(ii) As it can be readily seen in Figure 4, the maximum overlap in the $\sigma(C_1-C_2)$ bond orbital in the transition state occurs out of the internuclear axis, and that constitutes another important destabilization factor. This is due to the fact that C_2 is forced to maintain an average sp hybridization along the reaction coordinate, while the transition state geometry imposes a $C_1-C_2-O_3$ angle of 150.3°. The $sp^{0.40}$ hybrid orbital at C_2 is then forced out of the C_1-C_2 internuclear straight line in order to maintain a bonding direction approximately opposite to that of the $sp^{1.41}$ component of C_2 in the $\sigma(C_2-O_3)$ bond orbital. In conclusion, the visualization of an elementary reaction in terms of LMOs results in a new way of looking at chemical reactions (provided that the wavefunction remains monodeterminantal along the reaction path[38]), which could be summarized as follows: any elementary chemical reaction involves a geometrical rearrangement of the nuclei along the reaction coordinate, together with a relocation and/or rehybridization of the LMOs (which represent the "classical" electron pairs) of the system. A substantial part of the energetic barrier associated to the transition state could then be due to the fact that *at least one electron pair*, which will be always presumably a bonding one, *is not able to follow adequately the movement of the nuclei*, so that it is not possible for the transition state to maintain a bonding situation comparable to that of reactants and products. An important point that arises from the present study is that *the bonds which are mainly responsible for the energetic destabilization of the transition state are not necessarily those which are made or broken during the reaction*, contrary to what is implied or stated in elementary textbooks; in the present case, the bond orbital which is the most destabilized in the transition state is the σ-component of the acetylenic C_1-C_2 triple bond, which does not "intervene" essentially in the reaction since it ends up in the products also as a σ-component of a multiple bond between the same atoms (i.e., the σ-component of the C_1-C_2 double bond of ketene). It would be interesting to know if this fact is more general and work along these lines is currently in progress in our laboratory.

Acknowledgment. The calculations were performed with the IBM 3083 computer at the "Centre d'Informàtica de la Universitat de Barcelona". Financial support from the CAICYT (Grant 3218/83) is gratefully acknowledged. We also thank Dr. Juan C. Paniagua and Dr. Santiago Olivella for helpful discussions.

Registry No. **2a**, 927-80-0; **2b**, 36678-59-8; **2c**, 89489-28-1; **3a**, 14273-06-4; **3b**, 89489-29-2; **3c**, 89896-71-9; 4, 14272-91-4; D_2, 7782-39-0.

Supplementary Material Available: Cartesian coordinates of the optimized molecular structures and relevant bond indices in the optimized TS's at the MINDO/3, MNDO, and AM1 levels and the AM1 LMOs for reactant, transition state, and products in the concerted elimination of ethylene from ethoxyethyne (36 pages). Ordering information is given on any current masthead page.

(38) For open shell systems, the problem of localizing the molecular orbitals is not so well defined as in the case of closed shell ones, and there is not a unique way of tackling it. See for instance: (a) Schlosser, H. *Int. J. Quantum Chem.* **1971**, *5*, 683. (b) Hirst, D. M.; Lirington, M. E. *Theor. Chim. Acta* **1970**, *16*, 55.

Dipolar Cycloaddition Reactions of Diazoazoles with Electron-Rich and with Strained Unsaturated Compounds

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Regiospecific net 1,7-cycloaddition reactions of electron-rich or strained olefins and electron-donor acetylenes occur readily (−70 to −10 °C) with diazoazoles having nitrogen in the 2-positions of their azole rings. Diazoazoles such as 5-*tert*-butyl-3-diazo-3*H*-pyrazole (**20**), 3-diazo-5-phenyl-3*H*-pyrazole (**24**), 2-diazo-2*H*-imidazole (**28**), 4,5-dicyano-2-diazo-2*H*-imidazole (**12**), 4-diazo-4*H*-imidazole (**63**), 4-diazo-5-phenyl-4*H*-1,2,3-triazole (**70**), 5-cyano-4-diazo-4*H*-1,2,3-triazole (**74**), 3-diazo-3*H*-1,2,4-triazole (**76**), and 3-diazo-5-phenyl-3*H*-1,2,4-triazole (**79**) thus usually add effectively to unsaturated reactants such as enamines, 1-alkoxyalkenes, ketene acetals, aryl isocyanates, norbornene, and norbornadiene to give new 1,7-cycloadducts. These cyclization reactions may be followed by tautomerization processes leading to new stabilized fused heterocycles or by elimination to novel highly delocalized heteroaromatic derivatives. 4,5-Dicyano-2-diazo-2*H*-imidazole (**12**) undergoes various accelerated cycloadditions to unsaturates and adds to norbornene and norbornadiene by exclusive exo dipolar proceses. Addition of activated acetylenes to representative α-diazoazoles also results in regiospecific 1,7-cyclization to give stabilized fused azolo heterocycles.

Regiospecific 1,7-cycloaddition reactions (eq 1 and 2) of 3-diazo-3*H*-pyrazoles (1, X = N, Y and Z = C–R), 4-diazo-4*H*-1,2,3-triazoles (1, X and Y = N, Z = C–R), and related diazoazoles with electron-rich olefins and acetylenes were discovered in this laboratory[1] and by Ege[2] and by Dürr[3] and their colleagues. Such additions were theorized to occur directly by thermally allowed ($4n + 2$ electron) 1,7-cyclic processes and/or by allowed ($4n + 2$ electron) 1,3-cyclizations followed by [1,5]-sigmatropic rearrange-

(1) (a) Shechter, H.; Magee, W. L. *J. Am. Chem. Soc.* **1977**, *99*, 633. (b) Magee, W. L., *Diss. Abstr. Int. B* **1975**, *34*, 3837.

(2) (a) Ege, G.; Gilbert, K.; Franz, H. *Synthesis* **1977**, 556. (b) Ege, G.; Gilbert, K. *Tetrahedron Lett.* **1979**, 1567.

(3) Dürr, H.; Schmitz, H. *Chem. Ber.* **1978**, *111*, 2258.

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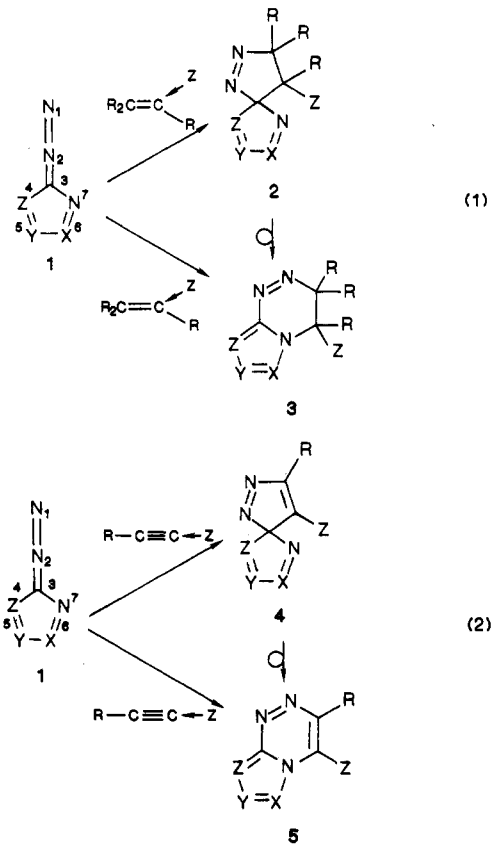
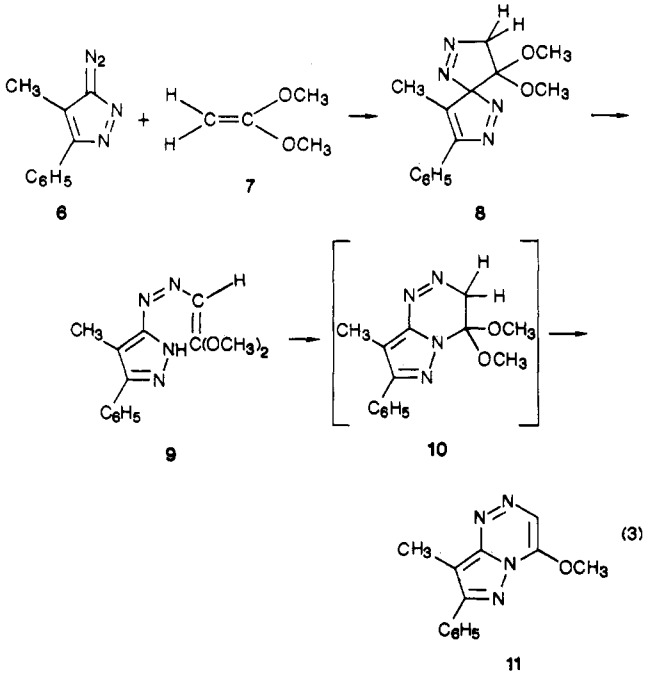


(1)

(2)

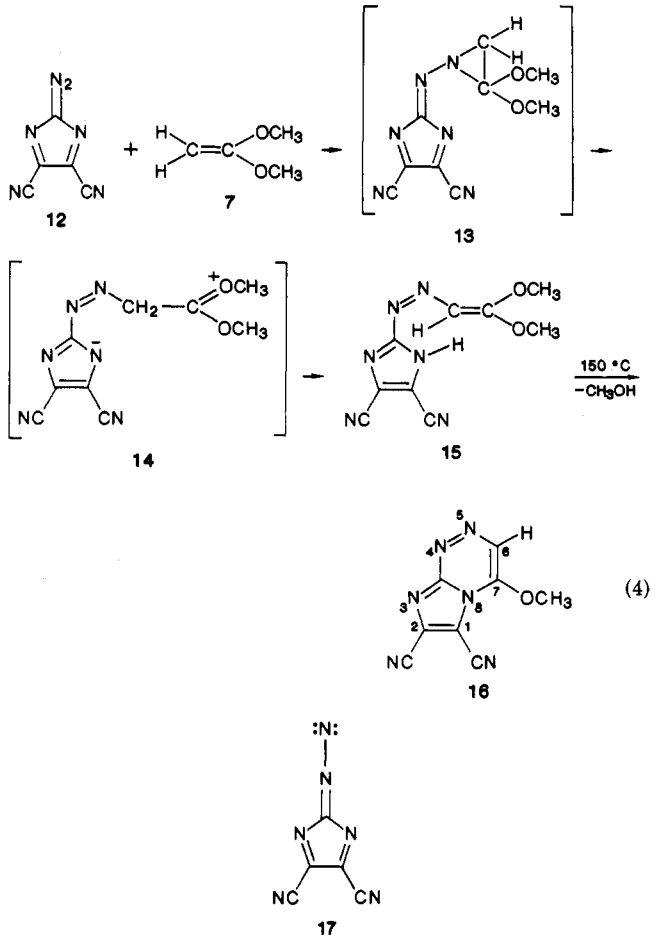
ments or/and ring openings and reorganization.[1] In a subsequent study of 3-diazo-3*H*-pyrazoles (1, X = N, Y and Z = C–R) and 3-diazo-3*H*-1,2,4-triazoles (1, X and Z = N, Y = C–R), Padwa et al.[4] found that 3-diazo-4-methyl-5-phenyl-3*H*-pyrazole (**6**) undergoes 1,3-dipolar addition to 1,1-dimethoxyethene (**7**) to give spiro-3*H*-pyrazole **8**, an isolable product, which isomerizes to **9** and then to the presumed intermediate **10**, which eliminates to pyrazolo-[5,1-*c*][1,2,4]triazine **11** (eq 3). Net 1,7-dipolar cycloadducts are also obtained from **6** and electron-deficient



(3)

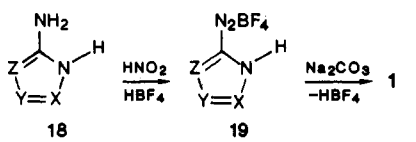
(4) (a) Padwa, A.; Kumagai, T. *Tetrahedron Lett.* **1981**, *22*, 1199. (b) Padwa, A.; Kumagai, T.; Woolhouse, A. D. *J. Org. Chem.* **1983**, *48*, 2330.

unsaturates such as acrylonitrile, methyl acrylate, and dimethyl acetylenedicarboxylate.[5] Of special note is that 4,5-dicyano-2-diazo-2*H*-imidazole[6] (**12**, eq 4) is reported to react with 1,1-dimethoxyethene (**7**) at 25 °C to give 2-(imidazylazo)-1,1-dimethoxyethene **15** (82%), which thermolyzes (150 °C) with ring closure and loss of methanol to yield 7-methoxyimidazo[2,1-*c*][1,2,4]triazine-1,2-dicarbonitrile (**16**, 85%).[7] The reaction of **12** to yield **15** is of additional interest in that **12** is theorized to undergo 1,1-cycloaddition as a nitrene (**17**) via **13**.[7]



(4)

We now report the behavior of varied diazoazoles with electron-rich and strained unsaturated derivatives. The diazoazoles (**1**) were usually prepared by diazotization of aminoazoles (**18**) with nitrous and tetrafluoroboric acids and neutralization of the subsequent azolediazonium tetrafluoroborates (**19**, eq 5). Our investigations result



(5)

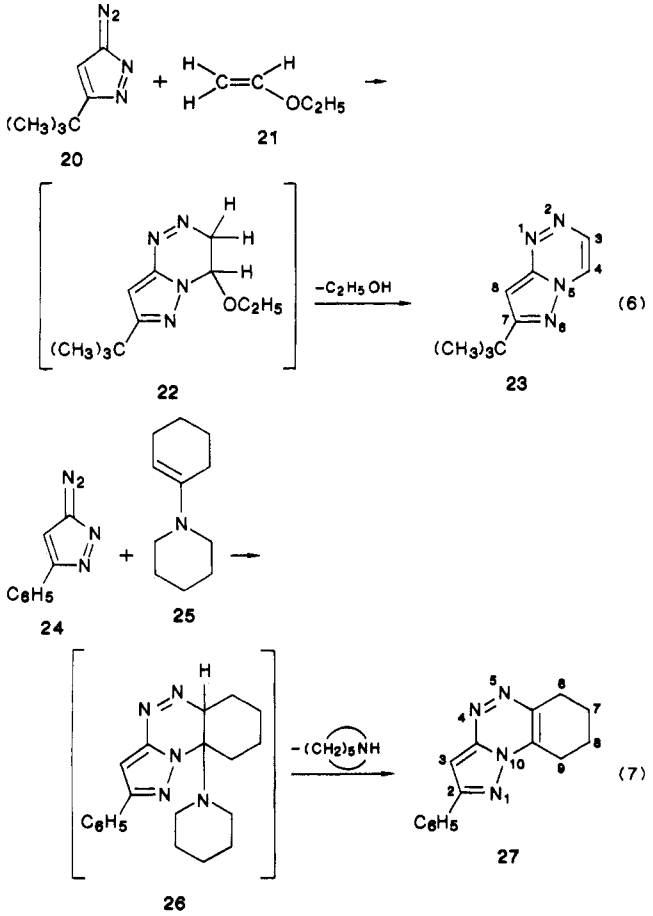
in general methodology for preparing various heterocycles and reveal that (1) nitrogen in a 2-position of a diazoazole leads to effective 1,7-cycloaddition to a multiply bonded center, (2) 1,7-cycloaddition occurs better with electron-deficient diazoazoles and with unsaturates that are electron-rich and/or sterically strained, (3) the addition reactions are remarkably regio- and stereoselective, and (4)

(5) Elmoghayar, M. R. H.; Fahmy, S. M.; Ibraheim, M. K. A.; Alnima, H. H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 216.
(6) Prepared by the method of Sheppard, W. A.; Webster, O. W. *J. Am. Chem. Soc.* **1973**, *95*, 2695.
(7) Padwa, A.; Tohidi, M. *J. Chem. Soc., Chem. Commun.* **1984**, 295.

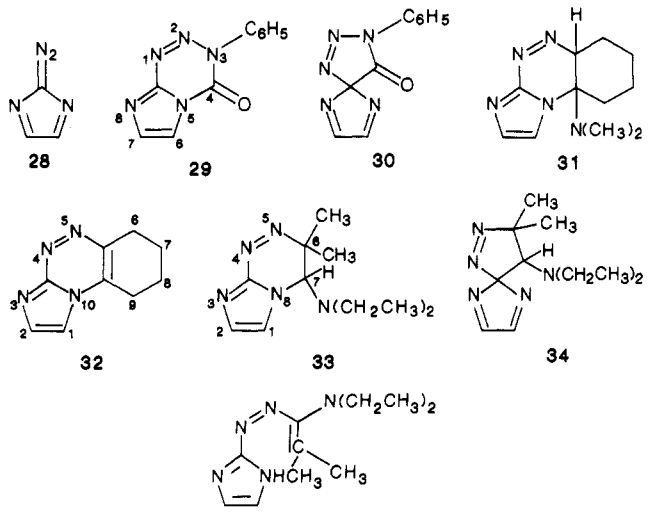
such cycloadditions are frequently accompanied or followed by isomerization, rearrangement, and/or elimination processes. The results are also of interest in that conventional theory rationalizes the regiochemistry of direct 1,7-cycloadditions or/and 1,3-cycloaddition processes in which there is electrical control in subsequent [1,5]-sigmatropic rearrangements.[8]

Results and Discussion

Our investigation of cycloaddition reactions of diazoazoles began with 5-*tert*-butyl-3-diazo-3*H*-pyrazole (**20**) and 3-diazo-5-phenyl-3*H*-pyrazole (**24**).[1] Diazoazole **20** does not react with varied alkenes, cycloalkenes, and conjugated dienes with nitrogen retention.[9] Net 1,7-cycloaddition (eq 6) of **20** and ethyl vinyl ether (**21**) occurs at −20 °C with elimination of ethanol on warming **22** to yield pyrazolo[5,1-*c*][1,2,4]triazine **23** (>60%). Similarly, **24** and 1-piperidinylcyclohexene (**25**) react by addition and then elimination of piperidine from **26** to give pyrazolotriazine **27** (eq 7). Products **23** and **27** are assigned, as are all others in this research (see the Experimental Section), from their analyses, by spectral methods, on the basis of their origins, and upon application of mechanistic principles.[1-4,7,8]



Cycloadditions of 2-diazo-2*H*-imidazole (**28**) were then investigated. Diazoazole **28** is an effective enophile with isocyanates and with electron-rich unsaturates such as enamines and ketene acetals.[10] Thus, phenyl isocyanate reacts with **28** at −70 °C to give imidazo[2,1-*d*]-1,2,3,4-tetrazin-4(3*H*)-one **29** (80%);[11a] 1,3-cycloadduct **30** was not detected in the cycloaddition product.[11b] Further, net 1,7-cyclization of 1-(dimethylamino)cyclohexene with **28** occurs, apparently with elimination of dimethylamine from **31**, to yield imidazotriazine **32**.[12] 1,7-Cycloaddition of 1-(diethylamino)-2-methylpropene also takes place with **28** (>53%) at −60 to −10 °C to give a yellow adduct assigned as 6,7-dihydroimidazotriazine **33**[13] rather than isomer **34** or **35**.



Of interest is that **28** has been found to react with 1,1-dimethoxyethene (**7**) by net 1,7-cycloaddition at −15 °C and then apparently by *hydrogen migration* in **36** to yield white crystals assigned as 1,4-dihydro-4,4-dimethoxyimidazo[2,1-*c*][1,2,4]triazine[14] (**37**) or, less likely, its NH tautomer **38** (eq 8). That the adduct is **37** rather than **38** is proposed on the basis that the aromaticity of the imidazole unit controls the stability and thus the structure

(8) (a) Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 565 and 633. (b) Huisgen, R. *J. Org. Chem.* **1968**, *33*, 2291; **1976**, *41*, 403. (c) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: New York, 1976. (d) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781.

(9) Storage of **20** or **24** at 0 °C with 1-octene, 2,3-dimethyl-2-butene, 2-methyl-1-butene, cyclohexene, cyclopentene, 1,3-butadiene, cyclopentadiene, and dimethyl acetylenedicarboxylate does not give tractable products of cycloaddition with nitrogen retention. The products of carbenic reactions of **20** and **24** with olefins will be reported in a subsequent publication.

(10) Decomposition of **28** occurs at −70 °C to −20 °C rather than cycloaddition with cyclohexene, cyclopentene, 2,3-dimethyl-2-butene, phenylacetylene, *tert*-butyl isocyanate, *p*-toluenesulfonyl isocyanate, phenyl isothiocyanate, and chloroketene.

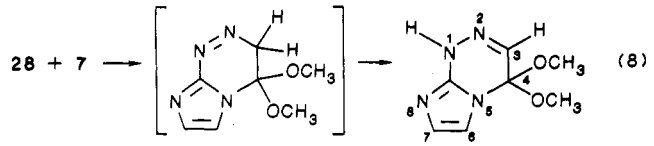
(11) (a) The structure of **29** is based primarily on its ^1H and ^{13}C NMR spectra (see the Experimental Section). Also, the appearance of two narrow ^1H NMR doublets (δ 7.80, J = 1.45 Hz; 7.92, J = 1.47 Hz) in the olefinic CH region indicates the presence of a 1,2-disubstituted imidazole. The off-resonance decoupled ^{13}C NMR spectra of the adduct consists of five doublets, a reflection of five carbon atoms each bearing one hydrogen. The phenyl ring can contribute a maximum of three doublets (one for the two *ortho*, one for two *meta*, and one for *para* carbons, and thus the remaining two doublets must belong to the two imidazole carbons (C_6 and C_7) bearing hydrogens. The IR carbonyl absorption for **29** (1745 cm^{-1}) is also consistent with the structural assignment. (b) In **30**, the two imidazole protons are magnetically equivalent and should appear as a ^1H NMR singlet. Also the imidazole carbons carrying these protons are equivalent and should show up as a single doublet in the off-resonance decoupled ^{13}C NMR spectra of **30**. The above NMR features were not found in the product of reaction of **20** and phenyl isocyanate.

(12) Attempts were not made to effect reaction such that the product(s) of cycloaddition were isolated. It was found best preparatively to conduct reaction of **28** with 1-(dimethylamino)cyclohexene and workup such that elimination occurs to give **32**.

(13) In the present research azo adducts such as **33** have always been found to be yellow.

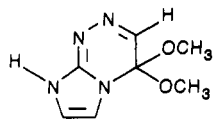
(14) (a) Net 1,7-cycloaddition of a diazoazole with an electron-rich olefin and subsequent tautomerization was first discovered by W. L. Magee[1b,14b] in that **24** reacts exothermically with **7** at −78 °C to −20 °C to give 7-*tert*-butyl-1,4-dihydro-4,4-dimethoxypyrazolo[3,2-*c*][1,2,4]triazine (a white solid, mp 176 °C) in 95% yield: IR (KBr) 3400 and 1490 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.23 [s, 9 H, C(CH_3)$_3$], 305 (s, 6 H, 2 OCH_3), 5.3 (s, 1 H), 6.3 (s, 1 H), and 11.1 (s, 1 H, N*H*); mass spectrum calcd 238, found *m/e* 238. (b) Magee, W. L. Ph.D. Dissertation, The Ohio State University, Columbus, Ohio, 1974.

of the product. Further, cycloadduct **37** from **7** and **28** is decidedly different in type as that reported[7] from **7** and **12** (eq 4).[15]



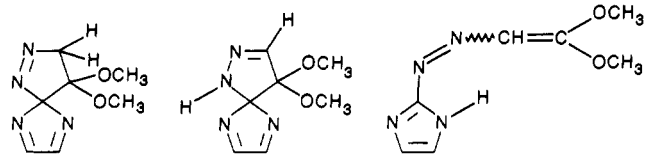
(8)

36 **37**



38

The structure as **37** (or **38**) is derivable from mass and IR spectral data and from NMR absorptions as summarized in the Experimental Section. The assignment as **37** (or **38**) is consistent with ^{1}H NMR evidence that the methoxy groups are equivalent and there are signals for three olefinic CH moieties. That the product has three nonequivalent hydrogens on sp^2 carbon atoms is supported by the three doublets (centered at δ 107.55, 126.48, and 126.78) in the olefinic region of the off-resonance decoupled ^{13}C NMR spectrum. Of significance also is that the ^{13}C NMR signal at δ 100.78 (singlet) is assignable to C_4, one of the sp^3 carbons in the adduct. The downfield distinguishing NMR absorption for C_4 thus arises from the effects of its nitrogen, its sp^2 carbon, and its two oxygen substituents. Further, the ^{1}H NMR and the ^{13}C NMR spectra of the product cannot be accommodated by structures **39**–**41** as explained as follows. The ^{1}H NMR

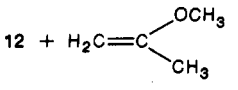


39 **40** **41**

spectrum of **39** would exhibit only one singlet for olefinic H, and the off-resonance decoupled ^{13}C NMR would display a single doublet for olefinic C. Structure **40** is expected to give two ^{1}H NMR and two ^{13}C NMR signals in the olefinic region. In isomer **41**, the two methoxy groups are magnetically nonequivalent whereas the two hydrogens of the imidazole ring and the corresponding carbons are equivalent. Therefore, the ^{1}H NMR spectrum of **41** should consist of two singlets for olefinic H and two singlets for its two methoxy groups. The off-resonance decoupled ^{13}C NMR spectrum of **41** should have two doublets and two singlets in olefinic-C and two quartets in sp^3-C regions. These expected features for **41** were not observed and constitute the basis for the rejection of the prior assignment.[15]

Reactions of 4,5-dicyano-2-diazo-2*H*-imidazole (**12**) with various olefins have also been investigated. A prime objective of this effort was to determine the effects of a strong electron-withdrawing group (C≡N) on the abilities of a 2-diazoimidazole to undergo cycloaddition. As will be illustrated, **12** is kinetically and preparatively superior to **28** for cycloadditions with electron-rich unsaturates.

Reaction of **12** has thus been found to occur effectively at −15 °C with 2-methoxypropene (**42**) and with 1-ethoxycyclohexene (**45**) by 1,7-cycloaddition and *tautomerization* to give white crystalline imidazotriazines assigned as **44** (52%, eq 9) and **47** (80%, eq 10). That the product



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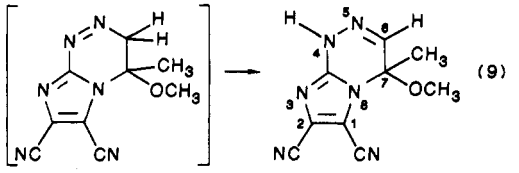
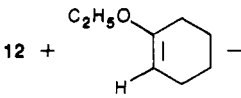


(9)

43 **44**



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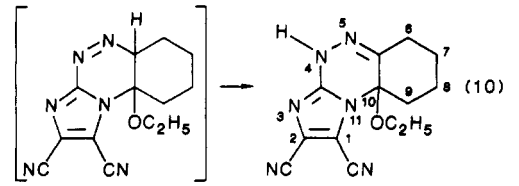


(10)

46 **47**

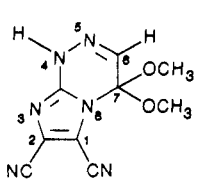
from **12** and **42** is **44** and not **43** or ring-opened isomers analogous to **15** or **35** is revealed by its white color, its ^{1}H NMR spectrum for olefinic CH (DCCl$_3$/DMSO-d_6; δ 6.56, s, 1 H, H_6), and its ^{13}C NMR spectrum for four sp^2 carbons (C_6, C_1, C_2, and C_{3a}), two nitrile carbons, and three sp^3 carbons (C_7, CH_3, and OCH_3). Adduct **47** is white, exhibits IR absorption for NH, undergoes rapid deuterium incorporation, and its ^{1}H NMR and ^{13}C NMR spectra are consistent (see the Experimental Section) with its assigned structure. The mechanisms by which the tautomerizations to **44** and **47** occur are not known. Among the possibilities resulting in **44** and **47** are ionization–recombination of **43** and **46** and/or reorganization and isomerization of ring-opened intermediates leading to or derived from **43** and **46**. It is emphasized that the tautomeric processes are similar *in result* to that found previously in reaction of **28** with **7** to give **37** (eq 8).

As has been summarized, **12** is reported to react nitrenically with **7** to give ring-opened adduct **15** (eq 4).[7] In the present research, however, reactions of (1) **28** with **7** (eq 8) and (2) **12** with **42** (eq 9) and **45** (eq 10) give products arising from *net 1,7-cycloaddition and tautomerization*. Also of concern are the prior observations that the NMR

(15) (a) After our work and this manuscript had been completed for publication, J. Farras and J. Vilarrasa (*J. Chem. Soc., Chem. Commun.* **1986**, 1127) reported that 4,5-dicyano-2-diazoimidazole (**12**) and 2-diazoimidazole (**28**) react with 1,1-dimethoxyethene (**7**) to give products assigned as 4,7-dihydro-7,7-dimethoxyimidazo[2,1-*c*][1,2,4]triazine-1,2-dicarbonitrile (**48**, mp 192 °C) and 1,4-dihydro-4,4-dimethoxyimidazo-[2,1-*c*][1,2,4]triazine (**37**, mp 137–140 °C). Although there are substantial differences in the melting points reported for **48** and **37** in the present work and that by Farras and Vilarrasa, comparison of the spectral properties of **48** and **37** as reported previously and as obtained by us reveal that the specific products from the two laboratories are identical and have the structures assigned independently by both groups. Further, Farras and Vilarrasa report that **48** thermolyzes at ~140–170 °C with loss of methanol and *methyl migration* to give 6,7-dicyano-1-methylimidazo[2,1-*c*]-*as*-triazin-4-one (mp 218–219 °C), a product isomeric with that assigned as **16** (mp 218–219 °C) in ref 7. We have also found that decomposition of **48** at 160 °C (4 h) yields 6,7-dicyano-1-methylimidazo[2,1-*c*]-*as*-triazin-4-one (68%, mp 217–218 °C) as a white solid: R_f 0.7 (25% acetone chloroform, UV); IR (KBr) 3425, 2240 (CN), 1725 (s, C=O), 1585, 1525, 1480, 1370, 1315, 1285, 1260, 1230, 1170, 1140, 1060, 885, 820, 780, 690 cm^{-1}; ^{13}C NMR δ (CDCl$_3$/DMSO-d_6) 39.54 (q, NCH$_3$), 100.95 (s, C_7), 106.72 (s, C_7-*C*N), 109.65 (s, C_6-*C*N), 122.93 (s, C_6), 129.13 (d, C_6), 143.45 (s, C_8), 147.60 (s, C_4). (b) Other cycloadditions of diazoazoles with unsaturates that occur with deep-seated rearrangement will be described in future publications.

spectra of the methoxy protons in **15** appear surprisingly as a 6 H *singlet* at δ 2.90[7] whereas those in **9** for OCH_3 absorb (as expected) as *singlets* (*3 H each*) at δ 3.31 and 3.46,[4a] respectively.

The behavior of **12** with **7** has been further investigated. Reaction of **12** with **7** at 0 to −15 °C yields a white crystalline solid (85%) whose melting point (200–201 °C) and ^1H NMR[15] spectrum are comparable to that published for **15**.[7] The ^{13}C NMR ($CDCl_3$/DMSO-d_6) and the ^1H NMR spectra of the product presently obtained (see the Experimental Section) are consistent, however, with **48** (4,7-dihydro-7,7-dimethoxyimidazo[2,1-*c*][1,2,4]triazine-1,2-carbonitrile) as derived by net 1,7-cycloaddition and *tautomerization* rather than ring-opening (eq 4): 51.03 (q, OCH_3), 100.00 (s, C_7), 100.52 (s, C_2), 106.98 (s, C_2-*C*N), 100.73 (s, C_1-*C*N), 122.23 (s, C_1), 127.70 (d, C_6), and 143.64 (s, C_{3a}). From the ^{13}C NMR, the product as **48** has eight kinds of carbon atoms: the carbons of the two methoxy groups show up as a single quartet and the remaining seven carbons are chemical shift nonequivalent. Further, in the ^1H NMR spectrum of **48**, the two methoxy groups are expected to appear as a six-proton singlet. Adduct **15** is clearly excluded because its off-resonance decoupled ^{13}C NMR spectra should consist of two quartets (one for each methoxy carbon), one doublet (sp^2 carbon), and four singlets (three for sp^2 and one for nitrile carbons). Further, C_2 in the imidazole nucleus and the olefinic carbon bearing the two methoxy groups in **15** are expected to absorb downfield from δ 130. Adduct **49** also is ruled out as the product because it contains only six different kinds of carbon atoms. Similarly, structure **50** cannot be the compound isolated since (1) its two cyano carbons are magnetically equivalent as are C_1 and C_2 and (2) it should exhibit only six ^{13}C NMR signals (three in the olefinic region).[15]



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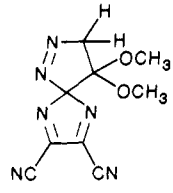

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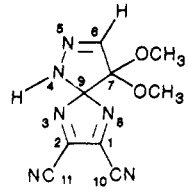
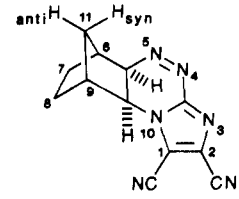


50

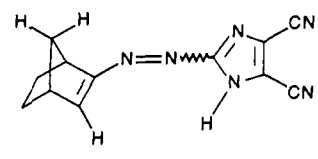
Study was then made of the efficacy and the stereochemistry of addition of **28** and **12** to strained cyclic olefins. Norbornene, norbornadiene, and dicyclopentadiene do not react with **28** at −15 °C (15 days). Additions of **12** to norbornene and norbornadiene at −15 °C occur smoothly, however, as now described.

Reactions of norbornene and **12** at −15 °C yields the yellow net exo 1,7-cycloadduct **51** (63%). The structure of the product as **51** rather than **52** or **53** is assignable from its ^1H and its ^{13}C NMR spectra (see the Experimental Section). Azo structure **52** as the *E* or the *Z* isomer cannot be the product because there is no absorption peak in the olefinic region of the observed ^1H NMR spectrum, and the off-resonance decoupled ^{13}C NMR spectrum should consist of one doublet and four singlets for sp^2 and nitrile carbons in addition to three triplets and two doublets for sp^3 carbons. Spiro structure **53** is also rejected because of the mismatch between the expected (10 signals: one for cyano carbons, one for sp^2 carbons, and eight for sp^3 carbons) and the observed broad band ^{13}C NMR absorptions.

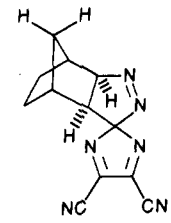
The stereochemistry of **51** as exo is assigned on the basis of ^1H NMR absorptions. The exo fusion in **51** is indicated by the observed multiplicities for two endo protons: H_{9a} (δ 4.42, dd, 1 H, J = 8.53 and 1.24 Hz) and H_{5a} (δ 4.83, d, 1 H, J = 8.54 Hz). The following values for coupling of



51

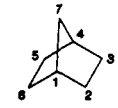


52



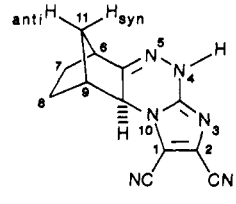
53

hydrogen in norbornyl systems (**54**) assist in determining the origins of coupling of ring juncture protons H_{5a} and H_{9a} in **51**: $J_{2,3(endo-endo)}$ = 6–7 Hz, $J_{2,3(exo-exo)}$ = 9–10 Hz, $J_{1,2(H_2\text{-}exo)}$ = 3–4 Hz, $J_{1,2(H_2\text{-}endo)}$ = 0–2 Hz, and $J_{2,3(endo-exo)}$ = 2.5–5 Hz. Irradiation of bridgehead protons H_6 and H_9 in **51** do not change the multiplicities of H_{5a} and H_{9a}, thus establishing the absence of coupling between H_9 and H_{9a} and H_6 and H_{5a}. Such coupling will not occur only when H_{5a} and H_{9a} are endo–endo. The major effects experienced by ring-juncture hydrogens H_{5a} and H_{9a} are thus endo–endo coupling (8.53 Hz) and long-range ω coupling (1.24 Hz) with $H_{11(anti)}$. (If indeed addition of **12** to norbornene had occurred endo, J for the above coupling constants would be in the ranges of 9–10 and 3–4 Hz, respectively.) The exo cycloaddition of **12** to norbornene is expected on the basis of steric factors and/or, among other ideas, that electrophilic addition of **12** occurs preferentially on the face of the olefinic center in norbornene having the higher electron density.[16]



54

Of additional interest is that **51** isomerizes to white crystalline imidazotriazine **55** (mp 255–256 °C) on standing in polar solvents (chloroform, dichloromethane, acetone, or methanol) at room temperature, on chromatography on silica gel, or on melting (mp 158–159 °C). Isomers **51** and **55** have greatly different solubilities. 1,7-Cycloadduct **51** dissolves readily in dichloromethane, chloroform, and acetone whereas tautomer **55** is sparingly soluble in these solvents. The structure of **55** is derivable from its ^1H



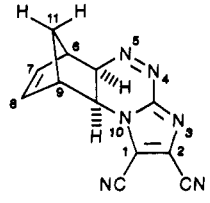
55

NMR spectrum (acetone-d_6): δ 0.93–1.56 (complex, 6 H, H_7, H_8, and H_{11}), 2.46 (br, 1 H, H_9), 2.89 (br, 1 H, H_6), 3.64 (br, 1 H, H_{9a}), and 9.90 (br, 1 H, H_4). The ^1H NMR spectrum of **55** reveals that one of the signals at δ ~3.0

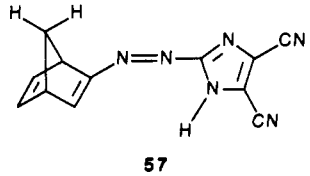
(16) (a) Inagaki, S.; Fujimoto, H.; Kukui, K. *J. Am. Chem. Soc.* **1976**, *98*, 4057. (b) Brown, F. K.; Houk, K. *Ibid.* **1985**, *107*, 1971.

for H_{5a} or H_{9a} in **51** is absent and a new signal is exhibited in **55** for H on N_4. Since the ^1H NMR spectrum of the product is incompatible with that expected for *E*- and *Z*-azo isomers **52**, rearrangements of endo-H at C_{5a} and the azo double bond at N_4–N_5 in **51** occur to yield thermodynamically stable tautomer **55**. The assignment as **55** is also supported by its ^{13}C NMR spectrum (see the Experimental Section).

Addition of norbornadiene to **12** also takes place effectively at −15 °C to yield net exo-1,7-cycloadduct **56** (85%) rather than **57** or **58**. The structure of **56** is assignable



56



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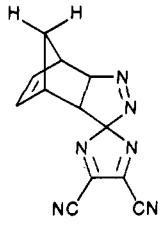
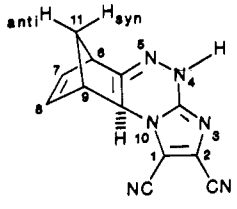


58

from its yellow color, its mass spectrum, and its NMR spectrum (see the Experimental Section). Major points with respect to the structural assignment as **56** are as follows: (1) the ^{13}C NMR spectrum reveals that the adduct has 12 unequivalent carbons (two nitrile carbons, three sp^2 carbons without any hydrogen, two sp^2 carbons each having one hydrogen, and five sp^3 carbons), (2) the ^1H NMR multiplets at δ 4.13 and 4.75 (J = 8.3 and 1.3 Hz) establish the endo,endo stereochemistry of H_{5a} and H_{9a}, and (3) irradiation of $H_{11(anti)}$ (δ 1.70) reduces the H_{5a} and H_{9a} multiplets to doublets (J = 8.3 Hz), thus revealing that the small coupling for H_{5a} and H_{9a} is due to long-range interaction.

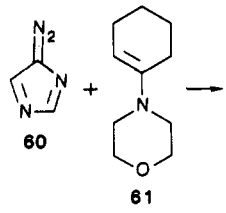
In behavior similar to isomerization of **51** to **55**, **56** tautomerizes to **59** on standing in dichloromethane, chloroform, or acetone or on column chromatography on silica gel. Isomeride **59** is a high-melting white solid (mp



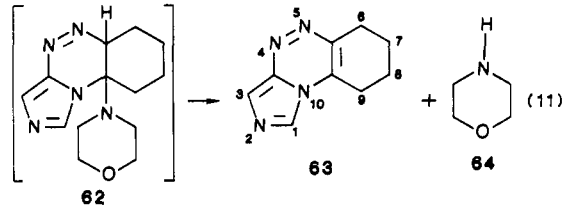
59

243–244 °C), which is sparingly soluble in the solvents in which it is formed. The structure as **59** is assignable from its IR spectrum, its ^1H NMR spectrum, which shows two olefinic C–H absorptions, and in particular its ^{13}C NMR spectrum for 12 carbon atoms that are nonequivalent (see the Experimental Section).

Study was then initiated of the ability of 4-diazo-4*H*-imidazole (**60**) to add to electron-rich dipolarophiles. Indeed, reaction of 1-morpholinylcyclohexene (**61**) with **60** (eq 11) occurs by net 1,7-cycloaddition and then elimination of morpholine (**64**) to yield imidazo[5,1-*c*][1,2,4]triazine **63** (100%). Further, phenyl isocyanate and 1-naphthyl isocyanate add to **60** at −80 °C to give imidazo-

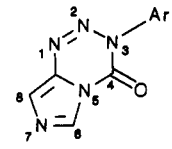


60 **61**



62 **63** **64** (11)

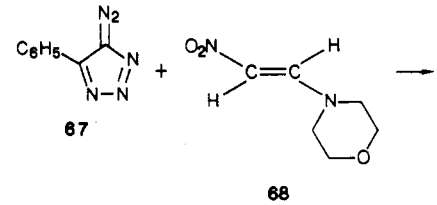
[5,1-*c*]-1,2,3,5-tetrazin-4(3*H*)-ones **65** (100%) and **66** (100%). As with the previous diazoazoles of this investigation, it is not known whether **60** reacts as an enophile by direct 1,7-cycloaddition or/and initial [3 + 2]-cycloaddition followed by [1,5]-sigmatropic isomerization. What is apparent, however, is that 4-diazo-4*H*-imidazoles will be satisfactory reagents for synthesis of varied imidazolo heterocycles by 1,7-cycloaddition (and elimination) processes.



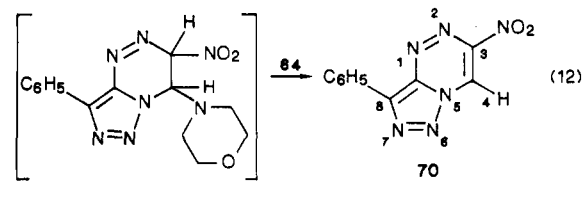
65, Ar = C_6H_5
66, Ar = 1-$C_{10}H_7$

The behavior of 4-diazo-4*H*-1,2,3-triazoles (1, X and Y = N, Z = CR) with possible dipolarophiles has also been of interest. A major concern was whether such diazoazoles are sufficiently reactive to add to unsaturated derivatives that are *less electron donating* than those that were effective in our previous studies.

4-Diazo-5-phenyl-4*H*-1,2,3-triazole (**67**) was thus found to react with 1-morpholinyl-2-nitroethene (**68**) in dichloromethane (20 °C) by net 1,7-cycloaddition and elimination of morpholine (**64**) to give the single product assigned as 3-nitro-8-phenyl[1,2,3]triazolo[5,1-*c*][1,2,4]triazine (**70**, eq 12; ≫48%). The regiospecificity of cyclo-



67 **68**

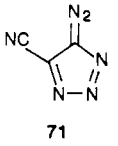


69 **64** **70** (12)

addition of **67** is believed to be predictable on the basis of the polarization in **68**. Of greater significance is the realization that a diazoazole undergoes extended cycloaddition to a dipolarophile, which is *both highly electropositively and electronegatively substituted*. Such addition reactions greatly increase the synthetic utility of diazoazoles and raise the interesting question as to the

mechanistic roles of dipolar factors and tandem effects in *both* the diazoazole and the dipolarophile during cycloaddition.

Of further note with respect to the behavior of 4-diazo-4*H*-1,2,3-triazoles (1, X and Y = N, Z = CR) is that 5-cyano-4-diazo-4*H*-1,2,3-triazole (**71**) adds to phenylacetylene. On the basis of the analytical and spectral properties of the product and that phenylacetylene functions as a *nucleophile* during net 1,7-cycloaddition, the structure of the adduct is assigned as 7-phenyl[1,2,3]triazolo[5,1-*c*][1,2,4]triazine-3-nitrile (**72**).



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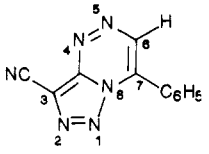
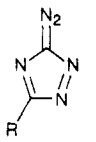


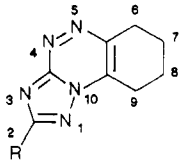
72

The synthetic utility and the regiochemistry of addition of representative 3-diazo-3*H*-1,2,4-triazoles (1, X and Z = N, Y = CR; see **73** and **75** below) to unsaturated acceptors have also been evaluated. Such diazoazoles offer the possibility of competitive 1,7-cycloadditions on nitrogen at the 2- and the 4-positions of their triazole moieties.

3-Diazo-3*H*-1,2,4-triazole (**73**) reacts exothermically with 1-ethoxycyclohexene (**45**), 1-morpholinylcyclohexene (**61**), and 1-piperidinylcyclohexene (**25**) at −60 °C to give the single addition–elimination product: 6,7,8,9-tetrahydro-[1,2,4]triazolo[5,1-*c*][1,2,4]benzotriazine (**74**).[17] Similarly, 3-diazo-5-phenyl-3*H*-1,24-triazole (**75**) is converted rapidly at −60 °C by **61** or **25** via cycloaddition and elimination to the single isomer, presumably 6,7,8,9-tetrahydro-2-phenyl[1,2,4]triazolo[5,1-*c*][1,2,4]benzotriazine (**76**).[17]

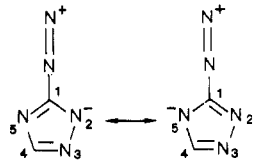


73, R = H
75, R = C_6H_5



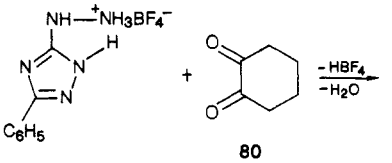
74, R = H
76, R = C_6H_5

Adducts **74** and **76** are assigned from their analytical and spectral properties and, in particular, on the premises that, in 3-diazo-3*H*-1,2,4-triazoles, nitrogen is more nucleophilic in the 2- than in the 5-positions (**77** and **78**, respectively) and this effect will control the regiochemistry of polar 1,7-cycloadditions. There is precedent[2,4] along with in-

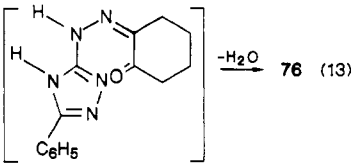


77 **78**

tuitive and sophisticated theory,[8] that are consistent with electronic control as proposed for reactions of **73** and **75** above. Of further note is that **76** is identical with the product obtained from reaction of 1,2-cyclohexanedione (**80**) with 5-phenyl-1,2,4-triazole-3-hydrazinium tetrafluoroborate (**79**, eq 13) as prepared by reduction of 5-phenyl-1,2,4-triazole-3-diazonium tetrafluoroborate with stannous chloride.[18]



79 **80**



81

76 (13)

The present study thus reveals the versatility and the practicality of cycloadditions of electron-rich olefins and strained olefins and of acetylenes with diazoazoles having nitrogen in the 2-positions of their azole rings. Investigation of the kinetic factors in the behavior of unsaturates with diazoazoles containing nitrogen in their 2- or 3-positions is in progress. The roles of electronic effects and steric factors on whether such reactions occur by initial nitrenic, 1,1-, or/and 1,7-cycloaddition processes are to be evaluated. Further chemistry and the biological and the medical properties of the various heterocyclic products described herein will be reported in subsequent publications.

Experimental Section

3-Amino-5-*tert*-butylpyrazole. 4,4-Dimethyl-3-oxopentanenitrile[19] (18.5 g, 0.15 mol) in ethanol (200 mL) was added dropwise to hydrazine hydrate (15 g, 0.3 mol) at 0 °C. The mixture was kept at 0 °C for 30 min, refluxed for 1 h, poured into water, and extracted with diethyl ether. After the ether extract had been dried (Na_2SO_4) and concentrated, crystallization of the residue from benzene/cyclohexane yielded 3-amino-5-*tert*-butylpyrazole (18.2 g, 82%) as an air-sensitive solid: mp 80 °C; IR (KBr) 3400 (NH), 1550 (C=N) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.3 [s, 9 H, $(CH_3)_3C$], 5.3 (s, 1 H, C*H*), 5.7 (br t, N*H*). Anal. Calcd for $C_7H_{13}N_3$: C, 60.40; H, 9.40. Found: C, 60.37; H, 9.35.

3-Benzamido-5-*tert*-butylpyrazole, prepared from 3-amino-5-*tert*-butylpyrazole and benzoyl chloride (1 equiv) in pyridine and recrystallization from benzene/ethanol, melts at 215–216 °C. Anal. Calcd for $C_{14}H_{17}N_3O$: C, 69.11; H, 7.04; N, 17.27. Found: C, 69.26; H, 7.17; N, 17.40.

5-*tert*-Butyl-3-pyrazolediazonium Tetrafluoroborate. Sodium nitrite (1.5 g, 21 mmol) dissolved in a minimum amount of water was added (10 min) to 3-amino-5-*tert*-butylpyrazole (2.74 g, 20 mmol) in fluoroboric acid (20 mL of a 48% solution) at 0 °C. A solid precipitated, and the mixture was allowed to warm to room temperature. Water was added dropwise until the precipitate dissolved. The solution on storage at −5 °C yielded long white needles of 5-*tert*-butyl-3-pyrazolediazonium tetrafluoroborate (4.2 g, 90%): mp >140 °C dec; IR (KBr) 2700 (NH), 2290 (CN_2^+), 1475 (C=N), 1450 (C=N), and 1060 cm^{-1}.

5-*tert*-Butyl-3-diazo-3*H*-pyrazole (20). 5-*tert*-Butyl-3-pyrazolediazonium tetrafluoroborate (2.31 g, 10 mmol) suspended in methylene chloride (50 mL) was stirred while cooled externally (ice/HCl bath). Aqueous sodium carbonate (10 mL, 10% solution) was added, and stirring was continued (30 min). The yellow organic layer was separated and dried (Na_2SO_4). Removal of solvent under vacuum at 0 °C in the dark yielded **20** (1.0 g, 67%). Recrystallization from diethyl ether produced clear squares of **20**, which are light sensitive and piezosonic: explodes at 97 °C; IR (KBr) 2970 (CH), 2190 (C=N_2), 1120, 1050 cm^{-1}.

Reaction of 5-*tert*-Butyl-3-diazo-3*H*-pyrazole (20) with Ethyl Vinyl Ether. A solution of **20** (0.3 g, 2 mmol) in ethyl

(17) Efforts to prepare the net 1,7-cycloadducts from reactions of **73** and **75** with the substituted cyclohexenes (**45**, **61**, and **25**) at lower temperatures and shorter reaction times have not been made.

(18) The sequence for synthesis of the product assigned as **76** is indicative but does not serve as an absolute proof of structure.

(19) Justoni, R.; Terruzzi, M. *Gazz. Chim. Ital.* **1948**, *78*, 176.

vinyl ether (25 mL) was placed in a freezer (−5 °C) overnight. Concentrating the mixture at reduced pressure left an orange solid, which on crystallization from benzene yielded 7-*tert*-butylpyrazolo[5,1-*c*][1,2,4]triazine (**23**; 0.19 g, 60%): yellow needles; mp 135–136 °C; IR (KBr) 2980, 1510, 1490, 1380, 1140, 922, 848, 805 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.45 [s, 9 H, $C(CH_3)_3$], 7.1 (d, 1 H, J = 1 Hz), 8.58 (q, 1 H, J = 1 and 5 Hz), and 8.8 (d, 1 H, J = 5 Hz); exact mass calcd for $C_9H_{12}N_4$ 176.1062, found 176.1065. Anal. Calcd for $C_9H_{12}N_4$: C, 61.34; H, 6.87. Found: C, 61.23; H, 7.06.

5-Phenyl-3-pyrazolediazonium Chloride and 5-Phenyl-3-pyrazolediazonium Tetrafluoroborate. A solution of 3-amino-5-phenylpyrazole[20] (3.18 g, 20 mmol) in hydrochloric acid (25 mL) was cooled to 0 °C. Sodium nitrite (1.5 g, 21 mmol) in water (5 mL) was added, and the resulting yellow solution was stirred at 0 °C for 15 min. Addition of ice water resulted in precipitation of tan needles of 5-phenyl-3-pyrazolediazonium chloride (4.1 g, 99%), which decompose above 200 °C: IR (KBr) 2600 (NH), 2280 (C≡N_2), 1490 (CN_2^+), 1440 (C=N), 1150, and 770 cm^{-1}.

In an alternate procedure, 5-phenyl-3-pyrazolediazonium tetrafluoroborate was prepared by dropwise addition of sodium nitrite (0.49 g, 7.0 mmol) in water (2.5 mL) to 3-amino-5-phenylpyrazole (0.8 g, 5.3 mmol) suspended in 48% tetrafluoroboric acid (15 mL) at 0 °C. After ~45 min, the product was filtered to give 5-phenyl-3-pyrazolediazonium tetrafluoroborate (1.14 g, 4.8 mmol) in 90% yield.

3-Diazo-5-phenyl-3*H*-pyrazole (24). Reaction of 5-phenyl-3-pyrazolediazonium chloride with aqueous sodium carbonate (as for **20**) yields **24** as long yellow needles (light and shock sensitive), which explode at 115 °C: IR (KBr) 2170 (C≡N_2), 1090, 760, and 690 cm^{-1}.

Reaction of 3-Diazo-5-phenyl-3*H*-pyrazole (24) with 1-Piperidinylcyclohexene (25). Excess **25** (18.6 g) was added dropwise to **24** (1.0 g, 5.88 mmol) at −30 to −40 °C. The temperature of the mixture was allowed to rise slowly. At ~10 °C, the mixture became deep red and reaction appeared complete. After 12 h, excess **25** was removed by distillation, and the red residue, after chromatography on silica gel (benzene/ethyl acetate as eluent) and crystallization from benzene, yielded 2-phenyl-6,7,8,9-tetrahydropyrazolo[5,1-*c*][1,2,4]triazine (**27**; 0.7 g, 2.80 mmol, 48%): mp 161–162 °C; IR (KBr) 2960, 1540, 1510, 1475, 1370, 1330, 1275, 1150, 1130, 1090, 980, 785, 710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.01–8.17 (m, aromatic H), 7.26–7.98 (m, aromatic H + one vinyl H), 4.04–3.00 (m, cyclohexenyl H); exact mass calcd for $C_{15}H_{14}N_4$ 250.121, found 250.122. Anal. Calcd for $C_{15}H_{14}N_4$: C, 72.00; H, 5.60; N, 22.40. Found: C, 72.04; H, 5.88; N, 22.18.

2-Diazo-2*H*-imidazole (28). Aqueous sodium nitrite (1.0 g, 14.4 mmol, 2 mL H_2O) was added dropwise to a stirred solution of 2-aminoimidazole sulfate[21] (1.32 g, 5 mmol) in aqueous tetrafluoroboric acid (48%, 13 mL) at −30 °C. In 20 min, a white precipitate separated. After an additional 20 min, the heterogeneous mixture was neutralized below 0 °C by addition of (tiny portions of) solid sodium carbonate. The reaction solution was extracted at ~0 °C with precooled dichloromethane (3 × 80 mL) or diethyl ether (5 × 80 mL). The cold extracts were combined, dried over anhydrous magnesium sulfate, and filtered. Vacuum evaporation of the cold filtrate yielded **28** (0.534 g, 5.8 mmol, 59%) as a yellow residue: IR (CH_2Cl_2) 2150 (C≡N_2) cm^{-1}. As a solid, **28** is shock sensitive. Thus, in all reactions presently reported, **28** was always freshly prepared and handled in solution.

Reaction of 2-Diazo-2*H*-imidazole (28) with Phenyl Isocyanate. Phenyl isocyanate (0.6 g, 5.0 mmol) in dichloromethane (10 mL) was added dropwise to **28** (as derived from 2.5 mmol of 2-aminoimidazole sulfate) stirred in dichloromethane (90 mL) at −70 °C. The mixture was stirred at −70 °C for 3 h and then at room temperature overnight. After the solvent had been evaporated, the residue was washed repeatedly with cold diethyl ether and recrystallized from acetone/petroleum ether to yield 3-phenylimidazo[2,1-*d*]-1,2,3,5-tetrazin-4(3*H*)-one (**29**; 0.921 g, 4.3 mmol, 86%): white flakes; mp 159–160 °C; R_f 0.73 (25% acetone/chloroform, UV); IR (KBr) 1745 (C=O), 1400, 760, and 700 (monosubstituted benzene) cm^{-1}; ^1H NMR ($CDCl_3$/DMSO-d_6) δ 7.52–7.67 (m, 5 H, phenyl H), 7.80 (d, 1 H, H_7, J = 1.45 Hz), 7.92 (d, 1 H, H_6, J = 1.47 Hz); ^{13}C NMR ($CDCl_3$/DMSO-d_6) δ 118.48 (d, C_7), 125.15 (d, ortho or meta C of phenyl), 128.15 (d, ortho or meta C of phenyl), 128.52 (s, para C of phenyl), 134.42 (d, C_6); MS, m/e 213 (M^+), 119 (100); exact mass calcd for $C_{10}H_7N_5O$ 213.0649, found 213.0646.

Reaction of 2-Diazo-2*H*-imidazole (28) with 1-(Dimethylamino)cyclohexene. A solution of 1-(dimethylamino)-cyclohexene[22] (0.75 g, 6.0 mmol) in dichloromethane (5 mL) was added slowly to **28** (0.267 g, 2.9 mmol) in dichloromethane (150 mL) at −70 °C. The mixture turned red upon addition of the enamine and then became dark brown. The mixture was allowed to warm to −40 °C and then stored at −15 °C for 2 days. After the dichloromethane had been vacuum evaporated, the residue was chromatographed, eluted with 15 and then 20% acetone/chloroform, crystallized, and rechromatographed. 6,7,8,9-Tetrahydroimidazo[2,1-*c*]benzotriazine (**32**) was thus obtained (0.243 g, 1.3 mmol, 45%) as a red solid: mp (dichloromethane/petroleum ether) 167–168 °C; R_f 0.18 (25% acetone/chloroform, UV); IR (KBr) 1500, 1480, 1320, 1285, 765 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.00–2.09 (complex m, 4 H, H_7 and H_8), 2.92–2.98 (m, 2 H, H_6), 3.28–3.33 (m, 2 H, H_9), 7.51 (d, 1 H, H_2, J = 1.05 Hz), 8.10 (d, 1 H, H_1, J = 1.30 Hz); exact mass calcd for $C_9H_{10}N_4$ 174.0907, found 174.0909.

Reaction of 2-Diazo-2*H*-imidazole (28) with 1-(Diethylamino)-2-methylpropene. 1-(Diethylamino)-2-methylpropene[23] (0.86 g, 6.6 mmol) in dichloromethane (5 mL) was added dropwise to a cold (−60 °C) solution of **28** (0.133 g, 1.45 mmol) in dichloromethane (50 mL). After the mixture had been stored at −10 °C for a week, the solvent was evaporated at room temperature, and the residue was chromatographed on MN Kiselgel-60 silica gel. Elution with chloroform gave an oil, which crystallized from dichloromethane/petroleum ether to give 7-(diethylamino)-6,7-dihydro-3,3-dimethylimidazo[2,1-*c*][1,2,4]triazine (**33**; 0.171 g, 0.7 mmol, 53%): yellow needles; mp 90–91 °C dec; R_f 0.41 (25% acetone/chloroform, UV); IR (KBr) 1355, 1215, 1075, 775 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.52 (t, 6 H, NCH_2CH_3, J = 7.1 Hz), 0.70 [s, 3 H, CH_3 cis to $N(CH_2CH_3)_2$], 1.61 [s, 3 H, CH_3 trans to $N(CH_2CH_3)_2$], 1.71 (sextet, 2 H, NCH_2), 2.07 (sextet, 2 H, NCH_2), 4.25 (s, 1 H, H_7), 6.28 (br s, H_2), 7.24 (d, 1 H, H_1, J = 1.1 Hz); ^{13}C NMR ($CDCl_3$) δ 12.32 [q, methyl C of $N(CH_2CH_3)_2$], 23.12 [q, CH_3 cis to $N(CH_2CH_3)_2$, CH_3 trans to $N(CH_2CH_3)_2$], 24.33 [q, CH_3 trans to $N(CH_2CH_3)_2$], 43.26 [t, two CH_2 of $N(CH_2CH_3)_2$], 65.76 (s, C_6), 75.14 (d, C_7), 117.69 (d, C_2), 130.55 (d, C_1); MS, m/e 221 (M^+), 165 (100), 127, 112, 72; exact mass calcd for $C_{11}H_{19}N_5$ 221.1641, found 221.1639.

Reaction of 2-Diazo-2*H*-imidazole (28) with 1,1-Dimethoxyethene (7). To a solution of **28** (0.133 g, 1.45 mmol) in dichloromethane (100 mL) at −15 °C was added **7** (1.360 g, 15.0 mmol). After the mixture had been refrigerated at 0 °C for 4 days, the solution was concentrated to 50 mL, stored at −10 °C for 5 days, reduced to a volume of 25 mL, and refrigerated. White crystals of 1,4-dihydro-4,4-dimethoxyimidazo[2,1-*c*][1,2,4]triazine (**37**; 0.107 g, 0.58 mmol) separated.[15] Evaporation of the filtrate yielded additional **37**, which was chromatographed three times and crystallized from acetone/cyclohexane: mp 163–164 °C dec; IR (KBr) 1575, 1230, 1120, 1095 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.30 (s, 6 H, 2 OCH_3), 6.62 (s, 1 H, H_3), 7.00 (d, 1 H, H_7), 7.10 (d, 1 H, H_6); ^{13}C NMR ($CDCl_3$) δ 51.56 (q, OCH_3), 100.78 (s, C_4), 107.55 (d, C_7), 126.48 (d, C_6), 126.75 (d, C_3), 143.55 (s, C_{8a}); MS, m/e 182 (M^+), 151 (100, M − 31), 136, 100.59; exact mass calcd for $C_7H_{10}N_4O_2$ 182.0802, found 182.0806.[15]

Reaction of 4,5-Dicyano-2-diazo-2*H*-imidazole (12) with 1-Ethoxycyclohexene (45). A solution of **45** (0.126 g, 1.0 mmol) and **12** (0.144 g, 1.0 mmol) in dichloromethane (25 mL) was stored at −15 °C for 30 days. The dark red solution was concentrated and then chromatographed. Elution with chloroform and crystallization from acetone/cyclohexane yielded white crystals of 10a-ethoxy-4,6,7,8,9,10-hexahydroimidazo[2,1-*c*][1,2,4]benzotriazine-1,2-dicarbonitrile (**47**; 0.142 g, 0.52 mmol, 52%): mp (from

(20) Ridi, M. *Gazz. Chim. Ital.* **1955**, *85*, 1160.
(21) Storey, B. T.; Sullivan, W. W.; Mayer, C. L. *J. Org. Chem.* **1964**, *29*, 3118.
(22) Prepared from cyclohexanone and dimethylamine as above.[21]
(23) 1-(Diethylamino)-2-methylpropene was prepared from isobutyraldehyde and diethylamine following the general procedure by Mannich, C.; Davidsen, H. *Ber. Dtsch. Chem. Ges. B* **1936**, *69*, 2106.

acetone/cyclohexane) 217–218 °C; R_f 0.44 (10% acetone/chloroform, UV); IR (KBr) 2240 (m), 2205 (s), 1600, 1320, 1060 cm^{-1}; ^1H NMR (CD_3OD) δ 1.22 (t, 3 H, CH_3), 1.75 (m, 1 H), 1.97 (m, 4 H), 2.48 (m, 2 H), 2.95 (m, 2 H), 3.32 (m, 1 H), 4.1 (br s, 1 H); MS, *m/e* 270 (M^+), 241, 225 (100, M – OEt); ^{13}C NMR ($CDCl_3$/DMSO-d_6) δ 14.25 (q, CH_3), 21.36 (t, C_7 or C_8), 25.10 (t, C_8 or C_7), 30.51 (t, C_9), 37.78 (t, C_6), 59.23 (t, OCH_2), 85.41 (s, C_{10}), 101.46 (s, C_{11}), 108.68 (s, C_2-*C*N), 111.62 (s, C_1-*C*N), 123.32 (s, C_1), 141.05 (C_{5a}), 144.23 (s, C_{3a}); exact mass calcd for $C_{13}H_{14}N_4O$ 270.1228, found 270.1218.

Reaction of 4,5-Dicyano-2-diazo-2*H*-imidazole (12) with 2-Methoxypropene (42). 2-Methoxypropene (**42**, 0.75 g, 1.04 mmol) was added to a precooled solution (–10 °C) of **12**[6] (0.144 g, 1.0 mmol) in dichloromethane (25 mL), and the mixture was stored at –10 °C for 6 days. Upon evaporation of the dichloromethane, a white solid was obtained, which on crystallization from acetone is assigned as 4,7-dihydro-7-methoxy-7-methylimidazo-[2,1-*c*][1,2,4]triazine-1,2-dicarbonitrile (**44**; 0.192 g, 0.88 mmol, 88%): mp (acetone) 200–201 °C; IR (KBr) 2235 (CN), 1580, 1320, 1140, 1035 cm^{-1}; ^1H NMR ($CDCl_3$/DMSO-d_6) 1.98 (s, 3 H, CH_3), 3.07 (s, 3 H, OCH_3), 6.56 (s, 1 H, H_6); MS, *m/e* 216 (M^+), 201 (M – CH_3), 185 (M – OCH_3); ^{13}C NMR (DMSO-d_6) δ 25.73 (C_7-CH_3), 51.43 (C_7-OCH_3), 84.67 (C_7), 102.38 (C_2), 109.31 (C_2-CN), 112.48 (C_1-CN), 122.51 (C_1), 133.31 (C_6), 143.85 (C_{3a}); exact mass calcd for $C_9H_8N_6O$ 216.0758, found 216.0742.

Reaction of 4,5-Dicyano-2-diazo-2*H*-imidazole (12) with 1,1-Dimethoxyethene (7). A mixture of **7** (0.188 g, 2.0 mmol) and **12**[6] (0.144 g, 1.0 mmol) in dichloromethane (25 mL) was stored at –15 °C for 5 days. Upon removal of the solvent and recrystallization of the residue from acetone/petroleum ether, white crystals of 4,7-dihydro-7,7-dimethoxyimidazo[2,1-*c*][1,2,4]triazine-1,2-dicarbonitrile (**48**; 0.193 g, 0.83 mmol, 83%) were obtained: mp 200–201 °C; ^{13}C NMR ($CDCl_3$/DMSO-d_6) 51.03 (q, OCH_3), 100.00 (s, C_7), 100.52 (s, C_2), 106.98 (s, C_7-*C*N), 110.73 (s, C_1-*C*N), 122.23 (s, C_1), 127.70 (d, C_6), 143.64 (s, C_{3a}).[15]

Reaction of 4,5-Dicyano-2-diazo-2*H*-imidazole (12) with Norbornene. A mixture of **12**[6] (0.144 g, 1.0 mmol) and norbornene (0.094 g, 1.0 mmol) in dichloromethane (30 mL) was stored at –15 °C for 15 days. Evaporation of the solvent provided a yellow adduct (0.23 g, 0.99 mmol, 100%), which upon crystallization from dichloromethane/petroleum ether was identified as (5aα,6β,9β,9aα)-5a,6,7,8,9,9a-hexahydro-6,9-methanoimidazo-[2,1-*c*][1,2,4]benzotriazine-1,2-dicarbonitrile (**51**): mp 158–159 °C; R_f 0.63 (10% acetone/chloroform, UV); IR (KBr) 2240 (CN), 1480 + other absorptions cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.21 (md, 1 H, $H_{11(anti)}$, $J_{geminal}$ = 11.63 Hz), 1.59 (md, 1 H, $H_{11(syn)}$, $J_{geminal}$ = 11.63 Hz), 1.70–205 (complex, 4 H, H_7 and H_8), 2.90 (br s, 1 H, H_9), 3.39 (br s, H_6), 4.42 (dd, 1 H, H_{9a}, $J_{H_{9a}-H_{5a}}$ = 8.53 Hz, $J_{H_{9a}-H_{11(anti)}}$ = 1.24 Hz) and 4.84 (d, 1 H, H_{5a}, $J_{H_{5a}-H_{9a}}$ = 8.53 Hz); ^{13}C NMR ($CDCl_3$) δ 26.04 (t, C_8), 26.79 (t, C_7), 33.09 (t, C_{11}), 43.22 (d, C_9), 44.21 (d, C_6), 57.25 (d, C_{9a}), 73.55 (d, C_{5a}), 106.98 (s, C_2), 109.48 (s, C_2-*C*N), 110.62 (s, C_1-*C*N), 123.34 (s, C_1), 140.26 (s, C_{3a}); MS, *m/e* 238 (M^+, 100), 197, 169, 67; exact mass calcd for $C_{12}H_{10}N_6$ 238.0966, found, 238.0932.

(6aα,9aα,9aβ)-4,6,7,8,9,9a-Hexahydro-6,9-methanoimidazo-[1,2-*a*]quinazoline-1,2-dicarbonitrile (55). Adduct **51** isomerizes at its melting point (158–159 °C), on chromatography on silica gel or on storage in dichloromethane, chloroform, or acetone, to a white crystalline product assigned as **55** (100%, see text) upon recrystallization from acetone/petroleum ether: mp 255–256 °C; R_f 0.31 (10% acetone/chloroform, UV); IR (KBr) 3200 (s, NH), 1580, 2230 (CN) cm^{-1}; ^{13}C NMR (DMSO-d_6) δ 22.87 (t, C_8), 26.52 (t, C_7), 37.28 (t, C_{11}), 41.68 (d, C_6), 56.44 (d, C_{9a}), 103.85 (s, C_2), 110.11 (s, C_2-*C*N), 112.82 (s, C_1-*C*N), 121.00 (s, C_1), 147.96 (s, C_{3a}), 155.28 (s, C_{5a}); MS, *m/e* 238 (M^+, 100%), 197, 165, 112, 67; exact mass calcd for $C_{12}H_{10}N_6$ 238.0966, found 238.0986.

Reaction of 4,5-Dicyano-2-diazo-2*H*-imidazole (12) with Norbornadiene. To a stirred solution of norbornadiene (0.430 g, 4.6 mmol) in anhydrous diethyl ether (20 mL) at –50 °C was slowly added **12**[6] (0.144 g, 1.0 mmol) in dichloromethane/diethyl ether (1/1, 40 mL). The mixture was stirred for 30 min at –50 °C and then stored for 15 days at –15 °C. Removal of the solvents by aspiration and crystallization of the product from dichloromethane/petroleum ether provided yellow crystals of (5aα,6β,9β,9aα)-5a,6,9,9a-tetrahydro-6,9-methanoimidazo[2,1-*c*][1,2,4]benzotriazine-1,2-dicarbonitrile (**56**; 0.149 g, 0.63 mmol, 63%): mp turns orange at 135 °C, blackens at ~285 °C; R_f 0.61 (10% acetone/chloroform, UV); IR (KBr) 2225 (CN), 1475, 1320, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.02 (md, 1 H, $H_{11(syn)}$, $J_{geminal}$ = 10.5 Hz), 1.70 (md, 1 H, $H_{11(anti)}$, $J_{geminal}$ = 10.5 Hz), 3.42 (br s, 1 H, H_9), 3.90 (br s, 1 H, H_6), 4.13 (dd, 1 H, H_{9a}, $J_{H_{9a}-H_{5a(endo-endo)}}$ = 8.3 Hz, $J_{H_{9a}-H_{11(anti)}}$ = 1.3 Hz), 4.75 (td, 1 H, H_{5a}, $J_{H_{5a}-H_{9a(endo-endo)}}$ = 8.3 and 1.3 Hz), 6.40 (dd, 1 H, H_8, $J_{H_7-J_8}$ = 5.6 Hz, $J_{H_8-H_9}$ = 3.1 Hz), 6.56 (dd, 1 H, H_7, J = 5.6 and 3.1 Hz); ^{13}C NMR ($CDCl_3$) δ 42.56 (C_{11}), 49.00 (C_9), 49.56 (C_6), 52.76 (C_{9a}), 69.84 (C_{5a}), 106.92 (C_2), 109.36 (C_2-*C*N), 110.53 (C_1-*C*N), 123.03 (C_1), 136.68 (C_8), 138.05 (C_7), 141.27 (C_{3a}); exact mass calcd for $C_{12}H_8N_6$ 236.0809, found 236.0807.

(6aα,9aα,9aβ)-4,6,9,9a-Tetrahydro-6,9-methanoimidazo[2,1-*c*][1,2,4]benzotriazine-1,2-dicarbonitrile (59). Isomerization of **56** occurs on chromatography or on storage in dichloromethane, chloroform, methanol, acetone, or dimethyl sulfoxide to give **59** (100%) as white crystals upon recrystallization from acetone/petroleum ether: mp 243–244 °C; R_f 0.32 (10% acetone/chloroform, UV); IR (KBr) 2230 (CN), 1575, 1325, 1235, 790 cm^{-1}; ^1H NMR ($CDCl_3$/DMSO-d_6) δ 1.75 (d, 1 H, $H_{11(syn)}$, $J_{geminal}$ = 9.8 Hz), 2.44 (md, $H_{11(anti)}$, $J_{geminal}$ = 9.7 Hz), 3.64 (br, 1 H, H_9), 3.82 (br, 1 H, H_{9a}), 4.01 (br, 1 H, H_6), 6.44 (dd, 1 H, H_8, $J_{H_8-H_7}$ = 5.6 Hz; $J_{H_8-H_9}$ = 2.8 Hz), 6.55 (dd, 1 H, H_7, $J_{H_7-H_8}$ = 5.6 Hz, $J_{H_7-H_6}$ = 3.3 Hz); ^{13}C NMR ($CDCl_3$/DMSO-d_6) δ 42.49 (d, C_9), 47.49 (d, C_6), 49.53 (t, C_{11}), 53.73 (d, C_{9a}), 103.48 (s, C_2), 109.57 (s, C_2-*C*N), 112.09 (s, C_1-*C*N), 122.81 (s, C_1), 135.13 (d, C_8), 137.15 (d, C_7), 149.49 (s, C_{3a}), 153.04 (s, C_{5a}); MS, *m/e* 236 (M^+, 100), 221, 208, 195, 104, 92; exact mass calcd for $C_{12}H_8N_6$ 236.0809, found 236.0809.

4-Diazo-4*H*-imidazole (60). Solid *tert*-butyl 4-imidazolecarbamate[24] (1.0 g, 5.5 mmol) was added to concentrated hydrochloric acid (5 mL) at –15 °C. Immediate evolution of carbon dioxide occurred, indicating rapid hydrolysis of the carbamate. The mixture was stirred until the 4-aminoimidazole dihydrochloride precipitated completely (10 min). The dihydrochloride was vacuum filtered: mp 140–145 °C dec; IR (KBr) 3500–2400 (several broad peaks, NH_3^+), 1640, 1480, 1310 (aromatic skeletal stretch) cm^{-1}; NMR (D_2O) δ 10.10 (br s, NH), 8.70 (s, 1 H, CH), 6.90 (s, 1 H, CH).

The 4-aminoimidazole dihydrochloride was suspended in concentrated hydrochloric acid (5 mL) and cooled to –20 °C. Sodium nitrite (1 g, 12 mmol) in water (1 mL) was then added, while the temperature of the reaction mixture was kept below –15 °C. The resulting solution was stirred for 30 min and neutralized with an aqueous suspension of sodium bicarbonate (excess) until there was no further evolution of gas. After the reaction mixture was extracted with cold dichloromethane (5 × 100 mL), the yellow extracts were combined, dried over anhydrous sodium sulfate, and concentrated in vacuo. The concentrate was cooled to –40 °C, and petroleum ether was added dropwise until the mixture became cloudy. After 15 min at –40 °C, **60**, a white crystalline solid, precipitated. Upon filtration, **60** converts to a black oil without evolution of nitrogen. 4-Diazo-4*H*-imidazole (**60**), prepared as previously described, was stored in solution in dichloromethane: IR (CH_2Cl_2) 2140 (C=N_2 stretch) cm^{-1}; ^1H NMR (CH_2Cl_2) δ 8.64 (s, 1 H, CH), 7.48 (s, 1 H, CH). For determining the approximate yields of **60**, the dichloromethane solutions were evaporated in vacuo at 0 °C to a black oil (0.36 g, 3.8 mmol, 69%, assuming no loss of nitrogen). It is assumed in calculating yields that **60** was always prepared in 69% efficiency.

Reaction of 4-Diazo-4*H*-imidazole (60) with 1-Morpholinylcyclohexene (61). To **61** (0.8 g, 4.8 mmol) in dichloromethane (10 mL) at –80 °C was added **60** (0.18 g, 1.9 mmol) in dichloromethane (20 mL). The mixture was stirred for 2 h, allowed to warm to room temperature, and concentrated in vacuo to a volume of 10 mL. Diethyl ether was added until the mixture became turbid. The reaction mixture was refrigerated overnight. Filtration afforded 6,7,8,9-tetrahydroimidazo[5,1-*c*][1,2,4]benzotriazine (**63**; 0.33 g, 1.9 mmol, 100%): white crystals; mp 120 °C dec; IR (KBr) 3600–3300, 2950, 2880, 1600, 1460, 1130 cm^{-1}; exact mass calcd for $C_9H_{10}N_4$ 174.0905, found 174.0916.

Reaction of 4-Diazo-4*H*-imidazole (60) with Phenyl Isocyanate. Phenyl isocyanate (1.0 g, 8.4 mmol) in dichloromethane (20 mL) was added dropwise to **60** (0.18 g, 1.9 mmol) in di-

(24) Kirk, K. L.; Cohen, L. A. *J. Am. Chem. Soc.* **1973**, *95*, 4619.

chloromethane (5 mL) at −80 °C. The mixture was stirred 30 min, warmed to room temperature overnight, and then concentrated in vacuo to a volume of approximately 10 mL. Diethyl ether was added dropwise until cloudiness occurred, and the mixture was stored at −5 °C overnight. Filtration afforded 3-phenylimidazo[5,1-*c*]-1,2,3,5-tetrazin-4(3*H*)-one (**65**; 0.40 g, 1.9 mmol, 100%): white crystals, mp 110 °C dec; IR (KBr) 3520–3300, 2110, 1740, 1450, 1365, 1315, 1270, 1120, 1030, 915, 760, 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.6 (s, 1 H), 8.2 (s, 1 H), 7.6 (br s, 5 H, phenyl H); exact mass calcd for $C_{10}H_7N_5O$ 213.0651, found 213.0655. Anal. Calcd for $C_{10}H_7N_5O$: C, 56.37; H, 3.31. Found: C, 56.30; H, 3.41.

Reaction of 4-Diazo-4*H*-imidazole (60) with 1-Naphthyl Isocyanate. To 1-naphthyl isocyanate (0.23 g, 1.4 mmol) in dichloromethane (10 mL) at −80 °C was added dropwise a solution of **60** (0.09 g, 0.9 mmol) in dichloromethane (10 mL). The mixture was stirred for 30 min at −80 °C and left at ~25 °C overnight. After concentration of the solution to a volume of 5 mL, diethyl ether was added until the mixture became cloudy. The mixture was refrigerated overnight. Filtration yielded 3-(1-naphthyl)-imidazo[5,1-*c*]-1,2,3,5-tetrazin-4(3*H*)-one (**66**; 0.34 g, 1.3 mmol, 100%): tan crystals; mp 124 °C dec; IR (KBr) 1740, 1450, 1375, 1275, 1210, 920, 805, 775 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.5 (s, 1 H), 8.1 (s, 1 H), 7.7–7.4 (m, 7 H, naphthyl H). Anal. Calcd for $C_{14}H_9N_5O$: C, 63.88; H, 3.82. Found: C, 63.36; H, 3.40.

4-Diazo-5-phenyl-4*H*-1,2,3-triazole (67). A stirred solution of 4-amino-5-phenyl-1,2,3-triazole[25] (1.6 g, 0.01 mol) in 2 N hydrochloric acid (10 mL) was cooled to 0 °C. Sodium nitrite (0.76 g, 0.011 mol) in water (1 mL) was added. The mixture was stirred 10 min. Dichloromethane (100 mL) was added, and the aqueous solution was neutralized with sodium carbonate. When carbon dioxide evolution ceased, the dichloromethane and the aqueous layers were separated. The aqueous solution was then extracted repeatedly with dichloromethane (300 mL). The organic layers were combined and dried over anhydrous magnesium sulfate. The solvent was removed to yield yellow crystalline **67** (11.6 g, 68%): mp 134–135 °C (explodes); IR (CH_2Cl_2) 2150 (=N=N), 1170 (CN); ^1H NMR ($CDCl_3$) δ 7.48 (m, 3 H, phenyl H), 7.70 (m, 2 H, phenyl H); UV (methanol) λ_{max} 285 nm.

Reaction of 4-Diazo-5-phenyl-4*H*-1,2,3-triazole (67) with 1-Morpholinyl-2-nitroethene (68). To **67** (0.62 g, 6.5 mmol) in dichloromethane (30 mL) was added **68** (1.13 g, 7.2 mmol)[26] in dichloromethane (20 mL). The resulting mixture was refluxed 1 h. Solvent removal under reduced pressure afforded a yellow mass, which was washed several times with cold water and dried in vacuo. Several recrystallizations from aqueous methanol afforded 3-nitro-8-phenyl[1,2,3]triazolo[5,1-*c*][1,2,4]triazine (**70**; 0.76 g, 48%): yellow solid; mp 247–248 °C; IR (KBr) 3075, 1595, 1580, 1570, 1545, 1315, 780, 695 cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.5 (m, 3 H, phenyl H), 8.25 (m, 2 H, phenyl H), 9.60 (s, 1 H, triazine H); exact mass calcd for $C_{10}H_6N_6O_2$ 242.1085, found 242.1130. Anal. Calcd for $C_{10}H_6N_6O_2$: C, 49.59; H, 2.50. Found: C, 49.23; H, 2.74.

5-Cyano-4-diazo-4*H*-1,2,3-triazole (71). To 4-amino-5-cyano-1,2,3-triazole[27] (1.09 g, 10 mmol) in 2 N hydrochloric acid (10 mL) at 0 °C was added sodium nitrite (0.76 g, 11 mmol) in a minimal amount of water. Dichloromethane (100 mL) was added to the light yellow mixture, and the aqueous solution was neutralized with sodium carbonate. After the organic layer had been separated, the aqueous solution was extracted with dichloromethane (800 mL). The fractions were combined and desiccated over anhydrous magnesium sulfate. Dichloromethane was totally removed to yield tan crystalline **71** (0.74 g, 62%): mp 125–126 °C (explodes); IR (CH_2Cl_2) 2200 (=N=N), 1490, 1350, 1333, 1160, 1100 cm^{-1}; UV (methanol) λ_{max} 279 nm.

Reaction of 5-Cyano-4-diazo-4*H*-1,2,3-triazole (71) with Phenylacetylene. To **71** (0.37 g, 3.1 mmol) in dichloromethane (50 mL) was added phenylacetylene (0.35 g, 3.50 mmol) in dichloromethane (20 mL). The resulting mixture was refluxed 16 h at which time its IR spectrum contained no diazo band. The solvent was removed under reduced pressure, and the yellow brown residue was recrystallized several times from aqueous ethanol to give 7-phenyl[1,2,3]triazolo[5,1-*c*][1,2,4]triazine-3-nitrile (**72**; 0.26 g, 38%): mp (aqueous ethanol) 159–160 °C; IR (KBr) 3100, 3075, 3000, 2900, 2840, 2240, 1605, 1270, 1220, 772, 683 cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.3–7.6 (m, 3 H, phenyl H), 7.8–8.02 (m, 2 H, phenyl H), 8.18 (s, 1 H, triazine H); exact mass calcd for $C_{11}H_6N_6$ 222.0984, found 222.0989.

3-Diazo-3*H*-1,2,4-triazole (73). 3-Amino-1,2,4-triazole[28] (1.0 g, 11.9 mmol) and sodium nitrite (1.0 g, 14.4 mmol) in water (10 mL) were added to concentrated nitric acid (2 mL) at 0–10 °C at a rate such that the temperature of the diazotizing mixture remained below 0 °C. The resulting slightly yellow degassing solution was stirred for 5 min in an ice bath. This procedure consistently gave solutions of 1,2,4-triazole-3-diazonium nitrate, which were used for preparing **73** as follows.

An aqueous solution, obtained as described above, was cooled below −4 °C and made basic (pH 9 to 11) with 2.6 N aqueous potassium hydroxide. The resulting cold red degassing solution was diluted with water to a volume of 40 mL. This procedure led to the destruction of any precipitate formed and consistently gave aqueous solutions of **73** usable immediately.

A freshly prepared aqueous solution of **73** was extracted with dichloromethane (four 50-mL portions) at 0 °C. (Because of the hazard involved in isolating **73**, no attempts were made to maximize the yield of the diazoazole.) To the combined extracts was added the reagent for cycloaddition, and the resulting solution was left standing at 0 °C for 12–18 h. The mixture was then concentrated to a solid at reduced pressure and worked up as described in the individual experiments.

Reaction of 3-Diazo-3*H*-1,2,4-triazole (73) with 1-Ethoxycyclohexene (45). Reaction of **45** (5 mL) and **73** was effected as above. After the mixture had been evaporated at reduced pressure, the concentrate was chromatographed over silica gel (20 g), eluting with ethyl acetate (100 mL) to give [1,2,4]triazolo-[5,1-*c*]cyclo[*c*][1,2,4]triazine (**74**; 0.152 g, 0.87 mmol): mp (1,2-dichloroethane) 184–185 °C; ^1H NMR ($CDCl_3$) δ 7.8 (s, 1 H, triazole H), 2.2 (m, 4 H), 1.8 (m, 4 H); IR (KBr) 3250–2800 (s, br d), 1650 (m), 1600 (s), 1200 (s), 970 (m), 910 (m), 900 (m), 800 (s); MS (70 eV), *m/e* (M^+ − fragment, relative intensity) 175.0861 (M^+, 100.00).

Reaction of 3-Diazo-3*H*-1,2,4-triazole (73) with 1-Morpholinylcyclohexene (61). A solution of **73** and **61** (5 mL) yielded a solid. Chromatography on silica gel and elution with ethyl acetate (150 mL) gave **74**: ^1H NMR ($CDCl_3$) δ 7.8 (s, 1 H, triazole H), 2.2 (m, 4 H), and 1.8 (m, 4 H).

Reaction of 3-Diazo-3*H*-1,2,4-triazole (73) with 1-Piperidinylcyclohexene (25). 1-Piperidinylcyclohexene (**25**, 5 mL) was added to **73** in dichloromethane at 25 °C. After addition was complete, the mixture was concentrated. The oily residue, on chromatography over silica gel (25 g) and elution with ethyl acetate (300 mL), yielded **74** (0.427 g, 2.4 mmol) identical with that described previously: ^1H NMR ($CDCl_3$) δ 7.8 (s, 1 H, triazole H), 2.2 (m, 4 H), and 1.8 (m, 4 H).

5-Phenyl-1,2,4-triazole-3-diazonium Tetrafluoroborate. To a stirred suspension of 3-amino-5-phenyl-1,2,4-triazole[29] (1.6 g, 10 mmol) and water (1 mL) was added tetrafluoroboric acid (48%, 15 mL) in small portions. The amine dissolved upon initial addition of acid and then its salt precipitated as further acid was introduced. After the final suspension had been cooled to 0 °C, concentrated aqueous sodium nitrite (0.7 g, 10 mmol) was added, and the mixture was stirred 10 min. The white solid formed, 5-phenyl-1,2,4-triazole-3-diazonium tetrafluoroborate, was collected on a sintered glass funnel in near-quantitative yield (2.5–2.6 g): IR absorption at 2300 cm^{-1} (N_2^+). The diazonium salt is a safe compound (it could not be detonated), but was used immediately after synthesis because it slowly colorized on standing.

3-Diazo-5-phenyl-3*H*-1,2,4-triazole (75). To a stirred mixture of dichloromethane (50 mL), water (150 mL), and 5-phenyl-1,2,4-triazole-3-diazonium tetrafluoroborate (2.6 g, 10 mmol) cooled in an ice bath was added excess sodium bicarbonate, and the mixture was stirred 30 min. The dichloromethane solution was removed, dried with anhydrous sodium sulfate, and concentrated in vacuo. The residue, **75** (1.44–1.49 g, 8.4–8.7 mmol, 84–87%), is a yellow solid that is light and highly shock sensitive, but can

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be weighed in tared flasks without incident. Triazole **75** exhibits intense IR absorption at 2200 cm^{-1} (=N_2). *Dry* **75** was typically used as soon as it was prepared, but could be stored in the dark at room temperature for several weeks without incident or apparent decomposition. In solution, **75** decomposes in a matter of hours at room temperature.

Reaction of 3-Diazo-5-phenyl-3*H*-1,2,4-triazole (75) with 1-Morpholinylcyclohexene (61). A solution of **75** (0.80 g, 4.7 mmol) in dichloromethane (10 mL) was added to **61** (1.0 g, 5.9 mmol) in dichloromethane (5 mL) at -60 °C. On warming the clear red solution (1 h) to room temperature, a precipitate formed. Evaporating the reaction mixture yielded a residue, which crystallized from hot 1,2-dichloroethane to give 6,7,8,9-tetrahydro-2-phenyl[1,2,4]triazolo[5,1-*c*][1,2,4]benzotriazine (**76**; 0.73 g, 62%) as a pale tan solid: mp (1,2-dichloroethane) 242 °C; IR (KBr) 2945 and 2920 (aliphatic CH), 1618 (aromatic), 1564, 1538, 1445, 1364, 1282, 798, and 690 cm^{-1}; ^1H NMR (DMSO-d_6) δ 8.50-8.20 (m, 2 H, Ph 2,6-H), 7.90-7.60 (m, 3 H, Ph 3,4,5-H) 3.00-250 (m, 4 H, 6,6,9,9-H of benzo group), and 2.35-2.00 (m, 4 H, 7,7,8,8-H of benzo group). Anal. Calcd for $C_{14}H_{13}N_5$: C, 66.92; H, 5.21; N, 27.87. Found: C, 67.03; H, 5.60; N, 27.70.

Reaction of 75 with 1-Piperidinylcyclohexene (25). To a solution of **25** (0.95 g, 5.7 mmol) in dichloromethane (5 mL) at -60 °C was added **75** (0.80 g, 4.7 mmol) in dichloromethane (10 mL). A solid precipitated from the red solution as the mixture warmed to room temperature (1 h). After evaporation of the solvent and recrystallization of the residue, **76** (0.75 g, 64%) was obtained identical with that from **75** and **61**. Additional products were isolated from the mother liquors, but the yield of **76** did not change by altering the time between addition and workup.

Synthesis of 6,7,8,9-Tetrahydro-2-phenyl[1,2,4]triazolo-[5,1-*c*][1,2,4]benzotriazine (75) from (5-Phenyl-1,2,4-triazol-3-yl)hydrazinium Tetrafluoroborate (79) and 1,2-Cyclohexanedione (80). 5-Phenyl-1,2,4-triazole-3-diazonium tetrafluoroborate (2.6 g, 10 mmol) was added in small portions to a stirred solution of stannous chloride (9.0 g, 20 mmol) in concentrated hydrochloric acid (5 mL) and 48% tetrafluoroboric acid (5 mL) at 0 °C. After the mixture had been stirred for 5 min, solid (5-phenyl-1,2,4-triazol-3-yl)hydrazinium tetrafluoroborate was collected. The wet solid was immediately added to **80** (1.20 g, 10 mmol) in acetonitrile (10 mL). The mixture was stirred for 1 h, diluted with 2 volumes of water, and neutralized with excess sodium bicarbonate. The solid was recrystallized from 1,2-dichloroethane, yielding **76** (0.60 g, 23%). This product is identical with that from reactions of **75** with enamines **61** and **25**.

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Registry No. **7**, 922-69-0; **12**, 51285-29-1; **20**, 62072-11-1; **23**, 62072-19-9; **24**, 62072-18-8; **25**, 2981-10-4; **27**, 111005-20-0; **28**, 50846-98-5; **29**, 111005-21-1; **32**, 111005-22-2; **33**, 111005-23-3; **37**, 105851-05-6; **44**, 111005-24-4; **45**, 1122-84-5; **47**, 111005-25-5; **48**, 105851-04-5; **51**, 111005-26-6; **55**, 111005-27-7; **56**, 111005-28-8; **59**, 111025-76-4; **60**, 89108-47-4; **61**, 670-80-4; **63**, 111005-29-9; **65**, 111005-30-2; **66**, 111005-31-3; **67**, 64781-77-7; **68**, 18169-20-5; **70**, 111005-32-4; **71**, 16968-06-2; **72**, 111005-33-5; **73**, 64781-78-8; **74**, 111005-34-6; **75**, 80670-36-6; **76**, 111005-35-7; **79**, 111005-36-8; **80**, 765-87-7; $NCCH_2COC(CH_3)_3$, 59997-51-2; $H_2C{=}CHOC_2H_5$, 109-92-2; C_6H_5NCO, 103-71-9; $(C_2H_5)_2NCH{=}C(CH_3)_2$, 16826-16-7; 1-$C_{10}H_7NCO$, 86-84-0; $C_6H_5C{\equiv}CH$, 536-74-3; $H_2C{=}C(OCH_3)CH_3$, 116-11-0; 3-amino-5-*tert*-butylpyrazole, 82560-12-1; 3-benzamido-5-*tert*-butylpyrazole, 111005-15-3; 3-amino-5-phenylpyrazole, 1572-10-7; 5-phenyl-3-pyrazolediazonium chloride, 60270-00-0; 2-aminoimidazole sulfate, 42383-61-9; 1-(dimethylamino)cyclohexene, 13815-46-8; norbornene, 498-66-8; norbornadiene, 121-46-0; *tert*-butyl 4-imidazolecarbamate, 34665-48-0; 4-aminoimidazole dihydrochloride, 111005-19-7; 4-amino-5-phenyl-1,2,3-triazole, 32416-41-4; 4-amino-5-cyano-1,2,3-triazole, 16968-08-4; 3-amino-1,2,4-triazole, 61-82-5; 3-amino-5-phenyl-1,2,4-triazole, 4922-98-9; 5-*tert*-butyl-3-pyrazolediazonium tetrafluoroborate, 111005-17-5; 5-phenyl-3-pyrazolediazonium tetrafluoroborate, 111005-18-6; 5-phenyl-1,2,4-triazole-3-diazonium tetrafluoroborate, 28151-85-1; 1,2,4-triazole-3-diazonium nitrate, 59104-93-7.

Intramolecular Diels-Alder Reactions of 3*H*-Pyrroles Resulting from the Thermal Rearrangements of 2*H*-Pyrroles

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The syntheses of methyl- and phenyl-substituted 2*H*-pyrroles 8 bearing a but-3-enyl or pent-4-enyl side chain are reported. The thermolyses of 8 yielded tricyclic derivatives with the 2-azabicyclo[2.2.1]hept-2-ene moiety resulting from the intramolecular Diels-Alder additions of 3*H*-pyrrole intermediates. No product resulting from the intramolecular cycloaddition of 2*H*-pyrroles or of 1*H*-pyrroles was observed. Thermochemical analysis and ab initio STO-3G calculations on model compounds suggested that the 2-azabicyclo[2.2.1]hept-2-enes derivatives are the only possible products under the conditions of our thermolyses. The rates of the isomerizations of 8 into the corresponding 3*H*-pyrroles intermediates, as well as those of their cyclizations could be enhanced in the presence of the cation-radical $(4\text{-}BrC_6H_4)_3NSbCl_6$ or of a Lewis acid.

Introduction

The 2*H*- and 3*H*-pyrroles[1] are 1-aza and 2-aza dienes, respectively, that are potential synthetic precursors for the preparation of polycyclic heterocycles via Diels-Alder cycloadditions.[2-4] To our knowledge, only the 2,2,3,4,5-pentachloro-2*H*-pyrrole (1) has been explored thus far for

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