one can accurately correlate with the $lN + mY$ equation (2) the solvolysis data for *tert*-butyl halides in a wide range of solvents (Table V); the value of l shows the significant sensitivity to solvent nucleophilicity. This establishes quantitatively a link between classical studies on the correlation of solvolysis rates[4,5] and contemporary studies of stable carbocations (Table VI).

Equations like (2), (4), and (5) should provide useful mechanistic probes of the roles of solvent in many systems, both organic and inorganic. Solvolyses in fluorinated alcohols indicate that the role of solvent as nucleophile in more nucleophilic aqueous or alcoholic solvents has in the past been significantly underestimated.

Experimental Section

Purification of Chemicals. 1-Adamantyl chloride (I, X = Cl) and bromide (I, X = Br; available from Aldrich) were prepared and purified by literature methods.[8,12a] Trifluoroacetic acid was fractionally distilled through a triple-pass Widmer column. Acetone,[8] ethanol,[2a] methanol,[8] trifluoroethanol,[7] acetic acid,[8] and formic acid[2a] were purified by standard methods.

Kinetic Methods. Stock solutions were checked by studying rates of solvolyses of *tert*-butyl chloride.[4b] For many solvolyses in aqueous media, the substrate was first dissolved in the organic solvent and solutions were prepared by using matched calibrated pipettes.[2a] Conductance measurements were made as described previously,[14c] using CO$_2$-free solvents for the more dilute solutions (10^{-5} M). Titrations of quenched aliquots (ca. 0.005 M) from sealed ampules were carried out on a Radiometer RTS 822 recording titration system fitted with a 2.5-cm^3 autoburet, except for the Volhard titrations, carried out on 0.02 M solutions using nitrobenzene to coat the precipitated silver chloride.[35]

Acknowledgment. This work was supported by the Science Research Council (Grants GR/A77105 and GR/B25988). We are grateful to Professor P. v. R. Schleyer for many helpful contributions to this research program.

Registry No. I (X = Cl), 935-56-8; I (X = Br), 768-90-1; *tert*-butyl chloride, 507-20-0.

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(35) Laitinen, H. A. "Chemical Analysis"; McGraw Hill: New York, 1960; p 214.

Photochemical and Thermal Denitrogenations of Azoalkanes as Mechanistic Probes for the Diradical Intermediates Involved in the Di-π-methane Rearrangement of Dibenzobarrelene

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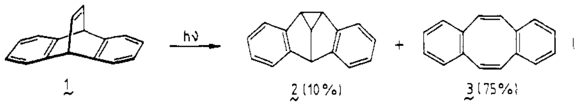
Contribution from the Institut für Organische Chemie, Universität Würzburg, Am Hubland, D-8700 Würzburg, BRD, Departamento de Quimica, Universidad de Puerto Rico, Rio Piedras, Puerto Rico 00931, and the Max-Planck-Institut für Festkörperforschung, D-7000 Stuttgart 80, BRD. *Received October 12, 1981*

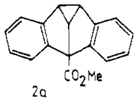
Abstract: The azoalkanes **9** and **10** were prepared from the corresponding urazoles **14** and **15**, which in turn were obtained by reaction of dibenzobarrelene (**1**) with *N*-methyl-1,2,4-triazoline-3,5-dione (MTAD). Thermolysis, direct photolysis at 350 and 254 nm, and benzophenone sensitization lead on denitrogenation respectively to the diradicals **6** and **7**, which are postulated in the di-π-methane rearrangement of dibenzobarrelene (**1**). It is shown that the singlet-state diradicals lead to dibenzobarrelene (**1**) and dibenzocyclooctatetraene (**3**) as minor products and dibenzosemibullvalene (**2**) as major product. Thus, the extent of retro-di-π-methane rearrangement of the diradical **7** derived from azoalkane **10** is small. Formation of benzocyclobutadiene dimer (**4**) via rearrangement of diradical **7** into **8**, a hitherto unrecognized di-π-methane route of dibenzobarrelene (**1**), takes place only to a very small extent in the 254-nm photolysis of azoalkane **10**. The triplet-state diradicals **6** and **7** only afford dibenzosemibullvalene (**2**). The mechanistic implications in reference to the di-π-methane process of dibenzobarrelene are discussed.

The photochemistry of dibenzobarrelene (**1**) has been reported

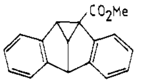


(1)

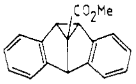
some time ago[1] to afford dibenzosemibullvalene (**2**) and *sym*-dibenzocyclooctatetraene (**3**). Analogous to related di-π-methane rearrangements,[2] it was proposed[1b] that the semibullvalene product **2** was formed via the triplet excited state of **1** and the cyclooctatetraene **3** via its singlet excited state. The regioselectivity of this photorearrangement was tested[1b] with the 1-carbomethoxy (**1a**) and 7-carbomethoxy (**1b**) derivatives, leading respectively to the semibullvalenes **2a**, **2a′**, and **2b**. A detailed mechanism



2a



2a′



2b

of this di-π-methane rearrangement[2] is given in Scheme I in terms of the diradical intermediates that might be involved. If one assumes the cyclopropyldicarbinyl diradical **6**, formed by C$_3$–C$_8$

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(1) (a) Ciganek, E. *J. Am. Chem. Soc.* **1966**, *88*, 2882. (b) Radideau, P. W.; Hamilton, J. B.; Friedman, L. *Ibid.* **1968**, *90*, 4465.

(2) (a) Zimmerman, H. E. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press; New York, 1980; Vol. 3, pp 131-166. (b) Zimmerman, H. E.; Grunewald, G. L. *J. Am. Chem. Soc.* **1966**, *88*, 183. (c) Zimmerman, H. E.; Binkley, R. W.; Givens, R. S.; Sherwin, M. A. *Ibid.* **1967**, *89*, 3932. (d) Zimmerman, H. E.; Givens, R. S.; Pagni, R. M. *Ibid.* **1968**, *90*, 4191.

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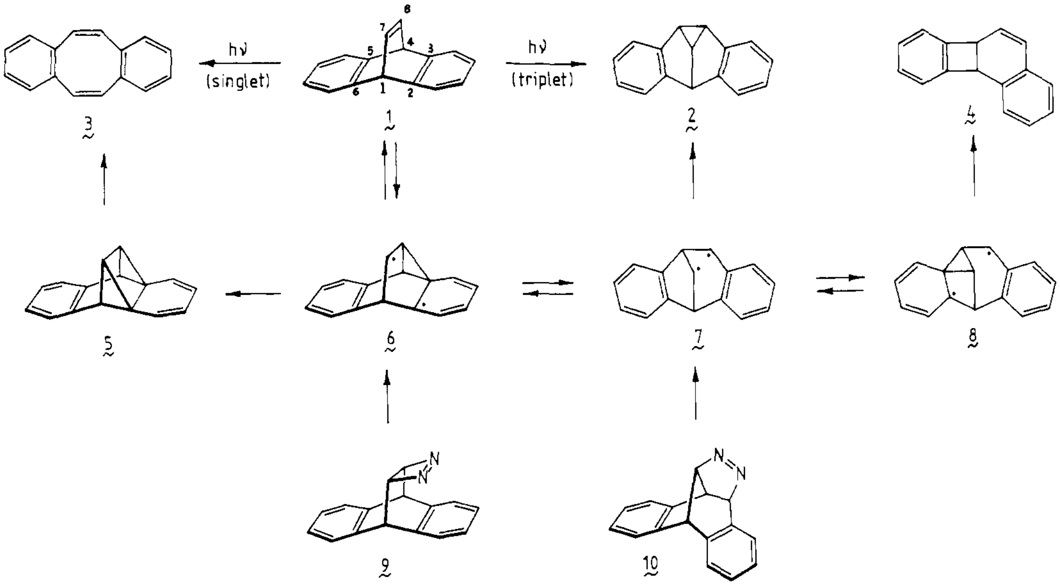
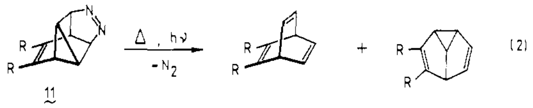
Scheme I

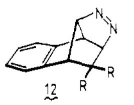


bonding in the excited **1**, is the key intermediate, cyclization via C_2–C_7 bonding into the labile **5** and subsequent isomerization would give dibenzocyclooctatetraene (**3**). Of course, this photochemical transformation could take place also directly from the singlet excited state of **1** without trespassing the cyclopropyldicarbinyl diradical **6**. On the other hand, dissociation of the C_3–C_4 bond in the cyclopropyldicarbinyl diradical **6** would produce the rearranged diradical **7**, and subsequent cyclization via C_4–C_7 bonding would afford dibenzosemibullvalene (**2**), the di-π-methane product of **1**. Alternatively, diradical **7** could via C_7–C_5 bonding result in the cyclopropyldicarbinyl diradical **8**, and subsequent breaking of the C_4–C_5 bond leads to **4**. The path **7** → **8** → **4** represents a retro-di-π-methane process, which engages the rearranged cyclopropyldicarbinyl diradical **8** instead of the initially formed cyclopropyldicarbinyl diradical **6**. The formation of **4** as photoproduct of dibenzobarrelene (**1**) has not been previously reported, although a number of unidentified products are obtained in this di-π-methane reaction.[1]

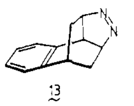
Zimmerman et al.[3] demonstrated that the denitrogenation of the azoalkanes **11** is a convenient entry into the diradical manifold of the di-π-methane rearrangement of barrelenes into semibullvalenes (eq 2). Similarly, we utilized azoalkanes **12** and **13** as mechanistic probes for the elucidation of the diradicals postulated in the di-π-methane rearrangements of benzonorbornadienes[4] and 6,7-benzobicyclo[3.2.1]octa-2,6-dienes,[5] respectively. Consequently, it was of interest to employ the azoalkanes **9** and **10** as precursors to the diradicals, which are postulated in the di-π-methane rearrangement of dibenzobarrelene (**1**) as shown in Scheme I. We hoped to demonstrate that these azoalkanes serve as mechanistic probes in the elucidation of diradical transformations that are postulated in the complex photochemistry of Scheme I. The specific mechanistic questions that we posed were as follows: (i) Do azoalkane **9** and **10** serve as thermal and photochemical sources for the diradicals **6** and **7**? (ii) Does diradical **7** undergo the retro-di-π-methane process **7** → **6** → **1** and **7** → **8** → **4**, of which the latter has hitherto not been reported for dibenzobarrelene? (iii) Is dibenzocyclooctatetraene (**3**) a direct singlet-state product, i.e., **1** → **5** → **3**, or is diradical **6** also an intermediate for this product, i.e., **1** → **6** → **5** → **3**? (iv) Are the transformations of the diradicals **6** and **7** spin state dependent; i.e., does the product distribution differ in the thermal (singlet-state diradicals) vs. ketone sensitized (triplet-state diradicals) denitrogenations of azoalkanes **9** and **10**? Presently we describe the results of our investigation on the thermal and photochemical denitrogenation of the azoalkanes **9** and **10** that are derived from dibenzobarrelene.



11

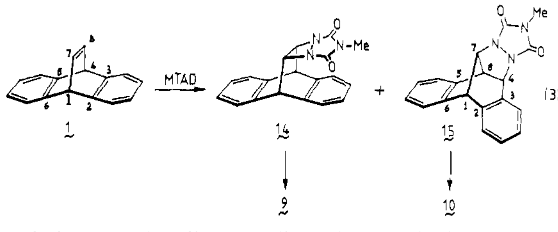


12



13

Results



Preparation of Azoalkanes 9 and 10. (2 + 2) cycloaddition[6] and dipolar cycloaddition with rearrangement[7] of triazolindione (TAD) with dibenzobarrelene (**1**) has recently been reported, leading respectively to the urazoles **14** and **15** (eq 3). With *N*-methyl-1,2,4-triazoline-3,5-dione (MTAD), **14a** (R = CH_3) was obtained in 23% yield and **15a** (R = CH_3) in 25% yield (after silica gel chromatography and recrystallization). Elemental analyses and spectral data (^1H and ^{13}C NMR and IR) support the proposed structures. For example, the ^1H NMR spectrum of urazole **14** in $CDCl_3$ consists of two symmetrical multiplets at 4.68 and 4.87 ppm, a complex aromatic pattern at 7.10–7.57 ppm, and a singlet for the N–CH_3 protons at 2.75 ppm. Decoupling experiments show that the two symmetrical multiplets are coupled to each other. The ^{13}C NMR spectrum consists of six aromatic and two aliphatic resonances and one carbonyl carbon for the urazole moiety. These NMR data are consistent only with structure **14** for this urazole. Urazole **15** presents a more complicated ^1H NMR spectrum, consisting of unsymmetrical multiplets at 4.43 and 5.05 ppm, which are too close to one another

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(3) Zimmerman, H. E.; Boettcher, R. J.; Buehler, N. E.; Keck, G. E.; Steinmetz, M. G. *J. Am. Chem. Soc.* **1976**, *98*, 7680.

(4) (a) Adam, W.; De Lucchi, O. *J. Am. Chem. Soc.* **1980**, *102*, 2109. (b) Adam, W.; De Lucchi, O. *J. Org. Chem.* **1981**, *46*, 4133.

(5) Adam, W.; Carballeira, N.; De Lucchi, O. *J. Am. Chem. Soc.* **1980**, *102*, 2107.

(6) Adam, W.; De Lucchi, O *Tetrahedron Lett.* **1981**, *22*, 929.

(7) Adam, W.; De Lucchi, O.; Erden, I. *J. Am. Chem. Soc.* **1980**, *102*, 4806.

to allow decoupling experiments. The ^{13}C NMR spectrum presents four distinct aliphatic doublets in the 50.8–67.2-ppm region and the expected aromatic and urazole carbon resonances. These data are in accord with the proposed structure **15** for this urazole. A rigorous structure assignment of urazole **15** rests on an X-ray analysis (cf. Experimental Section).

Oxidative hydrolysis with methanolic KOH, followed by cupric chloride treatment, led to the desired azoalkanes **9** and **10** in 50 and 38% yields, respectively. The structures of the azetidine **9** and pyrazoline **10** are based on correct elemental composition and appropriate spectral data (cf. Experimental Section). The ^1H NMR spectrum of diazetidine **9** was very similar to its precursor urazole **14**, while the ^1H NMR spectrum of pyrazoline **10** was much better resolved than the spectrum of its precursor urazole **15**. For example, besides the aromatic resonances at 7.10 ppm, it exhibited two triplets at 3.82 and 6.02 ppm and two doublets at 4.05 and 5.65 ppm, all possessing the same coupling constants of 5.4 Hz. Although it is difficult to assign these four-proton resonances among the bridgehead positions with certainty on the basis of their chemical shifts, the more upfield multiplets are designated as H_8 to 3.82 ppm and as H_1 to 4.05 ppm and the more downfield multiplets as H_4 to 5.65 ppm and H_7 to 6.02 ppm.

Thermal and Photochemical Denitrogenations of Azoalkanes 9 and 10. The possible products of the denitrogenation of azoalkanes **9** and **10** are dibenzobarrelene (**1**), dibenzosemibullvalence (**2**), *sym*-dibenzocyclooctatetraene (**3**), and 4,5,7,8-dibenzobicyclo[4.2.0]octa-2,4,7-triene (**4**) (cf. Scheme I). Authentic samples of **1** were on hand, while those of **2** and **3** were prepared from **1** by photochemical rearrangement.[1b] A sample of **4** was obtained by dimerization of benzobutadiene.[8]

The thermal denitrogenations were carried out by heating the neat azoalkanes above their melting points (ca. 170–200 °C) until complete cessation of nitrogen gas evolution (ca. 5 min). The residual hydrocarbon mixture was then analyzed quantitatively by capillary GC. Alternatively, the azoalkanes were pyrolyzed on the column directly in the GC, with the injector temperature at 275 °C. The results are summarized in Table I. Control experiments confirmed that the potential products **1–4** did not suffer thermal interconversion at the conditions of the thermolysis of the azoalkanes.

The direct photochemical denitrogenations were carried out by photolysis of the azoalkanes in acetonitrile at 350 nm (n,π^* excitation of azo chromophore) and 254 nm (π,π^* excitation of benzene chromophore), using a Rayonet photoreactor equipped with the appropriate lamps. Control experiments revealed that the potential photoproducts **1–4** isomerized inefficiently compared to the azoalkanes under the conditions of the present 350-nm irradiation. The quantitative results are summarized in Table I.

However, on 254-nm irradiation dibenzobarrelene (**1**) undergoes photorearrangement into the semibullvalene **2** (di-π-methane product) and the cyclooctatetraene **3**, while products **2** to **4** are photostable under these conditions. The quantitative results of the 254-nm photodenitrogenation of azoalkane **9** in Table I had to be corrected, therefore, for the amount of conversion of the photoproduct **1** into **2** and **3**. This was particularly critical for the 254-nm photolysis of the diazetidine **9**, since significant amounts of dibenzobarrelene (**1**) are formed as primary denitrogenation product. Photolysis of **9** at 254 nm to low conversion (<10%) alone was not feasible because the remainder of **9** would thermally denitrogenate into dibenzobarrelene (**1**) during GC quantitative analysis, thereby obscuring the "true yield" of **1** that is formed in the 254-nm photolysis.

Fortunately, the triple-sensitized photolysis gives quantitatively the semibullvalence **2**. Thus, after partial denitrogenation (8 min) of **9** at 254 nm, the remainder of **9** was destroyed by benzophenone-sensitized photolysis, and GC quantitation afforded the yield of dibenzobarrelene (**1**). Control experiments with authentic **1** confirmed that the amount of di-π-methane rearrangement $1 \rightarrow 2$ under these 254-nm photolysis conditions was less than 0.1% and thus negligible. The yield of semibullvalene **2** product from the 254-nm photolysis of the diazetidine **9** was established by partial denitrogenation (8 min) at 254 nm, followed by GC analysis. Since the remaining diazetidine **9** denitrogenates exclusively into dibenzobarrelene (**1**), the yield of semibullvalene **2** from **9** corresponds to that of the 254-nm photolysis.

Table I. Product Composition of the Thermal, Direct Photochemical, and Triplet-Sensitized Denitrogenation of Azoalkanes 9 and 10

		% product composition[a,b]			
azoalkane	method[c]	1	2	3	4
9	Δ[d]	100	traces		
	350 nm	12	85.5	2	
	254 nm	18 ± 2	79 ± 3	3 ± 1	
	$Ph_2C{=}O$ (300–330 nm)[e]		100		
10	Δ[d]	1	93[g]	6	
	350 nm		98.5[g]		traces
	254 nm	*f*	97	1.5	0.5
	$Ph_2C{=}O$ (300–330 nm)[e]		100[g]		

[a] A minor product (<1%) is formed in the 350-nm photolysis of azoalkanes 9 and 10, which could not be identified. [b] Determined by GC as described in the Experimental Section; experimental error less than 5% except when specified. [c] The photolyses were carried out in CH_3CN as solvent, using ca. 10^{-2} M solutions of the azoalkanes. [d] Heating of neat sample at its melting point and on-column decomposition in the GC. [e] K_2CO_3-$K_2Cr_2O_7$ filter was used to prevent direct excitation of the azo chromophore. [f] A little dibenzobarrelene (1) could have been formed, which would have been converted to semibullvalene 2. [g] A qualitative ^1H NMR check was made; it showed a product balance of better than 90%.

The triplet-sensitized denitrogenations were performed also in a Rayonet photoreactor, using benzophenone as sensitizer and a $K_2Cr_2O_7$–K_2CO_3 filter[3] that only transmits 300–330-nm radiation. Control experiments confirmed that the potential photoproducts **1–4** isomerized inefficiently compared to the azoalkanes under the benzophenone-sensitized photolysis conditions. The quantitative results are given in Table I.

Mechanistic Considerations. With the help of Scheme I we shall now attempt to rationalize the product data of Table I in terms of the diradical intermediates that have been postulated in the di-π-methane rearrangement of dibenzobarrelene. Some mechanistically important conclusions emerge from our results on this interesting photochemical process. It is significant to mention that control experiments confirmed[1] that semibullvalene **2** is the exclusive triplet-state product of barrelene **1**. Benzophenone sensitization and more convincingly tetramethyl-1,2-dioxetane chemienergization (a convenient and efficient thermal source of acetone triplets[9]) or barrelene **1** both gave exclusively semibullvalene **2** as photoproduct. Neither cyclooctatetraene **3** nor benzocyclobutadiene dimer (**4**) is formed in these triplet reactions of dibenzobarrelene (**1**). The cyclooctatetraene **3** photoproduct is only observed in the direct photolysis of the barrelene **1** at 254 nm. Also here control experiments verify that no benzocyclobutadiene dimer (**4**) is produced. Thus, cyclooctatetraene **3** appears to be a singlet-state product of the barrelene **1**. Furthermore, neither the cyclooctatetraene **3** nor the benzocyclobutadiene dimer (**4**) interconvert photochemically at 254 nm or 350 nm, nor do they transform under these conditions into barrelene **1** and semibullvalene **2**, as again confirmed through control experiments. This already implies that the hydrocarbons **3** and **4** do not allow us to enter the diradical manifold of the di-π-methane rearrangement of dibenzobarrelene (**1**) via the pathways $3 \rightarrow 5$ and $4 \rightarrow 8$.

The situation is quite distinct for the azoalkanes **9** and **10**. Let us consider first their thermal denitrogenations, since in the thermal process a singlet-state diradical is generated, at least initially. As the product data in Table I show, the diazetidine

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(8) (a) Cava, M. P.; Napier, D. R. *J. Am. Chem. Soc.* **1957**, *79*, 1701. (b) Nenitzescu, C. D.; Avram, M.; Dinu, D. *Chem. Ber.* **1957**, *90*, 2514.

(9) Adam, W. *Pure Appl. Chem.* **1980**, *52*, 2591.

9 dinitrogenates thermally quantitatively into dibenzobarrelene (**1**). Only traces of dibenzosemibullvalene (**2**) are produced. Consequently, **9** denitrogenates directly into **1**, analogous to related diazetidines,[10] without trespassing the diradical **6**, although a very small amount of diradical **6** must have been formed to explain the trace quantities of semibullvalene **2** that were observed, presumably via the **9** → **6** → **7** → **2** route.

In this respect the thermolysis of pyrazoline **10** was mechanistically more informative. As the data in Table I reveal for this azoalkane, the major product (93%) is the semibullvalene **2**, but significant amounts of barrelene **1** (1%) and cyclooctatetraene **3** (6%) are produced. Again the benzocyclobutadiene dimer (**4**) is absent as thermolysis product. Formation of the semibullvalene **2** via the **10** → **7** → **2** pathway is the expected course,[11] but the fact that barrelene **1** and cyclooctatetraene **3** are formed, although in small quantities, in the thermolysis of azoalkane **10** suggests that the singlet-state diradical **7** rearranges into the cyclopropyldicarbinyl diradical **6**, which is postulated as the initial intermediate in the di-π-methane rearrangement of dibenzobarrelene (**1**). Without the retro-di-π-methane process **10** → **7** → **6** → **1**, it would be difficult to account for the formation of the barrelene **1** from azoalkane **10**. Of course, it should be kept in mind that this retro-di-π-methane reaction,[12] analogous to that derived from the azoalkane of benzonorbornadiene,[4b] is quite inefficient.

Still more significant mechanistically speaking is the fact that dibenzocyclooctatetraene (**3**) is formed in the thermolysis of azoalkane **10**. Presumably the **10** → **7** → **6** → **5** → **3** route obtains in order to rationalize this observation. Thus, the singlet-state diradical **6** that is formed in the thermolysis of **10** via rearrangement of diradical **7** predominantly cyclizes by C_2–C_7 bond closure into the strained hydrocarbon **5**, the precursor to the cyclooctatetraene **3**, instead of fragmenting the C_3–C_8 bond to afford the barrelene **1**. As the product distribution shows (Table I), the yield of cyclooctatetraene **3** predominates over barrelene **1** by sixfold in the thermolysis of azoalkane **10**. Our thermolysis data of the azoalkanes **9** and **10** suggest that denitrogenation of diazetidine **9** into barrelene **1** does not engage diradical **6**, because we should have obtained significant amounts of semibullvalene **2**, and cyclooctatetraene **3**. Furthermore, and mechanistically more importantly, the singlet-state diradical **6** is the precursor to the cyclooctatetraene **3** and barrelene **1** products that are formed from pyrazoline **10**.

Next we shall discuss the benzophenone-sensitized denitrogenations of azoalkanes **9** and **10**, which involve triplet-state intermediates. Both azoalkanes give quantitatively dibenzosemibullvalene (**2**), as revealed by the product data in Table I. Since dibenzobarrelene (**1**) is photostable compared to the azoalkanes under these conditions, irrespective at what points we enter the diradical manifold of this di-π-methane rearrangement (Scheme I), i.e., with diradical **6** via denitrogenation of the diazetidine **9** or with diradical **7** via denitrogenation of the pyrazoline **10**, their triplet states generate exclusively and directly, i.e., not via secondary photolysis of intermediary dibenzobarrelene (**1**), the di-π-methane product **2**. Clearly, for the triplet-state intermediates, diradical **7** represents the reaction funnel, since the cyclopropyldicarbinyl diradical **6** is completely converted into **7** and neither produces diradical **8**. Furthermore, once one is on the triplet-state energy surface, even the cyclopropyldicarbinyl diradical **6** and certainly the diradical **7** do not give rise to dibenzobarrelene (**1**) and dibenzocyclooctatetraene (**3**). In other words these products are derived from singlet-state reactions of the diradical intermediates.

Considerably more complex are the direct photodenitrogenations of azoalkanes **9** and **10**. Here we carried out photolyses at 350 and 254 nm, respectively, representing excitation of the azo and benzene chromophores. Only minor alterations in the product distributions are observed (Table I) on excitations at these two wavelengths. For example, at both 254 and 350 nm the diazetidine **9** gives predominantly semibullvalene **2** (80–85%), and barrelene **1** (12–18%) and cyclooctatetrene **3** (2–3%) as minor products, but no benzocyclobutadiene dimer (**4**) is formed. In view of what has been said already for the triplet-sensitized denitrogenation of azoalkane **9**, both the barrelene **1** and cyclooctatetraene **3** must be singlet-state products, if diradical **6** is their precursor. This is hardly arguable for the cyclooctatetraene **3** photoproduct; but as in the thermolysis of azoalkane **9**, so also in its photolysis, direct denitrogenation might be a source for the barrelene **1** photoproduct. The semibullvalene **2** photoproduct of azoalkane **9** must have undoubtedly the triplet-state diradical **6** as precursor. Since intersystem crossing appears to be slow at the diradical stage (otherwise we should have formed significant quantities of semibullvalene **2** in the thermolysis of **9**, it presumably takes place quite efficiently for the singlet excited diazetidine **9**.

Similar results (Table I) are obtained for azoalkane **10**, except that here the direct photodenitrogenation does not afford barrelene **1**, but for the first time small amounts (<1%) of benzocyclobutadiene dimer (**4**) are formed as photoproduct. Furthermore, there are some differences in the product distribution with respect to wavelength. For example, the 350-nm direct photolysis is quite clean, leading predominantly (99%) to semibullvalene **2**. Only traces of **4** are formed, and barrelene **1** and cyclooctatetraene **3** are completely absent. The major course of photodenitrogenation at 350 nm is most probably triplet state derived, since products **1** and **3**, which are formed to some extent in the thermolysis, are not produced. The fact that traces of **4** are formed, presumably via the **10** → **7** → **8** → **4** route, suggests that the photochemically generated singlet-state diradical **7** is sufficiently energetic to afford this unusual di-π-methane product. In fact, this hypothesis is not unreasonable, since the amount of **4** is larger in the 254-nm photodenitrogenation of azoalkane **10**. However, it is surprising that such a more energetic singlet-state diradical (presumably vibrationally excited, i.e., a "hot" species) is so inefficient in executing the retro-di-π-methane process **7** → **6**, since the amounts of cyclooctatetraene **3** product in the 254-nm photolysis are appreciably smaller than those in the thermolysis of azoalkane **10**. Unfortunately, it is not possible to determine how much barrelene **1** is produced in the 254-nm photolysis of azoalkane **10**, because control experiments show that at 254 nm the di-π-methane process **1** → **6** → **7** → **2** is more efficient than the photodenitrogenation of azoalkane **10**. Thus, if barrelene **1** is formed in the 254-nm photodenitrogenation of **10**, it should not accumulate.

In summary, on the basis of the product data in Table I, analogous to Zimmerman's pioneering study,[3] we can extract the following mechanistic conclusions in reference to the initial questions we asked about the di-π-methane rearrangement of dibenzobarrelene (**1**): (i) Azoalkanes **9** and **10** are convenient precursors respectively to the diradicals **6** and **7**, which are postulated in the di-π-methane rearrangement of dibenzobarrelene (**1**). (ii) The singlet-state diradical **7** does undergo retro-di-π-methane rearrangement via diradical **6**, but inefficiently; only the direct photolysis of azoalkane **10** at 254 nm affords measurable amounts of the hitherto unobserved benzocyclobutadiene dimer (**4**) as photoproduct, presumably via diradical **8**; the triplet-state diradical **7** does not engage in retro-di-π-methane reaction, since it only cyclizes into semibullvalene **2**. (iii) The singlet-state diradical **6** is the precursor to the cyclooctatetraene **3** product by cyclizing presumably into the strained hydrocarbon **5**. (iv) The chemical behavior of the diradicals **6** and **7** is strongly spin state dependent, the triplets leading exclusively to semibullvalene and the singlets producing as well benzobarrelene[1] and cyclooctatetraene **3**.

We feel that tailor-made azoalkanes constitute convenient and effective mechanistic probes for the elucidation of the diradical intermediates that are involved in photochemical reactions such as the di-π-methane rearrangement.[3]

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(10) (a) Turro, N. J.; Cherry, W. R.; Mirbach, M. F.; Mirbach, M. *J. J. Am. Chem. Soc.* **1977**, *99*, 7388. (b) Pincock, J. A.; Druet, L. M. *Tetrahedron Lett.* **1980**, *21*, 3251.

(11) Adam, W.; De Lucchi, O. *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 762.

(12) Zimmerman, H. E.; Factor, R. E. *Tetrahedron* (*Suppl. 1*) **1981**, *37*, 125.

Experimental Section

Melting points and boiling points are uncorrected. Melting points were taken of recrystallized material on a Reichert Thermovar Kofler apparatus. Infrared spectra were taken on a Beckman Acculab **4** or on a Perkin-Elmer 157G spectrophotometer and ^{1}H NMR spectra on a Varian T-60 or on a Hitachi Perkin-Elmer R-24B spectrometer at 60 MHz. ^{13}C NMR spectra were kindly run for us by Professor Hopf's staff (Braunschweig). Gas chromatography was carried out on a Carlo Erba Fractovap 2900 capillary GC, equipped with a Spectraphysics integrator. A 50-m, OV-101 capillary column was used, which was operated at an oven temperature of 200 °C and an injector and a detector temperature of 275 °C. A flame ionization detector was always used, and the carrier gas (N_2) was controlled at a pressure of 1.5 kg/cm^2. Detection limit was better than 0.1%. A Rayonet photoreactor (Ultraviolet Corp.), equipped with either 254-, 300-, or 350-nm lamps, was used in the photolysis experiments. Microanalyses were performed in house. Commerical reagents and solvents were purified to match reported physical and spectral data. Known compounds used in this research were either purchased from standard chemical suppliers or prepared according to literature procedures and purified to match the reported physical and spectral data. Percent yields are before recrystallization.

Synthesis of Urazoles 14 and 15. A sample of 0.5 g (2.4 mmol) of dibenzobarrelene (**1**) and 0.3 g (2.5 mmol) of MTAD in ca. 15 mL of freshly distilled tetrachloroethane was heated at ca. 70 °C overnight. The resulting pale yellow solution was tested by TLC, eluting with CH_2Cl_2, for the presence of unreacted dibenzobarrelene (**1**). Small portions of MTAD (ca. 50 mg each) were added, and heating was continued until complete disappearence of starting material. The solution was concentrated on the rotoevaporator (ca. 70 °C (14 torr)) and chromatographed on a silica gel (70–230 mesh) column (ca. 30:1 ratio adsorbant to substrate), eluting with CH_2Cl_2. The first eluted substance was urazole **14**, affording 158 mg (23% yield): mp 281–283 °C (prisms from EtOH); correct elemental composition by combustion analysis; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 2.75 (3 H, N–CH_3, s), 4.68 (2 H, symmetrical m), 4.87 (2 H, symmetrical m), 7.10–7.57 (8 H, C_6H_4, m); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 25.79 (q), 46.81 (d), 64.94 (d), 125.53 (d), 126.89 (d), 127.05 (d), 127.51 (d), 137.94 (s), 138.29 (s), 162.14 (s); IR (KBr) ν (cm^{-1}) 3070, 2970, 1775, 1710, 1460, 1440, 1390, 1340, 1300, 1275, 1190, 1160, 1035, 1000, 965, 950, 835, 750, 625. The second product eluted was the rearrangement urazole (**15**), affording 195 mg (25% yield): mp 283–284 °C (prisms from EtOH), correct elemental composition by combustion analysis; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 2.68 (3 H, N–CH_3, s), 4.43 (2 H, m), 5.05 (2 H, m), 7.00–7.47 (8 H, C_6H_4, m); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 25.24 (q), 50.80 (d), 53.85 (d), 62.02 (d), 67.19 (d) and aromatic and carbonyl carbons frequencies; IR (KBr) ν (cm^{-1}) 3070, 3000, 1770, 1705, 1455, 1395, 1270, 1165, 1030, 965, 915, 800, 770, 760, 740.

Synthesis of Diazetidine (9). Urazole **14** (120 mg, 0.38 mmol) was dissolved in ca. 3 mL of reagent grade MeOH, and ca. 105 mg of KOH was added in one portion. The pale yellow solution was refluxed overnight and the solvent rotoevaporated (ca. 50 °C (14 torr)) to leave a residue, which was treated with 2 mL of distilled water and neutralized with few drops of 2 N HCl. More water was added, followed by thorough extraction with CH_2Cl_2 (3 × 30 mL). The organic phase was rotoevaporated (20 °C (14 torr)) and the residue treated with water and a little CH_3OH. $CuCl_2$ (ca. 400 mg) was added and the mixture stirred at room temperature for 1 h. The red copper complex that was formed was collected on a filter, washed with a little water, and treated with 2 N NH_4OH. Extraction with CH_2Cl_2 and usual workup afforded a yellow oil, which was purified by passing through a short silica gel (70–230 mesh) column (ca. 10:1 ratio adsorbant to substrate), eluting with CH_2Cl_2 to afford colorless crystals, 44 mg (50% yield): mp 185–186 °C (plates from ether), with nitrogen evolution; correct elemental composition by combustion analysis; ^{1}H NMR ($CDCl_3$–CCl_4, Me_4Si) δ 4.48 (2 H, dt, J = 5.4 and 1.5 Hz), 4.78 (2 H, symmetric m), 7.05–7.45 (8 H, C_6H_4, m); IR (KBr) ν (cm^{-1}) 3060, 3030, 3000, 2960, 2940, 1460, 1450, 1270, 1190, 1170, 1050, 950, 750, 740, 620; UV (CH_3CN) λ (nm) (ϵ) 352 (163), 343 (183).

Synthesis of Pyrazoline (10). The rearranged urazole **15** (120 mg, 0.38 mmol) and ca. 110 mg of KOH were dissolved in 6 mL of reagent grade CH_3OH and treated at reflux overnight. The resulting mixture was rotoevaporated and the solid residue dissolved in ca. 5 mL of distilled water and carefully neutralized with 2 N HCl. Above 30 mL of water was added and extracted with 3 × 30-mL portions of CH_2Cl_2. Rotoevaporation (20 °C (14 torr)) of the solvent afforded an oil, which was dissolved in a few drops of CH_3OH. A concentrated aqueous solution of $CuCl_2$ (ca. 400 mg) was added and stirred until the copper complex separated. It was collected on a filter, washed with a little water, and treated with 2 N NH_4OH. The resulting dark blue solution was extracted with CH_2Cl_2, and after rotoevaporation a pale yellow semisolid was obtained that was chromatographed on a short silica gel (70–230 mesh) column (ca. 10:1 ratio adsorbant to substrate), eluting with CH_2Cl_2 to afford colorless crystals, 41 mg (37% yield), mp 165–168 °C (needles from ether) with N_2 evolution, correct elemental composition by combustion analysis: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 3.82 (1 H, H_8, t, $J_{7,8}$ = 5.4 Hz), 4.05 (1 H, H_1, d, $J_{1,7}$ = 5.4 Hz), 5.65 (1 H, H_4, d, $J_{4,8}$ = 5.4 Hz), 6.02 (1 H, H_7, t), 7.10 (8 H, C_6H_4, narrow m); IR (KBr) ν (cm^{-1}) 3070, 3040, 3020, 2990, 1510, 1470, 1460, 1275, 1220, 1185, 1163, 1025, 1015, 955, 790, 765, 745, 615; UV (CH_3CN) λ (nm) (ϵ) 350 (132).

Preparation of Dibenzobarrelene (1). Hydrocarbon **1** was prepared in 55% overall yield by the reaction of *cis*-dichloroethylene and anthracene, followed by dehalogenation with Zn–Cu couple as already described,[13] mp 117–118 °C (lit.[11] mp 119–120 °C), colorless crystals from EtOH.

Preparation of Dibenzosemibullvalene (2) and *sym*-Dibenzocyclooctatetraene (3). Direct photolysis at 254 nm of dibenzobarrelene (**1**) in THF for 24 h afforded a ca. 9:1 mixture of dibenzocyclooctatetraene (**3**) and dibenzosemibullvalene (**2**).[1b] The mixture was separated by column chromatography on neutral alumina, eluting with pentane, which afforded ca. a 60% yield of **3** as the first eluted product, mp 108–109 °C (lit.[14] mp 109.2–109.4 °C) from ethanol. The second product eluted was **2**, which was obtained in ca. 5% yield, mp 103–105 °C (lit.[15] mp 105 °C), from pentane.

Preparation of 4,5,7,8-Dibenzobicyclo[4.2.0]octa-2,4,7-triene (4). Treatment of 1,2-dibromobenzocyclobutene with lithium amalgam as described by Nenitzescu et al.[8b] gave the hydrocarbon **4** in ca. 60% yield, mp 73–74 °C (lit.[8b] mp 74 °C) from ethanol.

Thermolysis of Azoalkane 9 and 10. Thermolysis of Diazetidine (9). Azoalkane **9** (1 mg, 4.3 μmol) was placed into a Kofler melting point apparatus and heated at ca. 190 °C. Gas evolution was evident when the temperature surpassed the melting point. The temperature was kept constant until denitrogenation had ceased (ca. 5 min), and the product was taken up with sufficient CH_3CN and analyzed by capillary GC. The results are shown in Table I.

Hydrocarbons **1**, **2**, and **3** proved to be thermostable under these conditions. Alternatively, azoalkane **9** was thermally decomposed directly in the injector of the chromatograph at 275 °C. The same product composition was obtained by these two thermolysis methods.

Thermolysis of Pyrazoline 10. Azoalkane **10** (1 mg, 4.3 μmol) was thermolyzed in a manner identical with that for isomer **9** by heating at 180 °C for 5 min in the Kofler melting point apparatus or directly in the injector of the chromatograph, heated at 275 °C. The results are given in Table I.

350-nm Photolysis of Azoalkanes 9 and 10. Diazetidine 9. A 10^{-2} M solution of azoalkane **9** in acetonitrile was placed into a Pyrex test tube, capped with a rubber septum, and deoxygenated with a flow of nitrogen gas. The test tube was transferred into the Rayonet photoreactor, equipped with RPR 3500-Å "black light" phosphor lamps, and irradiated continuously, keeping the temperature below 40 °C by cooling with the fan. The progress of the reaction was monitored by periodic GC analysis of small aliquots. The results are given in Table I. Hydrocarbons **1–4** are stable under these photolysis conditions.

350-nm Photolysis of Pyrazoline 10. A 10^{-2} M solution of azoalkane **10** in acetonitrile was irradiated in the same way as described for diazetidine **9**. The results are given in Table I.

254-nm Photolysis of Azoalkanes 9 and 10. Diazetidine 9. A 0.5-mL aliquot of a 2 × 10^{-2} M solution of diazetidine 9 in acetonitrile was placed into a quartz test tube and capped with a rubber septum. The solution was deoxygenated by passing a vivid stream of nitrogen gas. The test tubes were transferred into the Rayonet photoreactor, equipped with RPR 2537-Å lamps, and irradiated for 5–8 min, maintaining the photolysis temperature at ca. 40 °C by cooling with the fan. The photolysate sample was divided into two portions of 0.1 and 0.4 mL. The first sample was submitted to capillary GC analysis to assess the extent of conversion of the azoalkane **9** into dibenzocyclooctatetraene (**3**) and dibenzosemibullvalene (**2**). To the second sample was added benzophenone (30 mg, 16 mmol); the solution was then transferred into a Pyrex test tube and irradiated for 75 min in the Rayonet photoreactor, equipped with RPR 3000 Å lamps, employing a $K_2Cr_2O_7/K_2CO_3$ filter.[3] The samples were then tested by capillary GC for dibenzobarrelene (**1**) and dibenzocyclooctatetraene (**3**) conversion. Control experiments showed that a 2 × 10^{-2} M solution in acetonitrile of dibenzobarrelene (**1**) is photostable for at least 8 min at 254 nm, the conditions used for the 254-nm photolysis of diazetidine **9**. Extensive irradiation times afforded dibenzocyclooctatetraene (**3**) and dibenzosemibullvalene (**2**) in a ca. 9:1 ratio, in

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[13] Cristol, S. J.; Lim, W. Y. *J. Org. Chem.* **1969**, *34*, 1.

[14] Griffin, C. E.; Peters, J. A. *J. Org. Chem.* **1963**, *28*, 1715.

[15] Emerson, G. F.; Watts, L.; Pettit, R. *J. Am. Chem. Soc.* **1965**, *87*, 131.

Table II. Positional and Thermal Parameters (Å^2) of Urazole 15[a]

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	0.1049 (2)	0.1446 (1)	−0.0303 (4)	0.037 (2)	0.038 (2)	0.028 (2)	−0.002 (1)	−0.003 (1)	0.004 (1)
C(2)	0.1244 (2)	0.0925 (1)	0.0665 (4)	0.027 (1)	0.029 (1)	0.035 (2)	0.000 (1)	0.004 (1)	−0.002 (1)
C(3)	0.1680 (2)	0.0989 (1)	0.2109 (4)	0.026 (1)	0.040 (2)	0.037 (2)	0.006 (1)	0.003 (1)	−0.001 (1)
C(4)	0.1737 (2)	0.1565 (2)	0.2851 (4)	0.035 (2)	0.059 (2)	0.030 (2)	−0.007 (2)	0.001 (1)	−0.011 (2)
C(5)	0.2384 (2)	0.1946 (1)	0.0217 (4)	0.054 (2)	0.025 (1)	0.036 (2)	0.000 (1)	0.008 (2)	−0.001 (1)
C(6)	0.1962 (2)	0.1630 (1)	−0.0937 (4)	0.041 (2)	0.029 (1)	0.032 (2)	0.005 (1)	0.000 (1)	0.003 (1)
C(7)	0.0840 (2)	0.1934 (1)	0.0836 (4)	0.049 (2)	0.035 (2)	0.043 (2)	0.004 (2)	0.010 (2)	0.009 (2)
C(8)	0.1764 (2)	0.2035 (1)	0.1595 (4)	0.057 (2)	0.033 (2)	0.050 (2)	−0.011 (2)	0.013 (2)	−0.013 (2)
C(21)	0.1087 (2)	0.0391 (1)	0.0071 (5)	0.045 (2)	0.046 (2)	0.060 (2)	−0.017 (2)	0.019 (2)	−0.011 (2)
C(22)	0.1375 (3)	−0.0072 (2)	0.0930 (6)	0.073 (3)	0.030 (2)	0.108 (4)	−0.001 (2)	0.004 (3)	−0.004 (2)
C(23)	0.1813 (3)	−0.0008 (2)	0.2328 (7)	0.070 (3)	0.048 (2)	0.103 (4)	0.038 (3)	0.041 (3)	0.024 (2)
C(24)	0.1963 (2)	0.0518 (2)	0.2937 (5)	0.037 (2)	0.068 (2)	0.057 (2)	0.026 (2)	0.012 (2)	0.011 (2)
N(41)	0.0830 (2)	0.1693 (1)	0.3568 (3)	0.044 (2)	0.058 (2)	0.035 (2)	−0.013 (1)	0.006 (1)	−0.010 (1)
C(42)	0.0416 (2)	0.1259 (2)	0.4420 (4)	0.035 (2)	0.072 (2)	0.028 (2)	−0.007 (2)	0.000 (1)	−0.007 (2)
N(43)	−0.0356 (2)	0.1127 (1)	0.3621 (3)	0.035 (1)	0.056 (2)	0.031 (1)	0.001 (1)	0.000 (1)	−0.004 (1)
C(44)	−0.0416 (2)	0.1413 (1)	0.2196 (4)	0.034 (2)	0.051 (2)	0.038 (2)	−0.003 (2)	0.001 (1)	0.009 (2)
N(45)	0.0269 (2)	0.1796 (1)	0.2200 (3)	0.045 (2)	0.042 (2)	0.041 (2)	−0.003 (1)	0.007 (1)	0.008 (1)
C(51)	0.3255 (2)	0.2128 (1)	−0.0010 (4)	0.059 (2)	0.040 (2)	0.043 (2)	−0.006 (2)	0.008 (2)	−0.016 (2)
C(52)	0.3688 (2)	0.1984 (1)	−0.1398 (4)	0.051 (2)	0.040 (2)	0.046 (2)	0.001 (2)	0.008 (2)	−0.009 (2)
C(53)	0.3269 (2)	0.1661 (1)	−0.2528 (4)	0.049 (2)	0.040 (2)	0.039 (2)	0.006 (2)	0.011 (2)	0.000 (2)
C(54)	0.2391 (2)	0.1480 (1)	−0.2313 (4)	0.051 (2)	0.038 (2)	0.028 (2)	0.001 (1)	−0.002 (2)	0.001 (2)
O(420)	0.0679 (2)	0.1049 (1)	0.5626 (3)	0.046 (1)	0.136 (3)	0.034 (1)	0.016 (2)	−0.007 (1)	−0.018 (2)
C(430)	−0.0968 (2)	0.0695 (2)	0.4141 (5)	0.042 (2)	0.076 (3)	0.052 (2)	0.012 (2)	0.000 (2)	−0.011 (2)
O(440)	−0.0986 (2)	0.1350 (1)	0.1195 (3)	0.042 (1)	0.095 (2)	0.042 (1)	0.011 (1)	−0.009 (1)	0.005 (1)

[a] U_{ij} is defined for $\exp[-2\pi^2(U_{11}h^2a^2 + \ldots 2U_{12}hka^*b^* + \ldots)]$. The standard deviations are given in parentheses.

Table III. Bond Lengths (pm) and Angles (Deg) for Urazole 15[a]

Bond lengths

C(1)–C(2)	152.3 (4)	C(4)–C(8)	155.1 (5)	C(7)–N(45)	147.6 (4)	N(41)–N(45)	145.4 (4)
C(1)–C(6)	153.5 (4)	C(4)–N(41)	152.1 (4)	C(21)–C(22)	139.5 (6)	C(42)–N(41)	141.4 (5)
C(1)–C(7)	154.9 (4)	C(5)–C(6)	139.0 (4)	C(22)–C(23)	136.3 (8)	C(42)–N(43)	137.8 (4)
C(2)–C(3)	139.6 (4)	C(5)–C(8)	150.8 (5)	C(23)–C(24)	138.1 (6)	C(42)–O(420)	120.6 (4)
C(2)–C(21)	139.6 (4)	C(5)–C(51)	138.9 (5)	C(51)–C(52)	138.8 (5)	N(43)–C(430)	145.2 (5)
C(3)–C(4)	152.3 (5)	C(6)–C(54)	138.1 (4)	C(52)–C(53)	138.2 (5)	C(44)–N(43)	139.2 (4)
C(3)–C(24)	139.4 (5)	C(7)–C(8)	154.7 (5)	C(53)–C(54)	139.8 (5)	C(44)–N(45)	137.8 (4)
						C(44)–O(440)	121.4 (4)

Angles

C(2)–C(1)–C(6)	104.6 (2)	C(1)–C(6)–C(5)	108.5 (3)	C(4)–N(41)–C(42)	116.8 (3)
C(2)–C(1)–C(7)	108.8 (2)	C(1)–C(6)–C(54)	129.6 (3)	C(4)–N(41)–N(45)	103.5 (2)
C(6)–C(1)–C(7)	100.4 (2)	C(5)–C(6)–C(54)	121.6 (3)	C(42)–N(41)–N(45)	106.2 (2)
C(1)–C(2)–C(3)	118.3 (3)	C(1)–C(7)–C(8)	101.3 (3)	N(41)–C(42)–N(43)	106.7 (3)
C(1)–C(2)–C(21)	121.7 (3)	C(1)–C(7)–N(45)	115.9 (3)	N(41)–C(42)–O(420)	126.7 (3)
C(3)–C(2)–C(21)	119.6 (3)	C(8)–C(7)–N(45)	103.2 (3)	N(43)–C(42)–O(420)	126.6 (3)
C(2)–C(3)–C(4)	119.2 (3)	C(4)–C(8)–C(5)	116.5 (3)	C(42)–N(43)–C(44)	111.6 (3)
C(2)–C(3)–C(24)	119.8 (3)	C(4)–C(8)–C(7)	98.6 (3)	C(42)–N(43)–C(430)	123.0 (3)
C(4)–C(3)–C(24)	120.6 (3)	C(5)–C(8)–C(7)	102.0 (3)	C(44)–N(43)–C(430)	125.1 (3)
C(3)–C(4)–C(8)	112.2 (3)	C(2)–C(21)–C(22)	119.2 (4)	N(43)–C(44)–N(45)	106.2 (3)
C(3)–C(4)–N(41)	107.3 (2)	C(21)–C(22)–C(23)	120.9 (4)	N(43)–C(44)–O(440)	126.2 (3)
C(8)–C(4)–N(41)	98.7 (3)	C(22)–C(23)–C(24)	120.4 (4)	N(45)–C(44)–O(440)	127.5 (3)
C(6)–C(5)–C(8)	109.9 (8)	C(23)–C(24)–C(3)	120.0 (4)	C(7)–N(45)–N(41)	109.1 (2)
C(6)–C(5)–C(51)	120.1 (3)	C(5)–C(51)–C(52)	118.8 (3)	C(7)–N(45)–C(44)	125.4 (3)
C(8)–C(5)–C(51)	130.0 (3)	C(51)–C(52)–C(53)	120.9 (3)	N(41)–N(45)–C(44)	108.6 (3)
		C(52)–C(53)–C(54)	120.8 (3)		
		C(53)–C(54)–C(6)	118.0 (3)		

[a] Standard deviations are given in parentheses.

accord with the Friedman results.[1b] Dibenzobarrelene (**1**) is also photostable under the benzophenone-sensitization conditions of diazetidine **9**, i.e., 300-nm irradiation for 75 min at the approximate concentration of **1** (ca. 2 × 10^{-4} M) at which it is produced in the photolysis.

Pryazoline 10. A 10^{-2} M solution of azoalkane **10** in acetonitrile was placed into a quartz test tube, capped with a rubber septum, and carefully deoxygenated by passing a stream of nitrogen gas. The solution was transferred into the Rayonet photoreactor equipped with RPR 2537-Å lamps and continuously irradiated, maintaining the photolysis temperature at ca. 40 °C by cooling with a fan. The products were quantitated by capillary GC, and the results are reported in Table I. The hydrocarbon products are photostable under these conditions.

Benzophenone-Sensitized Photolysis of Azoalkanes 9 and 10. Diazetidine 9. A rubber-septum-capped 5-mL Pyrex test tube was charged with a carefully deoxygenated solution of azoalkane **9** (1 mg, 4.3 μmol) and 10 mg of benzophenone (55 μmol) in 150 μL, of acetonitrile. The test tube was immersed into a wider test tube (ca. 2 mm wider) containing a filter solution, consisting of 0.42 g of $K_2Cr_2O_7$ and 4.2 g of K_2CO_3 in 200 mL of distilled water,[3] which transmits only 300–330-nm radiation. The irradiation was carried out in the Rayonet photoreactor, equipped with RPR 3000-Å "sunlight phosphor" lamps, keeping the temperature at ca. 40 °C by cooling with a fan. Product analysis by capillary GC gave the results shown in Table I. Hydrocarbons **2**–**4** are completely photostable under these conditions.

Pyrazoline 10. To a solution of 1.0 mg (4.3 μmol) of azoalkane **10** in 150 μL of acetonitrile was added 11 mg (60 μmol) of benzophenone. The solution was then irradiated under the same conditions as described for azoalkane **9**. Capillary GC analysis of periodic aliquots showed that only dibenzosemibullvalene **2** was produced (Table I).

X-ray Crystallography of Urazole 15. A clear colorless crystal of dimensions 0.2 × 0.2 × 0.1 mm was optically centered on a Syntex PI four-circle diffractometer. The orientation matrix and the cell parameters were determined on the basis of 15 reflections. The intensities of 3552 *hkl* reflections were measured according to the ω method (Mo Kα, graphite monochromator), using a scan range of 1° and a scan speed between 0.5 and 24.0° min^{-1} as a function of the intensities of the re-

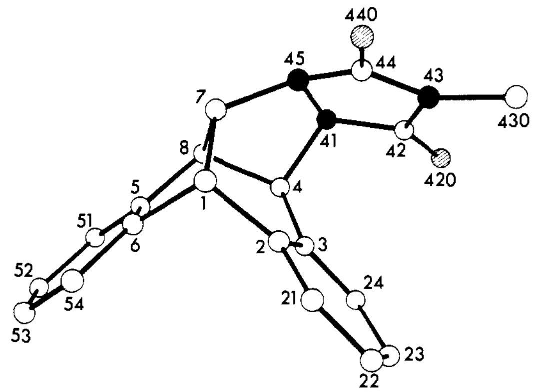

Figure 1. Perspective drawing of the urazole **15** with the labeling of the atoms corresponding to Tables I and II; white, black, and hatched spheres represent carbon, nitrogen, and oxygen atoms, respectively.

flections. In the range 3.0° ≤ 2θ ≤ 55.0°, 2307 reflections were obtained which were utilized for the structure determination. For the evaluation the SHELXTL system on a Eclipse S250 at the Max-Planck-Institut für Festkörperforschung was employed. The structure was solved by direct phase determination. The phases of 342 strong reflections were determined and on the resulting E map approximate positions of all C, N, and O atoms could easily be determined. Positional and thermal parameters could be refined by anisotropic least-squares cycles to $R = 0.067$. The positions of the hydrogen atoms were calculated geometrically and considered isotropically in all refinements.

Urazole **15** crystallizes orthorhombically in the space group *Pbca* with $a = 1499.2$ (2) pm, $b = 2397.4$ (4) pm, and $c = 847.9$ (1) pm. The unit cell contains $Z = 8$ formula units, the density was calculated to be 1.383 Mg·m^{-3}. All atomic parameters are listed in Table II. The labeling of the atoms can be seen in Figure 1. Bond distances and bond angles are summarized in Table III.

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Registry No. 1, 2734-13-6; **2**, 2199-28-2; **3**, 262-89-5; **4**, 17509-84-1; **9**, 82639-35-8; **10**, 82639-36-9; **14**, 78500-30-8; **15**, 82639-37-0; MTAD, 13274-43-6.

Electroorganic Chemistry. 62. Reaction of Iminium Ion with Nucleophile: A Versatile Synthesis of Tetrahydroquinolines and Julolidines

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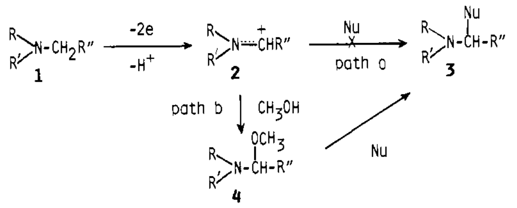
Abstract: A versatile synthetic method of tetrahydroquinolines and julolidines has been developed. The method involves the anodic oxidation of *N,N*-dimethylaniline in methanol to afford α-methoxylated or α,α'-dimethoxylated compounds and subsequent treatment of the products with Lewis acids in the presence of nucleophiles. Simple and electron-rich olefins such as alkenes, styrene, enol ethers, silyl enol ethers, enamines, and enol esters are usable as the nucleophiles. The intermediary formation of iminium ions from the methoxylated compounds is proposed as one of the key steps. The nucleophilic reaction of Grignard reagents with the methoxylated compounds in the presence of Lewis acid is also described.

Although anodic oxidation of amines or their derivatives (**1**) (Scheme I) has been known to be a versatile tool in generating iminium ion intermediates (**2**),[1] the trapping of **2** with carbanion or the like under conditions of anodic oxidation (path a) is almost impossible, since except cyanide ion,[2] the nucleophiles mentioned above are generally unstable under the reaction conditions.

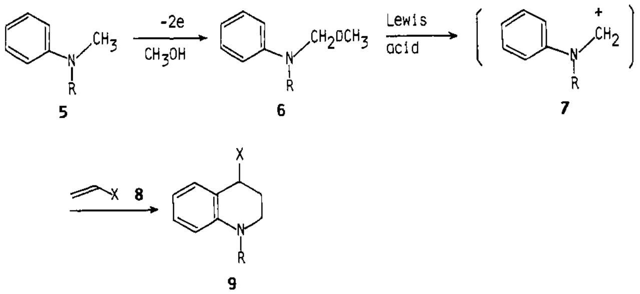
We have recently found, however, that **2** (R' = CO_2CH_3) can be trapped efficiently with a variety of nucleophiles when **2** is first trapped with methanol to give α-methoxylated carbamates (**4**, R' = CO_2CH_3) followed by regeneration of **2** from **4** with Lewis acid catalysts in the presence of nucleophiles (path b).[3] This concept of trapping and regeneration of iminium ion may be applicable to amines other than carbamates of aliphatic amines.

According to the above concept, we describe herein a versatile perparation of tetrahydroquinolines (**9**) and julolidines (**34** and **35**) starting from *N*-methyl-*N*-alkylanilines (**5**). Scheme II illustrates our method, which involves the anodic oxidation of **5** in methanol and subsequent treatment of the oxidized products (**6**) with Lewis acid to regenerate iminium ions (**7**) that can be

Scheme I



Scheme II



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[1] For examples, see (a) Barnes, K. K.; Mann, C. K. *J. Org. Chem.* **1967**, *32*, 1474. (b) Barry, J. E.; Finkelstein, M.; Mayeda, E. A.; Ross, S. D. *Ibid.* **1974**, *39*, 2695. (c) Shono, T.; Hamaguchi, H.; Matsumara, Y. *J. Am. Chem. Soc.* **1975**, *97*, 4264.

[2] Chiba, T.; Takaya, Y. *J. Org. Chem.* **1977**, *42*, 2973.

[3] (a) Shono, T.; Matsumura, Y.; Tsubata, K. *J. Am. Chem. Soc.* **1981**, *103*, 1172. (b) Shono, T.; Matsumura, Y.; Tsubata, K.; Takata, J. *Chem. Lett.* **1981**, 1121. (c) Shono, T.; Matsumura, Y.; Tsubata, K. *Tetrahedron Lett.* **1981**, *22*, 2411. (d) *Ibid.* **1981**, *22*, 3249.

0002-7863/82/1504-5753$01.25/0