Table I. The Absorbances of the 262-nm and 408-nm Bands, Measured at Various Temperatures

Temp, °C	262 nm ($\pi \rightarrow \pi^*$, PhCO)	408 nm ($\pi \rightarrow \pi^*$, S=CC=CO)
20	0.540	0.990
−60	0.504	1.160
−100	0.428	1.184
−150	0.360	1.266

Table II. Observed ^{1}H NMR Chelate Proton Chemical Shifts for the β-Thioxoketones **5**–**8**[a]

	Compd			
	5	**6**	**7**	**8**
δ (H^{chel})	13.53	15.09	14.95	15.98

[a] The shifts given are extrapolation shifts, referring to infinitely diluted tetrachloromethane solutions.[3,13,14]

for the reverse process (**2B** → **2C**) can be demonstrated. We interpret the effect of the vinyl group as being partly a conjugative stabilization of the enol structure (**2B**) and partly a destabilization of the enethiol structure owing to the possibility of vinylic conjugative stabilization of the carbonyl group competing with the SC=CC=O conjugation. The substitution of a vinyl group for the hydrogen atom in the X position (case III) has the opposite effect on the energy barriers, i.e., leads to a relative lowering of the barrier for the enol–enethiol conversion (**3B** → **3C**). This effect may be interpreted as arising partly from a relative stabilization of the enethiol structure (**3C**) by extended vinylic conjugation and partly from a destabilization of the enol structure (**3B**) owing to the competitive possibilities for conjugative stabilization of the thiocarbonyl group. Finally, the introduction of two vinyl groups effects an unmistakable lowering of both energy barriers (case IV). On the basis of these results we conclude that the introduction of conjugating X,Y substituents will give rise to a more rapid tautomeric interconversion process and, in the extreme case, possibly a "quasi-aromatic" common structure.

To gain further information concerning the latter possibility we studied the UV spectrum of monothiodibenzoylmethane (**8**) at different temperatures. It should be noted, at this point, that the UV spectrum of **8** is not easily explicable on the basis of the "quasi-aromatic" structure, whereas an interpretation in terms of the existence of the tautomer mixture **8B** ⇌ **8C** is consistent with the spectral features. In nonpolar solvents (e.g., cyclohexane) the spectrum shows three bands of high intensity at 262, 325, and 408 nm, together with a further band of low intensity at ~520 nm. These bands may be assigned to the transitions $\pi \rightarrow \pi^*$ (PhCO),[11] $\pi \rightarrow \pi^*$ (PhCS)[12] + $\pi \rightarrow \pi^*$ (O=CC=CS),[3,4] $\pi \rightarrow \pi^*$ (S=CC=CO),[3,4] and n → π^* (C=S),[12] respectively. We found that progressive lowering of the temperature from room temperature to −150 °C leads to a simultaneous increase in the intensity of the 408-nm band and a decrease in the intensity of the 262-nm band, corresponding nicely to a shift in the equilibrium **8B** ⇌ **8C** in favor of the enol tautomer **8B** (Table I). Against this background we therefore reject the possibility of a "quasi-aromatic" structure for **8**.

The theoretically evaluated effects of conjugative X,Y substituents on the equilibrium position for the enol–enethiol tautomerism are reflected qualitatively by the ^{1}H NMR chelate proton chemical shifts (Table II) of the β-thioxoketones **5**–**8** (the ^{1}H NMR spectra of these compounds are all characterized by the apparent presence of only one single species[3,13]). In reference to the UV spectroscopic findings above, the observed chelate proton shifts should be regarded as weighted average shifts of those for the chelate protons of the individual tautomers **B** and **C**; i.e., a relatively large δ value should correspond to a relatively large equilibrium concentration of the enol form (**B**) and vice versa (intramolecularly chelated enols exhibit their chelate proton shifts in the region δ 13–17 ppm,[7] whereas the mercapto proton signals of intramolecularly chelated enethiols have been found at δ 6–8.5 ppm[3,4,14,15]). It can be seen from Table II that the replacement of a methyl group by a phenyl group in the Y position (as in pairs **5** and **6** and **6** and **8**, respectively) gives rise to a general chelate proton shift displacement toward lower field, in accord

with the predicted increase in enol concentration (Figure 1; cf. pairs I and II and III and IV, respectively). Similar considerations hold for the pairs **6** and **7** and **5** and **8**, respectively. The apparent exceptions seen on comparison of results for **5** and **7** and **6** and **8**, respectively, does not necessarily reflect the breakdown of the above generalization, but emphasize rather its qualitative nature. Thus, for obvious reasons the model compounds and the β-thioxoketones actually investigated are not identical, and substituent screening effects on the chelate proton shifts have been totally neglected in this discussion.

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1-Aza-1,2,4,6-cycloheptatetraene

Sir:

The photolysis of aryl azides has attracted attention because of the commercial interest in making photoresists, the use of aryl azides in photoaffinity labeling, and the intriguing mechanism problems posed. We wish to report a new primary photochemical process in the photochemistry of phenyl azide and the spectroscopic observation of 1-aza-1,2,4,6-cycloheptatetraene.

Irradiation of phenyl azide (**1**) in solution in the presence of nucleophiles such as diethylamine gives 2-diethylamino-3*H*-azepine (**2**) in 70% yield[1-3] and small amounts of aniline and related products.[4] The quantum yield for formation of **2**
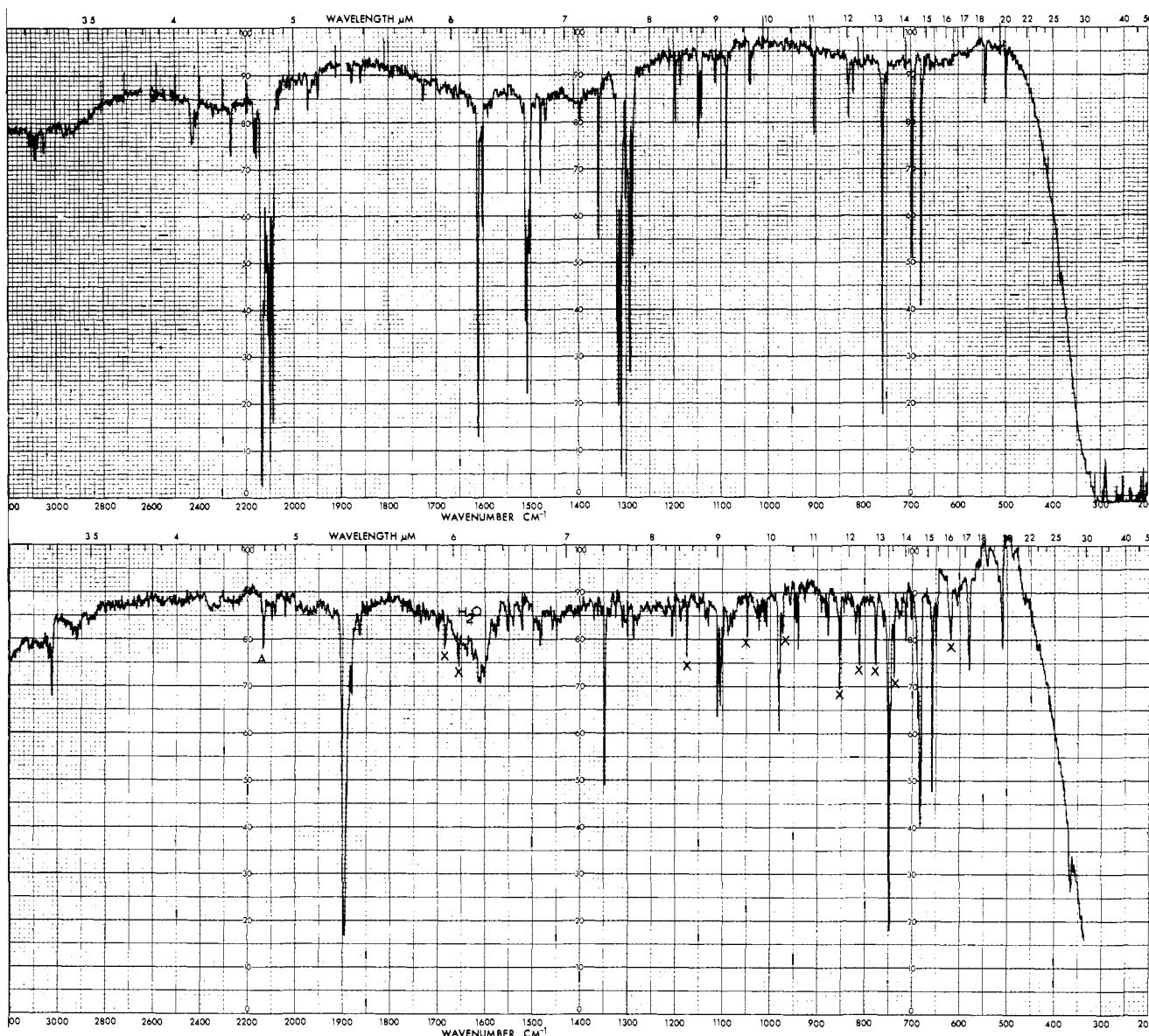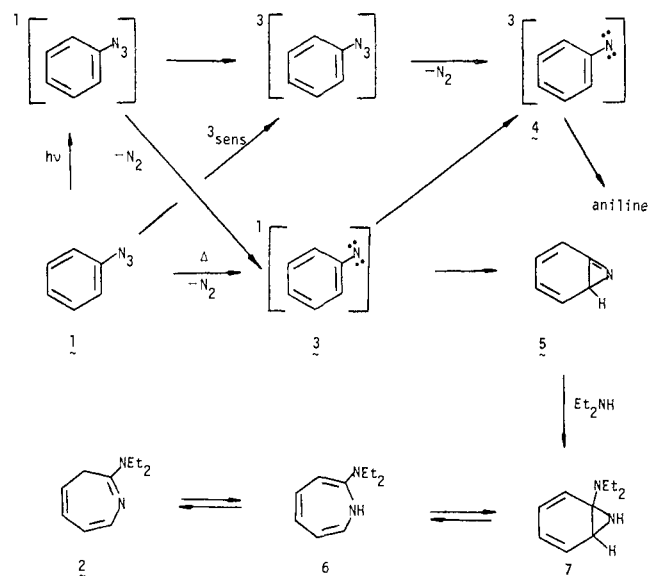
Figure 1. Top: infrared spectrum of phenyl azide matrix isolated in argon at 8 K. Bottom: infrared spectrum of 1-aza-1,2,4,6-cycloheptatetraene (**8**) matrix isolated in argon at 8 K. Bands marked A are due to residual phenyl azide and bands marked X are due to photoproducts of **8**.


is 0.42 ± 0.05.[3] Triplet sensitized decomposition of phenyl azide in diethylamine gives a low yield (7%) of azepine **2** and

aniline (70-80%).[5] Splitter and Calvin showed that azepine formation is a reaction of singlet excited phenyl azide and that aniline formation is a triplet reaction proceeding via ground-state triplet phenylnitrene (**4**).[5] The electron spin resonance[6,7] and ultraviolet[8] spectra of triplet phenylnitrene have been observed in the photolysis of phenyl azide at 77 K. Huisgen and Appl[9] suggested that the thermal conversion of phenyl azide to azepine derivatives might proceed via phenylnitrene and the bicyclic azirine (**5**). Doering and Odum[1] pointed out that this explanation also accounted for the photochemical formation of azepines. These mechanistic suggestions have been accepted in all subsequent studies. Flash photolysis studies of phenyl azide decomposition in hexane in the presence of di-n-butyl-amine showed two intermediates.[3] The azirine **5** was considered to be the most probable first intermediate on the basis of calculations[10] and other arguments.[3] The second intermediate decayed in a first-order process which was independent of amine concentration.[3] This intermediate was considered to be the 1H-azepine **6**.[3] No intermediate corresponding to **7** was observed.[3]

Irradiation ($\lambda > 3600$ Å) of phenyl azide matrix isolated in argon at 8 K gives a new product with an intense absorption at 1895 cm^{-1} and other significant bands at 3025, 1348, 1111,

1105, 980, 940, 748, 683, 658, 650, 580, 510, and 370 cm^{-1} (Figure 1). The product is not stable to light of λ >3600 Å and gives rise to new photoproducts which do not show infrared absorption characteristic of azirines such as **5**.[11] Shorter wavelength light (λ >2160 Å) gives a higher steady-state concentration of the primary product. This product can be obtained almost pure by irradiation (λ >2160 Å) of a thin film of phenyl azide in argon, deposition of more phenyl azide in argon, irradiation, and repetition of this cycle. The fresh phenyl azide deposited between the product and the ultraviolet source protects the product. The presence of the intense 1895-cm^{-1} band in the product suggested the presence of a strained heterocumulene (ordinary ketenimines show intense bands near 2000 cm^{-1}). This suggestion was confirmed by generating the product in an argon matrix containing oxygen (80:20 Ar:O$_2$) which on continued irradiation gave an isocyanate (ν_{NCO} 2270 cm^{-1}). Formation of a ketenimine as a primary product from phenyl azide, while initially shocking, is easily understood. Loss of nitrogen from phenyl azide and ring expansion gives 1-aza-1,2,4,6-cycloheptatetraene (**8**). The product identity was confirmed by an independent synthesis (vide infra).
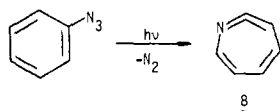
A second synthetic route to **8** has been devised and carried out. Irradiation of **9** matrix isolated in argon at 8 K gives first the expected 2-diazomethylpyridine (**10**, 2075, 2095 cm^{-1}), then **8**, and ultimately the photoproducts of **8**.
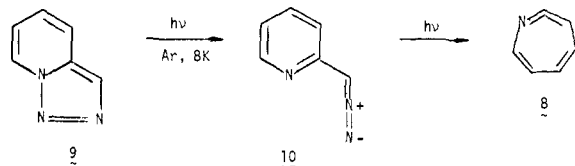
The photochemistry of α-azidostyrene (**11**) provides a spectroscopic model for **8**.[12] Irradiation (λ >3360 Å) of **11** matrix isolated in argon at 8 K gave the azirine (**12**, $\nu_{C=N}$ 1755 cm^{-1}). Irradiation (λ >2160 Å) of **12** gave a photostationary state containing the tautomer (**13**, 1930 cm^{-1}) and **12**. Irradiation (λ >3360 Å) of **13** gave the azirine (**12**). The heterocumulene stretch in **13** (1930 cm^{-1}) provides an excellent comparison for that in **8** (1895 cm^{-1}).
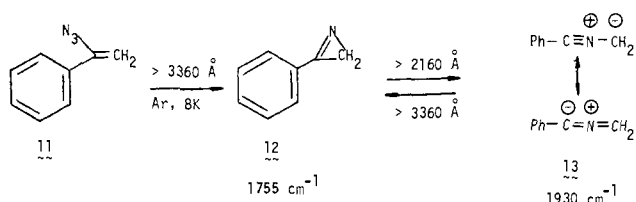
The electronic structure of 1-aza-1,2,4,6-cycloheptatetraene is of some interest. Two structures (**14** and **15**) may be
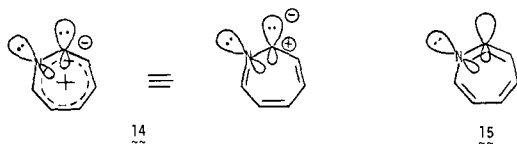
considered. Structure **14** has a six-electron π system and two adjacent, filled in-plane orbitals, while structure **15** has an eight electron π system and adjacent filled and vacant in-plane orbitals. The choice is thus between a combination containing a favorable π system and a repulsive in-plane interaction and a combination containing an unfavorable π system and a bonding in-plane interaction. The presence of the heterocumulene band at 1895 cm^{-1} in the infrared spectrum is con-

vincing evidence that structure **15** with the unfavorable eight-electron π system and the bonding in-plane interaction is the correct representation of the ground state. Several resonance structures can be written for 1-aza-1,2,4,6-cycloheptatetraene (**8**) which show its relationship to zwitterionic
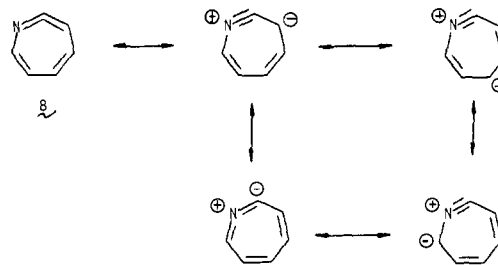
compounds such as **13**. Salem[13] has carried out ab initio calculations on **16** which show a broad, shallow minimum at a

C-N-C angle of 157°. If **8** is assumed to be a regular heptagon, the C-N-C angle would be 129°. Reduction of the N-C-N angle from 157 to 129° should produce relatively little increase in energy according to Salem's calculation. The relatively small difference (35 cm^{-1}) between the stretching vibrations of the heterocumulene units in **8** (1895 cm^{-1}) and **13** (1930 cm^{-1}) is in accord with Salem's prediction.

It is now clear that the singlet photochemistry of phenyl azide must be reinterpreted. The intermediate which reacts with nucleophiles is 1-aza-1,2,4,6-cycloheptatetraene (**8**). The nucleophilic trapping gives first the 1*H*-azepine **6** and then the
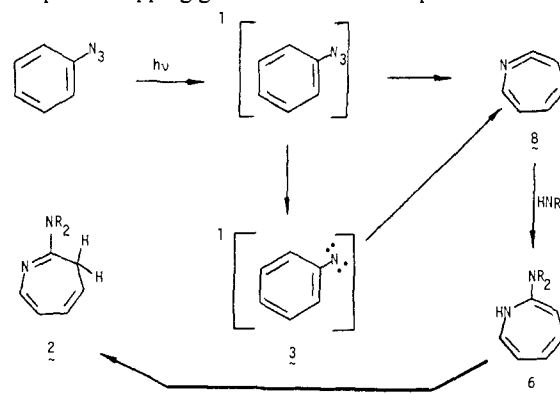
3*H*-azepine 2. The first intermediate observed in the flash photolysis study is thus 1-aza-1,2,4,6-cycloheptatetraene. It is an open question whether **8** is formed directly from singlet excited phenyl azide or via singlet phenylnitrene.

In retrospect it is interesting to reflect on the reasons for rejecting **8** as a candidate for the intermediate in phenyl azide photochemistry. Initially, the bias seems to have been that **8** was too strained to form, and the azirine **5** provided a reasonable alternative since vinyl azides were known to give azirines on irradiation.[14] Molecular orbital calculations placed **8** at higher energy than either azirine **5** or excited singlet phenylnitrene **3**[10] and thus reinforced the bias against **8**. Thermal transformations of aryl azides involving the interconversion of arylnitrenes and pyridylcarbene have been interpreted on the basis of analogues of **8** as intermediates.[15]

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## Synthesis and Thermolysis of 7,8-Diazabicyclo[4.2.2]deca-2,4,7-triene

Sir:

cis-Azoalkanes which possess vinyl substitution α to nitrogen, **1**, are isolable substances decomposing readily by loss of N_2 to give the corresponding allyl radical.[1] Cyclic analogues such as the diazacyclohexadiene **2** are represented by a number of species which have been generated in situ but rarely isolated or observed.[2] These extrude N_2 spontaneously by way of a
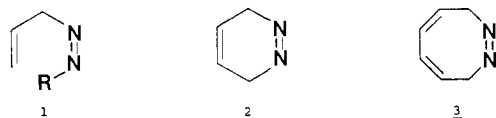
concerted retrocycloaddition. The latter can be attenuated, however, by replacing the carbon π unit with a three- or a four-membered ring.[2c,3] We now wish to report the first synthesis of a stable, simple derivative of the diazacyclooctatriene system **3** and a preliminary account of its thermal cycloreversion.[4]

Scheme I outlines the synthetic sequence. Addition of *N*-methyltriazolinedione to cyclooctatetraene iron tricarbonyl leads to cycloadduct **4**.[6] Treatment of **4** with hydrogen in the presence of PtO_2 yields the dihydro derivative **5** quantitatively, which by ceric ammonium nitrate oxidation gives adduct **6** (99%).[7] Oxidative hydrolysis with strongly basic hydrogen peroxide[8] delivers azo-*N*-oxide **7** in low yield (13%). Deoxygenation of the latter with hexachlorodisilane results in pale yellow crystals of azobicycle **8**: 46%; mp 46–48 °C (uncorr); IR ν_{max} (CHCl$_3$) 1542 cm^{-1} (N=N); UV λ_{max} (CH$_3$CN) 238 nm (ε 2100), 306 (ε 520), and shoulder extending to 430; NMR τ (CCl$_4$/TMS) 4.22 (4 H, m), 5.17 (2 H, m), 7.78 (2 H, m), 8.24 (2 H, m). In solution in the absence of light azodiene **8**

Scheme I
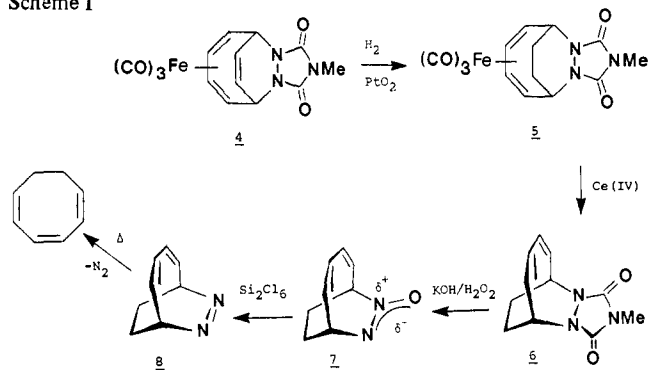
dissociates quantitatively to 1,3,5-cyclooctatriene (COTr) at temperatures slightly above ambient. First-order rates of decomposition were determined by following the disappearance of the absorption at 340 nm ($k_{isooctane}$ (48.4 °C) = 1.0×10^{-4} s^{-1}; $\Delta G^\ddagger$ = 24.7 kcal/mol).

Several pathways connecting azocycle **8** and COTr/N_2 are conceivable. Of those likely to involve intervening energy minima, either the diazenyl diradical **9** or the hydrocarbon diradical **10** could follow the starting material directly or exist as successive intermediates, respectively. Single-step nitrogen
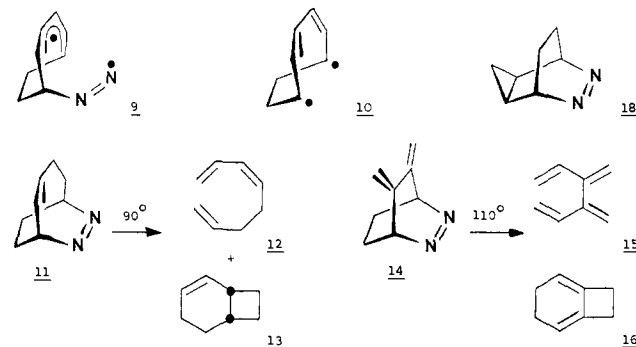
extrusion not involving radicaloid intermediates is possible by way of a least-motion forbidden route or a non-least-motion allowed path.[9] Although not rigorously applicable, several criteria have evolved to distinguish radical from concerted reactions where direct observation cannot be accomplished. Product composition, in particular structural and stereoisomerism, is primary while relative reaction rates are often, but not always, supportive.[2c,12]

In an attempt to shed some light on the thermolysis of **8**, the fragmentation of the model azobicycle **11**[7b] has likewise been investigated. It splits out nitrogen in a first-order process ($k_{isooctane}$ (90.4 °C) = 1.0×10^{-4} s^{-1}; $\Delta G^\ddagger$ = 28.1 kcal/mol) to give exclusively a mixture (25:75) of 1,3,7-octatriene (**12**) and bicyclo[4.2.0]oct-2-ene (**13**).[13,14] The appearance of both acyclic and bicyclic products signals the intermediacy of a biradical of type **9** or **10**.

A bicyclic isomer of diazacyclooctatriene **8**, i.e., **14**, exhibits the same pattern, losing N_2 at 110 °C in solution to give a 65% mixture of dimers, 30% polymer, and a 5% mixture (33:67) of the acyclic and cyclic hydrocarbons **15** and **16**, respectively.[15] The monomeric olefins **15** and **16** are produced exclusively in the same ratio in the gas phase (110 °C). Both a triplet and a singlet diradical have been inferred (CIDNP and ESR).[15] Similarly all other reports of diradical species, allylic and otherwise, disclose the ultimate formation of acyclic and/or ring-closure products.[1,2c,12,16] By comparison the butadiene-bridged azoalkane **8** in the condensed phase renders a single monocyclic hydrocarbon product (COTr) in quantitative yield. The formation of the COTr valence isomer, bicyclo[4.2.0]-octa-2,4-diene (**17**), as a primary product was ruled out by