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Metallated Ketenimines: Deprotonation of *N*-Isopropyl-diphenyl-ketenimine and Subsequent Trapping Reactions with Electrophiles A Theoretical and Experimental Study

Rolf Gertzmann[a1], Manfred H. Möller[b2], Ute Rodewald[b2], Roland Fröhlich[a3], Mathias Grehl[a3] and Ernst-Ulrich Würthwein*[a]

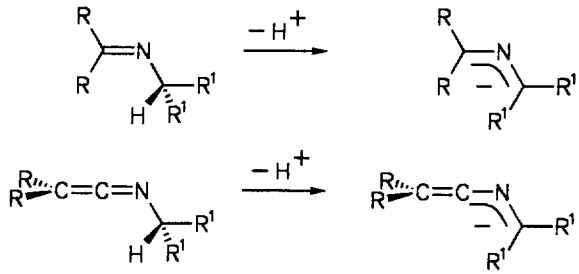
Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster, Corrensstr. 40, D-48149 Münster[a]

Anorganisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster, Wilhelm-Klemm-Strasse 8, D-48149 Münster[b]

Abstract: Deprotonation of *N*-isopropyl-diphenylketenimine **1** may be achieved by surplus strong organic base (2,2,6,6-tetramethylpiperidine, n-butyllithium, potassium *tert.*butylate in *tert.*butylmethyl ether). The resulting organometallic suspension is investigated by means of trapping reactions using various electrophiles. From the structures of the trapping products obtained the intermediacy of a substituted 1-methylene-2-aza-allyl anion **9** and of a 3-azapentadienyl anion **10** is deduced. Thus, proton sources yield a mixture of the 2-azabutadiene **2** together with two dimeric products, the 3-azahexatriene **3** and the heterocyclus **4.** Methyl iodide leads to the formation of a cross-conjugated dimeric product **5.** The 2-azabutadiene derivatives **6** and **7** are the trapping products using trimethylacetyl chloride or dimethyl disulfide, resp., as electrophiles, exhibiting multiple addition to intermediate substituted 3-azapentadienyl anion systems.- Quantum chemical calculations (MNDO, PM3, *ab initio*-methods) are used for the prediction of the gas phase acidities of *N*-isopropylformimine and *N*-isopropylketenimine as model systems; the structures obtained by complete geometry optimizations of the postulated monomeric anions and lithium compounds are discussed.

Ketenimines have found widespread use as reactive starting materials especially in heterocyclic synthesis.[4,5] Transition metal complexes of ketenimines are primarily useful for the generation of four-, five- and six-membered heterocyclic ring systems.[6] Regarding the metallation of ketenimines until recently attention was directed mainly towards the metallation at the nitrogen atoms of ketenimines (often by deprotonation of the appropriate nitriles);[7] reports on ß-carbon-metallated ketenimines are rare.[8]

In extension of previous studies [9] on the acidifying properties of imine functions on attached *N*-alkyl groups leading to 2-azaallyl anions we are interested in the question whether *N*-alkyl ketenimines can be deprotonated



Scheme 1.

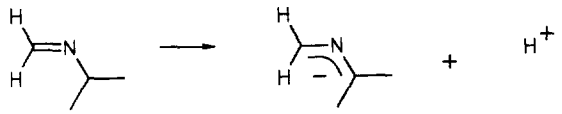
similarly in α-position of the *N*-alkyl group. This should lead to a new type of 2-azaallyl anions with an additional double bond at the 1-position (1-methylene-2-azaallylanions; see Scheme 1). Such organometallic intermediates deserve interest as polyfunctional synthetic building blocks. Furthermore, the structural properties of such species attract special attention with regard to the hybridization of carbon atom 1 and the position of the metal counterion. We also expect interesting aggregation phenomena of these highly reactive systems.

In this report we describe the deprotonation experiments of *N*-isopropyl-diphenylketenimine **1** and the subsequent trapping reactions of the organometallic intermediates with various electrophiles .[1] We have selected **1** as our target for investigation in spite of its expected slow deprotonation at the tertiary position; the corresponding *N*-ethyl derivative proved to give mixtures of compounds after deprotonation and quenching which were not separable.[1] The *N*-benzyl derivative is known to be subject to easy homolysis.[10] The emphasis of this study is mainly directed on the accurate analytical characterization of the trapping products in order to achieve a mechanistic overview of the reactive properties of these metallated ketenimines. Besides the experimental results we also present theoretical data on the acidity of the ketenimines, on the structures of the isolated anions and of the corresponding lithiated species in the gas phase.

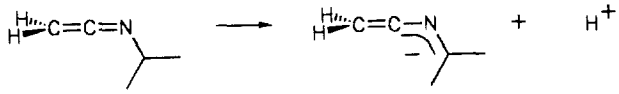
Quantum chemical Results

In order to get some insight into the structures and energies of ketenimines and their derived anions semiempirical (MNDO,[11] PM3[12]) and *ab initio*[13] (MP2/6-31+G*//6-31+G*) model calculations were performed. All structures presented here correspond to minima on the energy hyperface as it is shown by frequency analyses (NIMAG= 0). Zero point energy corrections were evaluated, but proved to be small (< 1kcal/mol) . They are therefore not taken into consideration in the following discussion. The primary question concerns the acidity of

Table 1. Calculated Heats of Formations ΔH_f [a], Total Energies E_{tot} [a] and Heats of Reactions ΔH_R [b] for the Deprotonation and Lithiation Reactions of N-Isopropylformimine and N-Isopropylketenimine in the Gas Phase.

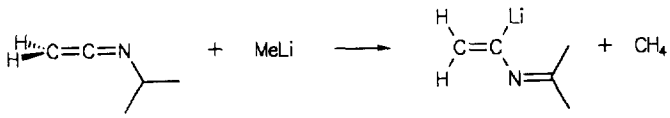


	$\Delta H_f/E_{tot}$	$\Delta H_f/E_{tot}$	$\Delta H_f/E_{tot}$	ΔH_R
MNDO	7.04	1.82	367.20	361.98
PM3	4.36	3.49	367.20	366.33
6-31+G*	-211.13700	-210.48793	0.0	407.28
MP2/ 6-31+G*	-211.82483	-211.20105	0.0	391.42



	$\Delta H_f/E_{tot}$	$\Delta H_f/E_{tot}$	$\Delta H_f/E_{tot}$	ΔH_R
MNDO	34.13	22.87	367.20	355.94
PM3	32.47	27.44	367.20	362.17
6-31+G*	-248.98247	-248.32951	0.00	409.73
MP2/ 6-31+G*	-249.79220	-249.16430	0.00	394.00

	$\Delta H_f/E_{tot}$	$\Delta H_f/E_{tot}$	$\Delta H_f/E_{tot}$	$\Delta H_f/E_{tot}$	ΔH_R
MNDO	7.04	-1.08	0.83	-11.95	-17.08
PM3	4.36	25.59	23.40	-13.02	-19.57
6-31+G*	-211.13700	-47.01760	-217.98313	-40.19567	-15.19
MP2/ 6-31+G*	-211.82483	-47.16670	-218.68995	-40.33395	-20.31



	$\Delta H_f/E_{tot}$	$\Delta H_f/E_{tot}$	$\Delta H_f/E_{tot}$	$\Delta H_f/E_{tot}$	ΔH_R
MNDO	34.13	-1.08	13.14	-11.95	-31.86
PM3	32.47	25.59	42.27	-13.02	-28.81
6-31+G*	-248.98247	-47.01760	-255.83785	-40.19567	-20.99
MP2/ 6-31+G*	-249.79220	-47.16670	-256.66382	-40.33395	-24.39

[a] $\Delta H_f/E_{tot}$: MNDO, PM3 (kcal/mol); *ab initio* methods (a.u.). [b] ΔH_R (kcal/mol).

ketenimines at the α-position of a *N*-isopropyl group in comparison to that of the corresponding imines.

From the calculated heats of formations (ΔH_f; semiempirical methods) or total energies (E_{tot}; *ab initio* MP2/6-31+G*//6-31+G*) acidities of ketenimines relative to imines for gas phase reactions were obtained (Heats of Reactions ΔH_R; Tab. 1). Whereas the semiempirical methods give slightly higher acidities for the ketenimines by 4-6 kcal/mol, the ab initio method favors by 2.6 kcal/mol imines in the deprotonation reactions.

For better comparison with the experiments, we also performed gas phase calculations for the metallation of imines and ketenimines using methyllithium as the model base (Tab. 1). From the energy lowest structures obtained (see below) we derived again a more easy metallation by 9-15 kcal/mol for the cumulene compared to the imine according to the semiempirical methods and by ca. 4 kcal/mol according to the *ab initio* method.

We conclude from these data, that both classes of compounds will show similar thermodynamic acidity in experimental gas phase deprotonation and metallation reactions; this may possibly be valid also for reactions in solution. Hence, deprotonation is predicted to be feasible using conventional strong organometallic bases.

The three quantummechanical methods give very similar geometries for the deprotonated species (anion without counterion; Fig. 1). As anticipated the structure is best described as a 1-methylene-2-azaallyl anion with a sp hybridized carbon atom bearing the methylene group. In other words, deprotonation of *N*-alkyl ketenimines yields an anion with a preserved ketenimine moiety; the negative charge is stabilized by 4π/3c conjugative allyl type interactions. The C=C double bond is orthogonal to the 2-azaallyl system and therefore not involved in the conjugation. This anion is very rich in energy: according to the ab initio method the isomeric 2-methyl-3-aza-pentadienyl anion, which prefers a planar, fully conjugated sickle-shaped 3-azapentadienyl chain, is predicted to be more stable by as much as 39.3 kcal/mol.

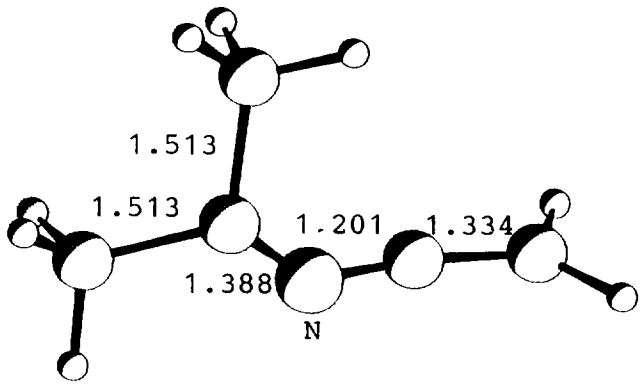


Figure 1. *Ab initio* optimized structure of the 1,1-dimethyl-3-methylene-2-azaallylanion with selected bond lengths [Å] (6-31+G*//6-31+G* *ab initio* result)

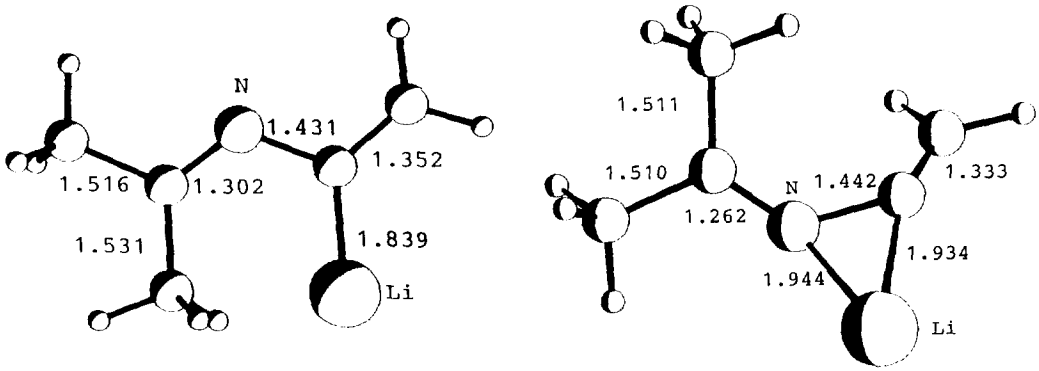


Figure 2. MNDO (left) and *ab initio* (6-31+G*//6-31+G*, right) optimized structure of the lithiated N-isopropyl ketenimine with selected bond lengths [Å]

The monomeric lithiated ketenimine is predicted by MNDO to have a planar 2-azabutadiene type structure with the lithium counterion monohapto bound to the carbon atom C3 (Fig. 2; left). PM3 and 6-31+G*//6-31+G* present a different picture of the energy lowest lithium compound (Fig. 2; right); in fact here also a 3-lithio-2-azabutadiene type structure is realized, yet not the planar s-trans, but a nonplanar cisoid gauche conformation (C=N-C=C dihedral angle: 67°(*ab initio*); 33° (PM3)) with the dihapto lithium cation bridging the N-C bond by utilizing the lone pair on nitrogen for internal complexation. It is known, that 2-azabutadienes show only small barriers for rotation around the central C-N bond.[14] The reason for the methodical difference lies most probably in the well known overestimation of carbon-lithium bonds by the MNDO method, which also underestimates a possible interaction to the lone pair at nitrogen.

Experimental deprotonation

The theoretical calculations predict similar thermodynamic acidities of *N*-alkyl groups attached to the nitrogen atoms of imines and of ketenimines. Hence, bases, which have found application in the synthesis of 2-aza-allylanions from *N*-alkyl imines [9] seem to be appropriate for the deprotonation of ketenimines. However, as it is well known from the chemistry of ketenes and ketenimines, the sp hybridized α carbon atom of these compounds is only little sterically shielded and very susceptible towards nucleophilic attack. Indeed, our experiments show that *n*- or *tert.*butyllithium and lithium diisopropylamide all attack at the α carbon atom of **1** leading to the corresponding enamine or amidine derivatives, resp.. (see also [4,15]) Deprotonation is not observed. On the other hand, the severely sterically crowded base lithium-2,2,6,6-tetramethylpiperidide (LiTMP) does not add, but for thermodynamic or kinetic reasons seems to be insufficient for deprotonation at a tertiary center such as in **1**. Even addition of TMEDA to the reaction mixture (*tert.*butylmethyl ether as solvent) and prolonged reaction times do not lead to deprotonation. However, addition of potassium *tert.*butylate rises the basicity and the rate of

deprotonation of the system considerably;[16] thus, complete deprotonation is achieved by treatment of one equivalent of ketenimine **1** with a mixture of two equivalents of potassium *tert.*butylate, two equivalents of 2,2,6,6-tetramethylpiperidine and two equivalents of *n*-butyllithium in *tert.*butylmethyl ether at low temperatures.

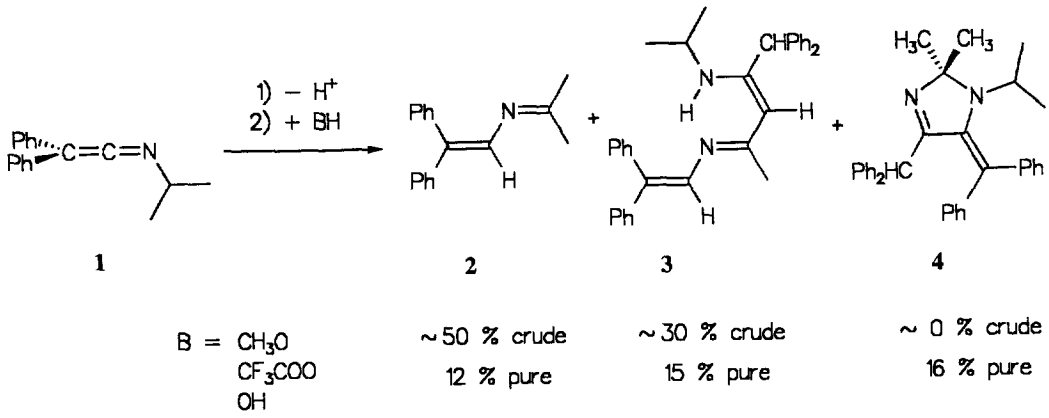
The deprotonation procedure has been optimized and standardized (see Experimental), and the resulting organometallic mixture has been treated with various electrophiles. We were able to obtain successful reactions with several proton sources, methyl iodide, trimethylacetyl chloride and dimethyl disulfide. These trapping reagents cover a wide range of reactivity, redox properties and hardness/softness. Less successful were trapping reactions with aldehydes, carbon dioxide, dimethylcarbonate, methyl chloroformate and trimethylsilyl chloride; in these cases, we were not able to isolate stable products from the very complex reaction mixtures. Possibly, decomposition of the highly functionalized, often quite sensitive products during work up may account for these failures; the same reason is most likely responsible for the less satisfying yields of pure material in the successful conversions. NMR spectra of the reactions mixtures (after evaporation of the solvent), however, often indicated quantitative conversions and fairly good yields of crude materials.

The complex nature of some of the products obtained required several X ray structure determinations for the complete assignment of constitutions and conformations.

Trapping with Various Proton Sources

Treatment of the organometallic reaction mixtures with methanol or trifluoroacetic acid or sodium hydrogencarbonate solution as proton sources yields a mixture of about 50% of 2-azabutadiene **2** and of about 30% of the dimer **3**, as estimated by the integration of the ^{1}H NMR spectrum of the crude reaction mixture after aqueous or non-aqueous work up (see Experimental, Scheme 2). Quick column chromatography allows the isolation of 15% of the dimer **3** and of 16% of the imidazole **4** which was not seen in the crude mixture and may well be generated during work up from a less stable intermediate. Isolation of the highly reactive 2-azabutadiene **2** by distillation of the crude reaction mixture is difficult and gives only poor yield (12%). If 6 mol equivalents of base (6 LiTMP + 6 KOtBu) are used for the deprotonation, after methanol addition and non-aqueous work up (see Experimental) the GC analysis indicates the preferred formation (ca. 90%) of the 2-azabutadiene **2** without dimeric compounds; however, isolation of pure material is still very difficult because of the reactive properties of this highly sensitive compound.

The constitution of the unexpected imidazole **4** was determined by X ray crystallography (see Fig. 3). It may regarded as a five-membered heterocyclus incorporating the cross conjugated π-system of a 3-amino-1-azabutadiene subunit.



1 **2** **3** **4**

Scheme 2.

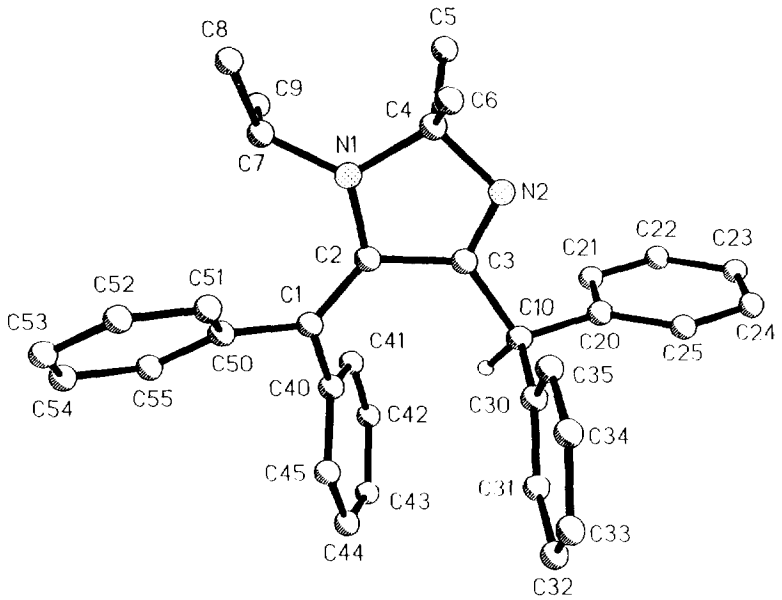
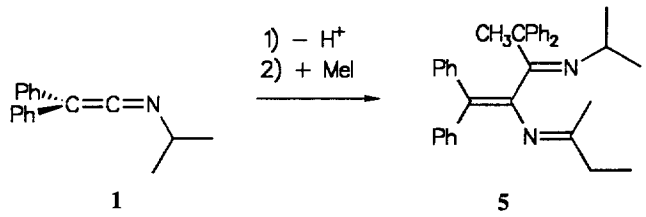


Figure 3. XS-Plot (SHELXTL-PLUS-Program [17]) for **4** with crystallographic numbering.

Trapping with Methyl Iodide

Trapping of the organometallic intermediates with methyl iodide results mainly in the formation of the dimeric product **5** (about 80% in the crude reaction mixture by ^{1}H NMR integration). Due to its instability only 18% of **5** may be obtained as crystals after chromatography (Scheme 3).



1 **5**

~ 80 % crude
18 % pure

Scheme 3.

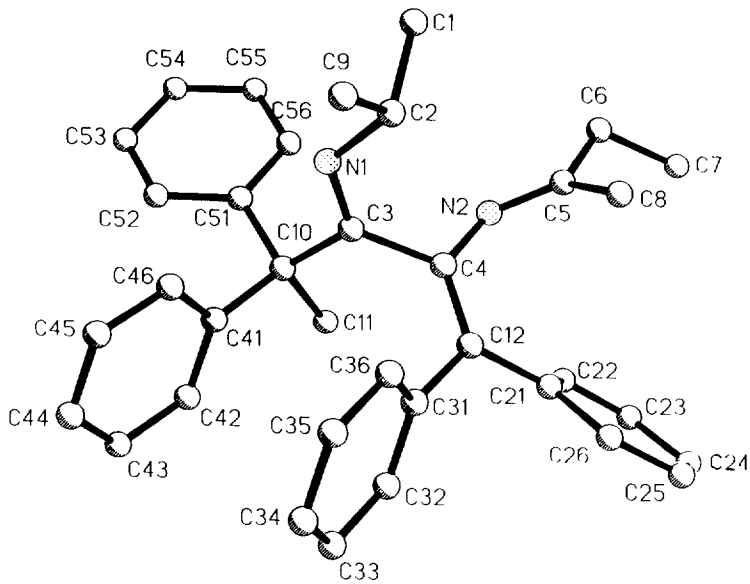
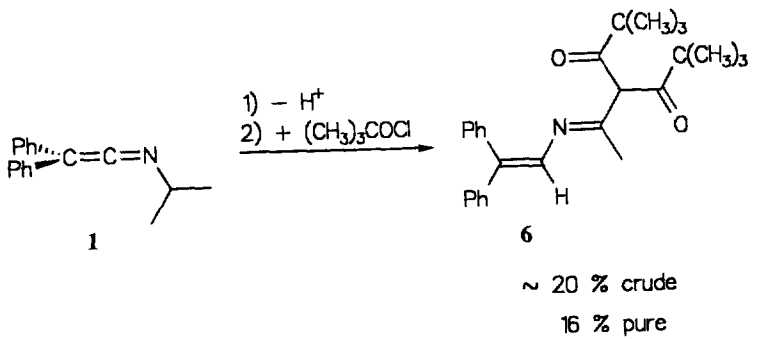


Figure 4. XS-Plot (SHELXTL-PLUS-Program [17]) for **5** with crystallographic numbering.

Again, the constitution and configuration of **5** was elucidated by X ray crystallography (see Fig. 4). The structure obtained clearly reveals the dimeric open chain structure with two additional methyl groups, resulting from a dianionic intermediate or two subsequent deprotonations. **5** is an interesting example of a cross-conjugated π-systems, consisting of 1- and 2-azabutadiene subunits sharing a mutual C=C double bond.

Trapping with Trimethylacetyl Chloride

Addition of trimethylacetyl chloride to the reaction mixture leads to a complex product distribution. However, after aqueous work up and chromatography 16% of a colorless solid **6** can be isolated (about 20% was seen by

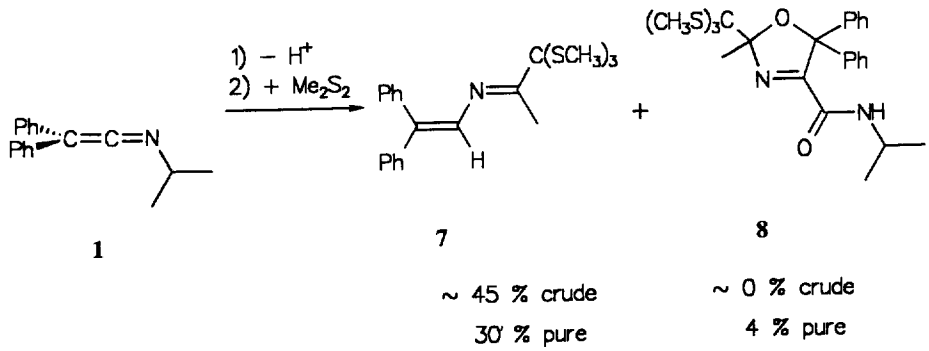


Scheme 4.

^{1}H NMR integration in the crude reaction mixture). Spectroscopic data clearly prove the two fold addition of the electrophiles to the same carbon atom C5 of the 3-azapenta-1.3-diene **6** (Scheme 4).

Trapping with Dimethyl Disulfide

Similarly, dimethyl disulfide attacks three fold and leads to the 3-azapenta-1,3-diene **7** in about 45% yield (estimated by ^{1}H NMR integration; 30% of pure material were obtained after HPLC). The very unexpected structure is the result of triple addition to the same carbon atom C5 (Scheme 5). Again, the constitution and the s-trans conformation were elucidated by X ray crystallography (see Fig. 5; left). Interestingly, the $(CH_3S)_3C$-subunit shows local C_s symmetry. Due to its poor solubility, small amounts (about 4%) of another crystalline material were detected in the reaction mixture, the 3-oxazoline derivative **8** (X ray, see Fig. 5; right). The presence of an oxygen atom in this ring system suggest its generation during work up. Diphenylmethylene compounds are known to be oxidized by air leading i.a. to benzophenone, which is also found in the reaction mixture.[18]



Scheme 5.

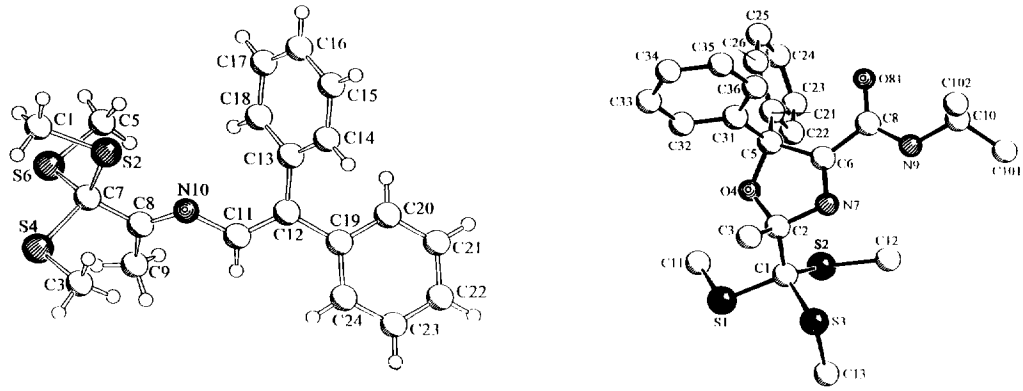


Figure 5. SCHAKAL-Plots [19] of **7** (left) and **8** (right) with crystallographic numbering

Mechanistic Considerations

In this chapter, we try to summarize and to clarify the results of the various trapping reactions. Scheme 6 gives an overview of experiments performed, indicating all substances isolated together with some reasonable intermediates, which may account for the observed products.

In the first stage of the reaction sequence, the deprotonation reaction, it is reasonable to assume that deprotonation first occurs at the α carbon atom of the *N*-isopropyl group of **1** yielding anion **9**. Indeed, the 2-azabutadiene **2** and the dimeric products **4, 5** may be considered to be direct trapping products of **9**. **2** may be

generated by proton addition to the central atom C3 of **9**. The dimeric products **4** and **5** give evidence for the presence of starting material **1** together with anion **9** in the course of the reaction. As anticipated the electrophilic α carbon atom of **1** may add to the corresponding central carbon atom C3 of **9** (umpolung by deprotonation), affording the intermediate **11** from which the products **4** and **5** are derived. In both cases, interesting cross-conjugated π systems are produced.

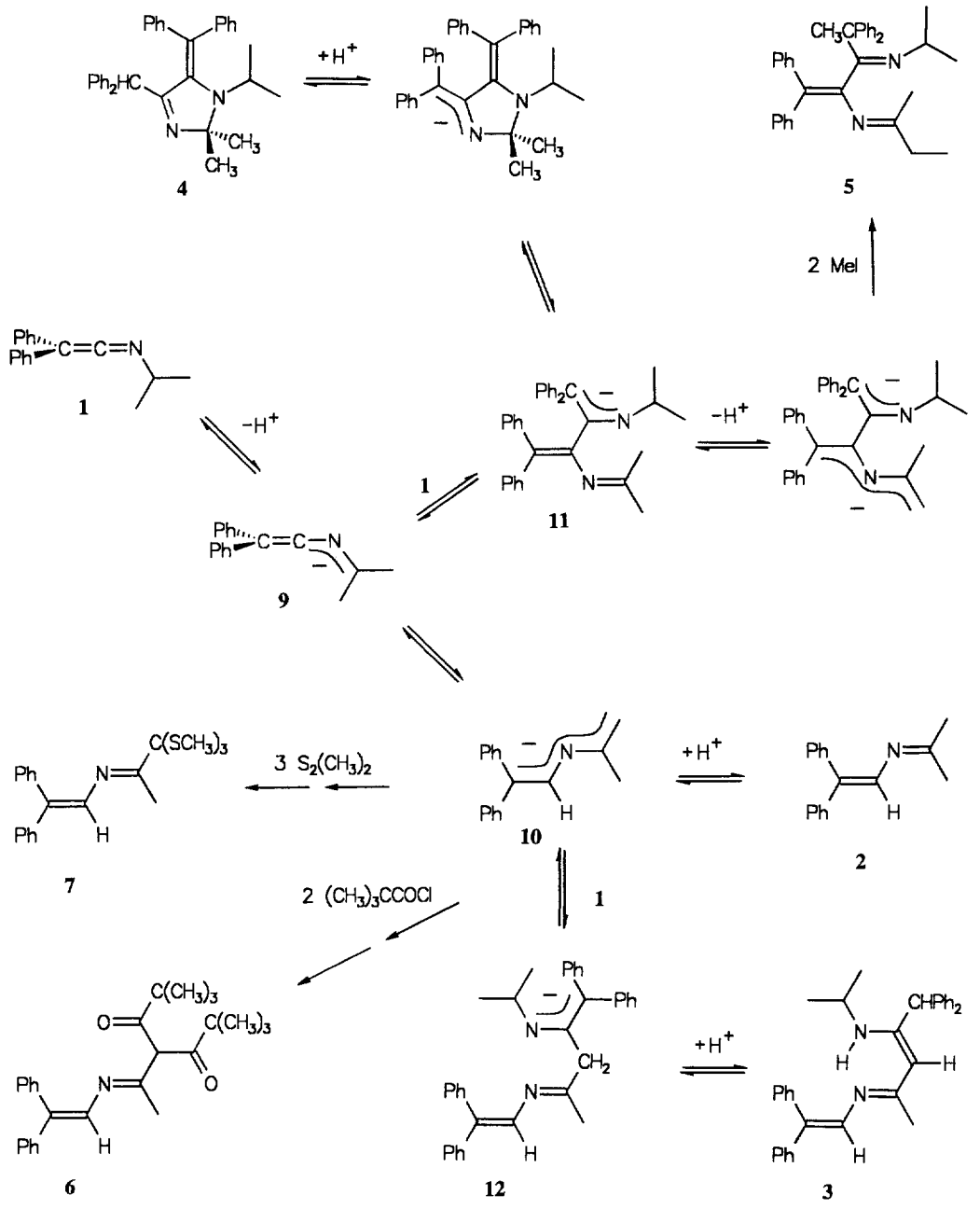
On the other hand, the isolated products **3, 6** and **7** clearly are all trapping products of the hitherto unknown 3-azapentadienyl anion **10**;[20] **2** also may be generated via **10**. As indicated by the calculations, the tautomerism from **9** to **10** is strongly exothermic; the reaction conditions employed (excess of base, presence of proton transfer reagents (*tert.*butanol, amines etc.)) are well suited for such an equilibration.

Similar to anion **9**, the 3-azapentadienyl anion **10** seems also to exist in the presence of **1** or in equilibrium with **1**. It is rational to postulate an attack of carbonatom C5 of **10** at the α carbonatom of **1** affording the 1,5-diazaheptatrienyl intermediate **12**. **12** is the prerequisite for the formation of the dimeric trapping product **3** as the most stable of several tautomers due to its chelating hydrogen bridge. The multiple trapping reactions with the electrophiles trimethylacetyl chloride and dimethyl disulfide affording **6** and **7** are easily explained by the increased acidity of the primary trapping products compared to **9** and by the excess of base used in the experiments.

In conclusion, deprotonation of **1** under the reaction conditions employed leads to a complex, possibly quickly equilibrating mixture of different anionic intermediates and the starting material (we consider the possibility of reversible dimerisation reactions in Scheme 6 without having direct experimental prove for it). The special properties of the electrophilic reagents are responsible for the reaction channel realized; e.g. protons as small, hard and quickly reacting electrophiles give reasonable overall yields of the trapping products since they seem to trap the equilibrating mixture at once; this indicates that all branches of Scheme 6 are open for trapping reagents simultaneously. Slower reacting electrophiles (methyl iodide, trimethylacetyl chloride and dimethyl disulfide) withdraw some intermediates from the reaction mixture and so, they govern to some extent the nature of the products obtained (see for instance the products **5**, **6** and **7**). However, the often not very satisfying material balance should be kept in mind, since the amounts of purely isolated products sometimes only represent a fraction of the total conversion.

Conclusion

In this study, we have presented the first experimental evidence for the successful deprotonation of suitable *N*-alkyl ketenimines in α-position of the N-alkyl group, similarly as it is known for the corresponding simpler N-alkyl imines. From the products of trapping reactions using various electrophiles we have deduced two major reaction pathways: a) the formation of dimeric products from reactions of the anions **9** and **10** with its precursor, the ketenimine **1**; and b) the generation of 2-azabutadiene derivatives as trapping products of an intermediate 3-azapentadienyl anion **10**. Slow deprotonation and the highly electrophilic nature of ketenimines clearly are responsible for the



Scheme 6. Mechanistic considerations regarding the trapping reactions of deprotonated **1** with various electrophiles.

observed formation of dimeric products. Base induced dimerisations as found in our study offer an interesting new synthetic pathway to unusual acyclic and heterocyclic conjugated systems. Another preparatively very valuable observation is the accessibility of 3-azapentadienyl anions by this route; open chain 3-azapentadienyl metal compounds, not incorporated into a heterocyclic ring system, are unknown to our knowledge. Besides deprotonations, transmetallation reactions also seem to be promising synthetic routes to these anionic intermediates. Further work is aimed towards this aspect of ketenimine chemistry.

EXPERIMENTAL SECTION

IR: Perkin-Elmer PE 298. - ^{1}H NMR: Bruker WM-300 (300 MHz), internal reference tetramethylsilane. - ^{13}C NMR: Bruker WM-300 (75.47 MHz) and AM-360 (90.56 MHz), internal reference tetramethylsilane. - MS: Finnigan MAT C 312. - GC/MS: Varian MAT CH7A with GC Varian 1400 and data system SS200; Finnigan MAT 8230 with Varian 3400 and data system SS300. Silica capiliary column OV 225 (30m).- CHN: Perkin Elmer CHN-Analysator 240.- HPLC: LiChrosorb Si60 (5µm or 7 µm, resp., length 250 mm, diameter 16mm).- Flash chromatography: Kieselgel 60 (Merck), 0.040-0.063 mm.- Melting points are uncorrected. - All solvents are rigorously dried by standard methods. All experiments are carried out with complete exclusion of moisture (argon; septum - syringe technique) in glass ware, which is thoroughly dried by repeated heating under argon and subsequent evacuation.

General procedure for the deprotonation of N-isopropyl-diphenylketenimine (1) using two eq. potassium tert.butoxide / 2,2,6,6-tetramethylpiperidine / n-butyllithium: [21,22] A 50 ml Schlenk flask, equipped with septum and argon inlet, is filled with 0.900 g (8.0 mmol) KO*t*Bu and *tert.*butylmethyl ether (20 ml) by use of a syringe. The mixture is cooled to -30°C, then 1.35 ml (8.0 mmol) of 2,2,6,6-tetramethylpiperidine is added. The suspension is cooled to -100°C and treated dropwise with 5.00 ml (8.0 mmol) of *n*-butyllithium (1.6 M solution in *n*-hexane). Within 25 min. the mixture is allowed to warm to -78°C. Now, 0.941 g (4.0 mmol) of *N*-isopropylketenimine **1**,[23] dissolved in *tert.*butylmethyl ether (10 ml), is added dropwise; after 5 min the suspension turns orange and later it becomes deep red. After complete addition the suspension is allowed to warm to -20°C within 2.5 h; this temperature is maintained for 1 h; then, the suspension of the *organometallic intermediates* is cooled again to -78°C.

General Procedure for the work up of the crude products after the trapping reaction:
Method A (aqueous work up): The crude reaction mixture is poured into a solution of diethyl ether (50 ml) and petroleum ether (200 ml); this mixture is washed with two portions of 30 ml of water. The combined organic layers are dried over $MgSO_4$, and the solvent is removed *in vacuo.*
Method B (non-aqueous work up): After evaporation of the *tert.*butylmethyl ether *in vacuo,* the residue is treated

with petroleum ether (150 ml); the resulting suspension is filtered twice in an argon atmosphere by use of a thoroughly dried filter funnel. Finally, the filtrate is freed from the solvent *in vacuo*.

Trapping of the organometallic intermediates with methanol: 5-Methyl-1,1,7,7-tetraphenyl-6-isopropylamino-3-aza-hepta-1,3,5-triene (**3**) *and 2,2-dimethyl-4-diphenylmethyl-5-diphenylmethylene-1-isopropyl-2,5-dihydro-1,3-imidazole* (**4**): Within 5 min 0.681 ml (16.8 mmol) of methanol is added to the -78°C cold suspension of the *organometallic intermediates*. During the addition, the color of the mixture turns from deep red to yellow. The reaction mixture (a ^{1}H NMR spectrum of the crude mixture indicates **2** : **3** ≈ 50% : 30%) is allowed to warm to room temperature overnight. At -60°C the color of the mixture turns green and later orange. The work up follows method B. Quick column chromatography (neutral Al_2O_3; activity 3, cyclohexane / ethyl acetate, (140 : 1) furnishes a first fraction of **4** [R_f(DC) = 0.24], which crystallizes very slowly at 6°C giving red prisms (150 mg, 16%); m.p. 125°C (from cyclohexane / ethyl acetate, 140 : 1). The next two fractions are combined and chromatographed again (cyclohexane / ethyl acetate, 120 : 1; R_f(DC) = 0.30), yielding the pure yellow oil **3** (152 mg, 15%). (The same products may be obtained by trapping the suspension of the *organometallic intermediates* with TFA resp. a satd. $NaHCO_3$ solution.) *5-Methyl-1,1,7,7-tetraphenyl-6-isopropylamino-3-aza-hepta-1,3,5-triene* (**3**): IR (Film): $\tilde{\nu}$ = 3390 cm^{-1} (w), 3080 (m), 3060 (m), 3020 (m), 2975 (m), 2920 (w), 2860 (w), 1650 (m,sh, C=N), 1635 (vs, C=C), 1590 (vs, C=C), 1560 (s, br, C=C), 1490 (vs, sh), 1480 (vs), 1440 (s), 1380 (s), 1365 (s), 1340 (s, sh), 1330 (s), 1310 (s), 1280 (s), 1270 (s, sh), 1250 (s, sh), 1160 (m), 1130 (s), 1075 (m), 1030 (m), 1020 (m, sh), 1000 (w,sh).- ^{1}H NMR ($CDCl_3$): δ = 0.51 [d, ^3J= 6.41 Hz, 6 H, CH(CH_3)$_2$], 1.89 (s, 3 H, CH_3C=N), 3.37 [sept, ^3J= 6.41 Hz, 1 H, CHCH$_3$)$_2$], 4.08 (s, 1 H, C*H*=CN), 5.10 (s, 1 H, C*H*Ph$_2$), 6.99-7.41 (m, 21 H, 20 aromatic H, C=C*H*N), 11.49 (s, 1 H, N*H*.- ^{13}C NMR ($CDCl_3$): δ = 21.02 (CH_3C=N), 23.41 [(CH_3)$_2$CH], 44.98 [(CH_3)$_2$*C*H], 53.37 (*C*HPh$_2$), 97.75 (*C*H=CN), 125.9 (*C*H$_{arom.}$), 126.4 (*C*H$_{arom.}$), 126.6 (*C*H$_{arom.}$), 127.3 (*C*H$_{arom.}$), 128.0 (*C*H$_{arom.}$), 128.3 (*C*H$_{arom.}$), 128.4 (*C*H$_{arom.}$), 129.4 (*C*H$_{arom.}$), 133.3 (*C*=CHN), 133.3 , 140.7 (2 *C*$_{ipso}$), 141.2 (2 *C*$_{ipso}$), 143.3 (C=*C*HN), 160.6 (CH=*C*N), 162.8 (CH_3*C*=N).- MS (70 eV), m/z (%): 470 (30) [M$^+$], 373 (36), 344 (34) [M$^+$-$C_{13}H_9$], 276 (30), 165 (87) [$C_{13}H_9^+$], 105 (52), 97 (72), 77 (100) [$C_6H_5^+$].- $C_{34}H_{34}N_2$ (470.66): calcd. C, 86.77; H, 7.28; N, 5.95; found C, 87.07; H, 7.38; N, 6.25. *2,2-Dimethyl-4-diphenylmethyl-5-diphenylmethylene-1-isopropyl-2,5-dihydro-1,3-imidazole* (**4**): - IR (KBr): $\tilde{\nu}$ = 3050 cm^{-1} (m, sh, CH), 3020 (m, CH), 2990 (m, CH), 2980 (s, CH), 1650 (m, sh, C=N), 1640 (m, C=C), 1580 (s, C=C), 1525 (s, br), 1500 (m, sh), 1470 (s), 1425 (m, sh), 1420 (s), 1370 (m), 1350 (s), 1340 (s), 1320 (s, sh), 1310 (s), 1285 (s, br), 1264 (s), 1245 (s), 1200 (s), 1180 (s), 1150 (s), 1130 (m), 1100 (s), 1050 (m), 1015 (s).- ^{1}H NMR ($CDCl_3$): δ = 1.00 [d, ^3J= 7.15 Hz, 6 H, (CH_3)$_2$CH], 1.49 (s, 6 H, 2 CH_3), 3.64 [sept., ^3J= 7.15 Hz, 1 H, (CH_3)$_2$C*H*, 4.55 (s, 1 H, C*H*Ph$_2$), 6.88-7.20 (m, 20 H, aromatic H).- ^{13}C NMR ($CDCl_3$): δ = 21.77 [(CH_3)$_2$CH], 28.24 (2 CH_3), 47.24 [(CH_3)$_2$CH], 50.19 (CHPh$_2$), 91.22 (*C*N$_2$), 125.6 (*C*H$_{arom.}$), 126.0 (*C*H$_{arom.}$), 126.4 (*C*H$_{arom.}$), 127.7 (*C*H$_{arom.}$), 128.0 (*C*H$_{arom.}$), 128.2 (*C*=C-N), 128.3 (*C*H$_{arom.}$), 129.0 (*C*H$_{arom.}$), 129.7 (*C*H$_{arom.}$), 131.7 (*C*H$_{arom.}$), 142.3 (2 *C*$_{ipso}$), 144.2 (*C*q), 144.3 (*C*q) 145.1 (*C*q) 170.5 (*C*=N).- MS (70eV), m/z (%): 470 (42) [M$^+$], 455 (44) [M$^+$-CH_3], 413 (18) (455-C_3H_6], 337 (12), 246 (14), 234 (17) [$C_{17}H_{16}N^+$], 193 (24) [$C_{14}H_{11}N^+$], 167 (100) [193-CN],

165 (40) [$C_{13}H_9^+$], 152 (32), 57 (22). - $C_{34}H_{34}N_2$ (470.66): calcd. C, 86.77; H, 7.28; N, 5.95; found C, 86.55; H, 7.50; N, 6.26.

X ray diffraction analysis of **4**:[24] A red, prismatic crystal $C_{34}H_{34}N_2$ (from n-hexane), crystal size 0.8 x 0.8 x 1.2 mm^3, was measured at room temperature by using an automatic CAD4 Turbo Diffractometer (Enraf-Nonius) with Mo-K_α radiation (λ = 0.71073 Å) and a graphite monochromator. 11204 reflexions were collected in the 2Θ range 4.4 << 2 Θ << 56° (scan speed variable; 3.3 to 5.5°/min). Crystal system: Monoclinic, space group P_1/c Z= 4, a= 9.450(2) Å, b= 31.651(6) Å, c= 9.914(2) Å, β = 109.89(3)°; V= 2788.4(10) $Å^3$; Dx = 1.121 g·cm^{-3}; μ = 0.65 cm^{-1}, no absorption correction. The structure was solved for the non-hydrogen atoms by direct methods (SHELXTL-PLUS program [17]) using 6708 independent reflexions. After the addition of the hydrogen atoms (coupled with respect to position and temperature parameters to the corresponding carbon atoms) anisotropic refinement led to agreement factors R= 0.0643 and w$R2$ = 0.2116 (weight = $1/[\sigma^2F_o^2) + (0.0647 \cdot P)^2 + 1.16 \cdot P]$, where $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$)[3512 reflections with $F_o > 4.0\sigma(F_o)$, 325 variable parameters, program SHELXL-93.[25] The molecular shape is presented in Fig. 3.

Deprotonation of N-isopropyl-diphenylketenimine (**1**) *using six eq. potassium tert.butylate / 2,2,6,6-tetramethyl-piperidine / n-butyllithium and subsequent trapping with methanol: 1,1-Diphenyl-4-methyl-3-aza-1,3-pentadiene* (**2**): 2.700 g (24.0 mmol) of KO*t*Bu is added to a 100 ml Schlenk flask, equipped with septum and argon inlet. *tert.*Butylmethyl ether (50 ml) and 4.05 ml (24.0 mmol) 2,2,6,6-tetramethylpiperidine (at -30°C) are added. Then, the suspension is cooled to -100°C, dropwise treated with 15.00 ml (24.0 mmol) of *n*-butyllithium (1.6 M solution in *n*-hexane) and slowly warmed to -78°C over a period of 25 min 0.941 g (4.0 mmol) ketenimine **1**,[23] dissolved in *tert.*butylmethyl ether (10 ml), is added dropwise, while the color of the suspension turns to red and later to deep red. After complete addition of the ketenimine the temp. of the suspension is kept at -60°C for 4h; then the mixture is cooled to -78°C. To this deep red suspension 2.10 ml (53.0 mmol) of methanol is added within 5 min; during the addition the color of the mixtures changes immediately to yellow. The mixture is allowed to warm to room temp. overnight and is worked up following method B [crude yield: 2 > 90% (GC)]. The subsequent Kugelrohr distillation yields a fraction (145°C/ 0.02 mbar), which consists of **2** (purity only 75%).- IR (Film): $\tilde{\nu}$ = 3100 (w, CH), 3080 (m, CH), 3050 (s, CH), 3020 (m, CH), 2990 (m, CH), 2930 (m, CH), 2900 (m, CH), 1690 (s, C=N), 1640 (s, sh, C=C), 1630 (vs), 1600 (vs, C=C), 1570 (m, C=C), 1490 (vs, C=C), 1440 (vs), 1430 (m), 1380 (m), 1370 (s), 1335 (w), 1320 (w, sh), 1310 (w), 1280 (m), 1240 (s), 1200 (m), 1180 (m, sh), 1155 (m), 1120 (m), 1075 (s), 1030 (m), 1000 (w).- ^{1}H NMR ($CDCl_3$): δ = 1.99 (s, 3 H, CH_3), 2.09 (s, 3 H, CH_3), 7.00-7.40 (m, 11 H, 10 aromatic H, CH=C).- ^{13}C NMR ($CDCl_3$): δ = 20.34 (CH_3), 29.00 (CH_3), 127.0 (CH_{ortho}), 127.5 (CH_{para}), 128.1 (CH_{meta}), 128.9 (CH_{para}), 130.3 (CH_{ortho}), 131.2 (CH_{meta}), 133.6 (CH=C), 138.3 (C_{ipso}), 138.4 (C_{ipso}), 142.3 (CH=C), 169.2 (C=N).- MS (GC-MS), m/z (%): 235 (92) [M^+], 220 (100) [M^+-CH_3], 178 (50) [$C_{14}H_{10}^+$], 165 (7) [$C_{13}H_9^+$], 152 (8), 77 (3) [$C_6H_5^+$].- $C_{17}H_{17}N$ (235.33): calcd. C, 86.77; H ,7.28; N, 5.95; found C, 85.56; H, 7.18; N, 5.30.

Trapping of the organometallic intermediates with methyl iodide: 3,8-Dimethyl-5-diphenyl-methylene-6-(1,1-diphenyl-ethyl)-4,7-diaza-3,6-nonadiene (**5**): At -78°C 1.05 ml (16.8 mmol) of methyl iodide is added within five min. to the deep red suspension of the *organometallic intermediates*; then the mixture is allowed to warm to room temp. overnight. Work up of the orange solution following *method B* furnishes **5** in about 80% crude yield. 0.460 g of the crude product is filtered over a short silica gel column (*n*-hexane / diethyl ether, 100 : 1); at -20°C, from the filtrate 100 mg light yellow, prismatic **5** crystallizes out, which is washed with cold *n*-hexane. The remaining oil is purified by HPLC [t_r value = 9.4 - 10.6 min; *n*-hexane / ethanol, 35 : 1; flow: 5ml/min] to yield 80 mg of additional **5** (total yield: 180 mg, 18%); m.p.: 132°C [*n*-hexane/diethyl ether (100 : 1)]. - IR (KBr): $\tilde{\nu}$ = 3070 cm^{-1}(w, sh, CH), 3050 (m, CH), 3000 (m, CH), 2980 (m,sh, CH), 2960 (s, CH), 2920 (m, CH), 2900 (m, CH), 2860 (m, CH), 1635 (s, sh, C=N), 1625 (s, C=C), 1590 (m, C=C), 1580 (m, sh, C=C), 1570 (m, sh, C=C), 1560 (w, sh, C=C), 1485 (m, C=C), 1450 (m), 1435 (s), 1420 (m, sh), 1370 (m), 1355 (m), 1330 (w), 1310 (m), 1260 (m), 1200 (m), 1180 (m), 1130 (m), 1065 (m), 1055 (m,sh), 1025 (m), 1000 (m).- ^{1}H NMR ($CDCl_3$): δ = 0.76 (t, ^3J= 7.36, 3 H, CH_3CH_2), 0.92 (d, ^3J= 6.56, 3 H, CH_3CH), 1.00 (s, 3 H, CH_3CH), 1.29 (s, 3 H, CH_3C=N), 1.78 (q, ^3J= 7.36 Hz, 1 H, CH_3CHH), 1.84 (q, ^3J= 7.65, 1 H, CH_3CHH), 1.86 (s, 3 H, CH_3CPh_2), 4.04 (sept, ^3J= 6.56, 1 H, $(CH_3)_2CH$), 6.85 - 7.23 (m, 20 H, aromatic H).- ^{13}C NMR ($CDCl_3$): δ = 9.68 (CH_3CH_2), 21.21 (CH_3C=N), 22.39 (CH_3CHCH_3), 22.85 (CH_3CHCH_3), 28.59 (CH_3CPh_2), 33.68 (CH_3CH_2), 53.94 (CH_3CHCH_3), 56.77 (CH_3CPh_2), 122.8 (C=CPh_2), 125.0 ($CH_{arom.}$), 125.4 ($CH_{arom.}$), 125.9 ($CH_{arom.}$), 126.9 ($CH_{arom.}$), 127.1 (CH_{arom}), 127.5 (CH_{arom}), 127.8 (CH_{arom}), 128.8 (CH_{arom}), 129.2 (CH_{arom}), 129.9 (CH_{arom}), 130.3 (CH_{arom}), 140.6 (C_{ipso}), 141.8 (C=CN), 148.9 (C_{ipso}), 149.7 (C_{ipso}), 168.9 (2 C=N).- MS (GC-MS), m/z (%): 498 (10) [M^+], 438 (2) [M^+-CH_3], 469 (2) [M^+-C_2H_5], 455 (2) [M^+-C_3H_7], 317 (100) [M^+-$C_{14}H_{13}$], 275 (97), 258 (28), 248 (96), 181 (82) [$C_{14}H_{13}^+$], 165 (44) [$C_{13}H_9^+$], 145 (29), 91 (27) ($C_7H_7^+$], 77 (20) [$C_6H_5^+$], 43 (22) [$C_3H_7^+$].- $C_{36}H_{38}N_2$ (498.71): calcd. C, 86.70; H, 7.68; N, 5.62; found C, 86.76; H, 7.78; N, 5.62.

X ray diffraction analysis of **5**:[24] A light yellow, prismatic crystal $C_{36}H_{38}N_2$ (from n-hexane/diethyl ether, 100:1), crystal size 0.6 x 0.5 x 0.4 mm^3, was measured at room temperature by using an automatic CAD4 Turbo Diffractometer (Enraf-Nonius) with Mo-K_α radiation (λ = 0.71073 Å) and a graphite monochromator. 13551 reflexions were collected in the 2Θ range 4.0 << 2 Θ << 60.0° (scan speed variable; 1.65 to 3.30°/min). Crystal system: Triclinic, space group *P*, *Z*= 2, *a*= 10.322(2) Å, *b*= 12.262(2) Å, *c*= 12.344(2) Å, α = 93.23(3)°, β= 93.49(3)°, γ = 107.18 (3)°; *V*= 1443.5(4) $Å^3$; *D*x = 1.147 $g{\cdot}cm^{-3}$; μ=0.7 cm^{-1}, no absorption correction. The structure was solved for the non-hydrogen atoms by direct methods (SHELXTL-PLUS program[17]) using 8388 independent reflexions. After the addition of the hydrogen atoms (coupled with respect to position and temperature parameters to the corresponding carbon atoms) anisotropic refinement led to agreement factors *R*= 0.0535 and w*R*= 0.0577 (weighting with $w^{-1} = \sigma^2(F) + 0.0002{\cdot}F^2$)[5604 reflections with $F_o > 4.0\sigma(F_o)$, 344 variable parameters, program SHELXTL-PLUS [17]]. The molecular shape is presented in Fig. 4.

Trapping of the organometallic intermediates with trimethylacetyl chloride: 4,7,7-Trimethyl-5-(2,2-dimethyl-1-oxo-propyl)-6-oxo-1,1-diphenyl-3-aza-1,3-octadiene (**6**): To the suspension of the *organometallic intermediates* 2.07 ml (16.8 mmol) of trimethylacetyl chloride is added dropwise during 5 min. by use of a syringe. After warming

to room temp. work up of the deep red reaction mixture proceeds following *method A*. The solvent is removed under reduced pressure, and **6** precipitates as delicate, colourless needles, which are recrystallized from *n*-hexane / diethyl ether, 50:1 (yield 216 mg, 13%). Chromatography of the red-brown residue (neutral Al_2O_3 (activity 3, cyclohexane / ethyl acetate, 90:1, R_f(DC) = 0.1) yields additional 48 mg of **6** (total yield: 264 mg; 16%); m.p. 135°C (*n*-hexane / diethyl ether). Other methods, even HPLC failed to furnish any other products.- IR (KBr): $\tilde{\nu}$ = 3080 (w, CH), 3060 (w, CH), 3010 (w, CH), 2960 (m, CH), 2920 (m, CH), 2860 (m, CH), 1710 (vs, C=O), 1690 (s, C=N), 1620 (m, C=C), 1600 (m, C=C), 1490 (w, C=C), 1470 (s), 1450 (m, sh), 1440 (m), 1390 (w), 1370 (m, sh), 1360 (m), 1300 (m), 1285 (m), 1230 (w), 1220 (w), 1070 (m), 1050 (m), 1035 (w), 1000 (m).- ^{1}H NMR ($CDCl_3$): δ = 1.13 [s, 18 H, 2 (CH_3)$_3$C], 2.11 (s, 3 H, CH_3C=N), 5.55 (s, 1 H, C*H*), 7.30-7.40 (m, 11 H, aromatic H, C*H*=C).- ^{13}C NMR ($CDCl_3$): δ = 18.58 (CH_3C=N), 26.91 [2 (CH_3)$_3$C], 45.43 [2 (CH_3)$_3$*C*), 67.70 [*C*H(C=O)$_2$], 127.2 (CH_{para}), 127.3 (CH_{ortho}), 127.4 (CH_{para}), 128.2 (CH_{meta}), 128.4 (CH_{ortho}), 131.1 (CH_{meta}), 132.2 (*C*H=C), 138.3 (C_{ipso}), 138.4 (C_{ipso}), 141.5 (CH=*C*), 166.0 (*C*=N), 208.4 (2 *C*=O).- MS (70 eV), m/z (%): 403 (24) [M^+], 358 (16), 346 (10) [M^+-C_4H_9], 318 (22) [M^+-C_5H_9O], 262 (29), 234 (38) [262-CO], 178 (24) [$C_{14}H_{10}^+$], 165 (19) [$C_{13}H_9^+$], 127 (24), 85 (28) [$C_5H_9O^+$], 57 (100) [$C_4H_9^+$].- $C_{27}H_{33}NO_2$ (403.56): calcd. C, 80.21; H, 8.23; N, 3.46; found C, 80.23; H, 8.45; N, 3.51.

Trapping of the organometallic intermediates with dimethyl disulfide: E-4-Methyl-1,1-diphenyl-5,5,5-tris-thiomethyl-3-aza-penta-1,3-diene (**7**) *and 2-methyl-2-(tris-thiomethyl-methyl)-5,5-diphenyl-4-(N-isopropylcarboxamido)-3-oxazoline* (**8**): During and after the dropwise addition of 1.51 ml (16.8 mmol) of dimethyl disulfide to the cold suspension of the *organometallic intermediates* no change in color is observed. However, after warming up of the suspension to room temperature overnight, the color has turned to red-brown. The work up follows *method A*. Isolation of **7**: chromatography of the crude product [neutral Al_2O_3 (activity 3), cyclohexane / diethyl ether, 100 : 3, R_f(DC) = 0.2] yields **7** as a light yellow oil, which crystallizes at 6°C from petroleum ether (582 mg, 39%); m.p. 79-80°C (from cyclohexane / diethyl ether, 100:3). For the isolation of **8** the crude product is filtered over a short SiO_2 column (n-hexane / diethyl ether, 100 : 3) and kept for 12 h at 6°C in the eluent. Then, the precipitated, viscous gum is removed, and the liquid layer is separated by HPLC [petroleum ether / diethyl ether, 100:2; flow: 5ml/min]. From the three fractions obtained the first one [t_r value: 18.0 - 21.0 min] yields 447 mg (30%) of **7**; the second fraction [t_r value = 21.0 - 24.0 min.] delivers a mixture of benzophenone and **8** (13 : 2). The third fraction is discarded. **8** can be separated from benzophenone by HPLC (t_r value: 33.5 - 41.0 min; *n*-hexane/ diethyl ether, 100 : 1, flow: 5ml/min) as a colorless oil, which crystallizes as rhombus at 6°C from $CHCl_3$ (30 mg; 4%); m.p. 71°C.

E-4-Methyl-1,1-diphenyl-5,5,5-tris-thiomethyl-3-aza-penta-1,3-diene (**7**): IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1}(w, CH), 3020 (s, CH), 2980 (s, CH), 2950 (s, CH), 1610 (m, C=N), 1585 (s, C=C), 1575 (m, sh, C=C), 1565 (m, sh, C=C), 1490 (m, C=C), 1440 (s), 1430 (s), 1410 (w), 1370 (m), 1355(m), 1310 (w), 1210 (m), 1075 (w), 1030 (w), 1000 (w).- ^{1}H NMR ($CDCl_3$): δ = 1.90 (s, 9 H, 3 SCH_3), 2.26 (s, 3 H, CH_3C=N), 7.30-7.50 (m, 11 H, 10 aromatic H, C*H*=C).- ^{13}C NMR ($CDCl_3$): δ = 13.34 (3 SCH_3), 15.50 (CH_3C=N), 81.33 [*C*(SCH_3)$_3$], 127.6 (CH_{para}), 127.7 (CH_{ortho}), 127.8

(CH_{para}), 128.5 (CH_{meta}), 128.9 (CH_{ortho}), 131.7 (CH_{meta}), 132.2 (HC=C), 137.9 (C_{ipso}), 138.6 (C_{ipso}), 141.7 (HC=*C*), 166.1 (*C*=N).- MS (70eV), m/z (%): 373 (17) [M^+], 327 (27), 326 (14) [M^+-SCH_3], 312 (18), 281 (12), 279 (12), 264 (18), 220 (100) [M^+-$C(SCH_3)_3$], 205 (18), 178 (72) [$C_{14}H_{10}^+$].- $C_{20}H_{23}N_3S_3$ (373.61): calcd. C, 64.30; H, 6.20; N, 3.75; found C, 64.30; H, 6.35; N, 3.84.

X ray diffraction analysis of **7**:[24] A yellow, irregular crystal $C_{20}H_{23}NS_3$ (from petroleum ether), crystal size 0.8 x 0.5 x 0.5 mm^3, was measured at room temperature by using an automatic CAD4 Turbo Diffractometer (Enraf-Nonius) with Mo-K_α radiation (λ = 0.71073 Å) and a graphite monochromator. 2916 reflexions were collected in the 2Θ range 5.30 << 2 Θ << 56.94° (scan speed variable 3.5 to 16.5°/min). Crystal system: Monoclinic, space group P_1, Z= 2, a= 9.3642(7) Å, b= 7.0229(6) Å, c= 15.556(2) Å, β = 93.128(8)°; V= 1022.1(2) $Å^3$; Dx = 1.214 $g \cdot cm^{-3}$; μ = 3.6 cm^{-1}, no absorption correction. The structure was solved by direct methods (SHELXS-86 program [26]) using 2777 independent reflexions. After the addition of the hydrogen atoms (coupled with respect to position and temperature parameters to the corresponding carbon atoms) anisotropic refinement led to agreement factors R= 0.036 and w$R2$ = 0.095 (2301 reflections with $I_o > 2.0\sigma(I_o)$, 222 variable parameters, program SHELXL-93[25]). In this final refinement an isotropic extinction coefficient χ of 0.006(3) was obtained; the Flack parameter is 0.2(1). The molecular shape is presented in Fig. 5 (left).

2-Methyl-2-(tris-thiomethyl-methyl)-5,5-diphenyl-4-(N-isopropylcarboxamido)-3-oxazoline (**8**): IR (KBr): $\tilde{\nu}$ = 3400 (s, NH), 3065 (w, CH), 3060 (w, sh, CH), 3000 (w, CH), 2970 (m, CH), 2920 (m, CH), 2915 (m, CH), 1680 (vs, C=O), 1626 (s, C=N), 1600 (w, C=C), 1520 (s, C=C), 1495 (m, C=C), 1460 (m), 1450 (m), 1430 (s), 1370 (m), 1180 (w), 1170 (w), 1010 (m).- ^{1}H NMR ($CDCl_3$): δ = 1.08 (d, ^3J= 6.34 Hz, 3 H, $CHCH_3$), 1.13 (d, ^3J= 6.34 Hz, 3 H, $CHCH_3$), 1.62 (s, 3 H, CH_3), 2.17 [s, 9 H, $C(SCH_3)_3$], 4.00 [dq, ^3J= 6.34 Hz, 1 H, $CH(CH_3)_2$], 6.71 (d, ^3J= 7.86, 1 H, NH), 7.10-7.30 (m, 6 H, aromatic H), 7.35-7.57 (m, 5 H, aromatic H), 7.70-7.77 (m, 1 H, CH).- ^{13}C NMR ($CDCl_3$): δ = 14.93 [$C(SCH_3)_3$], 21.88 (CH_3CHCH_3), 21.94 (CH_3CHCH_3), 23.15 (CH_3), 41.15 [$CH(CH_3)_2$], 77.14 [$C(SCH_3)_3$], 96.11 (CPh_2) 115.0 (CH_3CN), 127.2 (CH_{arom}), 127.6 (CH_{arom}), 128.0 (CH_{arom}), 128.2 (CH_{arom}), 128.6 (CH_{arom}), 130.0 (CH_{arom}), 132.3 (CH_{arom}), 140.3 (C_{ipso}), 159.2 (O=CNH), 165.2 (*C*=N).- MS (70 eV), m/z (%): 427 (34) [M^+-SCH_3], 304 (46) [M^+-170], 294 (34) [$C_{19}H_{18}N_2O$], 280 (42), 261 (53), 236 (57) [294-C_3H_8N], 220 (44), 167 (70), 153 (100) [$C_4H_9S_3^+$], 119 (76).- $C_{24}H_{30}N_2O_2S_3$ (474.69): calcd. C, 60.72; H, 6.37; N, 5.90; found C, 60.17; H, 6.17; N, 5.99.

X ray diffraction analysis of **8**:[24] A light yellow, prismatic crystal $C_{24}H_{30}N_2O_2S_3$ (from petroleum ether/diethyl ether, 100:2), crystal size 0.5 x 0.5 x 0.4 mm^3, was measured at room temperature by using an automatic CAD4 Diffractometer (Enraf-Nonius) with Cu-K_α radiation (λ = 1.54178 Å) and a graphite monochromator. 5338 reflexions were collected in the 2Θ range 4.12 << 2 Θ << 148.66° (scan speed variable 3.3 to 16.5° cm^{-1}). Crystal system: Monoclinic, space group P_1/c Z= 4, a= 10.860(2) Å, b= 12.509(3) Å, c= 18.684(4) Å, β= 100.71 (3)°; V= 2494.0(9) $Å^3$; Dx = 1.264 $g \cdot cm^{-3}$. μ = 28.9 cm^{-1}, no absorption correction. The structure was solved by direct methods (SHELXS-86 program[26]) using 5065 independent reflexions. After the addition of the hydrogen atoms (coupled with respect to position and temperature parameters to the corresponding carbon atoms) anisotropic refinement led to agreement factors R= 0.044 and w$R2$ = 0.122 (4415 reflections with $I_o > 2.0\sigma(I_o)$, 291 variable parameters, program SHELXL-93

[25]. In this final refinement an isotropic extinction coefficient χ of 0.0058(4) was obtained. The molecular shape is presented in Fig. 5 (right).

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We dedicate this paper to *Prof. Dr. P. v. R. Schleyer* at the occasion of his 65th birthday.

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