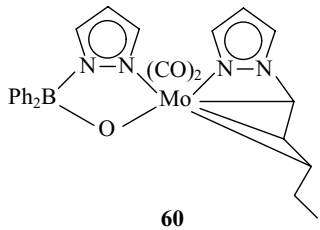


59

(R = Me) and two equivalents of [Pt(cod)$_2$]. A similar synthetic procedure (with two equivalents of [Ni(cod)$_2$]) applies to preparation of **59** (M = Ni, R = *p*-Tol). [(η^2-H$_2$Bpz$_2$)Mo(≡CPh)(CO)(PMe$_3$)$_2$] on reaction with *t*-BuC≡P undergoes the substitution of C(Ph) by C(*t*-Bu) and gives [(η^2-H$_2$Bpz$_2$)Mo(≡CBu-*t*)(CO)(PMe$_3$)$_2$] (89AGE210).

A remarkable transformation of [(η^2-Ph$_2$Bpz$_2$)Mo(CO)$_2$(η^3-pentadienyl)] (90OM1862) is the transformation with phosphines or phosphites of this 16-valence-electron species into 18-electron complexes; hydrolysis leads to profound changes in the coordination sphere yielding **60.**



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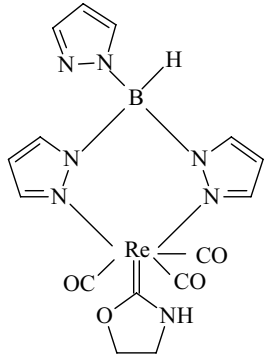
Tetraethylammonium dimethylbis(pyrazol-1-yl)gallate with hexacarbonyls of molybdenum and tungsten gives (NEt$_4$)[(η^2-Me$_2$Gapz$_2$)M(CO)$_4$] (M = Mo, W) (81CJC3123). The corresponding allyl complexes always contain the coordinated pyrazole, and the range of these products includes [(η^3-MeGapz$_3$)(Hpz)M(CO)$_2$(η^3-C$_3$H$_5$)] and [(η^3-MeGapz$_3$)(Hpz)M(CO)$_2$(η^3-C$_7$H$_7$)] (M = Mo, W). The dimethyl(pyrazol-1-yl)(2-methoxypyridyl) derivative of dimethylbis(pyrazol-1-yl) gallate exists as [(η^3-Me$_2$Gapz(OCH$_2$py)Mo(CO)$_2$(η^3-C$_3$H$_5$)], where the coordination of the pyrazol-1-yl-containing ligand is realized via the nitrogen atom of the pyrazol-1-yl ring, the oxygen atom, and the nitrogen heteroatom of the pyridyl moiety (88CJC355). Reaction of sodium salts of the anions [(η^3-Me$_2$Gapz*(OCH$_2$CH$_2$X))M(CO)$_3$]$^-$ (M = Mo, W; X = NMe$_2$, SEt), where coordination is effected via the pyrazole nitrogen, the oxygen atom, and the donor site of the X moiety, with tetraethylammonium chloride is the metathesis leading to the corresponding Et$_4$N$^+$ salts (90CJC109). Complexes [(η^3-Me$_2$Gapz*(OCH$_2$CH$_2$NH$_2$))Mo(CO)$_2$(η^3-C$_4$H$_7$)] (79CJC1335), [(η^3-Me$_2$Gapz*(OCH$_2$CH$_2$NH$_2$))Mo(CO)$_2$(η^3-C$_7$H$_7$)] (80CJC2278, 81CJC1665), and [(η^3-Me$_2$Gapz*(OCH$_2$CH$_2$SEt))Mo(CO)$_2$(L)] (L = NO, η^3-allyl, η^3-C$_7$H$_7$) (81CJC1331, 81CJC2391) are known. Anions [(η^3-MeGapz(OCH$_2$CH$_2$X))M(CO)$_3$]$^-$ (M = Mo, W; X = NH$_2$, NMe$_2$) and [(η^3-MeGapz*(OCH$_2$CH$_2$X)M(CO)$_3$]$^-$ (M = Mo, W; X = NH$_2$, NMe$_2$, SEt, SPh) also react with ClCH$_2$SMe to afford [(η^3-L)M(CO)$_2$(η^2-CH$_2$SMe)] (80CJC1080).

Bis(pyrazol-1-yl)- and bis(3,5-dimethylpyrazol-1-yl)methane and M(CO)$_6$ (M = Mo, W) produce [(η^2-CH$_2$pz$_2$)M(CO)$_4$] (M = Mo, W) and [(η^2-CH$_2$pz$_2^*$)M(CO)$_4$], respectively [87JCCS297, 89JOM(366)121, 90OM286, 90OM2632,

93JOM(453)201, 98POL3765]. With $RSnCl_3$ (R = Ph, Cl), the products yield the M—Sn compounds [(η^2-CH_2pz_2)$M(CO)_3SnCl_2R$] (M = Mo, W; R = Ph, Cl) and [(η^2-$CH_2pz_2^*$)$M(CO)_3SnCl_2R$] (M = Mo, W; R = Ph, Cl) (98POL3765). Dihydrobis(3(5)-phenylpyrazol-1-yl)methane with $Mo(CO)_6$ or [$Mo(CO)_4$ (piperidine)$_2$] gives [(η^2-H_2C(3-Phpz)(5-Phpz))$Mo(CO)_4$] [94JOM(469)169]. In a similar way, [(η^2-PhHCpz$_2^*$)$Mo(CO)_4$] and [(η^2-H_2C(3,5-Me_2-4-$PhCH_2pz_2$) $Mo(CO)_4$] can be obtained. [(η^2-PhHCpz$_2^*$)$Mo(CO)_4$] with allyl bromide gives [(η^2-PhHCpz$_2^*$)$Mo(CO)_2$(η^3-C_3H_5)Br] [91JOM(407)225].

V. Complexes of the Manganese Group

Potassium hydrotris(3,5-dimethylpyrazol-1-yl)borate and [Re(μ-Cl)$(CO)_4]_2$ form [(η^3-Tp*)$Re(CO)_3$] [79JOM(169)289]. Analogous η^3-Tp and η^3-Tp* complexes of manganese were also studied [72IC85, 93JOM(448)119] as well as [(η^3-Tp*)$Mn(CO)_2L$] [L = $P(OMe)_3$, $P(OPh)_3$, PMe_3] (74IC465). Photolysis of [(η^3-Tp)$Re(CO)_3$] prepared by the same technique in THF gives the product of displacement of CO by a solvent molecule, [(η^3-Tp)$Re(CO)_2$(THF)] [90JCS(D) 1895)]. It is subject to ligand substitution reactions by AN, py, PMe_2Ph, PPh_3, CyNC, and $Ph_2P(CH_2)_3PPh_2$. In the latter case, the product of monosubstitution is formed along with [(η^3-Tp)$(OC)_2$Re(μ-$Ph_2P(CH_2)_3PPh_2$) $Re(CO)_2$(η^3-Tp)]. Complex **61** was described [88JOM(352)157], which is remarkable for the switch of coordination mode upon photochemical decarbonylation to give **62.**



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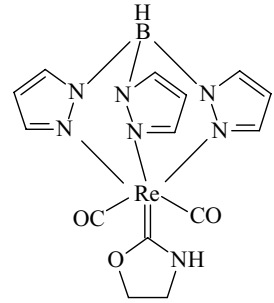


62

[(η^3-Tp)$Re(CO)_2$(THF)] with cyclopentene gives [(η^3-Tp)$Re(CO)_2$(η^2-cyclopentene)] (98JA8747), and with thiophene it gives another product of substitution of the THF ligand, [(η^3-Tp)$Re(CO)_2$(η^1(S)-C_4H_4S)]. However, with furan, 1-methylpyrrole, and naphthalene, the dinuclear bridging complexes of the

general formula [(η^3-Tp)Re(CO)$_2$(μ-η^2(CC)—L)Re(CO)$_2$(η^3-Tp)] (L = C_4H_4O, C_4H_4NMe, $C_{10}H_8$) follow. Nitrogen also gives the dinuclear species with a rare bridging N≡N group, [(η^3-Tp)Re(CO)$_2$(μ-N≡N)Re(CO)$_2$(η^3-Tp)]. The rhenium(III) complex [(η^3-Tp)ReCl$_2$(PMe$_3$)] is reduced by sodium amalgam in the presence of carbon monoxide and cyclohexene to the rhenium(I) derivative [(η^3-Tp)Re(CO)(PMe$_3$)(η^2-C_6H_{10})] (99JA6499). Silver triflate causes the one-electron oxidation of the latter and formation of the cationic complex [(η^3-Tp)Re(CO)(PMe$_3$)(η^2-C_6H_{10})](OTf), which on reflux dissociates cyclohexene off and forms [(η^3-Tp)Re(CO)(PMe$_3$)(OTf)]. Sodium amalgam reduces this rhenium(II) species in the presence of an aromatic(naphthalene) or heteroaromatic (thiophene or furan) ligand to give the η^2-coordinated via the double bond neutral species [(η^3-Tp)Re(CO)(PMe$_3$)(η^2-L)] (L = naphthalene, thiophene, or furan). These products are unstable, and the naphthalene ligand is easily substituted, even by acetone, affording [(η^3-Tp)Re(CO)(PMe$_3$)(η^2-Me$_2$CO)].

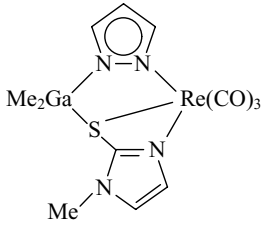
Another, more facile, method for the synthesis of [(η^3-Tp)Re(CO)(PMe$_3$)(η^2-C_6H_{10})] involves the reaction of [(η^3-Tp)ReCl$_2$(PMe$_3$)] with CO, cyclohexene, and sodium amalgam (00OM728). The η^2-cyclopentene complex was prepared similarly. The η^2-cyclohexene derivative with silver triflate gives the rhenium(II) complex [(η^3-Tp)Re(CO)(PMe$_3$)(η^2-C_6H_{10})](OTf). Reflux of the product in DME gives another rhenium(II) species, [(η^3-Tp)Re(CO)(PMe$_3$)(OTf)], where the triflate anion is covalently bound. Reduction of this product with sodium amalgam in the presence of naphthalene gives [(η^3-Tp)Re(CO)(PMe$_3$)(η^2-naphthalene)] and in the presence of cyclopentadiene, [(η^3-Tp)Re(CO)(PMe$_3$)(η^2-cyclopentadiene)]. The same reaction run in the presence of phenanthrene gives [(η^3-Tp)Re(CO)(PMe$_3$)(9,10-η^2-phenanthrene)]. The η^2-cyclohexene complex served as a starting material for the η^2-furanthiophene, and -2-methylthiophene derivatives. [(η^3-Tp)Re(CO)(PMe$_3$)(OTf)] on reaction with acetone gives the η^2-coordinated acetone species [(η^3-Tp)Re(CO)(PMe$_3$)(η^2-Me$_2$CO)].

Photolysis of [(η^3-Tp)Tc(CO)$_3$] [93ZN(B)227] with molecular nitrogen gives the nitrogen-bridged species [(η^3-Tp)Tc(CO)$_2$]$_2$(μ-N$_2$) [93JOM(455)137]. [(η^3-Tp)Tc(CO)$_2$(PPh$_3$)] is also known (92IC895). Species [(η^3-HB(3,5-(CF$_3$)$_2$pz)$_3$)Ag(THF)] reacts with BrMn(CO)$_3$ to give [(η^3-HB(3,5-(CF$_3$)$_2$pz)$_3$)Mn(CO)$_3$] (96OM2994). The 3-trifluropyrazol-1-yl analog follows from [(η^3-HB(3-CF$_3$pz)$_3$)Na(THF)] and BrMn(CO)$_5$.

The rhenium(V) oxophenyl species [(η^3-Tp)Re(=O)(Ph)(OTf)] are oxidized by pyridine *N*-oxide through the stage of [(η^3-Tp)Re(=O)$_2$(Ph)](OTf) to yield the rhenium(VII) phenoxide, [(η^3-Tp)Re(=O)(OPh)(OTf)], and catecholate [(η^3-Tp)Re(=O)((HO)$_2$C$_6$H$_4$)] species (96JA12119, 96JA12416, 98IC445). The rhenium(V) complexes can also be obtained from [(η^3-Tp*)Re(O)Cl$_2$] on reaction with phenyl magnesium chloride or diethyl zinc (00OM2781). When equimolar amounts of reactants are taken, [(η^3-Tp*)Re(O)(R)Cl] (R = Ph, Et) follow; in excess organomagnesium or organozinc reagents, [(η^3-Tp*)Re(O)R$_2$] (R = Ph, Et)

are the products. Complexes [(η^3-Tp*)Re(O)(R)Cl] enter the ligand exchange with silver triflate and produce [(η^3-Tp*)Re(O)(R)(OTf)].

Complexes [(η^2-Me_2Gapz_2)Re(CO)$_3$L] (L = CO, PPh_3, Hpz) can be prepared from the pyrazol-1-ylgallate ligand and $[Re(CO)_4Cl]_2$ with subsequent ligand substitution (84CJC1344, 85CJC703). Dimethylgallium pyrazol-1-yl-*o*-aminophenolate with $[Re(CO)_4Cl]_2$ gives [(η^3-$Me_2Gapz(OC_6H_4NH_2)$)Re(CO)$_3$], where coordination is effected via the ring nitrogen atom of pyrazolyl, oxygen atom and amino group of the *o*-aminophenolato framework (87CJC2469). [Mn(CO)$_5$Br] with Na[$Me_2Gapz(OCH_2pz)$] forms [(η^3-$Me_2Gapz(OCH_2pz)$)Mn(CO)$_3$] with coordination via the two heteroring nitrogens and oxygen atom of the OCH_2 group (88CJC101). The species with the pyridyl moiety instead of the pyrazol-1-yl group of OCH_2pz is prepared similarly (84CJC2783). The rhenium analog follows from the interaction of the same ligand with $[Re(CO)_4Cl]_2$. The complex [(η^3-$Me_2Gapz(OCH_2CH_2NH_2)$)Mn(CO)$_2$(η^3-C_3H_5)] is also known (79CJC167). Dimethylbis(pyrazol-1-yl)gallate with 2-mercapto-1-methylimidazole gives the product of monosubstitution, which with $[Re(CO)_4Cl]_2$ forms complex **63** (86CJC1643).



63

VI. Complexes of Iron, Ruthenium, and Osmium

[(η^3-Tp′)FeMe] [Tp′ = phenyltris(3-*tert*-butylpyrazol-1-yl)borate] (98JA10561) and [(η^3-Tp′)FeR] [Tp′ = hydrotris(3,5-diisopropylpyrazol-1-yl)borate; R = Et, CH_2CHCH_2, CH_2Tol-*p*] [98JCS(CC)973, 99JCS(CC)417] are prepared by methods similar to those described for the similar non-transition and late-transition metal alkyls.

[(η^3-Tp*)PCl_2] with $Na_2[Fe(CO)_4]$ gives the product [(η^2-Tp*)PFe(CO)$_4$], in which the dentacy of the pyrazol-1-ylborate group is changed (87JA6523).

Dihydrobis(pyrazol-1-yl)borate and hydrotris(pyrazol-1-yl)borate with [(C_3F_7)Fe(CO)$_4$I] produce [(η^2-pz_2BH_2)Fe(CO)$_3$(C_3F_7)] (76IC1861) and [(η^3-Tp)Fe(CO)$_2$(C_3F_7)], respectively (74JA1334). Potassium dihydrobis(pyrazol-1-yl)borate and [(η^3-C_3H_5)Fe(CO)$_3$I] undergo replacement of both iodide and allyl groups as well as decarbonylation of the iron species to yield *cis*-[(η^2-H_2Bpz_2Fe(CO)$_2$]

[72JOM(46)C53, 74JA1343]. Potassium hydrotris(pyrazol-1-yl)borate in similar conditions affords the iron(II) species $[(\eta^3\text{-Tp})_2\text{Fe}]$ as the major product (74JA1343), which is the same as the product of interaction with $[(\eta^5\text{-Cp})\text{Fe}(\text{CO})_3\text{I}]$ (67JA3170). The list of minor products includes $[(\eta^3\text{-C}_3\text{H}_5)\text{Fe}(\text{CO})_3\text{I}(\eta^3\text{-KTp})]$ and some products of cleavage of the boron–pyrazol-1-yl bond. Generally, organoiron compounds of pyrazol-1-ylborates are rare [93JCS(CC)266]; quite often, attempts to prepare these compounds and some organoruthenium species are complicated by the cleavage of the B—H or B—N bonds of a ligand [86JCS(D)109, 89POL1033, 90ICA(176)49, 97IC5991].

Bis(pyrazol-1-yl)methane and tris(pyrazol-1-yl)methane with $[\text{MI}(\text{Me})(\text{CO})_2(\text{PMe}_3)_2]$ (M = Fe, Ru) give the cationic species containing the acetyl group, *trans*-$[(\eta^2\text{-pz}_2\text{CH}_2)\text{M}(\text{COMe})(\text{CO})(\text{PMe}_3)_2]^+$ (M = Fe, Ru) and *trans*-$[(\eta^3\text{-pz}_3\text{CH})\text{M}(\text{COMe})(\text{CO})(\text{PMe}_3)_2]^+$ (M = Fe, Ru), as a result of the migration of the methyl group (96OM4349, 97OM2139). The same starting iron and ruthenium complexes react with Kpz_2BH_2 and NaTp to yield *trans*-$[(\eta^2\text{-pz}_2\text{BH}_2)\text{M}(\text{COMe})(\text{CO})(\text{PMe}_3)_2]$ (M = Fe, Ru) and *trans*-$[(\eta^2\text{-Tp})\text{M}(\text{COMe})(\text{CO})(\text{PMe}_3)_2]$ (M = Fe, Ru) [98JCS(D)947]. When M = Fe, further thermolysis leads to the transformation of the η^2- to the η^3-coordination mode of the hydrotris(pyrazol-1-yl)borate ligand followed by the elimination of the trimethylphosphine ligand, the product being $[(\eta^3\text{-Tp})\text{Fe}(\text{COMe})(\text{CO})(\text{PMe}_3)]$. $[\text{RuI}(\text{Me})(\text{CO})_3(\text{PMe}_3)]$ with NaTp gives $[(\eta^3\text{-Tp})\text{Ru}(\text{COMe})(\text{CO})(\text{PMe}_3)]$. $[(\eta^3\text{-Tp})\text{Ru}(\text{PPh}_3)(\text{CO})\text{Cl}]$ is known [97JCS(D)-4209].

The chain of transformations that starts from $[(\eta^4\text{-cod})\text{RuCl}_2]_n$ and H_2Bpz_2 gives $[(\eta^2\text{-H}_2\text{Bpz}_2)\text{Ru}(\eta^4\text{-cod})\text{Cl}_2]$ [93JCS(D)1935]. The product is converted into hydride $[(\eta^2\text{-H}_2\text{Bpz}_2)\text{Ru}(\eta^4\text{-cod})\text{HCl}]$ by LiBHEt_3, and then the reactions with KTp, KTp*, or TlTp′ (L) generate $[(\eta^3\text{-L})\text{Ru}(\eta^4\text{-cod})\text{H}]$, where Tp′ is hydrotris (3-isopropyl-4-bromopyrazol-1-yl)borate (94JA2635, 95JA7441). The Tp complex appears to be inert, while those based on Tp* and Tp′ reveal substantial reactivity, and some differences in structure are interpreted on the basis of the weaker *trans* influence and electron-releasing effect of the Tp′ moiety relative to Tp*. Moreover, there is a probability that these two cases represent different coordination situations. Thus, Tp* is coordinated in a traditional manner via three nitrogen atoms of the pyridine type, while Tp′ might be coordinated via two such atoms and the boron hydride moiety. Both $[(\eta^3\text{-Tp}^*)\text{Ru}(\eta^4\text{-cod})\text{H}]$ and $[(\eta^3\text{-Tp}')\text{Ru}(\eta^4\text{-cod})\text{H}]$ are hydrogenated to yield $[(\eta^3\text{-L})\text{RuH}_5]$ (L = Tp*, Tp′), while variations of temperature and the presence of the other ligands such as PCy_3, THT, py, and Et_2NH broaden the range of the hydrogenated products. Carbonylation of $[(\eta^3\text{-Tp}^*)\text{RuH}_5]$ allowed $[(\eta^3\text{-Tp}^*)\text{RuH}(\text{CO})_2]$ to be prepared.

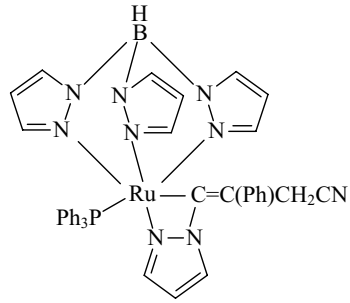
Potassium hydrotris(pyrazol-1-yl)borate with polymeric $[\text{RuCl}_2(\eta^4\text{-cod})]_n$ gives $[(\eta^3\text{-Tp})\text{RuCl}(\eta^4\text{-cod})]$ as one of the products [77JCS(D)1809, 95JCS(D)1629]. With $[(\eta^2\text{-pz}_2\text{CH}_2)\text{RuHCl}(\eta^4\text{-cod})]$, it gives $[(\eta^3\text{-Tp})\text{RuH}(\eta^4\text{-cod})]$. When treated with AlEt_3, MgEt_2, EtMgBr, or LiEt, $[(\eta^3\text{-Tp})\text{RuCl}(\eta^4\text{-cod})]$ produces a mixture of

[(η^3-Tp)Ru(η^4-cod)(Et)] and [(η^3-Tp)Ru(η^4-cod)H] (97BSCJ689). With trimethylaluminum, [(η^3-Tp)RuCl(η^4-cod)(Me)] is isolated. Species [(η^2-Tp′)RuH(η^4-cod)] [Tp′ = hydrotris(3,5-diisopropylpyrazol-1-yl)borate] (98OM4884) and [(η^2-Tp*) Ru(Me)(η^4-cod)] (97OM145) are characterized by a strong Ru $\cdots$ H—B agostic interaction and thus by the η^3(N,N,H) coordination mode (98OM145).

A similar situation is realized in the dihydrobis(3,5-di(trifluoromethyl)pyrazol-1-yl)borato complex [(η^2-H_2pz′$_2$)RuH(η^4-cod)], where the agostic interaction again predetermines the η^3(N,N,H) mode (97NJC847, 00OM2916). The bis(trifluoromethyl) derivative can also be prepared from the corresponding sodium salt and [(η^4-cod)$RuCl_2]_n$. With PR_3 (R = Ph, *i*-Pr) under hydrogen atmosphere, [(η^1-H_2pz′$_2$)RuH(η^2-H_2)(PR_3)$_2$] species are formed; here, the coordination mode may be regarded as η^2(N,H) because of the expressed agostic interaction. Without hydrogen, the η^2(N,H) species [(η^1-H_2pz′$_2$)RuH(η^4-cod)(PCy_3)] is formed; here, one pyrazol-1-yl group again is not involved in coordination but the agostic effect is apparent. Under hydrogen, this product gives a formally η^3(N,N,H)-coordinated species [(η^2-H_2Cpz′$_2$)RuH(η^2-H_2)(PCy_3)]. Complex [(η^2-H_2pz*$_2$)RuH(η^4-cod)] [95JMC(98)L5], which is formally characterized by η^3(N,N,H) coordination, behaves differently in a similar sequence of transformations (00OM2916). Its reaction with tricyclohexylphosphine and hydrogen gives [(η^1-H_2Bpz*$_2$)RuH (η^2-H_2)(PCy_3)$_2$] with the η^2(N,H) mode and [(η^2-H_2Bpz*$_2$)RuH(η^2-H_2)(PCy_3)] with the η^3(N,N,H) mode. Triphenylphosphine and hydrogen, however, give the η^2(N,H)-coordinated [(η^1-H_2Bpz*$_2$)RuH(η^4-cod)(PPh_3)] and [(η^2-H_2Bpz*$_2$)RuH (PPh_3)$_2$], the η^3(N,N,H) species. The bis(trifluoromethyl) complex [(η^2-H_2Bpz′$_2$) RuH(η^4-cod)] also reacts with *tert*-butylamine to give [(η^1-H_2Bpz′$_2$)RuH(η^4-cod) (η^1-NH_2Bu-*t*)], the structure of which is complicated by the agostic interaction and is best described by η^2(N,H) mode. In the presence of molecular hydrogen, [(η^2-H_2Bpz′$_2$)RuH(η^1-NH_2Bu-t)$_2$], the η^2(N,N,H) species, is formed. The hydride ligand is substituted by the chloride or iodide in reactions with methylene chloride and methyl iodide, respectively. The coordination mode in the substitution products remains unchanged. Reaction of [(η^2-H_2Bpz′$_2$)RuH(η^4-cod)] with mesitylene and hydrogen gives the substitution product [(η^2-H_2Bpz′$_2$)RuH(η^6-$Me_3C_6H_3$)] without the change in the coordination mode of the dihydrobis((trifluoromethyl) pyrazol-1-yl)borate ligand. With carbon monoxide, the product of CO insertion to the ruthenium–cyclooctadiene bond, [(η^2-H_2pz′$_2$)Ru(CO)$_2$(η^1-COC_8H_{13})], is formed.

[(η^3-Tp)Ru(η^4-cod)Cl] and DMSO give [(η^3-Tp)Ru(DMSO)$_2$Cl] (99OM2275). The product reacts further with HC≡CR (R = Ph, C_6H_9, COOMe, *n*-C_6H_{13}) and allyl alcohol to give the allyloxycarbenes [(η^3-Tp)Ru(=C(CH_2R)OCH_2CH= CH_2)Cl] (R = Ph, C_6H_9, COOMe, *n*-C_6H_{13}). Carbenes [(η^3-Tp)Ru(=CCH_2Ph-aapy))Cl]$\cdot$ OEt_2 (98OM827), [(η^3-Tp)Ru(=CHPh)(PCy_3)Cl_2] (98OM5384), and [(η^3-Tp)Ru(=C(OMe)CH_2COOMe)(dppe)](BF_4) [97ICA(259)77, 97OM5528] are known.

[(η^3-Tp)Ru(PPh_3)$_2$Cl] with phenylacetylene yields [(η^3-Tp)Ru(PPh_3)$_2$(C≡CPh)] (99OM982). The latter starts a chain of transformations. Thus, with ICH_2CN, the vinylidene species [(η^3-Tp)Ru(PPh_3)$_2$(=C=C(CH_2CN)Ph]$^+I^-$ results, and it can be deprotonated with sodium methylate to the cyclopropenyl neutral complex [(η^3-Tp)Ru(PPh_3)$_2$(*cyclo*-C=CPhCH(CN)]. One of the triphenylphosphine ligands is easily substituted by acetonitrile. Electrophilic agents cause the ring opening in the cyclopropenyl species. Thus, action of trifluoroacetic acid restores the original vinylidene compound. Trityl hexafluorophosphate gives [(η^3-Tp)Ru(PPh_3)$_2$(=CC(Ph)CH(CPh_3)CN] (PF_6), and $HgCl_2$ converts the cyclopropenyl moiety into vinylidene, affording [(η^3-Tp)Ru(PPh_3)$_2$(=CC(Ph)CH(HgCl)CN]Cl. Of interest is the reaction of the cyclopropenyl complex with pyrazole that gives metallacycle **64.**



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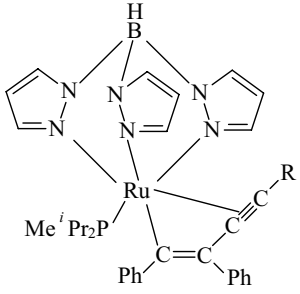
When reacted with terminal acetylenes HC≡CR (R = Ph, *t*-Bu) and sodium tetraphenylborate, species [(η^3-Tp)Ru(PR_3)$_2$Cl] (R_3 = Et_3, Me^{i}Pr$_2$) give the cationic vinylidenes [(η^3-Tp)Ru(=C=CHR)(PR_3)$_2$](BPh_4) (00OM1333). Another species of this nature can be prepared from [(η^3-Tp)Ru(PEt_3)$_2$(N_2)](BPh_4) with HC≡CCOOMe, and the product has the composition [(η^3-Tp)Ru(=CCHCOOMe)(PEt_3)$_2$](BPh_4). Further interaction of this species with the same acetylene derivative gives the product of alkyne coupling, [(η^3-Tp)Ru(=CC(COOMe)CH=CHCOOMe)(PEt_3)$_2$](BPh_4). With sodium borohydride, the η^1-butadienyl species [(η^3-Tp)Ru(CH=C(COOMe)CH=CHCOOMe)(PEt_3)$_2$] results. [(η^3-Tp)Ru(PMe^{i}Pr$_2$)$_2$Cl] also reacts with terminal acetylenes HC≡CR (R = Ph, *t*-Bu, $SiMe_3$) to afford the neutral vinylidenes [(η^3-Tp)Ru(=C=CHR)Cl(PMe^{i}Pr$_2$)], species similar to tricyclohexylphosphine [97JCS(D)2113] and triphenylphosphine [97JCS(D)4209] complexes. These complexes (R = Ph, *t*-Bu) enter alkyne coupling with diphenylacetylene and lithium diisopropylamide to yield **65** (00OM1333). Reaction with phenylacetylene occurs similarly.

[(η^3-Tp)Ru(η^4-cod)Cl] with HC≡CPh in the presence of potassium chloride gives a mixture of products (98JA6175, 98M221, 99EJIC1141), and the most interesting among them is **66.** This oxidative coupling occurs only for a terminal



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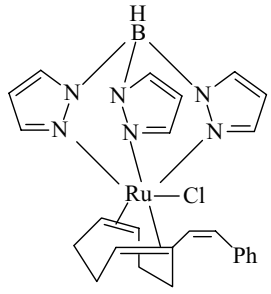
alkyne. With internal alkynes such as PhC≡CPh or MeOOCC≡CCOOMe, practically no reaction was observed, although some [(η^3-Tp)Ru(η^4-cod)H] is found in the reaction mixture. The latter reacts with phenylacetylene differently compared to the starting complex and gives the η^3-butadienyl species **67** (R = Ph). Similarly, [(η^3-Tp)Ru(η^4-cod)Cl] with HC≡CR (R = Ph, C_6H_9, Fc, CH_2Ph, *n*-Bu) but in the presence of NaOEt gives an isomeric mixture of **67** (R = C_6H_9, Fc, CH_2Ph, *n*-Bu) and **68** (R = Ph, C_6H_9, Fc, *n*-Bu). Complex **69** also reacts with terminal acetylenes HC≡CR (R = Ph, C_6H_9) in the presence of sodium ethylate to give **70** (R = Ph, C_6H_9) as well as the η^3-butadienyl derivatives.

KTp and [Ru(η^4-cod)(NH_2NMe_2)$_3$H]BPh_4 give the hydride species [(η^3-Tp)Ru(η^4-cod)H], and further interaction of the product with carbon tetrachloride or bromoform leads to [(η^3-Tp)Ru(η^4-cod)X] (X = Cl, Br) (96OM3998). The latter are used as precursors for numerous other syntheses [96JCS(D)4071, 96OM5275, 97IC1076] and as starting materials for valuable catalytic systems [98CL67, 98JOM(562)203, 99CCR(185)109]. These compounds also react with silver triflate in methylene chloride in an unexpected way, and the product is [(η^3-Tp)Ru(η^4-cod)(H_2O)]CF_3SO_3. The water molecule is easily substituted by acetonitrile, giving [(η^3-Tp)Ru(η^4-cod)(AN)]CF_3SO_3. The same complex follows if the reaction of [(η^3-Tp)Ru(η^4-cod)X] (X = Cl, Br) with silver triflate is conducted



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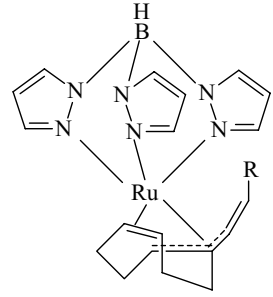

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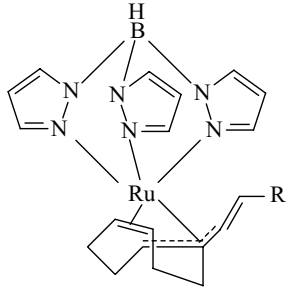

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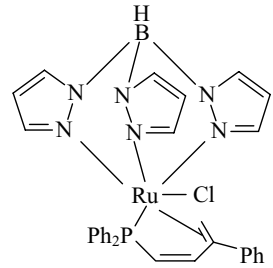

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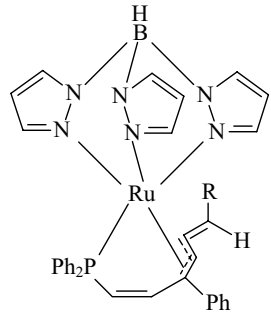

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in acetonitrile. If the medium is dimethyl sulfoxide or pyridine, [(η^3-Tp)Ru(η^4-cod)L]CF_3SO_3 (L = DMSO, py) result. Thermolysis of [(η^3-Tp)Ru(η^4-cod)Cl] in air, and further addition of another diene and zinc gives [(η^3-Tp)Ru(η^4-diene)Cl] (diene = 1,3-butadiene, isoprene, 2,4-hexadiene) (97OM2623). Species [(η^2-Tp′)RuH(cod)] where Tp′ is tris(3-isopropylpyrazol-1-yl)borate, i.e., there is a bulky ligand at position 3 of each pyrazolyl ring, contains the η^2-coordinated ligand (98OM4884). The role of agostic interactions is quite important in this species. [(η^3-Tp)Ru(η^4-cod)Cl] and ammonium hexafluorophosphate in AN give [(η^3-Tp)Ru$(AN)_3$](PF_6) (00IC382).

[(η^2-pz_2CH_2)RuHCl(η^4-cod)] with silver triflate gives the product of chloride substitution [(η^2-pz_2CH_2)RuH(OTf)(η^4-cod)] [96JOM(508)69]. In chloroform, the product is converted to [(η^2-pz_2CH_2)$RuCl_2$(η^4-cod)]. The triflate anion in the inner coordination sphere is easily substituted by dimethylphenylphosphine to yield *trans*-[(η^2-pz_2CH_2)RuH(PMe_2Ph)(η^4-cod)](CF_3SO_3), which coexists with minor amounts of the *cis* isomer on standing in solution. Trimethylphosphite acts similarly and gives *trans*-[(η^2-pz_2CH_2)RuH($P(OMe)_3$)(η^4-cod)](CF_3SO_3), which in chloroform can be converted to [(η^2-pz_2CH_2)$RuCl_2$(η^4-cod)]. At elevated temperatures, it isomerizes to the *cis* form. Similar substitution takes place with pyridine,

4-methyl-, or 3,5-dimethylpyridine in the presence of silver triflate, the products being isomeric mixtures of $[(\eta^2\text{-}pz_2CH_2)RuHL(\eta^4\text{-}cod)](CF_3SO_3)$ (L = py, 3-Mepy, 3,5-Me_2py). The starting complex was found efficient as a catalyst for hydrogenation and transfer hydrogenation reactions.

Potassium dihydrobis- and dimethylbis(pyrazol-1-yl)borates and $[(\eta^4\text{-}C_8H_{12})RuH(NH_2NMe_2)_3]PF_6$ or $[(\eta^4\text{-}C_8H_{12})RuClMe(AN)_2]$ give $[(\eta^2\text{-}H_2Bpz^*_2)Ru(\eta^4\text{-}C_8H_{12})X]$ (X = H, Me) where agostic B—H $\cdots$ Ru bonding is present (86OM2199, 87OM2014). The pure η^2-coordination is observed in $[(\eta^2\text{-}CH_2pz_2)Ru(CH{=}CH_2)(CO)(PPh_3)_2]$ (98OM4249).

Ruthenium complexes containing Tp and CO, Cp, or arene ligands are known [73JCS(CC)847, 73JOM(57)C61, 75IC3046, 86OM303, 90JCS(D)2991, 90JOM(395)C35, 90JOM(396)C31, 91OM3898, 92IC2906, 92JOM(429)229, 92JOM(434)341, 97OM1241, 97OM4464], in particular, $[(\eta^3\text{-}Tp)RuH(CO)(PPh_3)]$ obtained from NaTp and $[RuHCl(CO)(PPh_3)_3]$ [92JOM(434)341], as well as $[(\eta^3\text{-}Tp)_2Ru_2(CO)_4]$ [71JOM(31)269, 90JCS(D)2991, 92JOM(434)341, 95IC5199] which follows from KTp and $[Ru(CO)_2(O_2CMe)]$ [90JCS(D)2991]. This complex is characterized by its tendency to be oxidized chemically or electrochemically in different solvents to give $[(\eta^3\text{-}Tp)Ru(CO)_2(solv)]^+$ (solv = AN, THF, Me_2CO, H_2O) with the cleavage of the ruthenium–ruthenium bond (95IC-5199). The reactions between KTp* and $[RuHCl(CO)L_3]$ (L = PPh_3, $AsPh_3$), however, proceed differently and give $[RuHCl(CO)(Hpz^*)L_2]$ (99POL2625).

The cyclopentadienyl species $[(\eta^3\text{-}Tp)Ru(\eta^5\text{-}Cp)]$ [85JOM(282)C49, 87OM2199] as well as $[(\eta^3\text{-}Tp^*)Ru(\eta^5\text{-}Cp)]$, $[(\eta^3\text{-}Bpz_4)Ru(\eta^5\text{-}Cp)]$, and $[(\eta^3\text{-}Tp)Ru(\eta^5\text{-}Cp^*)]$ are characterized by the normal coordination situation. The mixed cyclopentadienyl–carbonyl complexes contain the η^2-coordinated pyrazol-1-ylborate ligand; these are $[(\eta^2\text{-}Tp^*)Ru(\eta^5\text{-}Cp)(CO)]$, $[(\eta^2\text{-}Bpz_4)Ru(\eta^5\text{-}Cp)(CO)]$, and $[(\eta^2\text{-}Bpz_4)Ru_2(\eta^5\text{-}Cp)_2(CO)_2](PF_6)$. The tetrakis(pyrazol-1-yl)borate ligand, which is η^2-coordinated with respect to each ruthenium site, is also present in the binuclear complex $[(Ph_3P)(OC)(MeCHCN)Ru(\mu,\eta^4\text{-}Bpz_4)RuCl(MeCHCN)(CO)(PPh_3)]$(82BCJ2356). Oxidation of $[(\eta^3\text{-}Tp^*)RuH(\eta^5\text{-}Cp)]$ with $AgPF_6$ gives $[(\eta^3\text{-}Tp^*)RuH(\eta^5\text{-}Cp)](PF_6)$ (86OM303). NaTp and $[MHCl(CO)(P^iPr_3)_2]$ (M = Ru, Os) at the first stage give $[(\eta^2\text{-}Tp)MH(CO)(P^iPr_3)_2]$, which transform into $[(\eta^3\text{-}Tp)MH(CO)(P^iPr_3)]$ on thermolysis (97OM4464).

Complex $[(\eta^1(N)\text{-}2,1,3\text{-benzothiazole})Os(CH{=}CHTol\text{-}p)(CO)Cl(PPh_3)_2]$ with potassium hydrotris(pyrazol-1-yl)borate at the first stage gives the η^2-coordinated $[(\eta^2\text{-}Tp)Os(CH{=}CHTol\text{-}p)(CO)Cl(PPh_3)_2]$, which eliminates triphenylphosphine on thermolysis and gives the η^3-coordinated $[(\eta^3\text{-}Tp)Os(CH{=}CHTol\text{-}p)(CO)Cl(PPh_3)]$ [98JCS(D)3501].

NaTp, $[Ru(\eta^6\text{-}p\text{-}Me_2C_6H_4)Cl_2]_2$, and ammonium hexafluorophosphate give rise to $[(\eta^3\text{-}Tp)Ru(\eta^6\text{-}p\text{-}Me_2C_6H_4)](PF_6)$ [97JCS(D)3367]. Reaction of $[(\eta^3\text{-}Tp)Ru(\eta^6\text{-}C_6H_6)](PF_6)$ [96POL2763, 97JCS(D)3367] with sodium tetrahydroborate gives $[(\eta^3\text{-}Tp)Ru(\eta^5\text{-}C_6H_7)]$ with the η^5-cyclohexadienyl framework [96JOM(507)291,

98JCS(D)3379]. A similar reaction course is observed when the starting complex is treated with methanolic sodium hydroxide or potassium cyanide, the products being [(η^3-Tp)Ru(η^5-C_6H_6OH)] and [(η^3-Tp)Ru(η^5-C_6H_6CN)], respectively. [(η^3-Tp)Ru(η^6-1-*i*-Pr-4-MeC_6H_4)](PF_6) with $NaBH_4$ gives [(η^3-Tp)Ru(η^5-1-*i*-Pr-4-MeC_6H_5)]. The analogous cyano and hydroxo complexes can be prepared as well. Species [(η^3-pz_3CH)Ru(η^5-C_6H_6CN)] is obtained in a similar way [98JCS-(D)3379].

Complex [(η^6-1-*i*-Pr-4-MeC_6H_4)Ru(O,N-quin)Cl] with KTp gives the η^1-coordinated [(η^6-1-*i*-Pr-4-MeC_6H_4)Ru(η^1-Tp)(O,N-quin)] substitution product [00JCS(D)2607], which can also be prepared in an indirect manner through the additional stage of treatment of the starting complex with silver triflate in acetonitrile. However, interaction of the starting complex with silver triflate in the presence of KTp leads to the destruction of the pyrazol-1-ylborate ligand and formation of [(η^6-1-*i*-Pr-4-MeC_6H_4)Ru(η^1-Hpz)(O,N-quin)].

With molecular hydrogen, [(η^3-Tp)RuH(AN)(PPh_3)] gives [(η^3-Tp)RuH(H_2)(PPh_3)] (97OM1241), the product revealing fluxional behavior between [(η^3-Tp)$RuH(H)_2(PPh_3)$] and [(η^3-Tp)RuH(η^2-H_2)(PPh_3)] species. The same starting complex with silanes $HSiR_3$ [R_3 = Et_3, $(EtO)_3$, Ph_3, HEt_2, HPh_2, H_2Ph] gives [(η^3-Tp)$Ru(PPh_3)(H)$(η^2-$HSiR_3$)] [R_3 = Et_3, $(EtO)_3$, Ph_3, HEt_2, HPh_2, H_2Ph] (99OM2484).

VII. Complexes of Cobalt, Rhodium, and Iridium

Species [(η^3-Tp)$SnCl_3$] reacts with $[Co(CO)_4]^-$ to yield the salt [(η^3-$Tp)_2Co]^+$ [*trans*-$((OC)_4CoCl_2Sn)_2Co(CO)_3]^-$ [90JOM(388)379].

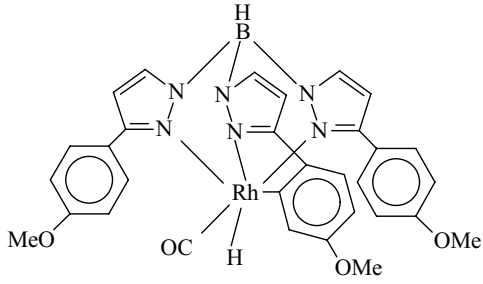
The cobalt(I) species [(η^3-(3-*t*-Bu-5-Mepz)$_3$B)Co] with RLi (R = Me, Et, *n*-Bu) gives cobalt(II) alkyls [(η^3-(3-*t*-Bu-5-Mepz)$_3$B)CoR] (R = Me, Et, *n*-Bu) (99OM-300). Complex [(η^3-(3-*t*-Bu-5-Mepz)$_3$B)Co(N_2)] reacts with ethylene and propylene to give the corresponding complexes [(η^3-(3-*t*-Bu-5-Mepz)$_3$B)Co(η^2-CH_2=CHR)] (R = H, Me) (99OM300). Species [(η^3-(3-*t*-Bu-5-Mepz)$_3$B)Co(CO)] should also be mentioned (96JA1703). A series of pyrazol-1-ylborates K(pz_nBH_{4-n}) (n = 2–4) with [(η^5-Cp)Co(CO)(R)I] (R = CF_3, C_2F_5, *n*-C_3F_7, and *i*-C_3F_7) gives different species that can be represented as [(η^5-Cp)Co(R)(η^2-$(pz)_2$BXY)] (X = Y = H; X = pz, Y = H; X = Y = pz) but have a common feature in the η^2-coordination of the pyrazol-1-ylborate moiety (74JA1334).

Cyclooctane-1,5-diyl-bis(pyrazol-1-yl)borate (L) with cobalt(II), nickel(II), and zinc(II) nitrates gives [(η^2-L)M] (M = Co, Ni, Zn) strongly stabilized by the C—H $\cdots$ M agostic interactions, which justifies their inclusion in the class of organometallic complexes [89AGE205, 91ICA(183)203, 92IC974].

Sandwiches of composition [(η^3-$HCpz_3$)Co(η^5-Cp*)]PF_6 and [(η^3-$HCpz_3$)Co(η^4-C_4Ph_4)]PF_6 are known [73JOM(57)C58].

Thallium tris(3-mesitylpyrazol-1-yl)borate and [(η^4-cod)$_2$RhCl] produce [(η^3-Tp′)Rh(η^4-cod)] (93IC3471). These complexes appeared to be good catalysts

for the polymerization of *p*-substituted phenylacetylenes (97OM4497). A similar derivative [(η^3-Tp′)Rh(η^4-nbd)] exists for Tp′ = hydrotris(3,5-diisopropylpyrazol-1-yl)borate (97OM4121). A series of [(η^3-Tp′)Rh(CO)$_2$] complexes [Tp′ = hydrotris(3-*tert*-butyl-, 3-isopropyl, 3-mesityl-, 3-phenyl-, 3,5-dimethyl-, 3-trifluoromethyl-5-methyl-, and 3-trifluoromethyl-5-thienylpyrazol-1-yl)borate] follows either from the appropriate salt and the rhodium(I) dimer [Rh(CO)$_2$Cl]$_2$ (94IC6361) or from carbonylation of the relevant [(η^3-Tp′)Rh(η^4-cod)] (94IC3666). These products are, however, characterized by the coexistence of the η^2- and η^3-coordinated forms in solution and in the solid state (98OM1552, 98OM3152). Another case of the coexistence of two coordinated forms concerns the hydrotris(3-*p*-anisylpyrazol-1-yl)borate ligand (L) in [(η^2-L)Rh(η^4-L′)] (L′ = cod, nbd) and in [(η^2-L)Rh(CO)$_2$] [00JOM(605)117]. In the latter, however, the *o*-C-H group of one of the *p*-anisylpyrazol-1-yl groups could be photochemically activated to yield **71.** For the Tp* ligand, the coexistence of the coordination modes is observed in the xenon solvates (00OM3442). In the case of more sterically demanding substituents at the pyrazolate ring, especially in position 3 or simultaneously in positions 3 and 5, the fraction of the η^2-coordinated species increases (95IC66, 96IC6354, 98HCA2127). Moreover, there is a trend that less bulky diene ligands (L_2) favor the η^3-coordination, which is sometimes the case for nbd but not for cod ligands.



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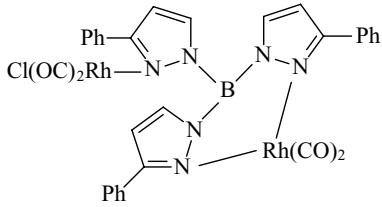
This type of isomerism is also observed for the rhodium(I) complexes containing the MeBpz′$_3^-$ and MePhB(3-Mepz)$_2^-$ ligands (95GCI181). The thallium salts TlTp*, Tl(3-CF$_3$-5-Mepz$_3$BH), and Tl(3,5-(CF$_3$)$_2$pz$_3$BH), when reacted with [RhClL$_2$]$_2$ [L$_2$ = (CO)$_2$, nbd, cod], give the corresponding [(η^3-Tp′)RhL$_2$] $\rightleftarrows$ [(η^2-Tp′)RhL$_2$] complexes [95ICA(240)631]. For the 3-mesityl derivative, exclusively the η^3-coordination mode was observed (93IC3471). The fact of $\eta^2 \rightleftarrows \eta^3$ coexistence has an interesting chemical consequence: namely, the synthesis of the dimer based on hydrotris(3-phenylpyrazol-1-yl)borate **72.** In the solid state, the 3-methylindazolate complex is η^2-coordinated (97IC5097), although some

fluxionality is noted in solution. 3-Methyl-4,5,6,7-tetrahydroindazolate complex [(η^2-Tp′)Rh(η^4-cod)] is also η^2-coordinated (00IC1333).



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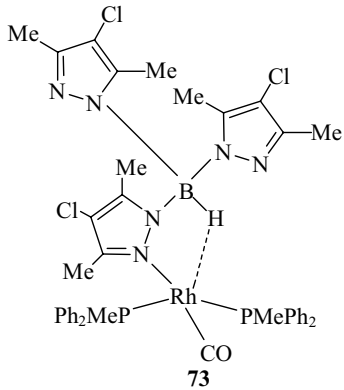
The observation that the η^2-coordinated rhodium(I) species [(η^2-Tp*)Rh(CO)(PPh_3)] may be oxidized to give the rhodium(II) isomer [(η^3-Tp*)Rh(CO)(PPh_3)] [96JCS(CC)2289] is of interest. Another unusual case refers to the reaction between [(η^3-HB(4-Clpz*)$_3$)Rh$(CO)_2$] and methyldiphenylphosphine [99JCS(D)-271]. If one equivalent of the phosphine is used, the η^2-coordinated species [(η^2-HB(4-Clpz*)$_3$) Rh(CO)($PMePh_2$)] results. However, in excess phosphine, the product is **73,** which is coordinated via only one nitrogen while the hydrogen atom of the B—H moiety occupies the other coordination site, so that B—H $\cdots$ Rh agostic interaction is realized. The coordination situation for the pyrazol-1-ylborate ligand may be regarded as η^2(N,H). This is unique, although the B—H $\cdots$ M agostic interactions often arise for similar ligands [95JCS(D)1709, 98EJIC425, 98JA361, 98JCS(CC)2011]. A similar phenomenon is observed when the dimer [Rh(μ-Cl)(cod)]$_2$ reacts with KTp* and (1-cyclohepta-2,4,6-trienyl)phosphine in any sequence to yield **74** (00ZAAC552).



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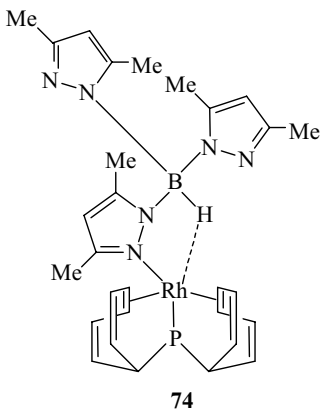

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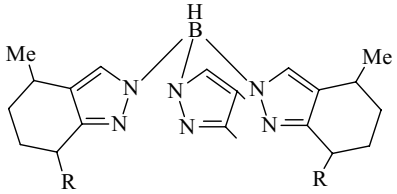
[(η^3-Tp*)Rh(CO)$_2$)] and trimethylphosphine give the product of ligand monosubstitution [(η^2-Tp*)Rh(CO)(PMe$_3$)] (96IC6354). In the solid state, it is a square-planar complex with the η^2-coordination of the pyrazol-1-ylborate ligand. In solution, some fluxionality is observed, which the authors relate not to the $\eta^2 \rightleftarrows \eta^3$ dynamics but rather to the exchange of the coordinated and noncoordinated pyrazol-1-yl groups. Another synthesis of this nature involves the reaction of potassium hydrotris(3-phenyl-5-methylpyrazol-1-yl)borate with [Rh(acac)(CO)$_2$] to yield [(η^2-Tp′)Rh(CO)$_2$] [00JOM(595)178]. If the reaction is conducted in the presence of triphenylphosphine, [(η^2-Tp′)Rh(CO)(PPh$_3$)] results. The formation of the square-planar complexes with the bidentate coordination of the bulky pyrazol-1-ylborate ligands takes place in the solid state, while in solution the $\eta^2 \rightleftarrows \eta^3$ fluxionality is noted, although this process is somewhat retarded in the case of PPh$_3$ substitution.

Sodium or potassium salts of Tp, Tp*, and Tp′ [hydrotris(3-R-pyrazol-1-yl) borate (R = Me, *i*-Pr), hydrotris(3,5-R,R′-pyrazol-1-yl)borate (R = CF$_3$, R′ = Me; R = Ph, R′ = Me; R = R′ = *i*-Pr), hydrotris(3,4,5-R,R′,R″-pyrazol-1-yl) borate (R = R′ = R″ = Me; R = R″ = Me, R′ = Cl, Br)] with the dimer [Ir(μ-Cl)(η^4-cod)]$_2$ give a series of complexes of general formulation [(Tp′)Ir(η^4-cod)] (97IC5991). In the solid state the parent pyrazol-1-ylborate is η^3-coordinated, while the Tp′ derivatives with R = R′ = Me, R″ = H, and R = R″ = Me, R′ = Cl are η^2-coordinated with signs of the B—H $\cdots$ Ir agostic interaction (X-ray data). Similar structures can be inferred for all the other complexes prepared on the basis of IR spectral data in the solid phase. In solution there is an $\eta^2 \rightleftarrows \eta^3$ dynamic equilibrium. When reacted with the rhodium(I) dimer [Rh(CO)$_2$Cl]$_2$, ligands **75** (R = *i*-Pr, *t*-Bu) form the η^2-coordinated species [(η^2-Tp′)Rh(CO)$_2$] (Tp′ represents ligands **75,** R = *i*-Pr, *t*-Bu) in the solid state, while some $\eta^2 \rightleftarrows \eta^3$ fluxionality was noted in solution (96OM4133). Moreover, these complexes appear to be good examples of the diastereoselective intramolecular C—H activation of the coordinated pyrazol-1-ylborate ligands when form **76** (R = *i*-Pr) is chosen to illustrate the predominating species. [(η^3-Tp)Rh(CO)$_2$] in chloroform is characterized by the equilibrium of the η^2- and η^3-coordination mode of the pyrazol-1-ylborate ligand (94IC3666). [(η^3-Tp)Rh(CO)$_2$] is protonated at the pyrazolate rings [89JCS(CC)341, 94AGE1983].



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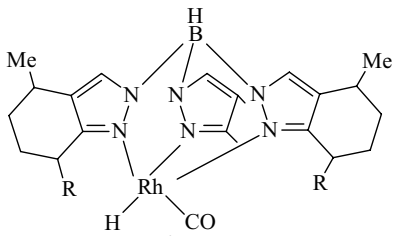

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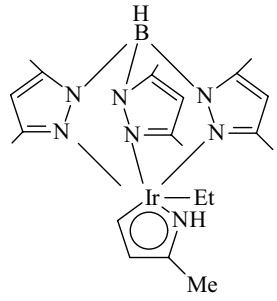
The potassium salt of hydrotris(3,5-diisopropylpyrazol-1-yl)borate (KTp′) with $[(\eta^2\text{-COE})_2RhCl]_2$ in CH_2Cl_2/AN gives $[(\eta^3\text{-Tp}')Rh(\eta^2\text{-COE})(AN)]$ (99OM3234). Such complexes are often characterized by agostic interactions and exhibit the η^4(N,N,N,H) mode of coordination (99OM2571). The ligand substitution reactions with diphosphines or carbon monoxide lead to the change in the coordination mode of the pyrazol-1-ylborate ligand and formation of $[(\eta^2\text{-Tp}')RhL_2(AN)]$ [L_2 = dppm, dppe, dppp, $(CO)_2$] with a possible fluxionality in solution. For the dicarbonyl complex, the prevalence of the η^3 mode is emphasized. Molecular iodine, diethylsilane, and phenylsilane oxidatively add to $[(\eta^3\text{-Tp}')Rh(\eta^2\text{-COE})(AN)]$ with no change of coordination mode but with elimination of COE. The products are formulated as $[(\eta^3\text{-Tp}')Rh(AN)(X)(Y)]$ (X = Y = I; X = H, Y = $SiHEt_2$; X = H, Y = SiH_2Ph).

$[(\eta^3\text{-Tp})Ir(CO)_2]$ (90JA7984) and $[(\eta^3\text{-Tp}^*)IrH_2(\eta^2\text{-COE})]$ (92NJC337) manifest the prevailing η^3 mode. Potassium hydrotris(pyrazol-1-yl)borate with $[(COE)_2IrCl_2]$ gives the cyclooctenyl hydride $[(\eta^3\text{-Tp})Ir(H)(\eta^3\text{-cyclooctenyl})]$ (89IC3444). Of non–C—H-activated alkenes, only ethylene is known to react in these circumstances, giving $[(\eta^3\text{-Tp})Ir(C_2H_4)_2]$. C—H activation of coordinated ethylene occurs on irradiation to yield $[(\eta^3\text{-Tp})Ir(H)(\eta^1\text{-CH=CH}_2)(\eta^2\text{-}C_2H_4)_2]$. H_nBpz_{4-n} Ir complexes containing alkenyl and carbonyl ligands are known [89JCS(D)2073, 91POL1595]. Sodium hydrotris(pyrazol-1-yl)borate with $[Ir(\mu\text{-Cl})(\eta^2\text{-COE})_2]_2$ gives the product of partial C—H activation of the COE ligand, $[(\eta^3\text{-Tp})IrH(\eta^1\text{-}C_8H_{13})(\eta^2\text{-COE})]$ [89JCS(D)2073]. Protonation of this species with tetrafluoroboric acid gives $[(\eta^3\text{-Tp})IrH(\eta^2\text{-COE})_2]BF_4$. Sodium hydrotris(pyrazol-1-yl)borate with $[IrCl(C_2H_4)_4]$ gives $[(\eta^3\text{-Tp})Ir(C_2H_4)_2]$. The latter with carbon monoxide gives $[(\eta^3\text{-Tp})Ir(CO)_2]$ (89IC3444), which with ethylene gives the product of monosubstitution, $[(\eta^3\text{-Tp})Ir(C_2H_4)(CO)]$ [93JOM(443)249]. Protonation of the ethylene complexes $[(\eta^3\text{-Tp})Ir(C_2H_4)_2]$ and $[(\eta^3\text{-Tp})Ir(C_2H_4)(CO)]$ with tetrafluoroboric acid leads to $[(\eta^3\text{-Tp})Ir(Et)(\eta^2\text{-}C_2H_4)](BF_4)$ and $[(\eta^3\text{-Tp})Ir(C_2H_5)(CO)](BF_4)$, respectively.

Photolysis of $[(\eta^3\text{-Tp}^*)IrH_2(\eta^2\text{-COE})]$ in benzene in the presence of trimethoxyphosphine gives $[(\eta^3\text{-Tp}^*)IrH(Ph)(P(OMe)_3)]$ (96IC1602), while in ether the process leads to $[(\eta^3\text{-Tp}^*)IrH_2(P(OMe)_3)]$. The product of photolysis of the starting complex in *tert*-butylacrylate is $[(\eta^3\text{-Tp}^*)IrH_2(CH_2\text{=CHCOOBu-}t)]$. Species $[(\eta^2\text{-Tp})IrH(CO)_2]$ [92JOM(438)337] forms $[(\eta^2\text{-Tp})IrH(COOH)(CO)]$ with water, $[(\eta^2\text{-Tp})IrH(COOMe)(CO)]$ with methanol, and $[(\eta^2\text{-Tp})IrH(COOEt)(CO)]$ with ethanol. On reflux, the hydroxycarbonyl derivative gives rise to $[(\eta^2\text{-Tp})IrH_2(CO)]$. The starting complex also reacts with primary amines to give $[(\eta^2\text{-Tp})IrH(CONHR)(CO)]$ (R = Alk) [92JOM(441)155].

Complex $[(\eta^3\text{-Tp}^*)Ir(\eta^2\text{-}C_2H_4)_2]$ (99OM139) on hydrogenolysis gives the Ir(V) species $[(\eta^3\text{-Tp}^*)IrH_4]$ (99JA346). The latter can be carbonylated to $[(\eta^3\text{-Tp}^*)IrH_2(CO)]$. The reaction of $[(\eta^3\text{-Tp}^*)IrH_2(SC_4H_4)]$ with triethylsilane is an oxidative addition followed by elimination of thiophene; the product is $[(\eta^3\text{-Tp}^*)IrH_3(SiEt_3)]$.

As some illustrations above show, the Tp* ligand is famous for the stabilization of the Rh(III) and Ir(III) oxidation states [87JA4726, 89JA375, 89JA5480, 90JOM(394)C31, 92JA7288, 94JA791, 96IC1602, 96JOM(526)341, 98JPC(A)1963] and promotion of the coordination number 6 (86JA1550, 92JA579). There is an indication that [(η^3-Tp*)Rh(CO)$_2$] oxidatively adds methyl iodide to give the rhodium(III) species [(η^3-Tp*)Rh(CO)(Me)(I)] [74IC1291, 76IC3117, 79JOM(165)383]. The latter effect may be illustrated by a facile rearrangement of [(η^3-Tp*)Ir(C$_2$H$_4$)$_2$] into [(η^3-Tp*)Ir(H)(CH=CH$_2$)(C$_2$H$_4$)], where the ethylene molecule undergoes the process of C—H activation [92JCS(CC)8, 92JCS(CC)558]. This approach is used for the activation of numerous organic molecules [94JA4519, 95JOM(504)147]. Thus, thermolysis of the AN solutions of [(η^3-Tp*)Ir(C$_2$H$_4$)$_2$] and [(η^3-Tp*)Ir(H)(CH=CH$_2$)(C$_2$H$_4$)] gives [(η^3-Tp*)Ir(H)(CH=CH$_2$)(Et)(AN)] (96OM2192). Further thermolysis leads to **77,** the isomeric iridapyrrole complex. A similar chain of transformations is known for the analogous propenyl compound.



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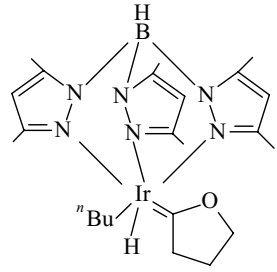
A detailed photochemical study of the intermolecular C—H activation of the hydrocarbon solvents by [(η^3-Tp*)Rh(CO)$_2$] [95IC424, 95JOM(504)107, 96IC675, 96IC7049, 96JA3769] is illustrated by the fact that the vinyl and ethylene frameworks undergo coupling to yield the allylic complex [(η^3-Tp*)Ir(H)(CH$_2$CHCHMe)]. The latter is formed upon thermolysis of the THF solution of [(η^3-Tp*)Ir(H)(CH=CH$_2$)(C$_2$H$_4$)], together with **78** (92JA7288). [RhCl(C$_2$H$_4$)$_2$]$_2$ with KTp (69JA588) and KTp* (95AGE231, 00IC180) gives [(η^3-Tp)Rh(C$_2$H$_4$)$_2$] and [(η^3-Tp*)Rh(C$_2$H$_4$)$_2$], respectively.

These complexes were sometimes speculated to be the η^2-coordinated structures [69JA588, 74JOM(65)C47, 74JOM(73)115], although this speculation found no further confirmation except for fluxionality in solution. On thermolysis, the Tp* derivative gives allylic species of composition [(η^3-Tp*)Rh(H)(η^3-*syn*-C$_3$H$_4$Me)] (00IC180), and other analogous allylic derivatives are also known (98OM3770). The product slowly converts into the butadiene species [(η^3-Tp*)Rh(η^4-C$_4$H$_8$)] on

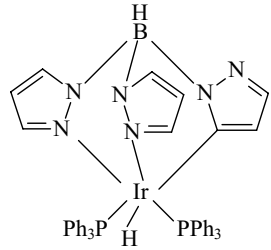


78

standing in benzene or cyclohexane solution (00IC180). At low temperatures in the presence of ethylene, $[(\eta^3\text{-Tp}^*)\text{Rh}(\text{C}_2\text{H}_4)_2]$ gives not only the aforementioned η^4-butadiene species but also the products of incorporation of the third ethylene molecule, allylic $[(\eta^3\text{-Tp}^*)\text{Rh}(\text{Et})(\eta^3\text{-}syn\text{-C}_3\text{H}_4\text{Me})]$ and dienic $[(\eta^3\text{-Tp}^*)\text{Rh}(\eta^4\text{-CH}_2{=}\text{CH}{-}\text{CH}{=}\text{CHCH}_2\text{CH}_3)]$. $[(\eta^3\text{-Tp}^*)\text{Rh}(\text{C}_2\text{H}_4)_2]$ easily substitutes one of the ethylene molecules with carbon monoxide, trimethylphosphine, *tert*-butyl isocyanide, and cyclohexyl isocyanide to give $[(\eta^3\text{-Tp}^*)\text{Rh}(\text{C}_2\text{H}_4)\text{L}]$ [L = CO (89JA-375), PMe_3, *t*-BuNC, CyNC (95AGE231, 96OM2678, 00IC180)]. Interestingly, the parent $[(\eta^3\text{-Tp})\text{Rh}(\text{C}_2\text{H}_4)_2]$ reacts with carbon monoxide and cyclohexyl isocyanide differently, yielding $[(\eta^3\text{-Tp})\text{Rh}]_2(\mu\text{-CO})_3$ and $[(\eta^3\text{-Tp})\text{Rh}]_2(\mu\text{-CyNC})_3$, respectively (82OM1125, 00IC180). Both the Tp and Tp* rhodium ethylene complexes, however, form the simple substitution products with tertiary (PMe_3, PMe_2Ph, PEt_3) and chelating (dmpe) phosphines (00IC180). Simple substitution is not the case for such entering ligands as acetonitrile and pyridine, when $[(\eta^3\text{-Tp}^*)\text{Rh}(\text{CH}{=}\text{CH}_2)(\text{CH}_2\text{CH}_3)(\text{L})]$ (L = AN, py) are formed. The product with L = AN transforms into the rhodium(I) derivative $[(\eta^3\text{-Tp}^*)\text{Rh}(\text{C}_2\text{H}_4)(\text{AN})]$ upon standing at elevated temperatures. Meanwhile, in benzene solution it causes the C—H activation of benzene, yielding $[(\eta^3\text{-Tp}^*)\text{Rh}(\text{C}_2\text{H}_5)(\text{AN})(\text{Ph})]$ and ethylene [88JCS(CC)1511]. With molecular oxygen, $[(\eta^3\text{-Tp}^*)\text{Rh}(\text{C}_2\text{H}_4)(\text{PR}_3)]$ (R = Me, Et) forms the η^2-dioxygen species, and with molecular hydrogen it forms the dihydrides (00IC180). Both $[(\eta^3\text{-Tp}^*)\text{Rh}(\text{C}_2\text{H}_4)_2]$ and $[(\eta^3\text{-Tp}^*)\text{Rh}(\text{C}_2\text{H}_4)(\text{PMe}_3)]$ in excess trimethyl phosphine give the rare η^1-coordinated species $[(\eta^1\text{-Tp}^*)\text{Rh}(\text{PMe}_3)_3]$ (00AGE218), although the possibility of the η^2(N,H) mode due to B—H $\cdots$ Rh interactions is not excluded completely.

$[(\eta^3\text{-Tp}^*)\text{Ir}(\eta^2\text{-C}_2\text{H}_4)_2]$ enters thermolysis with AN and DMSO (L) to yield $[(\eta^3\text{-Tp}^*)\text{Ir}(\text{C}_2\text{H}_4)(\text{Et})(\text{L})]$ (97CEJ860, 98CEJ2225). However, with PMe_3, PEt_3, PMe_2Ph, or CO (L), simple substitution products $[(\eta^3\text{-Tp}^*)\text{Ir}(\eta^2\text{-C}_2\text{H}_4)\text{L}]$ follow (98IC4538). The carbonyl complex (L = CO) in the aqueous medium gives rise to $[(\eta^3\text{-Tp}^*)\text{Ir}(\text{H})(\text{COOH})(\text{CO})]$. Bis(dimethylphosphino)ethane (L) in these conditions forms the dinuclear species $[\{(\eta^3\text{-Tp}^*)\text{Ir}(\eta^2\text{-C}_2\text{H}_4)\}_2(\mu\text{-L})]$. The Tp complex also enters this type of a reaction with triphenylphosphine (97OM467),

triethylphosphine, and dimethylphenylphosphine (98IC4538). [(η^3-Tp)Ir(C_2H_4)$_2$] with excess triphenylphosphine gives [(η^3-Tp)Ir(C_2H_4)(PPh_3)] (96JA12842, 00OM1670). On standing, this complex undergoes a unique rearrangement to **79** and eliminates ethylene. The η^1(C)-coordination of one of the pyrazolyl rings occurs, which implies the C—H activation of a pyrazolate ring of the ligand and formation of the iridium(III) complex. The product **79** can be protonated at the pyridine-type nitrogen atom by tetrafluoroboric acid, and the process is reverted by sodium hydroxide. In addition, complex **79** reacts with ethylene to restore the iridium(I) species [(η^3-Tp)Ir(C_2H_4)(PPh_3)]. In these complexes, the role of the metallacyclopropane resonance canonical form is sometimes stressed (92OM3427). With molecular hydrogen, a series of iridium(III) derivatives of the type [(η^3-Tp*)Ir(H)$_2$L] (L = PMe_3, PMe_2Ph, $\frac{1}{2}$ dmpe) and [(η^3-Tp)Ir(H)$_2$(PMe_2Ph)] was obtained (97JA11028, 98IC4538). Thermolysis of [(η^3-Tp*)Ir(η^2-C_2H_4)L] gives rise to the hydride–vinyl species [(η^3-Tp*)IrH(CH=CH_2)L] (L = PMe_3, PMe_2Ph) (98IC4538).



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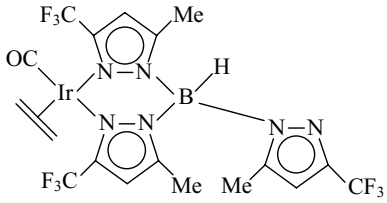
In the complex [(η^2-Tp*)Rh(CO)(η^2-C_2H_4)], the pyrazol-1-ylborate ligand is η^2-coordinated [88JCS(CC)1511]. The same situation is realized in complex **80** (89JA5480). At elevated temperatures isomerization of **80** into a hydridovinyl species **81** takes place. It is a process of intramolecular rearrangement with the change of coordination mode of the pyrazol-1-ylborate ligand from η^2 to η^3. These changes lead to the iridium(II) oxidation state, which appears to be more stable than that of iridium(I). The same situation is realized for the ligand hydrotris (3-trifluoromethyl-5-methylpyrazol-1-yl)borate when the iridium complex [(η^2-Tp′)Ir(CO)(η^2-C_2H_4)] is easily isomerized into [(η^3-Tp′)Ir(CO)(H)(CH=CH_2)] (90JA5480). This is not the case in the similar rhodium chemistry. This problem was tackled theoretically (97OM1962, 97SCI260). Thus, [(η^2-Tp*)Rh(CO)(H)(CH=CH_2)] is readily isomerized to [(η^2-Tp*)Rh(CO)(η^2-C_2H_4)]. Moreover, the chain of transformations starting from [(η^3-Tp*)Rh(CO)$_2$] in cyclohexane solution leads to a labile oxidative addition product [(η^3-Tp*)Rh(CO)(H)(Cy)], which upon interaction with ethylene produces a mixture of [(η^3-Tp*)RhH(CO)(CH=CH_2)] and [(η^2-Tp*)Rh(CO)(η^2-C_2H_4)]; the latter, which is a rhodium(I) species, predominates (87JA4726, 89JA375).



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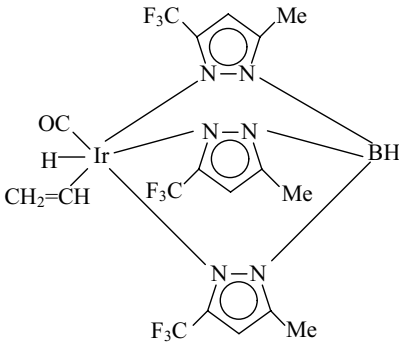
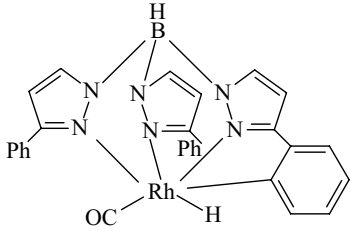


81

Species $[(\eta^3\text{-Tp}^*)\text{Rh(CO)}_2]$ (71IC1372, 80IC1582) on photolysis is decarbonylated to cause the C—H activation of both aromatic (benzene) and aliphatic (cyclohexane and a cyclohexane–methane mixture) hydrocarbons, the products being $[(\eta^3\text{-Tp}^*)\text{Rh(CO)(H)(R)}]$ (R = Me, Cy, Ph) (87JA4726). Meanwhile, the dicarbonyl complex based on hydrotris (3-phenylpyrazol-1-yl) borate reacts in benzene differently in the sense that it gives rise to the product of cyclometallation **82** (86JA7346). The same complex on photolysis with cyclopropane behaves in analogous way, giving first the product of intramolecular C—H activation **83,** which then rearranges to **84.** Species **84** also follows from the interaction of **82** with cyclopropane.



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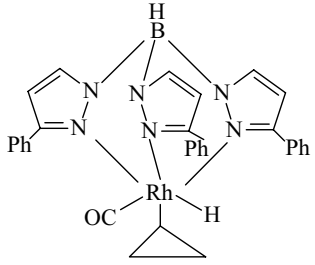

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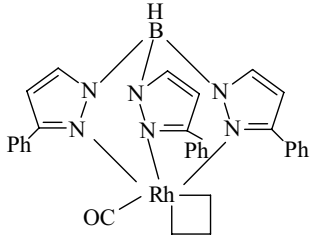
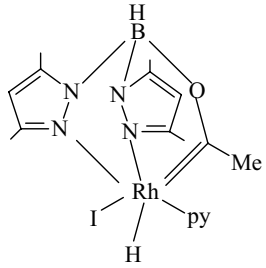


84

Another agent causing C—H activation [93JOM(444)223] is the stable 16-electron species [(η^2-$H_2Bpz^*_2$)Rh(CO)$_2$] [75JOM(87)365]. This complex when reacted with trimethylamine-*N*-oxide in pyridine medium gives the product of substitution of a carbonyl ligand, [(η^2-$H_2Bpz^*_2$)Rh(CO)(py)] (00OM2947). The product reacts with methyl iodide in an extraordinary manner, causing modification of the structure of pyrazol-1-ylborate ligand (loss of its innocence). The latter involves migration of one of the B—H protons to the rhodium site and insertion of carbon monoxide into the framework of pyrazol-1-ylborate to yield the oxycarbene **85.** Thermolysis of **85** leads to the migration of the Rh—H proton to the carbene center and formation of the coordinatively unsaturated rhodium atom, **86.**



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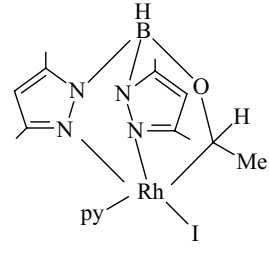
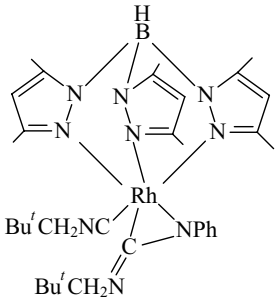


86

[(η^2-COE)Ir(μ-Cl)]$_2$, 1,3-diene, and then KTp or KTp* form a wide variety of the η^4-*s*-*cis*-dienic iridium(I) complexes of composition [(η^3-Tp)Ir(η^4-diene)] (diene = 1,3-butadiene, 2,3-dimethyl-1,3-butadiene) or [(η^3-Tp*)Ir(η^4-diene)] (diene = 1,3-butadiene, 2-methyl-1,3-butadiene, 2,3-dimethyl-1,3-butadiene, 1,3-cyclopentadiene, 1,3-cyclohexadiene) [97JOM(528)143]. Photolysis of [(η^3-Tp*)Ir(η^4-diene)] (diene = 1,3-butadiene, 2-methyl-1,3-butadiene, 2,3-dimethyl-1,3-butadiene) produces hydrido–allyl species, e.g., [(η^3-Tp*)IrH(η^3-$CH_2C(C(Me)=CH_2)CH_2$)]. Thermolysis of [(η^3-Tp*)Ir(η^4-2,3-dimethyl-1,3-butadiene)] with benzene in an atmosphere of nitrogen leads to the elimination of the 1,3-diene ligand and formation of [(η^3-Tp*)(Ph)(H)Ir(μ-N≡N)Ir(H)(Ph)(η^3-Tp*)]. Species [(η^3-Tp*)Ir(η^4-CH_2=C(Me)—C(Me)=CH_2)] with *p*-methoxybenzaldehyde yields the activated iridium(III) product of composition [(η^3-Tp*)Ir(η^1-*p*-Tol)(CO)(η^1-CH_2—C(Me)=CMe_2)] (99JA248). In addition, complex [(η^3-Tp*)Ir(η^4-CH_2=C(Me)—C(Me)=CH_2)] reacts with a variety of Lewis bases L (L = Me_3P, CO, THT, AN, py, PhCH=NMe) to yield the iridium(III) adducts [(η^3-Tp*)Ir(η^2-CH_2=C(Me)—C(Me)=CH_2)L], where the coordination mode of the butadiene moiety transforms from that embracing the delocalized π system to one of the σ^2 type via two terminal carbon atoms of the CC=CC framework (00OM3120).

While complex [(η^3-Tp)Rh(I)(Me)(PPh_3)] is η^3-coordinated [91AX(C)1732], [(η^2-Tp*)Rh($CNCH_2CMe_3$)$_2$] is characterized by bidentate coordination, which is

changed upon protonation with HBF_4 to the η^3 mode in $[(\eta^3\text{-Tp}^*)Rh(H)(CNBu\text{-}t)_2]BF_4$ (91IC778). Species **87** on photolysis in benzene eliminates carbodiimide $PhN{=}C{=}NCH_2Bu\text{-}t$ and oxidatively adds benzene to yield **88** (R = Ph, X = H) (89NJC725, 92JA6087). In cyclohexane, **88** (R = Cy, X = H) is formed (93JA554), which can be converted to **88** (R = Cy, X = Cl) in carbon tetrachloride. Similar reactions in cyclopentane or *n*-pentane give **88** (R = cyclopentyl, *n*-pentyl; X = H, Cl). With *n*-propane or mesitylene, **88** (R = *n*-Pr, Mes; X = H) were obtained. PhN_3 and $t\text{-}BuCH_2NC$ adds to $[(\eta^2\text{-Tp}^*)Rh(CNCH_2Bu\text{-}t)_2]$ to give the product, for which two alternative structures, **89** and **90,** were proposed (92OM1496). Some problems are encountered in this preparation (91IC778, 92OM1503).



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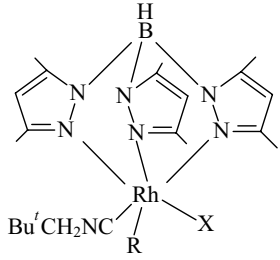

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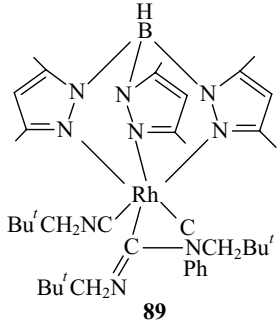

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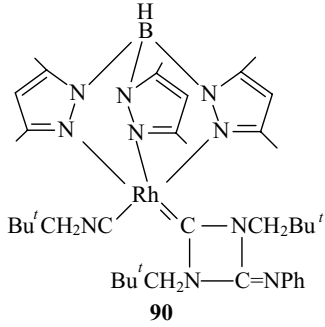

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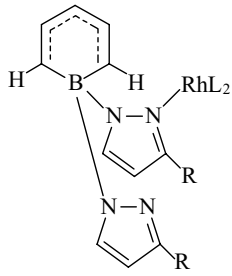
The vinyl chloride derivative $[(\eta^3\text{-Tp}^*)Rh(CNBu\text{-}t)(CH_2{=}CH)Cl]$ when reacted with Cp_2ZrH_2 gives the vinyl hydride $[(\eta^3\text{-Tp}^*)Rh(CNBu\text{-}t)(CH_2{=}CH)H]$ (99OM495). In C_6D_6 at room temperature, the product transforms into the ethylene complex $[(\eta^3\text{-Tp}^*)Rh(CNBu\text{-}t)(\eta^2\text{-}CH_2{=}CH_2)]$ by intramolecular isomerization. A similar complex, $[(\eta^3\text{-Tp}^*)Rh(CN\text{-}2,6\text{-xylyl})(\eta^2\text{-}CH_2{=}CH_2)]$, is also known (98OM4784, 98OM5148). Photolysis of $[(\eta^3\text{-Tp}^*)Rh(CNBu\text{-}t)(PhN{=}C{=}NBu\text{-}t)]$

in propylene gives the allyl hydride [(η^3-Tp*)Rh(CNBu-*t*)H(η^1-$CH_2CH{=}CH_2$)] (99OM495). It easily transforms into a propylene species [(η^3-Tp*)Rh(CNBu-*t*)(η^2-$MeCH{=}CH_2$)]. If photolysis is conducted in isobutylene, [(η^3-Tp*)Rh(CNBu-*t*)H(η^1-$CH_2CMe{=}CH_2$)] results; and in *tert*-butylethylene, [(η^3-Tp*)Rh(CNBu-*t*)H(η^1-$CH{=}CH{-}CMe_3$)] is obtained. Neither of these compounds undergoes intramolecular isomerization, but on standing in benzene give the product of C—H activation, [(η^3-Tp*)Rh(CNBu-*t*)H(Ph)]. Complex [(η^3-Tp*)(CNBu-*t*)(Me)Cl] gives [(η^3-Tp*)(CNBu-*t*)(Me)H] on reaction with either $LiAlH_4$ or Cp_2ZrH_2, the preparation being more efficient in the second case (99JA3974). The product on standing in benzene eliminates methane reductively and forms [(η^3-Tp*)(CNBu-*t*)(Ph)H]. [(η^3-Tp*)Rh(AN)Cl_2] with neopentyl isocyanide gives the product of substitution [(η^3-Tp*)Rh($NCCH_2$Bu-*t*)Cl_2]97IC2723). Addition of RMgX (R = Me, *n*-Pr, *i*-Pr, X = Cl; R = CD_3, X = I; R = *cyclo*-Pr, $CH_2{=}CH$, X = Br) to the product gives a variety of the alkyl halide species [(η^3-Tp*)Rh(NCBu-*t*)(R)X] (R = Me, *n*-Pr, *i*-Pr, X = Cl; R = CD_3, X = Cl, I; R = *cyclo*-Pr, X = Cl, Br; R = $CH_2{=}CH$, X = Cl, Br).

Alkylation of [(η^3-Tp*)Ir(PMe_3)Br_2] with methyllithium gives [(η^3-Tp*)Ir(PMe_3)(Me)Br], which with silver triflate enters the ligand substitution and generates [(η^3-Tp*)Ir(PMe_3)(Me)(OTf)] (00JA954). This is an extremely unreactive species. However, metathesis of the product with $NaB(3,5\text{-}C_6F_3(CF_3)_2)_4$ in methylene chloride under nitrogen unexpectedly gives the dinitrogen complex [(η^3-Tp*)Ir(PMe_3)(Me)(N_2)]($B(3,5\text{-}C_6F_3(CF_3)_2)_4$), while in the absence of nitrogen [(η^3-Tp*)Ir(PMe_3)(Me)(CH_2Cl_2)]($B(3,5\text{-}C_6F_3(CF_3)_2)_4$) was formed. These species are quite susceptible to ligand substitutions and give [(η^3-Tp*)Ir(PMe_3)(Me)L]($B(3,5\text{-}C_6F_3(CF_3)_2)_4$) (L = CO, AN) quite readily. Besides, the dinitrogen and methylene chloride cationic species appear to be quite promising C—H activation agents. Thus, benzene with the dinitrogen complex yields methane and [(η^3-Tp*)Ir(PMe_3)(Ph)(N_2)]($B(3,5\text{-}C_6F_3(CF_3)_2)_4$), while acetaldehyde and *p*-tolualdehyde lead to [(η^3-Tp*)Ir(PMe_3)(Me)(O=C(H)R)]($B(3,5\text{-}C_6F_3(CF_3)_2)_4$) (R = Me, *p*-Tol). Thermolysis of the latter affords [(η^3-Tp*)Ir(PMe_3)(R)(CO)]($B(3,5\text{-}C_6F_3(CF_3)_2)_4$) (R = Me, *p*-Tol).

Complexes [(η^2-Ph_2Bpz_2)RhL_2] [L_2 = $(CO)_2$, cod, nbd] and **91** [R = H, Me; L_2 = $(CO)_2$, cod, nbd] are characterized by a weak but significant Rh ··· H interaction [92OM2514]. Species [(η^3-Bpz_4)RhL_2] (L_2 = cod, nbd) [84OMR80, 85ICA(101)L45] and [(η^3-Bpz_4)RhI_2(CO)] (82OM1125) represent examples of the η^3-coordination of tetrakis(pyrazol-1-yl)borate complexes. It is interesting that [(η^2-Bpz_4)RhL_2] (L_2 = cod, nbd) is presented by the bidentate pyrazol-1-ylborate ligand, but when L_2 = duroquinone, the η^3-coordination is observed in the solid state (82OM1132), and the situation may become different in solution (82JMR168, 82OM1139). [$RhCl(C_2H_4)_2$] with the potassium salt of bis(3,5-dimethylpyrazol-1-yl)borate in the presence of 2,3-dimethylbutadiene gives [(η^2-$H_2Bpz^*_2$)Rh(η^4-2,3-$Me_2C_4H_4$)] [98ICA(273)244].



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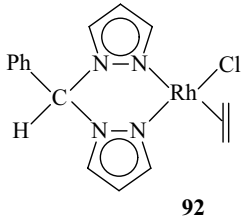
Bis(pyrazol-1-yl)phenylmethane in organorhodium complexes may offer a variety of coordination modes. Thus, with $[Rh(C_2H_4)Cl]_2$, the spectral data suggest a product that may have two possible arrangements—one where the ligand has a normal bidentate coordination, **92,** and the other where the dimeric complex contains two ligands with the monodentate mode, **93** [81JOM(219)409]. Bis(3,5-dimethylpyrazol-1-yl)phenylmethane in these circumstances behaves differently and forms only $[(\eta^2\text{-PhCHpz}_2^*)Rh(C_2H_4)_2Cl]$ containing two ethylene ligands. With $[Rh(\eta^4\text{-cod})Cl]_2$, the ligand-bridged structure **94** is the most probable product in the case of the pyrazol-1-ylmethane, while the ionic product of composition $[(\eta^2\text{-PhCHpz}_2^*)Rh(\eta^4\text{-cod})]Cl$ is formed when 3,5-dimethylpyrazol-1-ylmethane is used.



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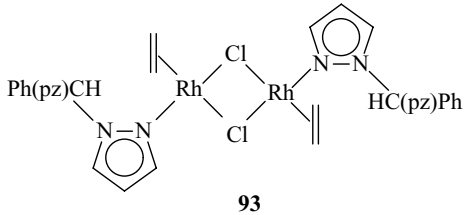

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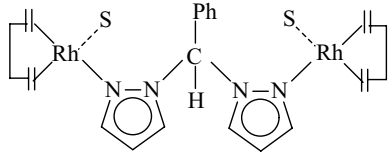


94

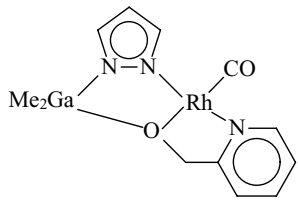
Ligands pz'_2CH_2 with dimers $[RhClL_2]_2$ (L_2 = tfb, cod, nbd) give a variety of complexes $[Rh(\mu\text{-}pz'_2CH_2)ClL_2]_2$ (L_2 = tfb, nbd, pz′ = pz, pz*, 3-NH_2pz, 4-Brpz;

L_2 = cod, pz′ = pz, 3-NH_2pz, 4-Brpz, 4-NO_2pz) [84JOM(276)79], where the pyrazol-1-yl ligands serve as the exo-bidentate bridges. Tris(pyrazol-1-yl) methane ligand in these conditions forms three types of rhodium(I) and iridium(I) products: [(η^3-pz_3CH)ML_2], [(η^3-pz_3CH)$MClL_2$]ClO_4, and [(η^3-pz_3CH)$MClL_2$] [MCl_2L_2] [88JOM(344)93, 89JOM(366)245]. [(η^2-H_2Cpz_2)$Ir(CO)_2$](BPh_4) oxidatively adds molecular hydrogen to give the iridium(III) species [(η^2-H_2Cpz_2) $Ir(CO)_2(H)_2$](BPh_4) and [$(H_2)(OC)_2$Ir(μ-η^2-$H_2Cpz_2)_2Ir(CO)_2$]($BPh_4)_2$ [00JCS(D) 2251].

Potassium hydrotris(pyrazol-1-yl)borate and *closo*-3,3-$(PPh_3)_2$-3-Cl-3,1,2-$RhC_2B_9H_{11}$ gives the sandwich product [(η^3-Tp)Rh(3,1,2-$C_2B_9H_{11}$)] (90IC2364). The sandwich containing a borole ligand, [(η^3-Tp)Rh(η^5-C_4H_4BPh)], is known (89CB615).

The derivative of the dimethylbis(pyrazol-1-yl)gallate, $Me_2Gapz(OCH_2py)^-$, reacts with the rhodium(I) dimer $[Rh(CO)_2Cl]_2$ to yield the monomeric rhodium(I) derivatives **95** and **96** (86CJC566). The product **95** oxidatively adds methyl iodide to yield the rhodium(III) species **97,** which further rearranges to **98.** Oxidative addition of molecular iodine gives the diiodo rhodium(III) complex. The rhodium(I) dimer also reacts with sodium dimethylbis(3,5-dimethylpyrazol-1-yl)gallate and triphenylphosphine to yield [(η^2-$Me_2Gapz_2^*$)Rh(CO)(PPh_3)] [85CJC503, 87JOM-(324)57]. The Me_2Gapz_2 analogs are prepared similarly (84CJC1057). The iridium(I) analog also follows from Na(Me_2Gapz_2) and $[Ir(\eta^4$-cod)$Cl]_2$ (85CJC692). The product is easily carbonylated to yield [(η^2-Me_2Gapz_2)$Ir(CO)_2$], which is convertible into [(η^2-Me_2Gapz_2)Ir(CO)(PPh_3)]. For $Me_2Gapz_2^{*-}$, only the monophosphine complex can be prepared. Complexes similar to **95** with the NH_2, NMe_2, SMe, or SPh moiety instead of the pyridine framework exist as well as their oxidative addition products [87JOM(324)57]. The complex [(η^3-MeGapz(OCH_2CH_2 NMe_2))Rh(CO)] that follows from the anionic pyrazol-1-ylgallate ligand and $[Rh(CO)_2Cl]_2$ oxidatively adds methyl iodide to yield [(η^3-MeGapz(OCH_2CH_2 NMe_2))Rh(COMe)I] (85CJC3019).

Binuclear complexes [(η^3-$REpz_3)_2Rh_2(\mu$-$CO)_3$] [R = Me, E = Ga (84CJC633); R = H, pz; E = B (83OM936)] are known.



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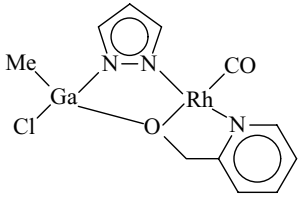

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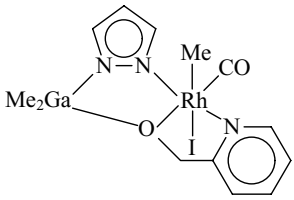

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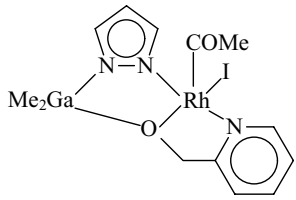
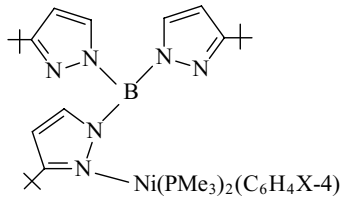


98

VIII. Complexes of Nickel, Palladium, and Platinum

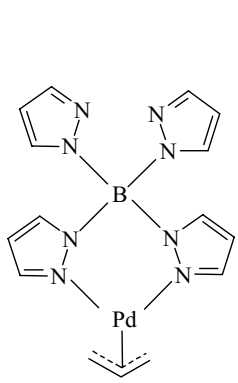
Potassium hydrotris(pyrazol-1-yl)borate and $[(\eta^3\text{-}C_3H_5)NiCl]_2$ form $[(\eta^3\text{-Tp})Ni(\eta^3\text{-}C_3H_5)]$ (91CB441). Thallium hydrotris(3-*tert*-butylpyrazol-1-yl)borate with *trans*-$[Ni(C_6H_4X\text{-}4)Br(PMe_3)_2]$ (X = H, Me, OMe) gives **99** (R = H, Me, OMe) [92JCS(D)2651], which is remarkable for the η^1-coordination of the pyrazol-1-ylborate ligand. The same coordination situation is observed in *trans*-$[(\eta^1\text{-Tp}')Ni(CO)(p\text{-Tol})(PMe_3)_2]$. A similar situation emerges when dihydrobis(3-*tert*-butylpyrazol-1-yl)borate ligand is used [98JOM(551)215]. Sodium dimethylbis(pyrazol-1-yl)gallate and $[(\eta^3\text{-}C_3H_5)]MCl]$ (M = Ni, Pd) give $[(\eta^2\text{-}Me_2Gapz_2)M(\eta^3\text{-}C_3H_5)]$ (M = Ni, Pd) (81CJC996).



99

The complex $[(\eta^2\text{-Tp})Pd(\eta^3\text{-}C_3H_5)]$, which is characterized by a bidentate coordination situation (69JA588), is the product of interaction of $[(\eta^3\text{-}C_3H_5)PdCl]_2$ and potassium hydrotris(pyrazol-1-yl)borate. The palladium(II) complex $[(\eta^2\text{-Tp})Pd(2\text{-}NMe_2CH_2C_{10}H_6)]$ contains the C,N-bonded amino ligand, and the hydrotris(pyrazol-1-yl)borate is coordinated via the two pyrazol-1-yl nitrogen atoms only (94OM2320). The same situation is realized in $[Pd_2(\eta^3\text{-}C_3H_5)_2(\mu\text{-}\eta^2\text{-}pz_3B{-}Bpz_3)]$, where pyrazol-1-ylborato moieties utilize two nitrogen atoms each for metal binding (88JA817). Two more groups of palladium(II) species follow from $[PdMe(SMe_2)(\mu\text{-I})]_2$ and $K(pz_3BR)$ (R = H, pz) in the presence of triphenylphosphine and thallium(I) hexafluorophosphate, or from [PdIPh(tmeda)] and $K(pz_3BR)$ (R = H, pz) in the presence of triphenylphosphine. The products are formulated as $[(\eta^2\text{-}pz_3BR)Pd(R')(PPh_3)]$ (R = H, pz; R′ = Me, Ph), all of them containing the

bidentate pyrazol-1-ylborato ligands [95JOM(489)153]. Potassium tetrakis (pyrazol-1-yl)borate and $[(\eta^3\text{-}C_3H_5)PdCl]_2$ give the products with the bidentate coordination of the pyrazol-1-ylborate ligand **100** (86IC87). It retains the donor potential, which is realized in the reaction with excess palladium(II) dimer to yield the cationic complex **101.**



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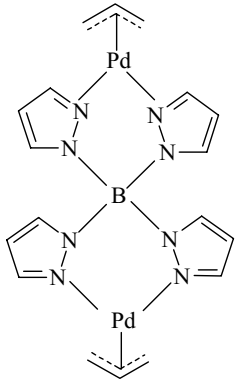


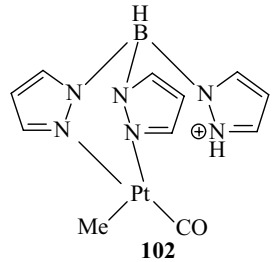
101

Palladium(IV) complexes usually follow from the oxidation of the palladium(II) species by water [92ACR83, 92JOM(435)C8, 97OM5331]. KTp and the pallada (II)cyclopentane species $[Pd(C_4H_8)(tmeda)]$ give the palladium(IV) complex $[(\eta^3\text{-}Tp)Pd(OH)(C_4H_8)]$ [95ACR406, 95JOM(490)C18, 96OM5713]. Hydrogen peroxide yields the same product. Palladium(IV) species $[(\eta^3\text{-}Tp)PdX(C_4H_8)]$ (X = Cl, Br, I) follow from the reaction of the same starting reagent, $[Pd(C_4H_8)(tmeda)]$ with phenyliodonium dichloride, molecular bromine, and iodine, respectively. In the representatives $[(\eta^3\text{-}Tp)PdMe_3]$ and $[(\eta^3\text{-}pz_4B)PdMe]$, both pyrazol-1-ylborato ligands are coordinated by their three nitrogen atoms [94JOM(471)C8]. The platinum(IV) derivative $[(\eta^3\text{-}Tp^*)PtMe_3]$ follows from potassium hydrotris (3,5-dimethylpyrazol-1-yl)borate and trimethylplatinum iodide (90IC3345) and can be brominated at position 4 of each pyrazol-1-yl ring. Reaction of KTp* or potassium tris(3,5-trifluoromethylpyrazol-1-yl)borate (KL) with $[PtMe_3(OTf)]_4$ gives $[(\eta^3\text{-}L)PtMe_3]$ (00OM3535). Substrates $PdMe_2(tmeda)$, PdMePh(tmeda), and pallada(II)cyclopentane $Pd(C_4H_8)(tmeda)$ are reacted with KTp and organic halides RX (MeI, EtI, $PhCH_2Br$, $CH_2{=}CHCH_2I$) simultaneously to give a wide variety of palladium(IV) products (95OM199): $[(\eta^3\text{-}Tp)PdMe_2R]$ (R = Me, Et, $PhCH_2$, $CH_2{=}CHCH_2$); $[(\eta^3\text{-}Tp)PdMePhR]$ (R = Me, Et, $PhCH_2$, $CH_2{=}CHCH_2$); $[(\eta^3\text{-}Tp)Pd(C_4H_8)R]$ (R = Me, Et, $PhCH_2$, $CH_2{=}CHCH_2$). $PdMe_3$ complexes of tris(pyrazol-1-yl)methane possess the same coordination mode (90OM826, 90OM1231). Another example is $[(\eta^3\text{-}pz_3CH)PtIPh_2](I)(I_3)$ [92JOM(424)381].

Addition of water to $[(\eta^3\text{-Tp})Pd^{II}(C_4H_8)]^-$ [95JOM(490)C18] gives the palladium(IV) species $[(\eta^3\text{-Tp})Pd(OH)(C_4H_8)]$ [95JOM(503)C16]. Addition of *m*-cresol to the latter gives $[(\eta^3\text{-Tp})Pd(OH)(C_4H_8)]\cdot 2(3\text{-}MeC_6H_4OH)$ and addition of pentafluorophenol gives $[(\eta^3\text{-Tp})Pd(OH_2)(C_4H_8)(C_6F_5O)]_2$. The first of the adducts has a hydroxyl group, which is hydrogen-bonded to two *m*-cresol molecules, while the second one has an aqua ligand hydrogen-bonded to the pentafluorophenolate.

KTp and $[PtMe_2(SEt_2)]_2$ give the platinum(II) derivative $[(\eta^2\text{-Tp})PtMe_2]^-$. The product further reacts with phenol to give the platinum(IV) complex $[(\eta^2\text{-Tp})PtHMe_2]$ (96OM2845). Similar processes are described (96JA5684). If the initial species is $K[(\eta^2\text{-Tp}^*)PtMe_2]$, it enters metathesis with (PPN)Cl and yields (PPN)$[(\eta^2\text{-Tp}^*)PtMe_2]$ (97JA10235, 99JA11900). $K[(\eta^2\text{-Tp}^*)PtMe_2]$ and $B(C_6F_5)_3$ in benzene give the η^3-coordinated product of C—H activation of benzene, $[(\eta^3\text{-Tp}^*)PtMe(Ph)H]$, together with $[(\eta^3\text{-Tp})PtMe_2H]$. $[(\eta^3\text{-Tp}^*)PtMe_2H]$ with triethylsilane yields $[(\eta^3\text{-Tp})Pt(SiEt_3)_3(H)_2]$, which in methanol can be converted to $[(\eta^3\text{-Tp})PtH_3]$ (00OM3748). In *n*-pentane and cyclohexane, also the products of C—H activation, $[(\eta^3\text{-Tp}^*)PtMe(R)H]$ (R = n-C_5H_{11}, Cy), result.

Another representative of this group of complexes is $[(\eta^3\text{-Tp})Pt(OH)Me_2]$ [95JOM(490)C18, 97OM2175], the product of the reaction of the platinum-containing complex anion and water. Complex $[(\eta^3\text{-Tp})PtMe(F_3C{\equiv}CF_3)]$ is characterized by the tridentate coordination of the pyrazolylborate ligand (74IC1843). Complexes $[(\eta^2\text{-Tp})Pt(Me)(CO)]$ [74JCS(CC)996, 76JOM(104)117] and $[(\eta^2\text{-Tp})Pt(Me)(CNBu\text{-}t)]$ (76IC2741) are fluxional in solution but become η^3-coordinated in the solid state. $[(\eta^3\text{-Tp})PtMe(CO)]$ (74IC1996, 76IC2354) and water give the stable product $[(\eta^3\text{-Tp})PtMeH_2]$ (99OM4677). Protonation of $[(\eta^3\text{-Tp})PtMe(CO)]$ with tetrafluoroboric acid gives **102,** where the protonation site is one of the uncoordinated nitrogen atoms of the pyrazol-1-yl group. Reaction of hydrotris(indazol-1-yl)borate (L) and $[PdMe_2(tmeda)]$ or $[PtMe_2(SEt_2)]_2$, followed by methyl iodide, gives the trimethylpalladium(IV) and -platinum(IV) species $[(\eta^3\text{-L})MMe_3]$ (M = Pd, Pt) [99JOM(287)27].



102

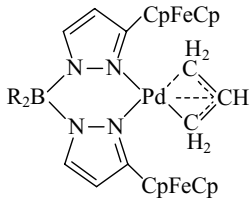
The cyclopalladated complexes of hydrotris(pyrazol-1-yl)borate and tetrakis(pyrazol-1-yl)borate have a common feature of bidentacy of the pyrazol-1-ylborate

ligand and dynamic equilibria of the coordinated and noncoordinated pyrazol-1-yl rings [76BCJ955, 80BCJ961, 80BCJ2540, 81JCS(D)962, 81JOM(209)123, 82CJC521].

The bridge around the platinum atom in [(η^2-$H_2Bpz^*_2$)$PtMe_3$] is formed not only by the nitrogen atoms of the pyridine type but by the B—H group as well (74JA1338). Platinum(II) complexes [(η^2-R_2Bpz_2)Pt(Me)L] (R = Et, Ph; L = PMe_3, *t*-BuNC, PhC≡CPh, PhC≡CMe) are known [74JOM(82)C51, 75JOM(101)347, 75JOM(102)245]. When acetylenes $F_3CC{\equiv}CCF_3$ and MeOOCC≡CCOOMe are used as precursors, the insertion products [(η^2-R_2Bpz_2)Pt(R′C=CR′Me)(PPh_3)] (R = Et, Ph; R′ = CF_3, COOMe) follow (74JOM(82)C51, 75JOM(101)347).

Potassium dihydrobis(pyrazol-1-yl)borates with [(η^4-cod)Pd(Me)Cl] in the presence of PR_3 (R = Ph, Cy) give [(η^2-H_2Bpz_2)Pd(Me)(PR_3)] and [(η^2-$H_2Bpz^*_2$)Pd(Me)(PR_3)] (R = Ph, Cy) (00EJIC1359). Carbonylation of the products leads to the insertion of the carbonyl group and formation of [(η^2-H_2Bpz_2)Pd(COMe)(PR_3)] and [(η^2-$H_2Bpz^*_2$)Pd(Me)(PR_3)] (R = Ph, Cy), respectively. The related complex is [(η^2-$H_2Bpz^*_2$)Pd(CH_2SiMe_3)(PMe_3)] [97JOM(549)167].

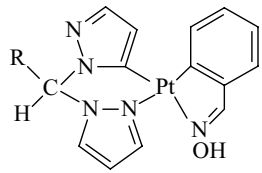
The thallium salt of cyclooctane-1,5-diyl-bis(pyrazol-1-yl)borate (L) and [Pd(η^3-CH_2CRCH_2)Cl]$_2$ (R = H, Me, Ph) yield [(L)Pd(η^3-CH_2CRCH_2)] (R = H, Me, Ph), in which the ligand is coordinated via two pyridine-type nitrogen atoms and is stabilized by C—H ··· Pd agostic interactions, where the C—H bond originates from the pyrazol-1-ylborate ligand [89AGE205, 89IC1091, 91ICA(183)203, 92IC974]. The same sort of interactions but originating from the allyl ligand is realized in complexes **103** (R = Et, R_2 = cyclooctane-1,5-diyl) the derivative of dihydrobis(3-ferrocenylpyrazolyl)borate (91IC524).



103

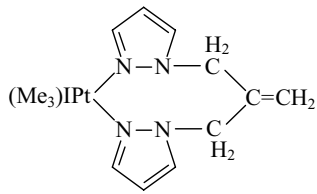
Phenyl-bis(3,5-dimethylpyrazol-1-yl)methane and pyridine-1-yl-bis(3,5-dimethylpyrazol-1-yl)methane with [(η^4-cod)$PdCl_2$] give [(η^2-RCHpz^*_2)$PdCl_2$] (R = Ph, py), which on alkylation with methyllithium are converted to [(η^2-RCHpz^*_2)$PdMe_2$] (R = Ph, py); with [(η^4-cod)Pd(Me)Cl], to [(η^2-RCHpz^*_2)Pd(Me)Cl] (R = Ph, py); with [(η^4-cod)Pd(C_6F_5)$_2$], to [(η^2-RCHpz^*_2)Pd(C_6F_5)$_2$] (R = Ph, py); with [(η^3-C_4H_7)PdS_2]X, to [(η^2-RCHpz^*_2)Pd(η^3-C_4H_7)] (R = Ph, py; X = PF_6, OTf) [00JOM(603)174].

Tris(pyrazol-1-yl)methane and [(η^4-cod)$PtMe_2$] gives [(η^3-$HCpz_3$)$PtMe_2$] [82JOM(226)C14, 83JCS(D)1253]. When dissolved in pyridine, it forms [(η^2-$HCpz_3$)Pt(py)Me]. With triphenylphosphine, [(η^1-$HCpz_3$)Pt(PPh_3)$_2$Me] results, which on thermolysis gives the cyclometallated product. The species [(η^3-$HCpz_3$)PtMe(CO)](PF_6) is known [81JOM(215)131]. Other cyclometallated complexes are **104** (R = H, pz) (78BCJ3209].



104

[(η^2-$Me_2Cpz^*_2$)$_2$$PdMe_2$], [($\eta^2$-$Me_2Cpz^*_2$)$PdMe_3$] (90OM210, 92MI1), [($\eta^2$-$CH_2pz^*_2$)$PtMe_3X$] (X = Cl, I, MeOCO, NO_3) [84JOM(270)365], [(η^2-$Me_2Cpz^*_2$)$PtMe_2X_2$] (X = I, NO_3) (83OM806), and [(η^2-$Me_2Cpz^*_2$)Pd(η^3-allyl)] (70JA5118) are known. Complex [(η^2-$Me_2Cpz^*_2$)$PdMe_3$] reacts with [$HNMe_2Ph$][$B(C_6F_5)_4$] to yield [(η^2-$Me_2Cpz^*_2$)PdMe(NMe_2Ph)]($B(C_6F_5)_4$) (99OM4758). The NMe_2Ph ligand can be substituted with ethylene to give [(η^2-$Me_2Cpz^*_2$)PdMe(η^2-C_2H_4)] ($B(C_6F_5)_4$). The ligand $(pzCH_2)_2C{=}CH_2$ was reacted with [$PtMe_2(SEt_2)$]$_2$ and then with methyl iodide to give **105,** the oxidative addition platinum(IV) product [92JCS(D)2663]. A similar compound, [PtI(Me_3)(pz_2CHMe)], is known [90JOM(385)429]. The *spiro* complex [$Bpz_2Pt(\eta^3$-$C_4H_7)$]$_2PF_6$ was described [92ICA(198)275].



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IX. Complexes of Copper, Silver, and Gold

[(η^3-Tp)Cu(CO)] [72JCS(CC)1124,72JOM(44)209,73JCS(D)2433,75IC2051] and [(η^3-Tp*)Cu(CO)] (76JA711, 79AJC1209, 82IS107) are normally made from the appropriate pyrazol-1-ylborate salt and a soluble copper(I) salt in a carbon

monoxide atmosphere. Complex [(η^3-Tp′)Cu(CO)] originates from hydrotris (3,5-diphenylpyrazol-1-yl)borate (89CL421, 91JA5664), hydrotris(3,5-diisopropylpyrazol-1-yl)borate [88JCS(CC)151, 92JA1277], hydrotris(3-*tert*-butylpyrazol-1-yl)borate (92JA4407, 93JA11285, 98JA11408), or hydrotris(3,5-trifluoromethylpyrazol-1-yl)borate [95IC5380, 96OM5374, 97ICA(263)357]. [(η^3-HB(3-CF_3pz)$_3$)Cu(CO)] may be obtained from the sodium salt of the ligand taken as a THF solvate, copper(I) triflate, and carbon monoxide (96OM2994). Complexes based on hydrotris(3-*tert*-butyl-5-methylpyrazol-1-yl)borate, hydrotris (3-*tert*-butyl-5-isopropylpyrazol-1-yl)borate, and hydrotris(3-phenyl-5-isopropylpyrazol-1-yl)borate were made from the potassium salt of the appropriate pyrazol-1-ylborate and copper(I) chloride in a carbon monoxide atmosphere (98IC3066). [(η^3-Tp′)Cu(AN)] [Tp′ = hydrotris(3-(*p*-*tert*-butylphenyl)-5-methylpyrazol-1-yl)] is carbonylated to give [(η^3-Tp′)Cu(CO)] (99IC906).The Cu^ICO complexes of tetrakis(pyrazol-1-yl)borate [75JOM(87)C15] and tetrakis(camphorpyrazol-1-yl) borate [93JOM(443)C16] are known. [(η^3-Tp*)Cu(η^2-C_2H_4)] (83JA3522) is a valuable catalyst (93OM261). Carbonylation of [(η^3-pz′$_3$CH)Cu(AN)](PF_6) (pz′ = 3,5-dimethylpyrazol-1-yl, 3-phenylpyrazol-1-yl-, and 3-*tert*-butylpyrazol-1-yl) gives the products of substitution of the acetonitrile molecules, [(η^3-pz′$_3$CH)Cu(CO)] (PF_6) (96OM2029). Lithium or thallium tris(3-*tert*-butylpyrazol-1-yl)methanesulfonate (L) forms [(η^3-L)Cu(CO)] (00AGE2464).

[(η^3-HB(CF_3)$_2$pz$_3$)Ag(THF)] in toluene gives [(η^3-HB(CF_3)$_2$pz)Ag(η^2-C_6H_4Me)] (97IC6205). With carbon monoxide, [(η^3-HB(CF_3)$_2$pz)Ag(CO)] results. Ethylene oxide or propylene sulfide gives the O- or S-coordinated substitution products of the η^2-coordinated toluene (00IC3724). With *N*-methyl-(2-methylamino) troponiminate germanium chloride, the silver–germanium adduct is obtained (00IC3890). The THF complex with ethylene gives [(η^3-HB(CF_3)$_2$pz$_3$)Ag(η^2-C_2H_4)], and that with *tert*-butyl isocyanide gives [(η^3-HB(CF_3)$_2$pz$_3$)Ag(η^1-CNBu-*t*)]. The *tert*-butyl isocyanide complexes of silver can be exemplified by [(η^3-Bpz$_4$)Ag(η^1-CNBu-*t*)] (79AJC1613), [HC(3-*t*-Bupz$_3$)Ag(CNBu-*t*)](OTf) (97OM349) and those of copper and gold by [(η^3-HB(CF_3)$_2$pz$_3$)Cu(η^1-CNBu-*t*)] (96IC2149) and [(η^3-HB(CF_3)$_2$pz$_3$)Au(η^1-CNBu-*t*)] (96IC3687). The toluene derivative with acetylene and phenylacetylene gives [(η^3-HB(CF_3)$_2$pz$_3$)Ag (η^3-C_2HR)] (R = H, Ph) (97IC6205).

Complexes [(η^3-HB(CF_3)$_2$pz$_3$)M(CO)] (M = Ag, Au) are known (95JA11381, 96IC267). The gold derivative was made from [(η^3-HB(CF_3)$_2$pz$_3$)Ag(THF)] or (NEt_4)[(η^3-HB(CF_3)$_2$pz$_3$)] and [Au(CO)Cl] (96IC3687). If the first of the aforementioned reactions is run in the presence of *tert*-butyl isocyanide, [(η^3-HB (CF_3)$_2$pz$_3$)Au($CNBu^t$)] results. Complex [(η^2-Tp)$AuMe_2$] contains the bidentate pyrazol-1-ylborate moiety [83AJC1107, 86JCS(D)645]. Potassium tetrakis (pyrazol-1-yl)borate and dimethylgold(II) nitrate give [(η^2-Bpz$_4$)$AuMe_2$] [85JCS-(D)1183]. Ligands CH_2pz_2 and $HCpz_3$ are both bidentate in the complexes [(η^2-H_2Cpz_2)$AuMe_2$]NO_3 and [(η^2-$HCpz_3$)$AuMe_2$]NO_3 [82JCS(D)1795].

In the complex [(η^2-Bpz$_4$)HgMe] with the bidentate coordination of the pyrazol-1-ylborate moiety, two mercury–nitrogen bonds are nonequivalent (87AJC1609). The mercury(II) species [(η^1-Tp*)HgR] (R = Alk, Ar, Fc) are regarded as containing the Tp* ligand in the monodentate coordination, but this conclusion follows from the extensive spectral data only (92RIMOC775).

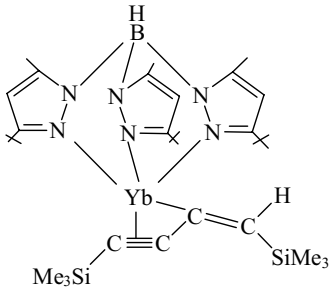
X. Complexes of Rare Earth Metals

In the complexes [(η^3-Tp)Ln(η^8-COT)], [(η^3-Tp*)Ln(η^8-COT)] (Ln = Ce, Sm) [93JOM(444)C15, 96JOM(508)275], and [(η^3-Tp)U(η^5-Cp)Cl$_2$] [79JCS(D)1241], the pyrazol-1-ylborate ligand is tridentate. The amide (RCONMe$_2$, R = Me, *t*-Bu) complexes of [(η^5-Cp)ThX$_3$] (X = Cl, Br) react with KTp to yield [(Tp)Th(η^5-Cp)X$_2$(amide)$_{1.5}$] (X = Cl, Br). For X = Cl, the spectral data point to the bidentate coordination of the Tp ligand, although for the bromide product the data are interpreted in terms of the formation of the binuclear species [(Tp)Th(η^5-Cp)(μ-Br)$_2$(amide)$_{1.5}$]$_2$. In the latter, one of the Tp ligands is postulated to be tridentate and the other, bidentate. [(η^5-Cp)UCl$_3$(Ph$_3$PO)] with KTp gives [(η^3-Tp)U(η^5-Cp)Cl$_2$]·Ph$_3$PO, which on sublimation at reduced pressure can be converted to [(η^3-Tp)U(η^5-Cp)Cl$_2$(Ph$_3$PO)]. In these cases, the tridentate coordination follows from the existing data. [(η^3-Tp*)$_2$Sm] and thallium cyclopentadienyl form [(η^3(N$_3$)-Tp*)(η^3(N$_2$, H)-Tp*)(Sm(η^5-Cp))] (99JA8110). One of the ligands is coordinated via two pyrazol-1-yl moieties, but there is an expressed Sm $\cdots$ H—B agostic interaction.

[(η^3-Tp*)$_2$Sm] and [(η^5-C$_5$H$_4$R)M(CO)$_3$]$_2$ (M = Cr, Mo, W) give [(η^3-Tp*)$_2$Sm(μ-OC)M(η^5-C$_5$H$_4$R)(CO)$_2$] (M = Cr, W, R = H; M = Mo, R = Me, *t*-Bu) [97JOM(528)209], where the bridging function of the carbonyl group is quite unusual, since there is bonding between samarium and carbonyl oxygen, and in this sense μ-OC is regarded as an isocarbonyl bridging moiety. The structurally similar complex [(η^3-Tp*)$_2$Sm(μ-OC)Mo(η^5-Cp)(CO)$_2$] (96IC76) is known. Another reaction of this nature is that between [(η^3-Tp′)Ln(THF)] (Ln = Sm, Yb) (Tp′ = 3-methyl-5-*tert*-butylpyrazol-1-ylborate) and Na[Mo(η^5-C$_5$H$_4$Me)(CO)$_3$] [98JCS(D)3871]. It gives [(η^3-Tp′)Ln(THF)(μ-OC)$_2$Mo(η^5-C$_5$H$_4$Me)(CO)]$_2$ (Ln = Sm, Yb; Tp′ = 3-methyl-5-*tert*-butylpyrazol-1-ylborate).

Complexes [(η^3-Tp′)LnI(THF)$_x$] [Ln = Yb, x = 1; Ln = Sm, x = 0, 2; Tp′ = hydrotris(3-*tert*-butyl-5-methylpyrazol-1-yl)borate] served as starting materials for [(η^3-Tp′)Ln(CHRSiMe$_3$)] (Ln = Yb, R = H; Ln = Sm, R = SiMe$_3$) [94JA8833, 97JAC(249)52]. Hydrogenolysis of [(η^3-Tp′)Yb(CH$_2$SiMe$_3$)(THF)] (94JA8833) gives the ytterbium(II) hydride [(η^3-Tp′)Yb(μ-H)]$_2$ (99AGE2233). In these and subsequent complexes mentioned below, Tp′ is hydrotris(3-*t*-butyl-5-methylpyrazol-1-yl)borate. With trimethylsilylacetylene, the product eliminates hydrogen and gives [(η^3-Tp′)Yb(μ-η^1:η^2-C≡C(SiMe$_3$)]$_2$. With carbon monoxide, the

reductive coupling takes place to yield *cis*-[(η^3-Tp′)YbOCH=CHOYb(η^3-Tp′)]. With the diyne $Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3$, species **106** is formed, which is monomeric and characterized by an addition of the hydride to the terminal carbon of one of the triple bonds. With cyclopentadienes, [(η^3-Tp′)Yb(η^5-C_5H_4R)] (R = H, $SiMe_3$) results [00JOM(596)95]. The coordination mode of the Tp′ ligand in the case of R = $SiMe_3$ (**107**) is rather unusual: Two pyrazol-1-yl rings are η^1-coordinated and the third ring is in the η^2-*endo*-bidentate mode, a feature quite typical for the organometallic chemistry of pyrazolate ligands [01AHC(80)157].



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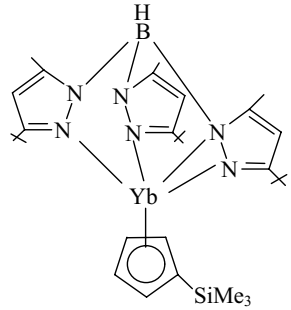

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In solution, both complexes reveal fluxionality, when the $\eta^3(N_3)$, $\eta^3(N_2H)$, and $\eta^2:\eta^2$(as described above) bonding modes could participate. (η^3-Tp*)$_2$Sm with mercury diphenylacetylide gives (η^3-Tp*)$_2$Sm(C≡CPh) (00OM1814). Thermolysis of the product leads to an interesting rearrangement of one of the Tp* ligands, when one of the 3,5-dimethylpyrazol-1-yl fragments is substituted by phenylacetylide, and the released 3,5-dimethylpyrazolate ligand is coordinated in an *endo*-bidentate fashion normal for the rare earth metal ions. The product is formulated as [(η^3-Tp*)Sm(η^2-HBpz$^*_2$)(C≡CPh))(η^2-pz*)]. Agostic Sm ··· H–B interaction can also be noted from the structural parameters. [(η^2-H_2Bpz_2)$_2$Np(η^5-MeC_5H_4)$_2$] and [(η^2-H_2Bpz_2)$_2$Np(η^5-C_5H_5)] are known (83IC503).

XI. Conclusions

1. Derivatives of beryllium, magnesium, zinc, and cadmium are normally characterized by the η^3-coordination of hydrotris(pyrazol-1-yl)borate ligands. The η^2-dihydrobis(pyrazol-1-yl)borates are typical, although the spectator role of $H_2Bpz'_2$ ligand may be violated and the derivatized ligand may emerge. Aluminum, gallium, and thallium derivatives often reveal the η^2 or η^1 modes

with uncoordinated pyrazol-1-yl moieties. In organothallium and organozinc chemistry, the new mixed-ligand hydrobis(2-mercapto-1-methylimidazol-3-yl)(pyrazol-1-yl)borate was found to possess remarkable coordinating properties depending on the nature of the complex-forming metal. Organotin derivatives are typically normal, although sometimes dynamic equilibrium of different coordination modes has been suspected.

2. Complexes of the titanium and vanadium groups are scarce but mainly follow the routine coordination modes. Sometimes for the dihydrobis(pyrazol-1-yl)borates, the role of M $\cdots$ H—B agostic interactions is significant.
3. Group VI complexes are among the best studied. The basis is the anionic series $[(\eta^3\text{-L})M(CO)_3]^-$ [L = Tp, Tp*, Tp′, new ligands such as hydrotris(3,5-dimethyl-1,2,4-triazol-1-yl)borate and methylbis(3,5-dimethylpyrazol-1-yl)silane], which gives rise to numerous transformations (protonation, ligand substitution, oxidation, oxidative halogenation, photolysis with nitriles and alkynes, ligation with other transition metal derivatives, σ-arylation followed by isomerization to the η^2-aroyl or η^1-chlorocarbyne species, and others). In these reactions, a ligand of interest remains innocent. In the allyl series of molybdenum complexes, there are a couple of anomalies when hydrotris(indazol-1-yl)borate is η^2-coordinated and Me_2NBpz_3 is coordinated via the dimethylamino group and two out of three pyrazol-1-yl moieties. Less common situations in the cyclopentadienyl series include the η^2-coordinated Tp ligand and μ-η^2-Cpz_4 and Bpz_4 derivatives manifesting a bridging function. Pyrazol-1-ylborates tend to stabilize the high oxidation states of group VI metals, especially Mo(VI) and W(VI). Group VI chemistry of dihydrobis(pyrazol-1-yl)borates is governed by B—H $\cdots$ M agostic interactions that can be minimized by adduct formation or ligand conformational constraints.
4. Among the less common features of complexes of group VII are the switch of the coordination mode from η^2 to η^3 upon photochemical decarbonylation and the stabilization of the μ-N≡N bridge in the rhenium species.
5. In the iron, ruthenium, and osmium derivatives, there are cases of $\eta^2 \rightarrow \eta^3$ re-switch on thermolysis followed by the elimination of small ligands. Organoruthenium species containing pyrazol-1-ylborate or -methane ligands with bulky substituents often have uncoordinated pyrazol-1-yl moieties and agostic R—B(C) $\cdots$ M interaction. The latter sometimes influences the properties of the η^3-coordinated species as well.
6. Organorhodium and -iridium complexes pose several structural and reactivity problems, among them dependence of the coordination mode on the bulk of substituents at the pyrazol-1-yl moieties and the nature of coligands. The dynamics of re-switch of the coordination mode involve not only exchange between the η^2 and η^3 or η^1 and η^2 modes but that between coordinated and uncoordinated pyrazol-1-yl groups. Existing chemistry allowed the discovery of new modes such as η^1(N) accompanied by agostic interactions for some hydrotris

(pyrazol-1-yl)borate ligands. Organometallic species of rhodium(I) and iridium(I) cause the C—H activation processes leading to stabilization of the Rh(III) and Ir(III) oxidation states and promotion of the coordination number 6. C—H activation processes are so prominent and facile that they may embrace one of the pyrazol-1-yl groups of Tp ligand and cause its η^1(C) coordination, which implies a rare case of innocence loss. C—H activation can also be accompanied by cyclometallation of the Tp′ ligand bearing the 3-phenyl substituent.

7. Organonickel derivatives also offer cases of the η^1-coordination of the substituted hydrotris(pyrazol-1-yl)borate ligand. For the palladium and platinum complexes, the M(II) → M(IV) (M = Pd, Pt) transformation is facile. Organopalladium chemistry offers a new type of agostic interactions, C—H · · · Pd, where the C—H bond belongs to one of the pyrazolate rings. Cyclopalladation of various pyrazol-1-ylborates and -methanes does not modify their structure.
8. Organometallic chemistry of the copper group offers practically no anomalies, although rare earth metal species are interesting in the sense of involvement of the η^2(N,N) *endo*-bidentate mode with and without splitting of a pyrazol-1-ylborate ligand and stabilization of the bridging isocarbonyl ligand.

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ADVANCES IN HETEROCYCLIC CHEMISTRY, VOL. 81

The Tautomerism of Heterocycles. Six-Membered Heterocycles: Part 1, Annular Tautomerism

BRANKO STANOVNIK AND MIHA TIŠLER

Faculty of Chemistry and Chemical Technology, University of Ljubljana, 1000 Ljubljana, Slovenia

ALAN R. KATRITZKY AND OLGA V. DENISKO

Florida Center for Heterocyclic Compounds, Department of Chemistry, University of Florida, Gainesville, FL 32611-7200

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I. Introduction

The first detailed survey of the prototropic tautomerism of heteroaromatic compounds appeared in four chapters in Volumes 1 and 2 of *Advances in Heterocyclic Chemistry* published in 1963. In 1976, a monograph entitled *The Tautomerism of Heterocycles* was issued as Supplement 1 to *Advances in Heterocyclic Chemistry* to update the work published in 1963.

The present chapter is part of an endeavor to provide a further update covering work that has appeared in the past 25 years. Volume 76 of this series contains three chapters, which cover (1) general topics and experimental and theoretical methods of the study of tautomerism and deal with (2) the tautomerism of five-membered rings with one heteroatom and (3) with several heteroatoms. In Volume 77, two other chapters are concerned with the tautomerism of heterocycles, covering (1) small and large rings and (2) polycyclic systems containing at least two five- or six-membered heterocyclic rings. This chapter, which deals with the annular tautomerism of monocyclic six-membered rings, continues this second major update of the subject.

The tautomerism of heterocyclic six-membered rings is the subject of one of the four original chapters that appeared in 1963 [63AHC(1)341] and is, furthermore, the subject of a main chapter in the 1976 Supplement (76AHCS1). Given the enormous amount of material published on the tautomerism of six-membered rings in the last 25 years, the present chapter deals exclusively with annular tautomerism. The substituent tautomerism of heterocycles containing potential OH, SH, NH_2, and CH_3 groups or exhibiting ring–chain tautomerism will be discussed in a subsequent volume of *Advances in Heterocyclic Chemistry.*

II. Tautomerism of Six-Membered Heterocycles: General Discussion

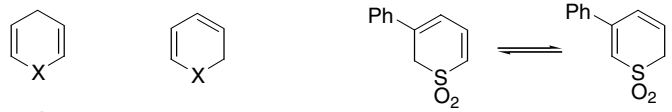
The most important change since 1976, when the monograph *The Tautomerism of Heterocycles* (76AHCS1) appeared, is the explosive development of the computational methods and studies arising from the computer science revolution. The level of calculations became high enough to ensure precision exceeding that of many experimental results (97MI1). Recent calculations of equilibrium constants include solvent effects with different approximations, as well as other refinements such as zero-point energy correction. On the other hand, many new experimental techniques have also been applied to the studies of tautomerism, including ^{1}H, ^{13}C, ^{15}N, and ^{17}O NMR techniques; homonuclear and heteronuclear coupling constant determinations; and photoelectron, fluorescence, and ion cyclotron spectroscopy. A general overview and a summary of methodology are provided by Elguero, Katritzky, and Denisko [00AHC(76)1].

Several other review articles cover various aspects of tautomerism in six-membered heterocycles. Various aspects of prototropic tautomerism have been covered in a review article by Katritzky [91H(32)329]: types of tautomerism, methods of study of aromatic tautomerism, and tautomeric equilibria in pyridines and other six-membered rings. Some generalizations have also been made. Another review article by Kurasawa, which appeared in two parts in 1995, covers, for the most part, the work of that author [95H(41)1805; 95H(41)2057].

III. Annular Tautomerism

A. Pyrans, Thiopyrans, and Dioxanes

No tautomeric interconversions have been observed between 4*H*-pyrans (**1,** X = O) and 2*H*-pyrans (**2,** X = O), 4*H*-thiopyrans (**1,** X = S) and 2*H*-thiopyrans (**2,** X = S), or their benzo-fused derivatives. Under normal conditions, all these compounds exist as sole isomers that are initially formed, both in solution and in the solid state. The only tautomeric equilibrium reported was that between the two possible 2*H* isomers of the unsymmetrical sulfone **3** (77TL1149).

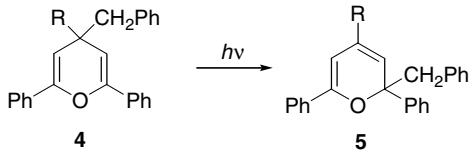


1 **2** **3a** **3b**

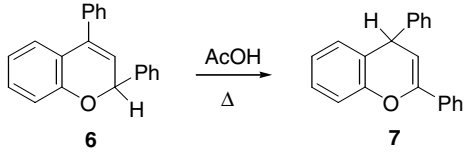
1. *Pyrans*

According to semiempirical CNDO/2 and nonempirical *ab initio* MO calculations, unsubstituted 4*H*-pyran is thermodynamically more favorable than the 2*H* isomer (81CCC759). However, most of the irreversible transformations reported so far involve the conversion of 4*H*-pyrans into the corresponding 2*H*-pyrans. These transformations usually occur in the presence of a strong acid (proton transfer) [77ACS(B)496] or under irradiation (carbonotropy) [77CJC2373; 85UK1971; 91JCS(P2)2061; 95CCC1621]; however, in most cases, the 2*H*-pyrans formed immediately undergo ring opening with formation of the corresponding dienones. The only reported reaction in which 2*H*-pyrans were stable enough to be isolated and characterized is the photochemically induced benzyl group migration, as in **4** → **5** (Scheme 1) (77CJC2373).

By contrast, heating benzo-2*H*-pyran **6** with acetic acid leads to the formation of the 4*H* isomer **7** (Scheme 2) [77ACS(B)496].



SCHEME 1

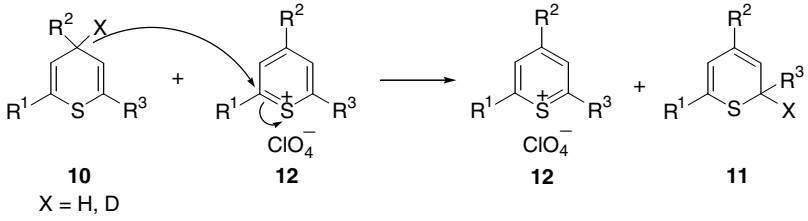


SCHEME 2

Transformations of 5,6-dihydro-2*H*-pyrans **8** into the corresponding 3,4-dihydro-2*H* derivatives **9** under basic conditions (88KGS291; 98TL2025), as well as the reverse conversion under irradiation [97H(46)451], have been explained by the intermediate formation of electron-delocalized heterocyclic systems, giving rise to two possible isomers.

2. *Thiopyrans*

Conversion of substituted 4*H*-thiopyrans **10** (X = H) into the corresponding 2*H* isomers **11** (X = H) (proton transfer) has been achieved thermally (80JOC2453) or in the presence of the analogously substituted thiopyrylium salt (Scheme 3) [77ACS(B)496; 81JHC1517] or a strong acid [76AHCS1, p. 76; 77ACS(B)496;



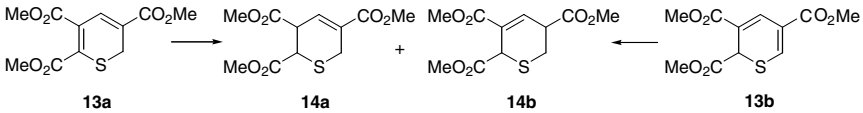
SCHEME 3

83AHC(34)145, pp. 255–256]. Considering that no H–D exchange was observed for the transformation **10** → **11** in the presence of the corresponding thiopyrylium salt [thus, 4-deuterio-2,4,6-triphenylthiopyran **10** ($R^1 = R^2 = R^3 = Ph$, X = D) gives exclusively 2-deuterated product **11** ($R^1 = R^2 = R^3 = Ph$, X = D)], the reaction was suggested to occur via the formation of the intermediate thiopyrylium salt **12** with subsequent intermolecular hydride transfer (Scheme 3). The kinetics of the process has been studied using ^{1}H NMR (81JHC1517), which revealed that the reaction rate does not depend on the concentration of the thiopyrylium salt, although its presence is necessary for the reaction to occur.

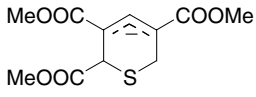
Electroreductions of 2*H*-thiopyrans **13a** and **13b** each afforded an equimolar mixture of isomeric dihydrothiopyrans **14a** and **14b** (Scheme 4) (97MI2). Although the products were not separated, no **13a** ⇌ **13b** or **14a** ⇌ **14b** interconversion was observed; therefore, the formation of isomers was explained by the intermediacy of the delocalized carbanion **15.**

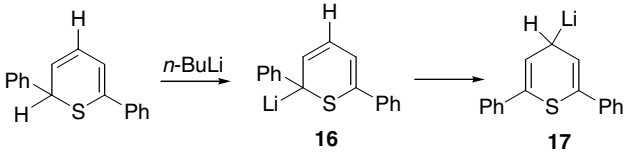
The relative stability of lithiated thiopyrans seems to depend upon the heterocyclic ring substitution. Thus, α-lithiated 2,6-diphenyl-2*H*-thiopyran **16** rearranges into the γ-lithiated derivative **17** (Scheme 5) (82JOC680), while the reverse transformation occurs on lithiation of 2,6-diphenyl-4-diethylphosphonylthiopyran (80JOC2453).

2*H*-Thiopyrans formed on irradiation of the corresponding 4*H* derivatives are less prone to ring opening than 2*H*-pyrans. This led to the study of the photochemistry of variously substituted 4*H*-thiopyrans. Irradiation of 3,5-unsubstituted

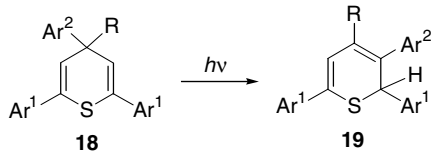


SCHEME 4



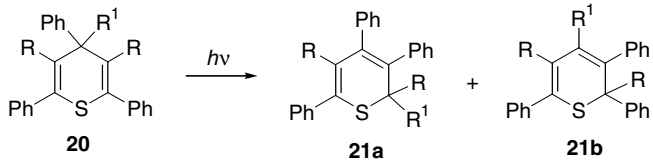


SCHEME 5



18 **19**

SCHEME 6



20 **21a** **21b**

R^1 = Ph, 4-$CF_3C_6H_4$, 4-MeC_6H_4

SCHEME 7

4*H*-thiopyrans **18** with two aryl groups in the 4 position leads to nonselective migration of one of these groups (Scheme 6), while in 4-aryl-4-alkyl-substituted analogs only the aromatic group migrates [92JCS(P2)1301; 94MI2]. The reaction readily occurs in methanol solution, as well as in the solid state, although the yields in solid-phase reactions are usually lower. The structures of the products were confirmed by ^{1}H NMR, (^{1}H–^{13}C) 2D NMR (94MI2), and X-ray analysis [91JCS(P2)2061], and a mechanism involving hypervalent intermediates was proposed (98CCC662). Introduction of substituents into the 3,5 positions alters the photochemical behavior of the system. In thiopyrans **20** (R = Ph) no photoisomerization occurs. However, irradiation of 3,5-dimethyl-substituted thiopyrans **20** (R = Me) gives mixtures of 2*H* isomers **21a** and **21b,** although the yields are lower than for 3,5-unsubstituted substrates (Scheme 7) (96MI1).

Considering the irreversibility of the reactions discussed above and the relatively harsh reaction conditions required (and hence the high activation energies of the processes), these transformations cannot be considered tautomeric processes.

3. *Dioxanes*

No annular tautomeric equilibrium transformations in compounds of the dioxane series have been reported yet; recently (97JCC1392), however, the optimized geometries and total energies of unsubstituted isomeric 3,4-dihydro-1,2-dioxin **22** and 3,6-dihydro-1,2-dioxin **23** were calculated using *ab initio* 3-21G, 6-31G*, and MP2/6-31G*//6-31G* methods. All the methods applied revealed that the total energies for half-chair conformations of **22** and **23** are approximately the same.

22

23

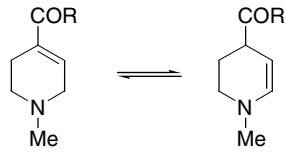
B. Dihydropyridines and Dihydroquinolines

1. *Dihydropyridines*

In 1976, most of the data on tautomerism of dihydropyridines were qualitative and rather scattered (76AHCS1, p. 77). Since then, various dihydropyridine isomers have been investigated for their stability using MINDO/3 program calculations. Theoretically, five isomeric dihydropyridines are possible. Most known dihydropyridines have either the 1,4- or the 1,2-dihydro structure, except in the few cases where steric hindrance or certain stabilizing groups lead to 2,3- or 3,4-dihydropyridines. Calculations revealed that the relative stability of the 1,4- and 1,2-dihydro isomers differs by 4.5 kcal/mol, in good agreement with previous experimental values. Moreover, the relative stability is not much affected by the introduction of a methyl group. 1-Methyl-1,4-dihydropyridine is about 5 kcal/mol more stable than the corresponding 1,2 isomer (78JA4946), the value being almost twice that of the results reported earlier by Fowler (76AHCS1, p. 77).

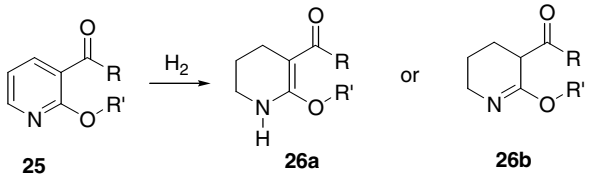
However, no tautomeric interconversions between 1,2-dihydro- and 1,4-dihydropyridine analogs have been observed, probably because a high energy barrier is inherent to this transformation.

In connection with the investigation of the relative thermodynamic stability of dihydropyridines, 1-methyl-4-acyl-1,2,5,6-tetrahydropyridines **24a** were investigated. Contrary to the previous view that six-membered acyclic allylamines (e.g., **24a**) are thermodynamically preferred over their enamine isomers (e.g., **24b**), the base-catalyzed equilibrative isomerizations of **24a** readily afforded 1-methyl-4-acyl-1,4,5,6-tetrahydropyridines **24b** (Scheme 8). The conjugation with the 4-acyl group is not required for these isomerizations, as it was shown that 1-methyl-1,2,5,6-tetrahydropyridine can be isomerized into 1-methyl-1,4,5,6-tetrahydropyridine, although using a stronger base (78T3027).



24a **24b**

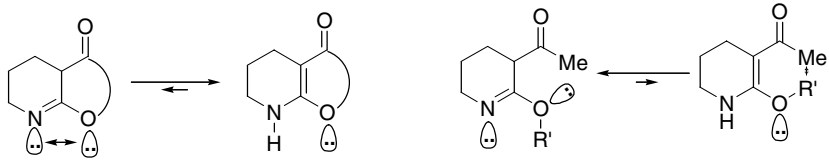
SCHEME 8



SCHEME 9

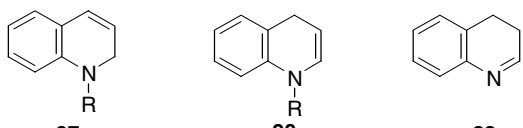
A different set of tautomeric tetrahydropyridines was obtained on partial hydrogenation of 2-alkoxy-3-acylpyridines **25** on PtO_2 or Pd/C catalyst (Scheme 9) (79JHC939). The tetrahydropyridines **26** formed exist exclusively as single tautomers, the type of tautomer, however, being determined by the substitution in the pyridine ring.

Thus, reduction of the bicyclic derivatives **25** ($RR' = CH_2$; $RR' = CH{=}C(Ph)$) affords the corresponding **26a**-type products, while hydrogenation of 2-ethoxy-3-acetylpyridine gives, along with the carbonyl group reduction product, the imine isomer **26b** (R = Me, R′ = Et). These results were explained by the so-called "internal strain" effect, e.g., by steric repulsion between the nitrogen and oxygen lone pair in rotationally restricted bicyclic derivatives or between the 2 and 3 substituents.



2. *Dihydroquinolines*

Three tautomeric structures (1,2-dihydro **27,** 1,4-dihydro **28,** and 3,4-dihydro **29**) are possible for N-unsubstituted dihydroquinolines, which retain the aromatic benzene ring, and two structures **27** and **28** for N-substituted derivatives. No information on the tautomerism of such dihydroquinolines and stability of the possible tautomers was available when the earlier review (76AHCS1) was published.

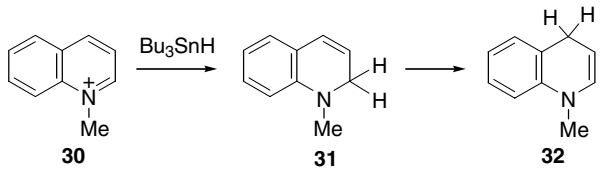


No 3,4-dihydroquinolines of type **29** have ever been isolated, or even detected by any spectroscopic method; however, their intermediacy was postulated for the disproportionation reaction of 1,2-dihydroquinolines (85CJC412) and for flash-vacuum thermolysis of triazoles (98JOC5779).

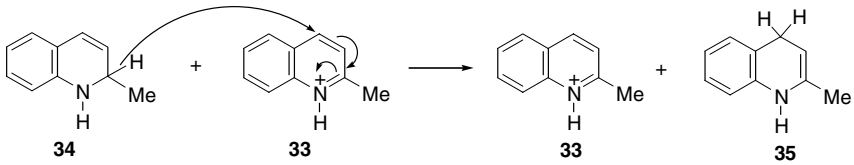
Formation of 1,2-dihydro- or 1,4-dihydroquinolines upon reduction of the corresponding quinolines or quinolinium salts depends strongly on the type of starting material, the substitution in the heteroaromatic ring, the reducing agent, and the reaction conditions. Thus, homogeneous hydrogenation of quinolines in the presence of a Ru catalyst occurs via 1,2-dihydroquinolines [98JMS(T)319], reduction of 3-unsubstituted quinolinium salts with sodium borohydride results in 1,2-dihydroquinolines (cf. **27**), while quinolines and quinolinium salts with an electron-accepting group at position 3 give 1,4-dihydro derivatives (cf. **28**) (89KGS1696). Reduction with $LiAlH_4$ affords an equimolar mixture of 1,2- and 1,4-dihydro isomers (93OM4291). 1-Methyl-1,2-dihydroquinoline **31,** initially formed on reduction of 1-methylquinolinium salt **30** with Bu_3SnH, was observed to isomerize gradually (70% in 70 min) to the corresponding 1,4-dihydro isomer **32** (Scheme 10) [94JCS(CC)287].

The mechanism suggested earlier for the similar isomerization **34** → **35** involving the reaction of a 1,2-dihydroquinoline molecule with the starting quinolinium salt **33** (Scheme 11) is analogous to that of 4*H*-thiopyran isomerization discussed above (cf. Scheme 3) and is supported by deuterated substrate studies (85CJC412). Further support for this mechanism is the absence of such isomerization for 4-substituted derivatives such as 1,4-dimethyl-1,2-dihydroquinoline [94JCS(CC)287].

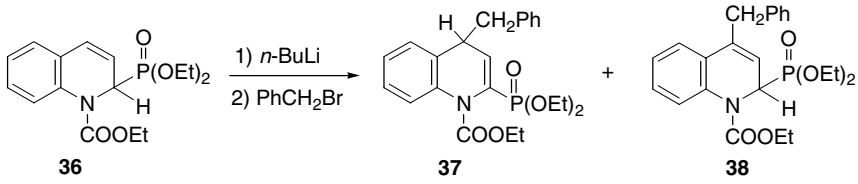
Interestingly, a reverse isomerization (1,4-dihydro → 1,2-dihydro) was observed when a 1,4-dihydroquinoline derivative was obtained by the reaction of lithiated 1-ethoxycarbonyl-1,2-dihydroquinoline-2-phosphonate **36** with benzyl bromide



SCHEME 10



SCHEME 11

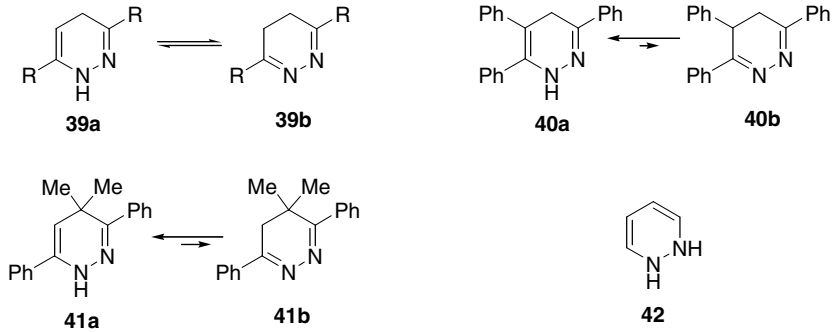


SCHEME 12

(82TL1709). 4-Benzylated 1,4-dihydroquinoline **37** was formed as a kinetic product at −20°C, while stirring the reaction mixture at 0°C for 15 min resulted in a mixture of 1,4- and 1,2-dihydroquinolines **37** and **38** and warming to ambient temperature gave exclusively 1,2-dihydro isomer **38** (Scheme 12).

C. DIHYDROPYRIDAZINES AND DIHYDROCINNOLINES

The conclusion drawn in 1976 that the 1,4-dihydropyridazine structure is the most stable (76AHCS1, p. 78) has been substantiated by later observations (for a review, see [95H(41)1805]). Thus, it was shown that dihydropyridazines **39** having alkyl or aryl substituents at ring positions 3 and 6 exist in solution in an equilibrium between a 1,4-dihydro tautomer **39a** and a 4,5-dihydro tautomer **39b,** with the former tautomer strongly predominating (Scheme 13). For example, in chloroform solution **39** (R = Ph) exists in an 8:1 ratio of 1,4-dihydro **39a** to 4,5-dihydro forms **39b.** The introduction of an aromatic substituent in the 5 position of the dihydropyridazine ring further increases the content of the 1,4-dihydro tautomeric form; thus, the 4,5-dihydro tautomer of **40b** is not observable even by NMR. Dihydropyridazine **41** exists in chloroform solution as a 78:22 mixture of 1,4-dihydro tautomer **41a** and 4,5-dihydro tautomer **41b** [83JHC855; 85AHC(38)1, p. 21].



SCHEME 13

SCHEME 14

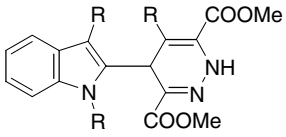
In this work the possibility of the existence of 1,2-dihydro isomer with the core structure **42** was not considered. Recently, however, it was shown that 1,2-dihydropyridazines could be prepared by careful electroreduction of the corresponding pyridazines, and that their stability depends significantly on the ring substitutions. Thus, dimethyl 1,2-dihydropyridazine-3,6-dicarboxylate **43a** (R = H) is reasonably stable and rearranges into the 1,4-dihydro tautomer **43b** only at a more negative potential, while the tautomerization in its tetrasubstituted analog **43a** (R = COOMe) occurs more readily (Scheme 14) [00TL647].

Most of the other examples of tautomeric interconversion in dihydropyridazines deal with the possibility of tautomerization of various 4,5-dihydropyridazines initially formed on the condensation of 1,4-diketones or 1,4-dithiones with hydrazine hydrate or monosubstituted hydrazines, or on Diels–Alder reactions with dimethyl 1,2,4,5-tetrazine-3,6-dicarboxylate. Thus, it was shown that, if the transformation into the most stable 1,4-dihydro tautomer is precluded by N-1 substitution, preformed 3,6-disubstituted 4,5-dihydropyridazines rearrange *in situ* into the corresponding 1,2-dihydro tautomers (87JHC1745). When conversion into 1,4-dihydro isomer is possible, the position of equilibrium depends significantly on the ring substitution. Thus, 3,6-disubstituted 4,5-dihydropyridazines bearing strong electron-donating groups (e.g., methoxy or dimethylamino groups) [85AHC(38)1, p. 40] or 3,4,5,6-tetrasubstituted derivatives with bulky substituents in the 3,6 positions (87JHC1745; 95T13261) exist as such. However, 3,6-di-*tert*-butyl [85AHC(38)1, p. 40] and 3,6-di(methoxycarbonyl) (92HCA901; 96TL921) derivatives were reported to exist as mixtures of 1,4-dihydro and 4,5-dihydro tautomers, although in the last case no adequate spectroscopic evidence for the tautomeric equilibrium was provided.

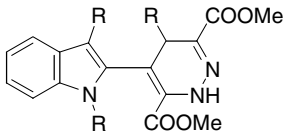
The differences in free energy, ΔG°, between 1,4-dihydro and 4,5-dihydro tautomers in $CDCl_3$ solution for some dihydropyridazines were calculated and have been found to be 1.24 kcal/mol for 3,6-diphenyldihydropyridazine **39** (R = Ph) and only 0.73 kcal/mol for 3,6-di-*tert*-butyldihydropyridazine **39** (R = *t*-Bu) [85AHC(38)1, p. 40].

A derivative of 5-(indol-2′-yl)dihydropyridazine **44** (R = H) exists in DMSO-d_6 solution exclusively as tautomer **44a** (within the limits of 400-MHz ^{1}H NMR detection). However, the introduction of methyl groups both into the indole ring and into the pyridazine ring favors a shift of the tautomeric equilibrium

to **44b.** Thus, using ^{1}H and ^{13}C NMR spectra, it was shown that the compound **44** (R = Me) exists as a single tautomer, **44b.** Atropoisomerism caused by steric repulsion between two methyl groups leads to the appearance of two sets of signals in the NMR spectra at 20°C with a coalescence temperature of 110°C (88TL3927; 89HCA65).



44a



44b

Since 1976, no further work has appeared on the tautomerism of dihydrocinnolines, which were previously shown to exist in the 1,4-dihydro form (76AHCS1, p. 78).

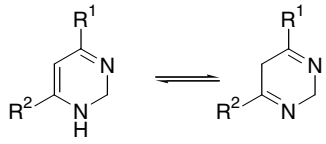
D. DIHYDROPYRIMIDINES

No data on tautomerism of dihydropyrimidines were available at the time of the early summary (76AHCS1), but much has been done since then. The results of tautomeric studies carried out during the period between 1976 and 1984 were reviewed comprehensively in [85AHC(38)1, pp. 63–77]. Later, Weis and van der Plas published an excellent review on the synthesis, structure, and tautomerism of dihydropyrimidines [86H(24)1433], where the tautomeric interconversions of these compounds were discussed in detail. In a more recent review on dihydropyrimidines (94MI1), the question of tautomerism in partially hydrogenated pyrimidines was also included.

On the basis of their tautomeric structures, most of the known dihydropyrimidines could be divided into two main groups: (1) 1,2- and 2,5-dihydropyrimidines and (2) 1,4-, 1,6-, and 4,5-dihydro derivatives. Although the photochemical rearrangement of 1,4- or 1,6-dihydropyrimidines into the corresponding 1,2-dihydro isomers has been reported [79JCS(P1)1228; 79JCS(P1)2393], no thermal interconversion between these two groups has yet been observed. Thus, the tautomeric transformations in these main groups will be discussed separately.

1. *1,2- and 2,5-Dihydropyrimidines*

According to *ab initio* calculations of unsubstituted dihydropyrimidines **45** ($R^1 = R^2 = H$), the 1,2-dihydro form **45a** is about 5 kcal/mol more stable than the



45a **45b**

2,5-dihydro structure **45b.** To study the influence of various factors on the position of the tautomeric equilibrium, a series of 1,2-/2,5-dihydropyrimidines **45** were synthesized by $LiAlH_4$ reduction of the corresponding pyrimidines (86JOC4623). The authors clearly demonstrated that the relative stability of these tautomers is highly dependent upon the electron-donating properties of the substituents R^1 and R^2 at positions 4 and 6 as well as the polarity of the solvent. Thus, although all known 1,2-dihydropyrimidines with alkyl substituents in positions 4 and 6 exist solely as such, in the ^1H NMR spectra of aryl-substituted 1,2-dihydropyrimidines signals of the corresponding 2,5-dihydro forms were also observed [84CL1773; 85H(23)1077; 86JOC4623].

The introduction of strong electron-donating groups into positions 4 and 6 (but not into position 2) leads to a further shift of the tautomeric equilibrium toward 2,5-dihydro tautomers as the result of stabilization induced by conjugation. This was shown on representative 4,6-dialkoxy compounds **45** ($R^1 = R^2 =$ OMe, OEt, OPr^n, OBu^n, OBu^t, OC_2H_4OEt), which exist in solution exclusively in 2,5-dihydro form **45b** independently of the polarity of the solvent used (86JOC4623).

In solution, the position of the tautomeric equilibrium of 1,2-dihydropyrimidines is highly influenced by the polarity of the solvent: The content of the more polar 1,2-dihydro tautomer is greatly increased in DMSO-d_6 due to strong intermolecular bonding with the solvent compared to that in $CDCl_3$, as shown in Table I.

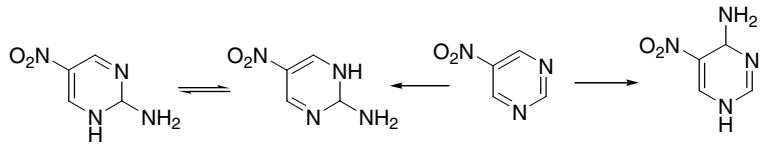
A simple calculation on the basis of ^1H NMR spectra involving concentrations of the both tautomers was carried out for 4,6-diphenyldihydropyrimidine and gave the value of ΔG° in $CDCl_3$ as 0.41 kcal/mol (84CL1773).

In the solid state, dialkoxydihydropyrimidine **45** ($R^1 = R^2 =$ OEt) exists exclusively in 2,5-dihydro form; no hydrogen-bond formation was detected in the crystal (86JOC4623).

TABLE I

TAUTOMERIC EQUILIBRIA OF 1,2-/2,5-DIHYDROPYRIMIDINES **45**

		Ratio **45a/45b** in Solvents		
R^1	R^2	$CDCl_3$	DMSO-d_6	Reference
Ph	Ph	2:1	only **45a**	84CL1773, 86H(24)1433
Ph	OMe	1:6	8:1	86JOC4623
SPh	SPh	1:3	8:1	86JOC4623



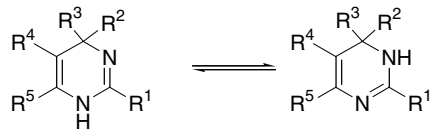
SCHEME 15

2. *1,4- and 1,6-Dihydropyrimidines*

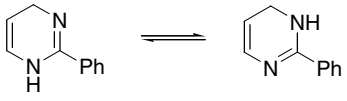
Van der Plas *et al.* (86JOC1147) demonstrated that the formation of identical tautomeric 1,2-dihydropyrimidines **46a** and **46a′** on amination of 5-nitropyrimidine is favored at a low temperature, while ammonia addition at room temperature produces the thermodynamically more stable 1,4-dihydro adduct **46b** (Scheme 15).

X-Ray analyses and solid-state IR spectra were recorded for a number of 1,4- and 1,6-dihydropyrimidines, demonstrating the dependency of the tautomeric composition in the crystal on the substitution in the pyrimidine ring and on the ability of these compounds to form intermolecular hydrogen bonds. Thus, 2,4,6-trisubstituted dihydropyrimidines exist in the solid state exclusively as 1,4-dihydro tautomers independently of the nature of the substituents (alkyl, aryl, heteroaryl, acyl, alkoxycarbonyl, etc.) [82H(19)493; 86H(24)233; 86T6429; 90JMC1510]. Introduction of another alkyl substituent into the 4 position shifts the equilibrium toward the 1,6-dihydro isomer. For example, 2-phenyl-4,4,6-trimethyldihydropyrimidine **47** (R^1 = Ph, $R^2 = R^3 = R^5$ = Me, R^4 = H) [82H(19)493] and dihydropyrimidine **47** [R^1 = Ph or Me, $R^2 = R^3$ = Me, R^4R^5 = $(CH_2)_2CH(Me)CH_2$] (86JHC705) were found to exist solely in their 1,6-dihydro tautomeric forms **47b** (Scheme 16).

A similar effect is produced by cocrystallization with protic solvents capable of forming a hydrogen bond–stabilized environment. Thus, dihydropyrimidine **47** ($R^1 = R^5$ = aryl, $R^2 = R^4$ = COOR, R^3 = H) cocrystallizes with water (1:1) exclusively as the 1,6 tautomer (98T9837). 2,4,6,6-Tetraphenyldihydropyrimidine **47** ($R^1 = R^2 = R^3 = R^5$ = Ph, R^4 = H) exists as the 1,6 tautomer in its solvate with



SCHEME 16



48a **48b**

SCHEME 17

i-PrOH [91AX(C)1656]. With loss of the solvent from the crystal, this compound partially tautomerizes into the 1,4-dihydro form.

X-Ray analysis of dihydropyrimidine **47** (R^1 = Me, R^2 = 2-ClC_6H_4, R^3 = H, R^4 = EtOCO, R^5 = Cl) hydrochloride exhibited its electron-delocalized structure (86T6429).

Tautomerism of simple monosubstituted 1,4-dihydropyrimidines in solution has been studied on an example of 2-phenyldihydropyrimidine **48,** prepared by condensation of benzamidine with acrolein [84H(22)657]. IR and ^{1}H and ^{13}C NMR spectra at $-60°$C in specially purified solvents showed that this compound exists as a tautomeric mixture of 1,4- and 1,6-dihydro tautomers (Scheme 17), with the relative amount of 1,4-dihydro isomer **48a** increasing with the polarity of the solvent.

Similarly, more highly substituted 1,4- and 1,6-dihydropyrimidines are usually reported to exist in solution as equilibrating mixtures of 1,4- and 1,6-dihydro tautomers, the ratios being dependent on the substitution pattern, polarity of the solvent, and temperature [82H(19)493; 82TL449; 84JA8021; 85AHC(38)1, pp. 63–77; 86H(24)233; 86H(24)1433; 86JCS(P1)83; 86JHC705; 86JOC1147; 86TL6377; 88JA4832; 93KGS1290; 93KGS1398; 94MI1; 97H(45)1967; 97KGS1587]. Increasing the solvent polarity shifts the equilibrium toward the more polar 1,4-dihydro form (84JA8021). Quantitative data on these effects are given in Table II.

Moreover, with a change of solvent, a new tautomeric form can arise owing to formation of intermolecular hydrogen bonds in place of the previously existent intramolecular hydrogen bonds. This situation is characteristic, for example, for pyrimidine derivatives **49,** for which the use of polar (DMSO, DMF, MeOH, HMPT) solvents or specifically solvating cosolvents (S) (e.g., a small amount of water or *N*-methylpyrrolidinone) leads to the appearance of ylidene tautomer **49b** with the *p*-quinonoid disposition of the double bonds (Scheme 18) [88KGS521; 90UK457].

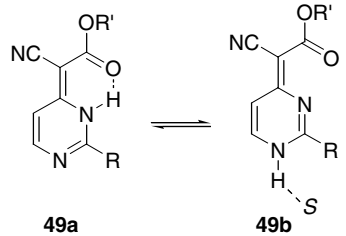
Although Weis *et al.* (84JA8021) demonstrated that the tautomeric ratio for 6-methyl-2,4-diphenyldihydropyrimidine **47** (R^1 = R^2 = Ph, R^3 = R^4 = H, R^5 = Me) does not depend on concentration (all other parameters being constant), a few years later Cho *et al.* (88JA4832) showed that for **47** (R^1 = CF_3, R^2 = 2-$O_2NC_6H_4$, R^3 = H, R^4 = $COOPr^i$, R^5 = Me) the ratio **47a:47b** gradually increases on concentrating its C_6D_6 solution. However, for the analogous

TABLE II

TAUTOMERIC EQUILIBRIUM IN 1,4-/1,6-DIHYDROPYRIMIDINES **47** IN SOLUTION AND ITS DEPENDENCE ON EXPERIMENTAL CONDITIONS

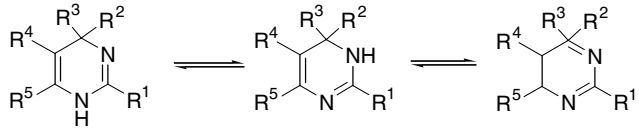
Substituents	*T* (°C)	Solvent	Ratio **47a/47b**	Reference
$R^1 = R^2 = Ph$, $R^3 = R^4 = H$, $R^5 = Me$	−60	$CDCl_3$	4:5	84JA8021
	20	$CDC1_3$	3:4	82H(19)493
	20	DMSO-d_6	3:2	82H(19)493, 84JA8021
	15	Dioxane-d_6	5:4	84JA8021
	20	HMPA-d_{18}	2:1	84JA8021
$R^1 = R^2 = Ph$, $R^3 = H$, $R^4 = MeC(O)$, $R^5 = Me$	50	$CDC1_3$	3.4:1	86JCS(P1)83
$R^1 = Ph$, $R^2 = 2$-furyl, $R^3 = R^4 = H$, $R^5 = Me$	20	DMSO-d_6	9:1	82H(19)493
$R^1 = Ph$, $R^2 = R^3 = R^5 = Me$, $R^4 = H$	20	DMSO-d_6	9:11	82H(19)493
$R^1 = Ph$, $R^2 = Ar$, $R^3 = H$, $R^4 = NO_2$, $R^5 = Me$	20	DMSO-d_6	only **47a**	93KGS1398, 97KGS1587
$R^1 = CF_3$, $R^2 = 2$-$O_2NC_6H_4$, $R^3 = H$, $R^4 = COOPr^i$, $R^5 = Me$	20	C_6D_6	2:1	88JA4832
$R^1 = OMe$, $R^2 = Ar$, $R^3 = H$, $R^4 = NO_2$, $R^5 = Me$	20	DMSO-d_6	1:3	93KGS1398, 97KGS1587
$R^1 = OMe$, $R^2 = Ph$, $R^3 = H$, $R^4 = COOEt$, $R^5 = Me$	20	$CDCl_3$	2:1	97H(45)1967
$R^1 = OMe$, $R^2 = 2$-ClC_6H_4, $R^3 = H$, $R^4 = COOEt$, $R^5 = Me$	20	$CDCl_3$	1:2	97H(45)1967
$R^1 = SMe$, $R^2 = 2$-$O_2NC_6H_4$, $R^3 = H$, $R^4 = COOPr^i$, $R^5 = Me$	20	C_6D_6	1:1.15	88JA4832

compound with R^1 = SMe, an opposite tendency was observed, which was explained by electronic effects of R^1 substituents. These discrepancies in behavior of compounds described by Weis and Cho could be ascribed to different deuterated solvents used for the experiments. For example, differences in aggregation effects for 1,4- and 1,6-dihydro forms could be more pronounced in the less polar C_6D_6 than in $CDCl_3$.



49a **49b**

SCHEME 18



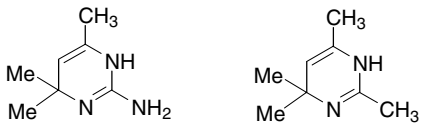
SCHEME 19

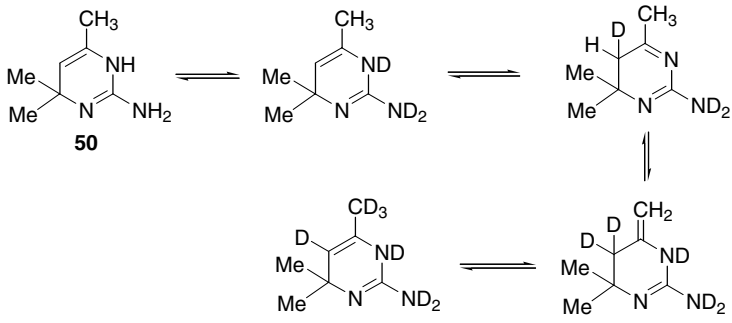
Cho *et al.* (88JA4832) also noted an increase in the relative amount of a 1,6-dihydro tautomer on warming the solution for both of the studied dihydropyrimidines.

Surprisingly, Kashima *et al.* (83TL209) reported the formation of individual 1,4-dihydro- and 1,6-dihydropyrimidines on desulfurization of the corresponding pyrimidine-2-thiones with Raney Ni and claimed that no tautomerization occurs under the reaction conditions (heating under reflux in MeOH).

In most of the papers discussing tautomerism in dihydropyrimidines, the possibility of the existence of 4,5-dihydro isomer **47c** (Scheme 19) was not even considered or was ruled out on the basis of ^{1}H NMR spectra. In 1985, however, Kashima *et al.* (85TL5057) reported that, although dihydropyrimidines **47** with $R^1 = H$ or Pr^i ($R^2 = R^3 = R^5 = Me$, $R^4 = H$) indeed exist only as mixtures of **47a** and **47b** tautomers, for analogs with $R^1 =$ Ph, OEt, or SMe, 4,5-dihydro tautomers **47c** were also observed in $CDCl_3$ solution in relative amounts of 10%, 20%, and 31%, respectively. The proportion of this tautomer rises to 45% in the case of the 2-dimethylamino-substituted derivative. The electronic effects of a heteroatom or an aromatic group in the 2 position were proposed as an explanation for this phenomenon. No 4,5-dihydropyrimidine has ever been found in the solid state.

Interesting results were also obtained on treatment of 2-amino-4,6,6-trimethyldihydropyrimidine **50** and 2,4,6,6-tetramethyldihydropyrimidine **51** with CD_3OD in the absence of a base (91TL2057). It was shown that, under these conditions, the 4-methyl protons of **50,** the 2,4-dimethyl protons of **51,** and H(5) in **50** and **51** undergo H–D exchange. The suggested mechanism involves annular (1,4-dihydro $\rightleftharpoons$ 4,5-dihydro) as well as substituent tautomeric equilibria, as shown in Scheme 20 for H–D exchange in **50.**

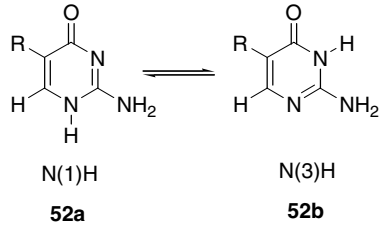




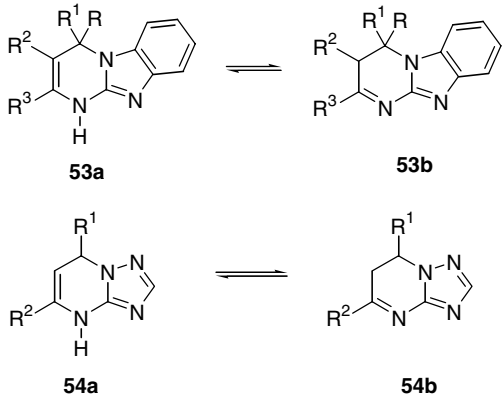
SCHEME 20

In tautomeric equilibria of some functionalized pyrimidine derivatives, such as isocytosine **52** (R = H) [77ZN(C)894] or pseudocytidine **52** (R = furanosyl) (99MI1), the potentially tautomeric oxo and amino groups are practically not involved, and only annular tautomeric interconversions N(1)H ⇌ N(3)H are observed. Using UV and NMR spectroscopy, it was shown that in solution these compounds exist as mixtures of both tautomeric forms **52a** and **52b,** slowly interconverting, with the N(3)H form **52b** usually predominating (Scheme 21). These experimental findings were confirmed by theoretical calculations, carried out for **52** (R = Me), which demonstrated the decreased stability of the N(1)H tautomer **52a** by 9.5 kcal/mol compared to that of N(3)H tautomer **52b** in the gas phase. However, this energy difference is essentially smaller in solution and, depending on the polarity of the solvent, could be as low as 2 kcal/mol (99MI1). The effect of the solvent polarity on the position of the tautomeric equilibrium in these oxo(amino)pyrimidines is essentially the same [77ZN(C)894] as that discussed above for nonfunctionalized dihydropyrimidines.

The tautomeric equilibrium in variously substituted imidazo- **53** (93KGS1353) and triazolo-fused pyrimidines **54** (88KGS1489; 91KGS1539; 93KGS1353; 93KGS1357) has been comprehensively studied by Desenko and colleagues, whose results were summarized in a special review (95KGS147).



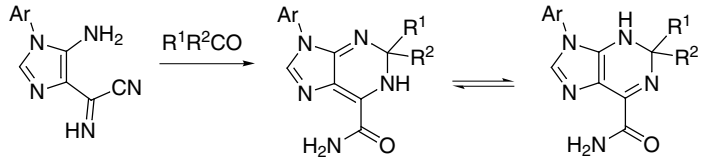
SCHEME 21



SCHEME 22

Quantum-mechanical calculations carried out for **53** and **54** showed that both enamine and imine forms (Scheme 22) have similar thermodynamic parameters. As a consequence, even small structural changes can affect the equilibrium position. Detailed investigation revealed similar changes in the tautomeric behavior of **53** and **54** with variations in the substitution pattern or in external conditions; hence the conclusions given below are applicable to both systems. Increasing the electron-donating character of the R^1 and/or R^3 substituent shifts the tautomeric equilibrium toward the 1,4-dihydro form **53a** (**54a**). Normally, the latter form is slightly more favored in DMSO than in $CDCl_3$ or alcohols; however, the difference in the tautomeric ratios becomes striking when the compound contains a substituent capable of forming intramolecular hydrogen bonds (for another example of an analogous solvent effect, see Scheme 18). The position of the equilibrium is also greatly affected by the presence of an acid: CF_3COOH addition shifts the equilibrium toward the more basic **53b** (**54b**) tautomer.

For unsymmetrical dihydropyrimidines with fully substituted 4(6) and 5 positions, such as **56,** a tautomeric equilibrium only between two 1,2-dihydro tautomers is possible. Thus, dihydropyrimidines **56,** obtained by condensation of the corresponding imidazole derivatives **55** and aldehydes or ketones, were shown to exist in acetone, DMSO-d_6, $CHCl_3$, or EtOH solution as mixtures of 1,2-dihydro tautomers **56a** and **56b** (Scheme 23) [94JCS(P2)1949]. From the detailed examination of ^1H and ^{13}C NMR spectra, it was established that in all the cases the major isomer in DMSO-d_6 is **56a;** however, the exact ratio **56a/56b** depends strongly on the substitution both in the pyrimidine ring and in the aryl group. For example, when Ar does not contain a strong electron-withdrawing substituent in the *para* position, the ratio **56a/56b** is somewhat higher for $R^1 = R^2 =$ Et (5–7 : 1) than for $R^1 = R^2 =$ Me or $R^1 =$ Ph, $R^2 = H$ (3–4 : 1). However, when Ar = 4-$O_2NC_6H_4$, only tautomer **56a** was found in DMSO-d_6 solution, independently



R^1 = H, Me, Et; R^2 = Me, Et, Ph

SCHEME 23

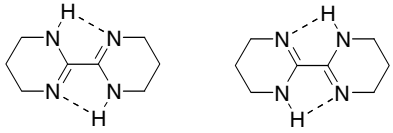
of the substitution in the pyrimidine ring. Introduction of an *ortho* substituent into the Ar aromatic ring shifts the equilibrium toward **56b.**

The effect of the substrate concentration on the rate of the tautomeric equilibrium also depends on substitution. Thus, for compounds **56** with R^1 or R^2 = H, the equilibrium rate is faster in concentrated solutions, while a change in concentration has a little effect for the 2,2-disubstituted derivatives. Tautomers **56a** and **56b** (Ar = Ph, $R^1 = R^2$ = Me) could be obtained in the pure tautomeric forms and do not equilibrate in the solid state.

The influence of various factors on the rate of tautomerization (and hence the possibility of observing the individual tautomers at relatively high temperatures) was studied in detail by Weis *et al.* [82TL449; 84H(22)657; 84JA8021; 85AHC(38)1, pp. 65–73; 86JCS(P1)83] and Cho *et al.* (88JA4832). The rate of tautomeric equilibrium and the coalescence temperature were found to be strongly dependent both on internal factors [e.g., the nature of the substituents, especially those in the 2 position (88JA4832)] and on external parameters, such as the polarity of the solvent (84JA8021), the purity of a deuterated solvent, microconcentrations of H^+ ions or paramagnetic impurities, or concentration of the dihydropyrimidine under investigation [82TL449; 85AHC(38)1, pp. 65–73]. Thus, it was shown that the tautomeric transformation is slower in more polar solvents, which was explained by hindering the proton transfer due to hydrogen-bond formation between the dihydropyrimidine and the solvent. Meanwhile, even small amounts of impurities strongly catalyze the tautomeric equilibrium, decreasing the coalescence temperature (t_c): thus, for 6-methyl-2,4-diphenyldihydropyrimidine **47** ($R^1 = R^2$ = Ph, $R^3 = R^4$ = H, R^5 = Me), t_c is about $-60°$C in commercial $CDCl_3$, but is about 60°C in specially purified $CDCl_3$. Admixtures of HCl or ammonium salts show a strong catalytic effect on the equilibrium (84JA8021; 99MI1).

Weis [85AHC(38)1, pp. 70–73] has also studied the kinetics of 1,4-dihydro to 1,6-dihydro transformation quantitatively using ^{1}H NMR line-shape analysis. The results indicated that two mechanisms (monomolecular and bimolecular reactions) are involved in the process, for which all the kinetic parameters were calculated.

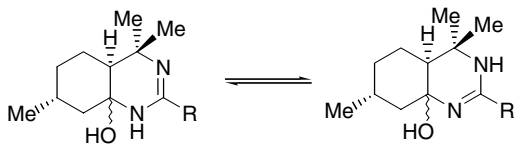
As tautomeric equilibration in monocyclic tetrahydropyrimidines is too fast to allow for observation of the individual tautomers (88MRC191), numerous attempts have been made to study the prototropic tautomerism in sterically hindered or hydrogen-bond–constrained derivatives. Shrerer and Limbach (94JA1230) used dynamic NMR experiments to investigate the possibility of tautomeric interconversion between two identical bis(tetrahydropyrimidine) tautomers, **57a** and **57b.** However, no such interconversion was observed in methylcyclohexane-d_{14} solution in the temperature range from 280 to 410 K, probably because a high activation energy is required. The latter was calculated to be more than 21 kcal/mol at 410 K.



57a **57b**

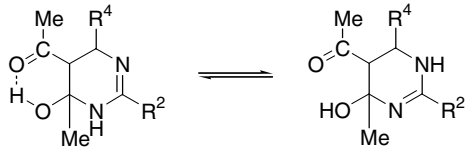
Annular tautomerism in tetrahydropyrimidines has also been studied for a few N-unsubstituted tetrahydropyrimidines bearing OH groups at the 6 position. X-Ray analysis of bicyclic **58** (R = H) revealed that its crystals are composed of two independent tautomeric molecules, **58a** and **58b** (Scheme 24), connected by three hydrogen bonds (86JHC705). According to ^{13}C NMR spectroscopy, the same tautomers **58a/58b** (R = H, Me) coexist in solution, their ratios being dependent on the solvent polarity.

Tetrahydropyrimidine **59** ($R^2 = R^4 = Ph$) with an acetyl group in position 5 crystallizes as a semihydrate, and exists exclusively as 3,4,5,6-tetrahydro derivative **59b** in the solid state [86JCS(P1)83]. Surprisingly, no intramolecular hydrogen bonding, as shown for **59a,** was observed. However, in $CDCl_3$ solution, compounds **59** exist as tautomeric mixtures whose tautomer ratio depends on heterocyclic ring substitution (Scheme 25). Thus, when $R^2 = R^4 = Ph$ or $R^2 = Me$, $R^4 = Ph$, the ratio **59a : 59b** = 1 : 1, while when $R^2 = Ph$, $R^4 = 3\text{-}O_2NC_6H_4$, the ratio is 4 : 1, with the 1,4,5,6-tetrahydro tautomer **59a** predominating.



58a **58b**

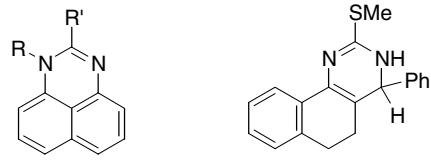
SCHEME 24



59a **59b**

SCHEME 25

The ^{13}C NMR spectrum of the parent perimidine **60** (R = R′ = H), the benzo-fused analog of tetrahydropyrimidines, is clearly consistent with a symmetrical structure, reflecting rapid prototropic tautomerism between the annular nitrogen atoms. However, the introduction of an alkylthio substituent into the 2 position (R = H, R′ = SMe or SEt) suppresses the rate of this interconversion. In these cases, the NMR spectra are characteristic of unsymmetrical molecules rather than of rapidly equilibrating 2-substituted perimidines (88MRC191). This anomalous effect was explained by enhancement of the differential electron density between the heterocyclic and carbocyclic rings due to electron donation from the sulfur atom. A relatively slow rate of tautomerism was observed for amide **60** (R = H, R′ = $CONHCH_2CH_2NMe_2$) in contrast to the rapidly equilibrating ester **60** (R = H, R′ = COOEt); this was attributed to intramolecular hydrogen bonding between the amide oxygen and the tautomeric annular proton.



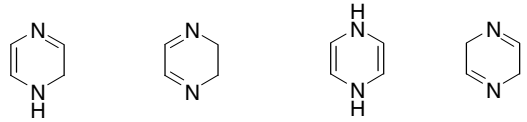
60 **61**

However, another representative of benzo-fused tetrahydropyrimidines, 3,4,5,6-tetrahydrobenzo[*h*]quinazoline **61,** was reported to exist exclusively as the tautomer shown, without any indication of the annular tautomeric equilibrium (91M209).

Tautomerism of 2-substituted hexahydropyrimidines has been studied (98OPP53), and free energies, enthalpies, and entropies of activation for this ring–chain tautomeric equilibrium have been measured [97JCS(P2)169].

E. DIHYDROPYRAZINES AND DIHYDROQUINOXALINES

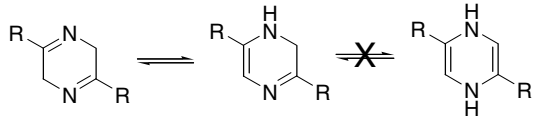
Four possible tautomeric forms, e.g., 1,2- (**62**), 2,3- (**63**), 1,4- (**64**), and 2,5- (**65**), exist for unsubstituted dihydropyrazines; however, information on the tautomeric interconversions and stabilities of these forms is sparse. It was demonstrated that, of the four tautomers, 1,4-dihydropyrazine **64** is the least stable (unsubstituted 1,4-dihydropyrazine has not yet been synthesized). This instability was explained by the cyclic conjugation of the 8π electrons of the heteroring, leading to an "antiaromatic" character, this was apparently confirmed by the ^{1}H NMR spectra of 1,4-disilylated derivatives [81AG(E)599; 84MI1]. However, this conclusion about the antiaromaticity of 1,4-dihydropyrazines was later disproved on the basis of X-ray analysis (88JOC5779) and theoretical calculations of isodesmic energy (at the MP2/6-31G* and B3LYP/6-31G* levels), which showed a substantial stabilizing effect (93CJC1123; 94IJQC575; 99CCC633). Even when substituent introduction forces the 1,4-dihydropyrazine structure to be planar (which should promote π delocalization), the diene character of the heteroring is maintained.



62 **63** **64** **65**

Armand and coworkers have shown that, while 1,4-dihydropyrazines are the initial products of the electrochemical reduction of pyrazines, they could not be isolated and readily isomerize in solution into 1,2- or 1,6-dihydropyrazines depending on the substitution pattern in the heterocyclic ring (74CJC3971; 84MI1). The rate of the isomerization depends on the type of pyrazine as well as the pH and the nature and amount of the cosolvent.

3,6- and 1,6-Dihydropyrazines **66a** and **66b** (R = Ph) (Scheme 26) were found to coexist in $CDCl_3$ solution in a thermodynamic equilibrium in a ratio of 30:70

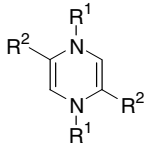


66a **66b** **66c**

SCHEME 26

[74CJC3971; 85AHC(38)1, p. 21]. Addition of deuterioacetone to this solution shifts the equilibrium toward the 1,6-dihydro isomer **66b.** A similar tautomeric equilibrium was earlier observed for the methyl-substituted analog (R = Me) in a neat liquid using ^{1}H NMR and IR spectroscopy (76AHCS1, p. 78). In this case, however, a large predominance of tautomer **66a** (up to 90%) was suggested, which is possibly explained by the lower polarity of the neat liquid compared to a $CDCl_3$ solution.

Compared to prototropic tautomerism, carbonotropic tautomerizations of dihydropyrazines have been studied more extensively. Thus, it was demonstrated that 1,4-dibenzyl-1,4-dihydropyrazines **67** and **68** (R^1 = $PhCH_2$, R^2 = Ph) on heating in benzene undergo 1,3-benzylic migration to give the corresponding 1,2-dihydropyrazines **69** and **70,** respectively (70JOC3987; 74JOC1998). Some bulky alkyl groups, such as cyclopentyl or cyclohexyl, demonstrate a similar ability to migrate (74JOC1998). However, when R^1 = Ar, the possibility of migration depends strongly on the substitution in the heterocyclic ring. Thus, the migration of R^1 = Ar was observed for compounds of type **67,** but not for **68** (R^2 = Ph) [87JCS(P1)1841]. This rearrangement has first-order kinetics and does not depend on the solvent polarity and the presence of a radical scavenger (74JOC1998). When the migrating group is chiral, the reaction proceeds with ≥95% stereoselectivity and configuration inversion (74TL179). These reaction features suggest that this is a unimolecular rearrangement with ≥88% of an intracage process. No 1,3-migration of the second benzylic group in **69** (R^1 = $PhCH_2$, R^2 = Ph) with the formation of **71** (R^1 = $PhCH_2$, R^2 = Ph) was observed (70JOC3987).



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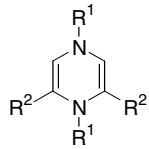

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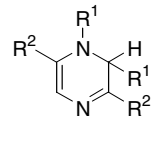

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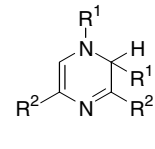

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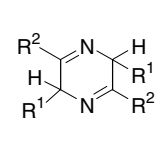
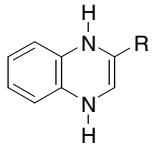


71

Since the earlier review (76AHCS1, p. 79), no additional data have become available on the tautomerism of dihydroquinoxalines. Although the fusion of a benzene ring renders 1,4-dihydroquinoxaline **72** essentially more stable than 1,4-dihydropyrazine **64** (82CJC2792; 84MI1), allowing unsubstituted **72** (R = H) to be prepared by electrochemical reduction of quinoxaline (74CJC3971), 1,4-dihydroquinoxaline **72** (R = Ph) is still thermodynamically less stable than the 1,2-dihydro tautomer **73** (R = Ph) and easily rearranges to the latter (76AHCS1, p. 79).



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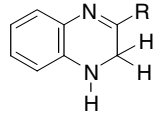
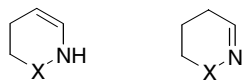


73

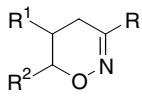
F. Oxazines and Thiazines

5,6-Dihydro-2*H*- **74** and -4*H*-1,2-oxazines and thiazines **75** are interrelated by prototropy, being enamines and imines, respectively. In the case of oxazines, the imine form **75** is favored, and there are several well established examples of this system, including the parent heterocycle **75** (X = O) [84MI2]. No tautomeric equilibrium between the 2*H* and 4*H* forms has been observed under normal conditions in solution or in the solid state. However, the formation of intermediate 2*H* isomers **77** was proposed both for the conversion of 3-phenyl-5,6-dihydro-4*H*-1,2-oxazine **76** (R = Ph, R^1 = R^2 = H) into 2-phenylpyrrole (89TL3471) under strong basic conditions and for thermal decomposition of cyclopentene-fused 1,2-oxazine **76** (R = Ph, 4-BrC_6H_4, 2-furyl, R^1R^2 = $-CH_2-CH=CH-$) [79JCS(P1)258].



74 **75**

X = O, S



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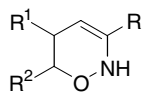

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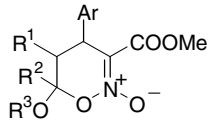

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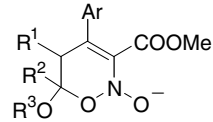
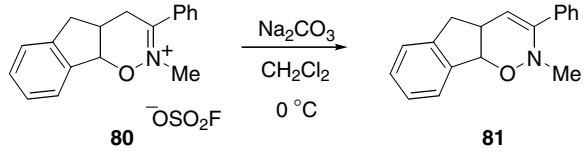


79

An analogous isomerization to the intermediate **79** was reported to occur upon the basic cleavage of oxazine *N*-oxides **78** (88BCJ461).

N-Substituted 5,6-dihydro-2*H*-1,2-oxazines were found to be significantly more stable than their N-unsubstituted analogs and could be distinguished from the corresponding 4*H* isomers using ^{1}H NMR spectroscopy. Thus, it was shown that oxazinium salt **80** isomerizes on treatment with sodium carbonate to tricyclic

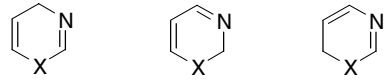


80 **81**

SCHEME 27

oxazine **81** (Scheme 27), which is stable enough to be investigated by ^{1}H NMR spectroscopy, but quickly decomposes on attempted purification [79JCS(P1)258].

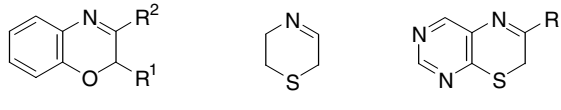
Representatives of all three types of isomeric 1,3-oxazines **82–84** (X = O) and 1,3-thiazines **82–84** (X = S) and of the corresponding partially hydrogenated derivatives are known. However, no tautomeric interconversions between these structures have been observed.



4H- *2H-* *6H-*

82 **83** **84**

Few monocyclic 1,4-oxazines are known and their chemistry is relatively unexplored; no systematic studies on the possible annular tautomerism of these compounds have been undertaken. However, it was shown that benzo-fused 1,4-oxazines **85** (R^1 = H, Me, R^2 = SMe; R^1 = R^2 = COR) exist exclusively in the 2*H* form and do not tautomerize under normal conditions (76AHCS1, p. 80; 80JHC1625).



85 **86** **87**

The parent 1,4-thiazine exists exclusively as the 2*H* tautomer **86,** independently of the medium used, as do its pyrimidino-fused derivatives **87** (76AHCS1, p. 80; 84MI2). However, the equilibrium could be affected significantly by a substitution pattern in the thiazine ring, as was shown in the example of 1,4-benzothiazine. Thus, 3-phenyl-1,4-benzothiazine **88** (R^1 = H, R^2 = Ph) is present in aqueous hydrochloric acid as a 4:1 mixture of 2*H* (**88a**) and 4*H* (**88b**) isomers

88a **88b**

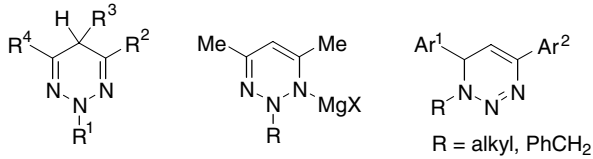
SCHEME 28

(Scheme 28) (84MI2). Introduction of an electron-accepting ethoxycarbonyl group into the 2 position ($R^1 =$ COOEt, $R^2 =$ Me) shifts the equilibrium completely toward the 4*H* form **88b** (76AHCS1, p. 80).

G. DIHYDRO-1,2,3-TRIAZINES

Available data on dihydro-1,2,3-triazines are limited. A short account on these compounds was published in [85AHC(38)1, p. 82], and since then only a few papers dealing with dihydro-1,2,3-triazines have appeared.

All the partially hydrogenated 1,2,3-triazines, prepared from the parent 1,2,3-triazines either by catalytic hydrogenation (H_2/Pd–C) [80JCS(CC)1182] or by reduction with sodium borohydride [85AHC(38)1, p. 82] or with lithium aluminum hydride (85LA1732), were assigned 2,5-dihydro structures **89** on the basis of ^{1}H and ^{13}C NMR and IR studies. Other approaches to tautomerizable dihydro-1,2,3-triazines, such as mild hydrolysis of 5,5-disubstituted 2,5-dihydro-1,2,3-triazines [90JCS(P1)3321] or Grignard reagent addition to 1,2,3-triazines [92H(33)631], were also reported to produce exclusively 2,5-dihydro isomers, although in the last case the unstable 1,2-adduct **90** was postulated as an intermediate to explain the formation of a pyrazole derivative as a side product.



89 **90** **91**

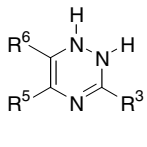
When N^1-substituted dihydro-1,2,3-triazines are formed, the products exist solely in 1,6-dihydro forms **91** as confirmed by ^{1}H and ^{13}C NMR studies [96H(43)1759].

As no 1,2- and 1,4-dihydro isomers were observed by any spectroscopic technique, and the existence of only one isomer, usually the 2,5-dihydro derivative,

was registered in each reaction where dihydro-1,2,3-triazines were formed, no tautomerism in dihydro-1,2,3-triazines has yet been discussed.

H. DIHYDRO-1,2,4-TRIAZINES

No data on the tautomerism of dihydro-1,2,4-triazines were available at the time of the previous reviews [76AHCS1; 85AHC(38)1, p. 83]; since then, however, much work has been done. For N-unsubstituted dihydro-1,2,4-triazines, nine possible isomers (**92–100**) could exist; however, only some of them (**92–95, 98,** and **99**) have been synthesized individually.



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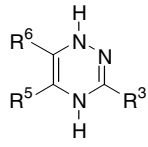

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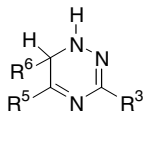

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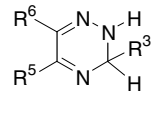

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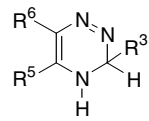

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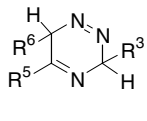

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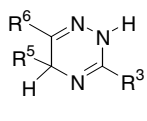

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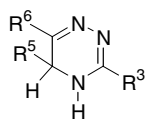

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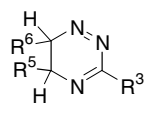


100

The first systematic theoretical study on dihydro-1,2,4-triazines was recently carried out (98JOC5824): the stabilities of all the possible unsubstituted dihydro-1,2,4-triazines were calculated using various theoretical methods. all reliable calculation methods consistently show that the 2,5-dihydro isomer **98** is the most stable. This is in perfect agreement with the experimental observations: all the synthetic methods used for the preparation of dihydro-1,2,4-triazines result in 2,5-dihydro isomer **98,** provided the structures of the reactants and the reaction mechanism allow its formation. Thus, although Metze and Scherowsky (59CB2481) claimed the formation of 1,2-dihydro-1,2,4-triazine **92** ($R^3 = R^5 = R^6 =$ Ph) in the reduction reaction of 3,5,6-triphenyl-1,2,4-triazine with acetic anhydride, this conclusion has been disproved in the favor of the 2,5-dihydro isomer **98** (99EJOC685).

In the ring-closure reaction of α-acylaminoketones with hydrazines, some dihydro-1,2,4-triazines were obtained. The possible 1,2-, 2,3-, or 5,6-dihydro structures were excluded by IR spectroscopic studies; however, this method, as well as the attempted preparation of fixed derivatives, failed to distinguish between

TABLE III

CALCULATED RELATIVE ENERGIES OF ISOMERIC DIHYDRO-1,2,4-TRIAZINES COMPARED TO 2,5-DIHYDRO-1,2,4-TRIAZINE **98**

Isomer	4,5-Dihydro **99**	1,6-Dihydro **94**	1,4-Dihydro **93**	2,3-Dihydro **95**
ΔG (kcal/mol)	8.89	9.33	9.46	10.39
Isomer	1,2-Dihydro **92**	3,4-Dihydro **96**	3,6-Dihydro **97**	5,6-Dihydro **100**
ΔG (kcal/mol)	14.48	15.13	16.08	18.39

2,5- and 4,5-dihydro structures. The assignment of the products as 2,5-dihydro-1,2,4-triazines was made on the basis of ^{1}H NMR studies, corroborated by the mass spectra of these compounds (77T1043). 2,5-Dihydro tautomeric structures have also been ascribed to the products of the reactions of 3-methyl-6-phenyl-1,2,4-triazine with Grignard reagents [85H(23)2807] and of the photochemical and electrochemical reduction of various triazines (99EJOC685). The predominance of the 2,5-dihydro tautomers in ethanolic solution has been confirmed by UV spectra of 3,5,6-triphenyl-dihydro-1,2,4-triazine and its N-2 and N-4 methylated derivatives (82MI1).

If the formation of a 2,5-dihydro isomer **98** is not allowed, other dihydro-1,2,4-triazines are formed according to their order of stability calculated by various theoretical methods (see Table III) (98JOC5824).

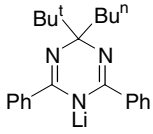
Although 1,4-dihydro-1,2,4-triazines **93** have long been assumed to be intermediates in electrochemical and photochemical reactions, the first representative of this series was isolated only recently as its *N,N*-diacetyl derivative (99EJOC685).

2,3-Dihydro-1,2,4-triazines **95** were obtained by base-induced ring expansion of 1-alkyl-1,2,3-triazolium salts, and their structure in the solid state was confirmed by X-ray analysis [92JCS(P1)147].

I. DIHYDRO-1,3,5-TRIAZINES

Sequential addition of *t*-BuCN and PhCN to *n*-BuLi in the presence of tetrahydrofuran produces an isolable lithium salt of 1,4-dihydrotriazine tris(THF) solvate, **101**·$(THF)_3$, characterized by both NMR spectroscopic and X-ray crystallographic methods [93JCS(CC)608]. An analogous potassium salt monosolvate was prepared using a similar procedure with *n*-BuK, and X-ray structural analysis of this compound revealed the polymeric zig-zag chain arrangement of alternating K^+ cations and 1,4-dihydro-1,3,5-triazinyl anions [94JCS(CC)2393]. The corresponding magnesium and sodium salts also include 1,4-dihydro-1,3,5-triazinyl moieties; however, unlike the potassium salt, they are found to be monomeric (97CB621).

Methanolysis of the lithium salt **101** gave no 1,4-dihydro-1,3,5-triazine **102;** instead, its 1,2-dihydro analog **103** was isolated as a monomethanolate [93JCS(CC)608]. While *ab initio* MO calculations (at the 6-31G level) indicated that the 1,4-dihydrotriazine arrangement is energetically preferred to the 1,2-dihydro alternative irrespective of the counterion (M^+ or H^+) [95JOM(486)79], it was suggested that this switch to a 1,2-dihydro-1,3,5-triazine on methanolysis is directed by the formation of an intermediate MeOH complex with a methanol molecule attached to a ring N atom.



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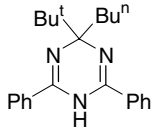

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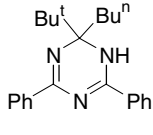
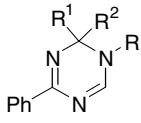


103

When a tautomeric equilibrium is possible, neutral dihydro-1,3,5-triazines exist predominantly or exclusively in their 1,2-dihydro forms. Thus, the formation of 1-substituted 1,2-dihydro-1,3,5-triazines **104** was reported on intramolecular cyclization of imidoylcarbodiimides (86CB3737). No corresponding 1,4-dihydro tautomers were observed by ^1H, ^{13}C NMR, or IR spectroscopy in solution.

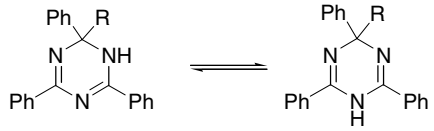


104

R = Me, Et, *i*-Pr, *t*-Bu, Ph, 2,6-$Me_2C_6H_3$
R^1 = H, Me; R^2 = Me, Ph

Base-catalyzed Dimroth rearrangements of 1-aryl-4,6-diamino-1,3,5-triazines or triflic acid–induced decomposition of 6-anilino-1,3,5-triazines led to the formation of the corresponding substituted 1,2-dihydro-1,3,5-triazines, whose structure was established on the basis of ^1H NMR spectra (93JHC849).

In an attempt to explain the peculiar photochemical behavior of 2,2,4,6-tetraphenyldihydro-1,3,5-triazine, Maeda and coworkers carried out extensive studies on the annular tautomerism of this compound and its variously substituted derivatives both in solution and in the solid state. Thus, spectroscopic studies (^1H NMR, IR, and UV) of 2,2,4,6-tetraphenyldihydro-1,3,5-triazine **105** (R = Ph) and some



105a **105b**

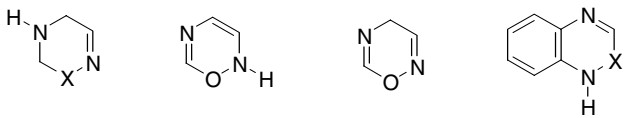
SCHEME 29

other tri- and tetraphenyldihydro-1,3,5-triazines **105** (R = H, Me, Et) showed that in chloroform and methylene chloride all these compounds exist as tautomeric mixtures of the corresponding 1,2- and 1,4-dihydro isomers, with the 1,2-dihydro tautomers **105a** predominating (Scheme 29) [85JCS(P2)887]. An analogous conclusion was drawn earlier by Weis and colleagues, who observed both **105a** and **105b** tautomers in $CDCl_3$ and DMSO-d_6 solutions using IR, ^{1}H NMR, and ^{13}C NMR techniques. They also noted the significant influence of the bulkiness of the R substituent on the rate of tautomerization. Thus, a change of substituents in the order R = *n*-Bu, Me, H clearly increases the rate of the tautomeric interconversion as measured by NMR [85AHC(38)1, p. 98].

Although the presence of the 1,4-dihydro tautomers **105b** (R = Me, Ph) in the solid state was suggested on the basis of IR spectra [85JCS(P2)887], this conclusion was later disproved by a number of X-ray structural determinations. Thus, X-ray analysis showed that dihydro-1,3,5-triazine **105** (R = Ph) and its solvates with ethanol, propylamine, and acetone exist in the solid state exclusively in their 1,2-dihydro tautomeric forms [88AX(C)704; 88BCJ2487; 89BCJ3171]. Indirect evidence for the predominance of the **105a** form for the triazine **105** (R = Ph) was provided by its methylation, which occurred at the N-1 atom. The structure of the N-methylated derivative thus prepared was confirmed by X-ray analysis [89AX(C)1115].

J. OXADIAZINES AND THIADIAZINES

Fully saturated and 5,6-dihydro-4*H*-1,2,5-oxadiazines **106** (X = O) have been reported (96MI3), whereas the 2*H*- and 4*H*-1,2,5-oxadiazines **107a** and **107b** are still unknown.

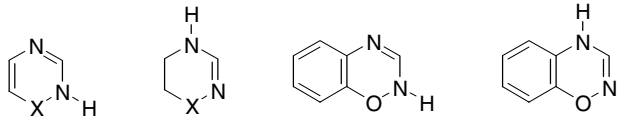


106 **107a** **107b** **108**

Also rare are the 1*H*-2,1,4-benzoxadiazines and 1*H*-2,1,4-benzothiadiazines **108** (X = O, S) and 1,2,5-thiadiazines **106** (X = S), the latter being known only as their 5,6-dihydro-4*H*-derivatives.

2*H*-1,2,4-Oxadiazines **109** (X = O) and their 4*H* and 6*H* isomers are also known mainly as the 5,6-dihydro (**110,** X = O) and tetrahydro derivatives (96MI2). 1,2,4-Benzoxadiazines are uncommon systems, but have been reported as both 2*H* (**111a**) and 4*H* (**111b**) isomers. However, no studies on tautomerism of either monocyclic or benzo-fused 1,2,4-oxadiazines have yet been performed.

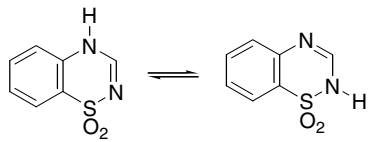
Although 2*H*- and 4*H*-thiadiazines with divalent sulfur are virtually unknown, both isomers have been prepared as the 1-oxides and, more commonly, as the 1,1-dioxides **109** (X = SO_2) and **110** (X = SO_2).



109 **110** **111a** **111b**

Studies of the tautomeric state of 1,2,4-thiadiazines have been more or less confined to the biologically active 1,2,4-benzothiadiazine 1,1-dioxides of type **112.** Initial UV spectroscopic investigations, performed as early as 1960, suggested that the parent benzothiadiazine **112** exists in ethanolic solution as a tautomeric mixture of 4*H* (**112a**) and 2*H* (**112b**) forms, with the 4*H* tautomer **112a** predominating (Scheme 30) (60JOC970). A few years later, however, Jakobsen and Treppendahl (79T2151) studied the tautomeric behavior of variously substituted benzothiadiazines in different solution using ^{13}C NMR spectroscopy. They observed the sole 4*H* tautomer of type **112a,** independently of the ring substitution, solvent, or temperature. Later, extended Hückel MO calculations confirmed the increased stability of the 4*H* tautomer **112a** relative to the 2*H* tautomer **112b** [90AHC(50)255].

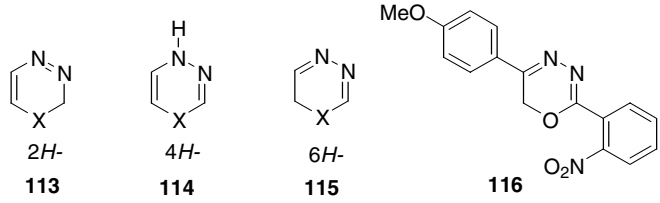
Although representatives of all the possible tautomeric 1,3,4-oxadiazines—2*H*- (**113,** X = O), 4*H*- (**114,** X = O), and 6*H*- (**115,** X = O)—are known, only a few isolated studies concerning the existence of tautomerism in these



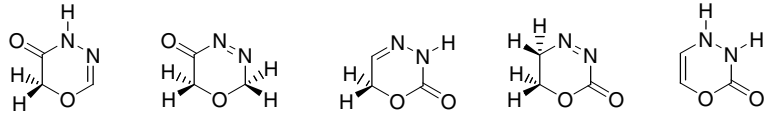
112a **112b**

SCHEME 30

systems have been carried out, and those almost exclusively deal with the substituent and ring–chain tautomerism (96MI5). For 2,5-diaryl-substituted 1,3,4-oxadiazines, the 6*H* form is presumably the most stable. Using X-ray analysis, it was demonstrated that **116** exists in the solid state exclusively as the 6*H* tautomer shown (85CB4026).



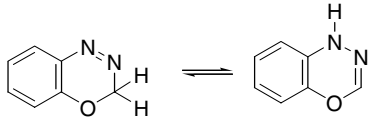
The enthalpies of all the annular tautomers of 1,3,4-oxadiazin-5-ones **117** and -2-ones **118** were calculated using the MNDO method (88CB887). The results clearly indicated that in both cases the hydrazone-type tautomers **117a** and **118a** are the most stable, while the formation of the tautomer **118c** is the least probable.



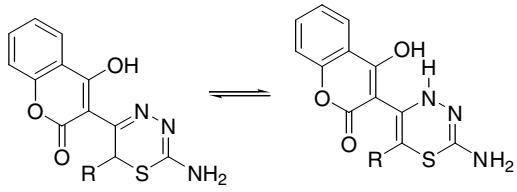
	117a	**117b**	**118a**	**118b**	**118c**
ΔH_f (kcal/mol)	- 47.3	- 38.7	- 48.6	- 45.4	- 37.5

Early studies on tautomerism of benzo-fused 1,3,4-oxadiazines (70CB331; 76AHCS1, p. 79) suggested the predominance of the 2*H* tautomer **119a,** which, however, easily tautomerizes to the 4*H* isomer **119b** on treatment with sodium alkoxide (Scheme 31).

Like their oxygen analogs, 1,3,4-thiadiazines have been reported mainly as their 6*H* derivatives **115** (X = S). However, Trkovnik *et al.* (85OPP206) showed that,



SCHEME 31

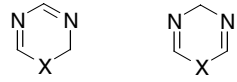


120a **120b**

SCHEME 32

although coumarin-substituted thiadiazines **120** indeed exist in DMSO and $CDCl_3$ solution predominantly as 6*H* tautomers **120a,** the 4*H* tautomer **120b** seems to be favored in the solid state (Scheme 32).

A variety of 2*H*- (**121,** X = O) and 4*H*- (**122,** X = O) 1,3,5-oxadiazines has been studied and characterized, whereas 2*H*-1,3,5-thiadiazines **121** (X = S), unlike the 4*H* isomers **122** (X = S), are uncommon. The most common type of tautomeric interconversions for such systems is ring–chain tautomerism. A few studies on substituent tautomerism have also been carried out; however, no data on annular tautomerism have yet appeared in the literature.

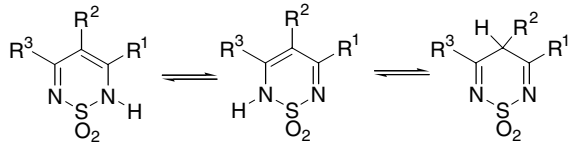


121 **122**

The 1,2,6-oxadiazine ring system is much less known. Some reports concerning heterocycles of this type are incorrect, while others are unsubstantiated (96MI4).

In contrast, 1,2,6-thiadiazines, especially their 1,1-dioxide derivatives, are common. N-Unsubstituted 1,2,6-thiadiazine 1,1-dioxides **123** can exist in three possible tautomeric forms: 2*H*- **123a,** 6*H*- **123b,** and 4*H*- **123c** (Scheme 33).

It was shown that, except in the cases of 4,4-disubstituted derivatives with the fixed **123c** form, nonfunctionalized thiadiazine 1,1-dioxides exist as tautomeric mixtures of 2*H* (**123a**) and 6*H* (**123b**) tautomers (70CRV593; 82JOC536). As



2H- **123a** 6*H*- **123b** 4*H*- **123c**

SCHEME 33

TABLE IV

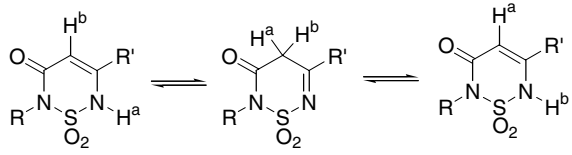
SUBSTITUENT EFFECTS ON THE POSITION OF THE EQUILIBRIUM OF THIADIAZINE 1,1-DIOXIDES **123**

Entry	Substituents	Solvent	Method	Ratio **123a/123b**	Reference
1	$R^1 = R^2 = R^3 = H$	Solid state	X-ray analysis	**123b** only	79JOC4191
2	$R^1 = Me$, $R^2 = R^3 = H$	DMSO-d_6	Interpolation	~40:60	82JOC536
3	$R^1 = Ph$, $R^2 = H$, $R^3 = Me$	DMSO-d_6	Interpolation	~20:80	82JOC536
4	$R^1 = Me$, $R^2R^3 = (CH_2)_3$	Solid state	^{13}C CP/MAS	**123a** only	94JCS(P2)1561
5	$R^1 = Me$, $R^2R^3 = (CH_2)_3$	DMSO-d_6	^{13}C NMR	**123a** predominates	94JCS(P2)1561
6	$R^1 = Me$, $R^2R^3 = (CH_2)_4$	Solid state	^{13}C CP/MAS	**123b** only	94JCS(P2)1561
7	$R^1 = Me$, $R^2R^3 = (CH_2)_4$	DMSO-d_6	^{13}C NMR	**123b** predominates	94JCS(P2)1561
8	$R^1 = NH_2$, $R^2 = R^3 = H$	Solid state	X-ray analysis	**123b** only	82JOC536
9	$R^1 = NH_2$, $R^2 = R^3 = H$	DMSO-d_6	Interpolation	**123b** predominates	82JOC536
10	$R^1 = NH_2$, $R^2 = Br$, $R^3 = H$	DMSO-d_6	^{13}C NMR	**123b** predominates	86JMC531
11	$R^1 = NH_2$, $R^2 = CONH_2$, $R^3 = H$	DMSO-d_6	^{13}C NMR	**123b** predominates	86JMC531
12	$R^1 = NH_2$, $R^2 = NO_2$, $R^3 = NH_2$	DMSO-d_6	^{13}C NMR	~50:50	86JMC531

equilibrium in monocyclic nonfunctionalized compounds **123** (R^1, R^2, R^3 = H, alkyl, aryl) is too fast to allow for the direct measurements of the equilibrium constants, a number of interpolation methods, based on ^{13}C chemical shifts and ^1H coupling constants, were used to evaluate the tautomeric ratios (82JOC536). The results indicated that thiadiazine **123** ($R^1 = Me, R^2 = R^3 = H$) exists in DMSO-d_6 as a mixture of **123a** and **123b** tautomers in a ratio of about 40:60, respectively. The position of the equilibrium depends significantly on steric demands and on the electronic effects of the thiadiazine ring substituents. In the case of unfunctionalized unsymmetrical thiadiazines ($R^1 \neq R^3$), the equilibrium is usually shifted toward the **123b** form, R^1 being the bulkiest substituent (Table IV). However, some exceptions were also observed (compare entries 4 and 6, and 5 and 7 in Table IV).

The effect of the R^2 substituent on the equilibrium position has been studied by Goya, Ochoa, and colleagues (76JHC793; 86FES862; 86MRC444), who later summarized their findings in a review [88AHC(44)81]. Using ^1H, ^{13}C, and ^{15}N NMR spectroscopy, these authors showed that, surprisingly, 4-unsubstituted 3,5-diamino-1,2,6-thiadiazine 1,1-dioxide **123** ($R^1 = R^3 = NH_2$, $R^2 = H$) exists in DMSO-d_6 solution mainly as the 4-CH tautomer **123c.** The signals corresponding to this tautomer have also been observed in the spectra of the compounds **123** ($R^1 = R^3 = NH_2, R^2 =$ NHCOMe, NHCOPh, or $NHCOC_5H_{11}$), although the degenerate tautomers **123a** and **123b** still predominate in these cases. Nevertheless, most of the 4-substituted derivatives studied, such as those with $R^2 = NH_2$, NO_2, $NHCOCF_3$, or $NHSO_2Tol$, were found to exist in DMSO-d_6 solution exclusively as mixtures of **123a** and **123b** tautomers.

The rate of the equilibrium is greatly accelerated upon addition of an acid (e.g., CF_3COOH) [86MRC444; 94JCS(P2)1561], although this does not affect the tautomeric ratio.



SCHEME 34

Quantum-chemical calculations have been carried out for **123** [R^1 = Me, $R^2R^3 = (CH_2)_n$, n = 3, 4] using two semiempirical methods: AM1 and PM3 [94JCS(P2)1561]. The heats of formation (ΔH_f°) and the population of each tautomer were calculated, the latter being in good agreement with experimental data.

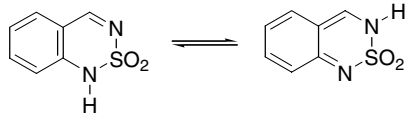
NMR signal broadening, ascribed to the hydrogen exchange between the 6 and 4 positions, was observed on heating DMSO-d_6 solutions of 3-oxo-1,2,6-thiadiazines **124** (R = *n*-Bu, Ph; R′ = Me) [88JCS(P2)859]. This was attributed to a dynamic equilibrium **124a** ⇌ **124c** ⇌ **124b** (Scheme 34). When R′ = NH_2, the equilibrium is shifted entirely toward the 4-CH tautomer **124c** (R = *n*-Bu, Ph) in all the solvents used. For R′ = Me, the content of the 4-CH tautomer **124c** depends significantly on the polarity of a solvent (the relative amount of **124c** increases on passing to a less polar solvent) and on the nature of the R substituent (it is almost double on replacing R = *n*-Bu with R = Ph in $CDCl_3$).

For the benzo-fused derivative of the parent 1,2,6-thiadiazine 1,1-dioxide, the aromatic tautomer **125a** (Scheme 35) was found to be the most stable (82JOC536).

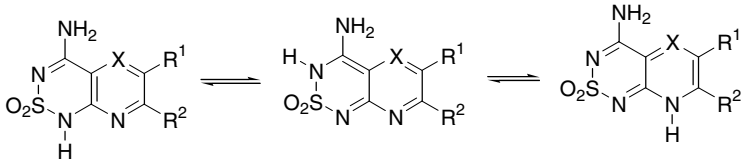
Tautomeric equilibrium in amino-substituted 1,2,6-thiadiazine 1,1-dioxides fused with five- or six-membered nitrogen heterocycles has been extensively studied by Goya and colleagues. No amino group participation in tautomeric equilibria in these systems has been observed.

Aminopyridothiadiazine 2,2-dioxides **126** (X = CR^3, R^1 = H) were found to exist in water (from UV spectra) and in DMSO-d_6 (from ^{13}C NMR spectra) exclusively as N(8)H tautomers **126c** [86CS607; 88AHC(44)81]. This was explained by the strongly acidifying effect of the SO_2 function, which makes the formation of a tautomer with the more distant acidic proton energetically more favorable.

Later, more detailed studies of analogous pyrazine-fused derivatives **126** (X = N) using UV, ^{13}C, and ^{15}N NMR spectroscopies showed that the position of



SCHEME 35



126a **126b** **126c**

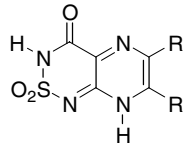
SCHEME 36

tautomeric equilibrium in these systems depends largely on the solvent polarity and on substitution in the pyrazine ring. The N(3)H isomers **126b** have not been observed by any method; and it was shown that in DMSO, $CHCl_3$, MeOH, and acetone solutions, N(1)H tautomers **126a** strongly predominate, independently of the substitution [88H(27)2201; 99JMC1698; 00JMC4219]. The broad signals in ^{15}N NMR spectra are due to the equilibrium **126a** $\rightleftharpoons$ **126c**, which is slow enough on the NMR time scale. However, in water solution the tautomeric ratio depends on 6,7-substitution (R^1 and R^2). While the compounds with electron-donating groups in the pyrazine ring ($R^1 = R^2 =$ Me, Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$) exist as N(8)H tautomers **126c** [88H(27)2201], unsubstituted derivatives ($R^1 = R^2 = H$) and those with electron-withdrawing substituents [$R^1 =$ CH(=NOR), $R^2 = H$; $R^1 = R^2 =$ 4-ClC_6H_4, 4-$O_2NC_6H_4$] were found to be mixtures of **126a** and **126c** tautomers [88H(27)2201; 91H(32)279; 98JCS(P2)1889]. The introduction of a thienyl group ($R^1 = R^2 =$ 2-thienyl) shifts the equilibrium completely toward the N(1)H tautomer **126a** [88H(27)2201].

The results of the gas-phase calculations of these three possible isomers **126a–c** ($X = N, R^1 = R^2 = H$), using semiempirical (AM1 and PM3), density functional theory (BLYP/6-31G*), and *ab initio* MO (RHF/6-31G*) methods, all showed that the most stable tautomer is the N(1)H **126a** with a very large energy difference from the second most stable tautomer N(8)H **126c** ($\Delta E =$ 10–15 kcal/mol) [98JCS(P2)1889]. The least stable tautomer is N(3)H **126b** ($\Delta E =$ 12–18 kcal/mol). These results indicate that only the tautomer **126a** should be present in the gas phase or in apolar media; this is in good agreement with experimental findings. Calculation of the dipole moments showed that all these structures are highly polar, the most polar being N(8)H isomer **126c** (9–11 Db), followed by **126b** (7–10 Db), and finally **126a** (6–8 Db). This enhanced polarity causes **126c** to form stronger hydrogen bonds on dissolution in water and, thus, on coordination with two molecules of water, decreases the energy difference between **126a** and **126c** to about 1 kcal/mol. This explains the significant shift of the tautomeric equilibrium toward **126c** in aqueous solutions.

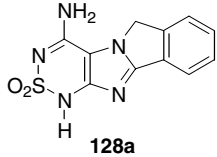
Independently of the substitution, in the solid state compounds **126** (X = N) were found to exist exclusively as N(1)H tautomers **126a** [88H(27)2201].

When the amino group is substituted by a keto group, the shift of the equlibrium toward the N(8)H tautomer is observed. Thus, in contrast to **126** (X = N), for which N(1)H tautomer **126a** predominates in MeOH solution [88H(27)2201], 4-oxo derivatives **127** exist in MeOH as N(8)H tautomers shown (84JHC861).

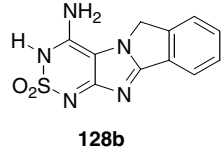


127

Imidazole-fused thiadiazine **128,** in principle, can exist as four possible tautomers **128a–d.** Experimental studies using UV spectroscopy and pK_a determination have shown that this compound exists in aqueous solution exclusively as tautomer **128a** [98H(48)1833]. Theoretical *ab initio* MO (RHF/6-31G*) and BLYP/6-31G* calculations indicated that the tautomers **128a** and **128b** are more stable than the nonaromatic tautomers **128c** and **128d** with respect to relative stability and dipole moment. After the consideration of the solvent effect, the relative energies (compared to **128a**) shown below were obtained. These results confirm the experimental findings and indicate that only the form **128a** should be present both in gas phase and in water.

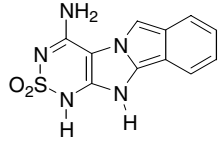


128a

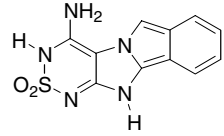


128b

	128a	**128b**
ΔE: RHF/6-31G* (BLYP/6-31G*) (kcal/mol)	0.0 (0.0)	9.2 (11.6)



128c

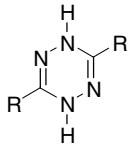


128d

	128c	**128d**
ΔE: RHF/6-31G* (BLYP/6-31G*) (kcal/mol)	41.3 (15.9)	41.0 (15.9)

K. DIHYDROTETRAZINES

The possibility of annular tautomerism in dihydro derivatives of 1,2,4,5-tetrazines has been investigated mostly in the solid state. X-Ray structural determinations showed unambiguously that symmetrical 1,4-dihydro tautomers of type **129** are preferred for all dihydro-1,2,4,5-tetrazines with aryl, heteroaryl, or carboxylic groups in positions 3 and 6, including neutral molecules [82JCS(P1)1165; 85JHC643], salts (97P2871), and transition metal complexes [91AX(C)2448]. The predominance of the 1,4-dihydro tautomer of dimethyl 1,2,4,5-tetrazine-3,6-dicarboxylate **130** in solution has been indirectly confirmed by condensation of this tetrazine with isocyanates leading exclusively to the formation of the linear annulation product **131** (Scheme 37) (92S879).

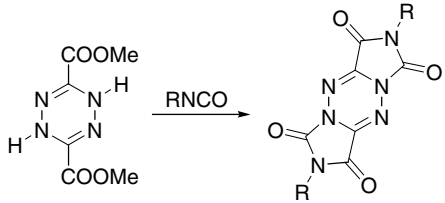


129

Interestingly, an alkyl substituent at the 6 position stabilizes the 1,6 tautomer, which was found to be the sole form both in the solid state (82JOC2856) and in solution (as confirmed by ^{1}H and ^{13}C NMR and IR spectroscopy) [76AHC1, p. 79; 81JOC2138; 96JCR(S)174].

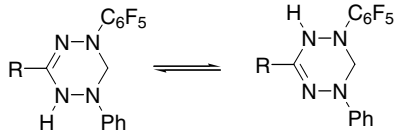
Tautomerism in tetrahydrotetrazines (also known as leucoverdazyls) has been studied by NMR spectroscopy, which showed that unsymmetrically substituted aryl leucoverdazyls **132** exist in solution in a tautomeric equilibrium of two stable forms (Scheme 38) (85KGS1425).

The tautomer **132a** usually slightly predominates in solution, with the ratio only slightly affected by the polarity of a solvent for most of the solvents studied. Somewhat greater stability of the **132a** form (**132a : 132b** = 70 : 30) was observed



130 **131**

SCHEME 37



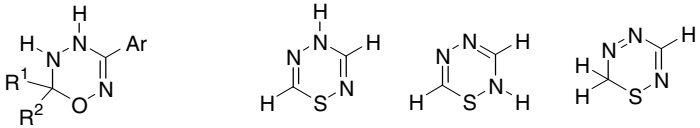
132a **132b**

SCHEME 38

only in CD_3CN solution. Negligible changes in the tautomeric ratios with the temperature variations were explained by a low value of the free energy of the tautomeric equilibrium (ΔG was calculated to be only 0.36 kcal/mol). The free energy of interconversion activation, calculated from the coalescence temperature, was found to be 18–20 kcal/mol.

L. OXATRIAZINES AND THIATRIAZINES

Just a few examples of oxatriazine systems capable of existing in different tautomeric forms, such as **133** [87H(26)2199], have been reported. However, according to their NMR and IR spectra, these compounds exist as preformed, and no annular tautomeric interconversions in oxatriazine series have yet been observed.

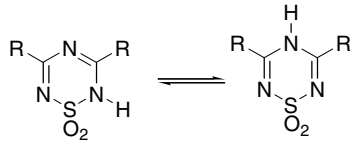


133 **134a** **134b** **134c**

The thermodynamic stabilities of three possible annular tautomers of the parent 1,2,4,5-thiatriazine **134** were compared using *ab initio* HF/6-31G* calculations (00JOC931). The 4*H* isomer **134a** appears to be the most stable (it is more stable than **134b** by 11.6 kcal/mol and more stable than **134c** by 15.5 kcal/mol), presumably because it allows low-energy distortion from planarity and formation of the boat conformation.

The 1,2,4,6-thiatriazine system is the most common in all the oxa- and thiatriazine series, and some investigations of the tautomeric behavior of 1,2,4,6-thiatriazine 1,1-dioxides **135,** which can exist as N[2(6)]H **135a** and N(4)H **135b** tautomers (Scheme 39), have been performed.

The parent thiatriazine **135** (R = H) exists predominantly in the 4*H* form **135b,** as shown by its ^{1}H NMR spectrum or by comparing its ^{13}C and ^{15}N NMR data with



135a **135b**

SCHEME 39

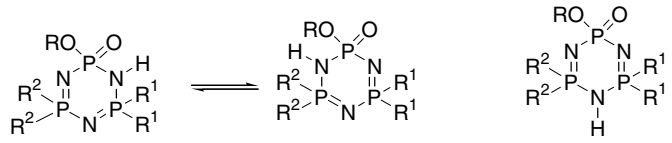
those of the corresponding 4-Me-substituted derivative (86MRC444). The symmetrical structure **135b** was also established for 3,5-di(trifluoromethyl)-1,2,4,6-thiatriazine **135** (R = CF_3) on the basis of a unique signal in the ^{19}F NMR spectrum [88AHC(44)81, pp. 156–157].

Later, *ab initio* calculations (on the 3-21G* and STO-3G* levels) were used to study the annular tautomerism in unsubstituted **135** (R = H). The 4*H* tautomer **135b** was found to be more stable [by 5.1 kcal/mol (STO-3G*) or 2.8 kcal/mol (3-21G*)] than **135a,** which is in agreement with all the previous experimental data [90H(31)197].

M. OTHER HETEROCYCLIC SYSTEMS

The tautomeric behavior of six-membered azaphospha heterocycles **136** has been studied in solution by variable-temperature ^{31}P NMR [82JCS(D)1549].

Tautomeric equilibrium in the symmetrical phenoxy-substituted derivative **136** (R = Ph, $R^1 = R^2$ = OPh) is fast at ambient temperature on the NMR time scale; however, at −84°C the proton exchange becomes frozen and both annular tautomers **136a** and **136b** can be observed (Scheme 40). The similar exchange was also found for *P*-aryl-substituted **136** (R = Me, Et, Ph; $R^1 = R^2$ = Ph). In these cases, the equilibrium is very slow, even at ambient temperature, which was attributed to increased steric demands of four phenyl substituents. Unsymmetrically substituted azaphosphorinanes ($R^1 \neq R^2$) provide even more interesting examples. These compounds (R^1 = Ph; R = Me, *n*-Pr; R^2 = MeO, *n*-PrO) were found to



136a **136b** γ-form **136c**

SCHEME 40

exist as mixtures of two α forms, **136a** and **136b,** with the form **136a** predominating. Basicity calculations carried out for **136** (R^1 = Ph, R = Me, R^2 = MeO) confirmed the enhanced stability of these α forms compared to the less favored γ form **136c.** The increasing proportion of the tautomeric form **136b** on passing from R^2 = MeO to R^2 =*n*-PrO was explained by the greater base-strengthening effect of the *n*-propoxy group compared to that of the methoxy group.

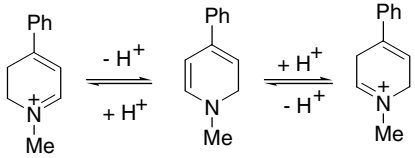
IV. Azine Cations

A. Pyridines and Quinolines

Various amino-substituted pyridines have been compared with respect to acidity (pK_{HA}, deprotonation at the amino group) and basicity (pK_{BH^+}, protonation at the ring nitrogen). As in amino-substituted heterocycles, the amino group is not the favored site of protonation; there is no correlation between pK_{HA} and pK_{HB^+} since protonation and deprotonation do not occur at the same site. The basicity of such amino groups was calculated using the Hammett equation with regard to the effect of the position of the ring nitrogen on the basicity and acidity of the 2- and 4-aminopyridines (78JOC3123). The determination of the equilibrium position of 2-aminopyridine/acetic acid - 2-aminopyridinium acetate in the acid–base complex was carried out by IR spectroscopy (97NKK100).

Basicity measurements of 4-amino-2,2′-bipyridyl and some of its N-substituted derivatives have shown that, when an electron-withdrawing substituent is present, the protonation occurs at the distant ring and derivatives with electron-donating substituents are protonated at N(1) of the substituted ring [78JCS(P2)1215].

An MNDO study of the oxidation process for 1-methyl-4-phenyl-1,2,3,6-tetrahydropyridine (MPTP) has been performed to explain the occurrence of 2,3-dihydropyridinium salt **137a** (but not the 2,5-isomer **137b**) in various tissue preparations (88JA6337). Calculations of semiempirical heats of formation (ΔH_f) showed that the isomer **137a** is more stable than **137b** by about 4.7 kcal/mol. The indicated equilibrium between **137a** and **137b** via **138** (Scheme 41) is known to occur *in vitro* since treatment of **137a** with nucleophiles (e.g., cyanide) gives rise to both the 5- and 2-substituted tetrahydropyridines.



137a **138** **137b**

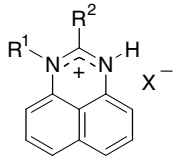
Scheme 41

B. Pyrimidines and Benzo-Fused Derivatives

Using ^{13}C NMR measurements, the percentage of the N(1) or N(3) monoprotonated form of methyl and amino(methyl) di- or trisubstituted pyrimidines has been evaluated. In TFA the form protonated on the nitrogen atom *para* to the methyl group predominates (~71%). In the case of 4-amino-6-methylpyrimidine, 4-amino-2,6-dimethylpyrimidine, and 4-amino-5,6-dimethylpyrimidine, the influence of the amino group predominates over that of the methyl group and the percentage of the form protonated on the nitrogen atom *para* to the amino group is increased to 95, 96, and 90%, respectively (77JA6838).

Natural-abundance ^{15}N NMR spectroscopy has been used to determine the site of protonation in vitamin B_1. The most common representations of vitamin B_1 show protonation at the N(3) atom of the pyrimidine ring or at the 4-amino group. Selective decoupling of individual protons of vitamin B_1 in water, D_2O, and ethylene glycol permitted assignment of the nitrogen resonance signals and hence the determination of the protonation site, which was found to be at the N(1) atom of the pyrimidine ring (77JA6423).

The ^{13}C NMR spectra of some 1- and 2-substituted perimidinium salts **139** are discussed and assigned. Several 2-substituted derivatives possess ^{13}C and ^{1}H NMR spectra that reflect relatively slow prototropic tautomerism due to hydrogen bonding with a solvent, intramolecular hydrogen bonding, or enhanced delocalization of the nitrogen lone pair (88MRC191).



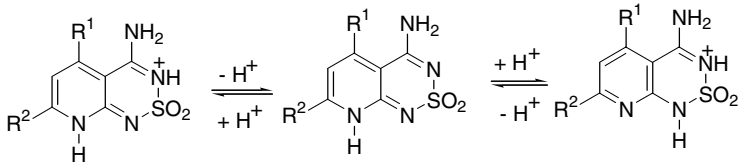
R^1 = H, Me
R^2 = H, Cl, SMe, SEt, NH_2
X = Br, I, $OCOCF_3$

139

C. Other Azine Cations

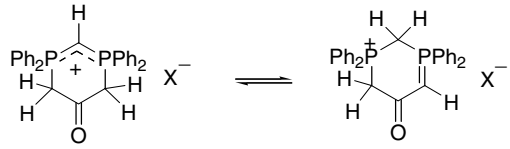
Protonation of pyrazine *N*-oxides takes place at the unsubstituted ring nitrogen as revealed by examination of their UV spectra and ionization constants in water. The same holds for unsubstituted quinoxaline *N*-oxide and the 3-amino derivative. Pyrazine and quinoxaline di-*N*-oxides are protonated at one *N*-oxide oxygen atom (74KGS1554).

Protonated aminopyrido[2,3-*c*]-1,2,6-thiadiazine 2,2-dioxides exist as mixtures of two cationic forms, **140a** and **140b** (Scheme 42), as was concluded from



140a **140b**

SCHEME 42



141a **141b**

SCHEME 43

comparisons of the UV spectra of these species with those of the corresponding N(1) and N(8) methyl derivatives [86CS607; 88AHC(44)81].

According to its IR spectrum, phospharinane **141** exists in the solid state exclusively as the tautomer **141b** possessing the localized electronic structure (Scheme 43) (83UK1761). However, by means of NMR and IR spectroscopy, it was shown that in $CDCl_3$ solution the delocalized structure **141a** is also present, although at a low relative concentration.

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