Fund, administered by the American Chemical Society, and the American Cancer Society (BC-348). NMR data which were useful in identifying the intermediates observed in this study were obtained at the Worcester Consortium NMR Facility, which is supported by the National Science Foundation (DMR 8108697). We also thank Dr. P. G. Gassman for making a copy of his communication available to us prior to its publication.

Supplementary Material Available: Physical and spectral data for solvolysis products 3–8 (3 pages). Ordering information is given on any current masthead page.

Thermolysis and Photolysis of the Azoalkane 4,5-Diaza-7,8,8-trimethyltricyclo[4.2.1.$0^{3,7}$]non-4-ene: 1,3-Diradical and Diazoalkane Formation

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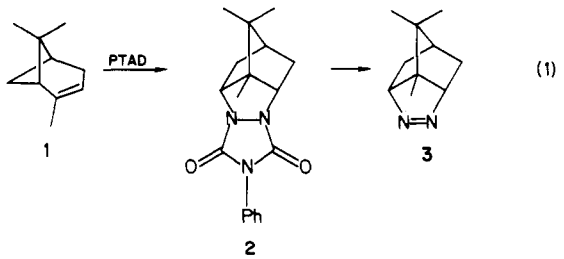
On benzophenone-sensitized photolysis at 350 nm the azoalkane **3** denitrogenates exclusively into 2,3,3-trimethyltricyclo[2.2.1.$0^{2,6}$]heptane (**5**), while direct photolysis at 350 nm affords the tricycloheptane **5** as major product and 2,3,3-trimethyl-4-vinylcyclopentene (**6**) as minor product. With increasing temperature the vinylcyclopentene **6** increases in the direct photolysis. On preparative laser photolysis at 333 nm the diazo-2-(2,3,3-trimethylcyclopenten-4-yl)ethane (**8**) accumulates, which on subsequent photolysis is shown to produce the vinylcyclopentene **6** via the corresponding carbene intermediate. The diazoalkane **8** does not cyclize back to the azoalkane **3**. The thermolysis leads essentially quantitatively to the tricycloheptane **5**, with only traces of the vinylcyclopentene **6**. These results are rationalized mechanistically in terms of a diazenyl diradical as common intermediate for all three denitrogenation modes. It is proposed that the divergent chemical behavior of the diazenyl diradicals produced in the three forms of activation (triplet-sensitized and direct photolysis and thermolysis) is best understood in terms of distinct spin multiplicities and electronic configurations of the diradical intermediates. In this tritopic process it is shown by means of a Salem diagram that the $D_{\sigma,\sigma}$ diazenyl diradical serves as precursor to the tricycloheptane **5** via the 1,3-diradical **4**, while the $D_{\sigma,\pi}$ diradical is responsible as intermediate for the vinylcyclopentene **6** via the diazoalkane **8**.

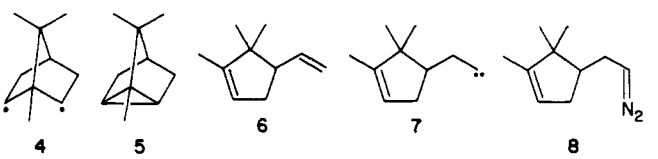
Introduction

Recently it was shown[1] that α-pinene (**1**) gives on cycloaddition with 4-phenyl-1*H*-1,2,4-triazole-3,5-dione (PTAD) the rearranged urazole **2** in fair yields (eq 1).

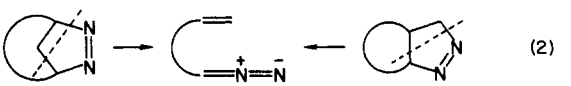


Since such urazoles can be readily converted into their corresponding azoalkanes on hydrolysis–oxidation,[2] it was of mechanistic interest to prepare the azoalkane **3** from urazole **2** and explore its thermolytic and photolytic behavior. Via nitrogen extrusion such azoalkanes serve as convenient precursors to 1,3-diradicals.[3]

In the particular case of azoalkane **3** the 1,3-diradical **4** was expected, which should cyclize into the tricycloheptane **5** or possibly rearrange via 1,2-shift to revert to α-pinene (**1**), although such diradical rearrangements are not common.[4] However, the unexpected formation of the



vinylcyclopentene **6** as minor product[5] implicated the carbene **7** as the immediate precursor, presumably formed from the intermediary diazoalkane **8** via nitrogen loss. Indeed, numerous examples of retrocleavages of azoalkanes into diazoalkanes (eq 2) have been documented during the



past years.[6] Consequently, a thorough investigation of the

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Table I. Product Distribution and Mass Balance in the Thermolysis and Photolysis of Azoalkane 3

	mode[a]	λ, nm	temp, °C	solvent	[3], 10^2M	[additive], 10^2M	product anal.[b] conversn, %[c]	distribution, % 5[d]	6[d]	balance, %[e]
1	VFT		450				100	100	traces	>98
2	DP	350	30	benzene	0.74		100	81	19	>98
		350	-78	THF	0.74		12	100	0	91
3	DP	350	0	THF	0.74		17	94	6	>98
		350	65	THF	0.74		53	74	26	>98
4	DP	350	70	benzene	1.4	35[f]	76	89	11	>98[g]
5	LP	333.6	20	benzene	10		100	91	9	>98
6	SP	350	30	pentane	1.1	19[h]	93	100	0	>98
7	SP	254	30	THF	5.5	5.16[i]	86	97.7	2.3	>98
8	QP	350	30	benzene	0.52	88[j]	61	88	12	>98

[a] VFT = Vacuum flash thermolysis. DP = direct photolysis (Rayonet). LP = laser photolysis (argon ion laser). SP = sensitized photolysis (benzophenone, triphenylene). QP = quenched photolysis (1,3-cyclohexadiene). [b] Capillary GC was run on a 50-m OV-101 column, operated at injector, column, and detector temperatures of 200, 100–180 (programmed at 20 °C min), and 200 °C, respectively, and a nitrogen pressure of 0.7 kg/cm^2; product yields are within 10% of stated values. [c] Amount of azoalkane consumed. [d] Relative yields, normalized to 100%. [e] Sum of absolute yields of recovered azoalkane **3**, tricycloheptane **5**, vinylcyclopentene **6** and unidentified product, unless specified. [f] Acetic acid. [g] Includes 19% acetate **12**. [h] Benzophenone. [i] Triphenylene. [j] 1,3-Cyclohexadiene.

thermolytic and photolytic comportment of azoalkane **3** seemed advisable, in the interest of rigorously testing the involvement of diazoalkane **8** as potential precursor to the minor hydrocarbon products. Herein we describe the full details of this investigation.

Results

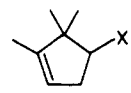
Synthetic Work. As outlined in eq 1, the azoalkane **3** was prepared from the urazole **2** according to the published procedure.[1] For an X-ray picture of urazole **2** and structural data see the paragraph at the end of the paper about supplementary material. Hydrolysis followed by oxidation[2] of urazole **2** afforded the azoalkane **3** in high yield. Its full characterization is given in the Experimental Section.

The unexpected vinylcyclopentene product **6** is known[7] and an authentic sample was prepared via pyrolysis of the acetate **12**. The latter was prepared in turn by the sequence **9** → **10** → **11** → **12** starting from camphor.

The 100-MHz ^{13}C NMR data for these cyclopentenes, along with other derivatives prepared, are in the supplementary material.

Considerable difficulties were encountered in the synthesis of the diazoalkane **8**, the presumed precursor to the vinylcyclopentene **6**. For example, under a variety of conditions the tosylhydrazone of the aldehyde **10** did not lead to detectable quantities of diazoalkane **8**. The difficulties in preparing diazoalkanes from aliphatic aldehydes via their tosylhydrazones are notorious.[8] Thus, no problems whatever were experienced with the preparation of diazoalkane **15** via the sequence **9** → **13** → **14** → **15**. As expected, diazoalkane **15** gave on decomposition the *cis,trans*-styrenes **16a,b** along with other products.

In view of the difficulties in preparing the diazoalkane **8** from aldehyde **10**, the known amine **17** was prepared from nitrile **9** by reduction with lithium aluminum hydride. Unfortunately, also the sequence **17** → **18** → **19** → **8** failed. Instead of the desired diazoalkane **8**, only hydrocarbon products including the vinylcyclopentene **6** were produced.



8, X = $CH_2CH{=}N_2$
9, X = CH_2CN
10, X = $CH_2CH{=}O$
11, X = CH_2CH_2OH
13, X = CH_2COPh
14, X = $CH_2C(Ph){=}NNHTs$
15, X = $CH_2C(Ph){=}N_2$

16a,b, X = CH=CHPh
17, X = $CH_2CH_2NH_2$
18, X = CH_2CH_2NHTs
19, X = $CH_2CH_2N(NO)Ts$
20, X = $CH_2CH_2NHCONH_2$
21, X = $CH_2CH_2N{=}C{=}O$
22, X = $CH_2CH_2N(NO)CONH_2$

Finally, the successful route proved to be the sequence **17** → **20** → **22** → **8**. The new compounds are characterized in the Experimental Section. For their ^{13}C NMR data see the paragraph at the end of the paper about supplementary material. The diazoalkane **8** is indeed a rather sensitive substance, decomposing readily on standing at room temperature. Its characteristic IR band at 2060 cm^{-1} and UV–vis absorption in the 400–500-nm region clearly establish the authenticity of this material. On photolysis and thermolysis it gives vinylcyclopentene **6**, together with other unidentified products, but no tricycloheptatriene **5** could be detected by capillary GC.

Product Studies. The qualitative results on the type of products formed in the thermolysis and photolyses are summarized in eq 3 and the quantitative capillary GC data are collected in Table I. The main product by far was the tricycloheptane **5**. The vinylcyclopentene **6** was at all times the minor product, the relative amounts of which depended dramatically on the reaction conditions. Other minor volatile products could also be sighted in the capillary GC, but their amounts were too small for preparative GC collection and characterization. However, as Table I shows, product balance was high in all cased, i.e., 90%, provided the yields were adjusted for the amount of azoalkane

(6) (a) Bianchi, G.; De Micheli, C.; Gandolfi, R. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 721. Cf. cited literature therein on retrocyclization of azoalkanes into diazoalkanes. (b) Aue, D. H.; Lorens, R. B.; Helwig, G. S. *J. Org. Chem.* **1979**, *44*, 1202. (c) Ege, G.; Gilbert, K.; Hahn, B. *Tetrahedron Lett.* **1979**, *1571*. (d) Franck-Neumann, M.; Dietrich-Buchecker, C. *Tetrahedron Lett.* **1980**, *21*, 671. (e) Schneider, M. P.; Bippi, H. *J. Am. Chem. Soc.* **1980**, *102*, 7363. (f) Schneider, M. P.; Bippi, H.; Rau, H.; Ufermann, D.; Hörmann, M. *J. Chem. Soc., Chem. Commun.* **1980**, 957. (g) Wilt, J. W.; Niinemae, R. *J. Org. Chem.* **1980**, *45*, 5402. (h) Padwa, A.; Ku, H. *Tetrahedron Lett.* **1980**, *21*, 1009. (i) Nishizawa, Y.; Miyashi, T.; Mukai, T. *J. Am. Chem. Soc.* **1980**, *102*, 1176. (j) Demuth, M.; Amrein, W.; Bender, C. O.; Braslavsky, S. B.; Burger, U.; George, M. V.; Lemmer, D.; Schaffner, K. *Tetrahedron* **1981**, *37*, 3245. (k) Padwa, A.; Rodriguez, A. *Tetrahedron Lett.* **1981**, *22*, 187. (l) Chang, M. H.; Dougherty, D. A. *J. Am. Chem. Soc.* **1982**, *104*, 2333. (m) Gstach, H.; Kish, H. *Chem. Ber.* **1982**, *115*, 2586. (n) Kumagai, T.; Ohba, Y.; Mukai, T. *Tetrahedron Lett.* **1982**, *23*, 439. (o) Padwa, A.; Caruso, T.; Nahm, S.; Rodriguez, A. *J. Am. Chem. Soc.* **1982**, *104*, 2865. (p) Padwa, A.; Kumagai, T.; Tohidi, M. *J. Org. Chem.* **1983**, *48*, 1834. (q) Dolbier, Jr., W. R.; Al-Fekri, D. M. *Tetrahedron Lett.* **1983**, *24*, 4047. (r) Adam, W.; Carballeira, N.; Gillaspey, W. D. *Tetrahedron Lett.* **1983**, *24*, 5473.

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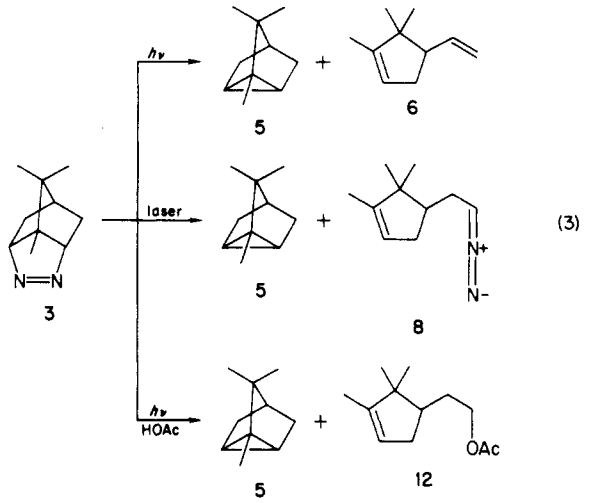
(8) Regitz, M. "Diazoalkane: Eigenschaften und Synthesen"; Georg Thieme Verlag: Stuttgart, 1977.



consumed. Both products were perfectly stable toward the thermolysis and photolysis conditions employed, as confirmed by control experiments on the authentic materials.

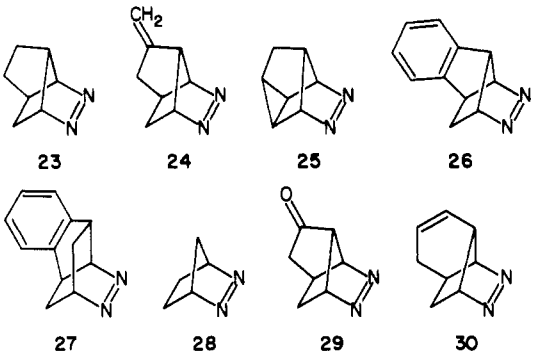
The vacuum flash thermolysis (VFT) at 450 °C (18 torr) gave essentially exclusively the tricycloheptane **5** (entry 1 in Table I); only traces of vinylcyclopentene **6** could be detected by capillary GC. The cleanest reaction, however, was the benzophenone-sensitized photolysis (entry 6 in Table I), which gave exclusively the tricycloheptane **5**. Therefore, the vinylcyclopentene **6** was formed only via singlet excitation. In this context, the triphenylene-sensitization (entry 7 in Table I) led to significant amounts (ca. 2.3%) of vinylcyclopentene **6**. Presumably singlet-sensitization by triphenylene took place.[9]

Direct photolysis of azoalkane **3** at 350 nm and elevated temperatures were the optimal conditions for the production of vinylcyclopentene **6** (entries 2 and 3 in Table I). Thus, at 65 °C in THF (but benzene makes no significant difference), as much as ca. 26% was formed. Of interest is the significant activation barrier to this photochemical reaction since at −78 °C no vinylcyclopentane **6** was formed (entry 3 in Table I). An attempt at probing for triplet quenching in the direct photolysis was made with 1,3-cyclohexadiene (entry 8 in Table I). However, as compared with entry 2 (Table I), essentially the same product distribution was observed in the absence and presence of the 1,3-cyclohexadiene. Presumably 1,3-cyclohexadiene quenched the azoalkane triplets inefficiently[3a] or no such triplets were involved in the direct photolysis. In other words, the tricycloheptane **5** was formed via singlet as well as triplet excitation, but the vinylcyclopentene exclusively via singlet excitation.

Significant and mechanistically informative as to the origin of the vinylcycloheptene **6** was the direct photolysis of azoalkane **3** in the presence of acetic acid (entry 4 in Table I). Besides the hydrocarbons **5** and **6** (produced in significantly reduced amounts), the acetate **12** was formed in an absolute yield of 19%, identified by comparison with authentic material. The most logical precursor to the acetate **12** was the diazoalkane **8**.[8] Despite intensive and deliberate efforts to observe the transient diazoalkane **8** spectroscopically (UV and vis) in the Rayonet irradiations at 350 nm, not even traces could be detected. For this purpose the authentic diazoalkane **8** was prepared. Control experiments confirmed that under the photolysis conditions the diazoalkane **8** disappeared faster than the azoalkane **3** and thus had no chance of accumulating. Of course, the photolysis product was the vinylcyclopentene among others. Also the use of a 1000-W Hanovia xenon–mercury lamp with appropriate filters or monochromator gave inconclusive results concerning the intermediacy of the diazoalkane **8** in the photolysis of azoalkane **3**. Too stringent filtering led to impractically low azoalkane conversion so that IR or UV detection of diazoalkane **8** was not sufficiently sensitive, at least with the instrumentation available to us.

The decisive experiment turned out to be laser photolysis (entry 5 in Table I), with the 333.6-nm line of the CR-18 Supergraphite argon ion laser with an output intensity of ca. 1 W. After several seconds of irradiation the photolysate turned yellow and after a few minutes the intensity of the coloration was maximal (UV–vis monitoring). On prolonged irradiation or standing in the dark the photolysate turned colorless. Capillary GC at that point confirmed the presence of the hydrocarbon products **5** and **6** (entry 5 in Table I). The UV–vis and IR spectra of the transient color at maximal intensity matched that of the authentic diazoalkane **8** (cf. Experimental Section). In fact, rotoevaporation of the solvent and the hydrocarbon products **5** and **6** afforded a mixture of azoalkane **3** and diazoalkane **8**, a convenient and attractive synthetic route to such elusive diazoalkanes. However, in this particular case isolation and purification of the diazoalkane **8** proved difficult in view of its labile nature. Nevertheless, preparative laser photochemistry could constitute a useful synthetic method of more stable diazoalkanes via retrocleavage of the appropriate azoalkane precursor.

Laser Photolysis of Other Azoalkanes. To probe the scope and generality of the photolytic retrocleavage of azoalkanes into diazoalkanes, the laser photolysis of the series of azoalkanes **23–30** was conducted under the conditions described for azoalkane **3**. Of these the first five



(structures **23–27**) gave diazoalkanes, as confirmed by IR and UV–vis detection, but the last three (structures **28–30**) did not. In all cases (except **25**) the amount of diazoalkane formation was small (a few percent) also at elevated temperature. Even a cursory inspection of this list of azoalkanes makes it apparent that no obvious structural feature commands the photoreversion of these azoalkanes into their respective diazoalkanes.

Discussion

The following experimental facts require mechanistic rationalization: (a) Triplet-sensitized photolysis of azoalkane **3** affords exclusively the tricycloalkane **5** as denitrogenation product. (b) Thermolysis also gives essentially quantitatively tricycloalkane **5** and only traces of the vinylcyclopentene **6**. (c) Direct photolysis leads mainly to tricycloalkane **5** and appreciable amounts of vinylcyclopentene **6**, the latter increasing with increasing photolysis temperature. (d) Photochemical retrocyclization of azoalkane **3** yields irreversibly diazoalkane **8**, the pre-

(9) Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker, Inc.: New York, 1973.

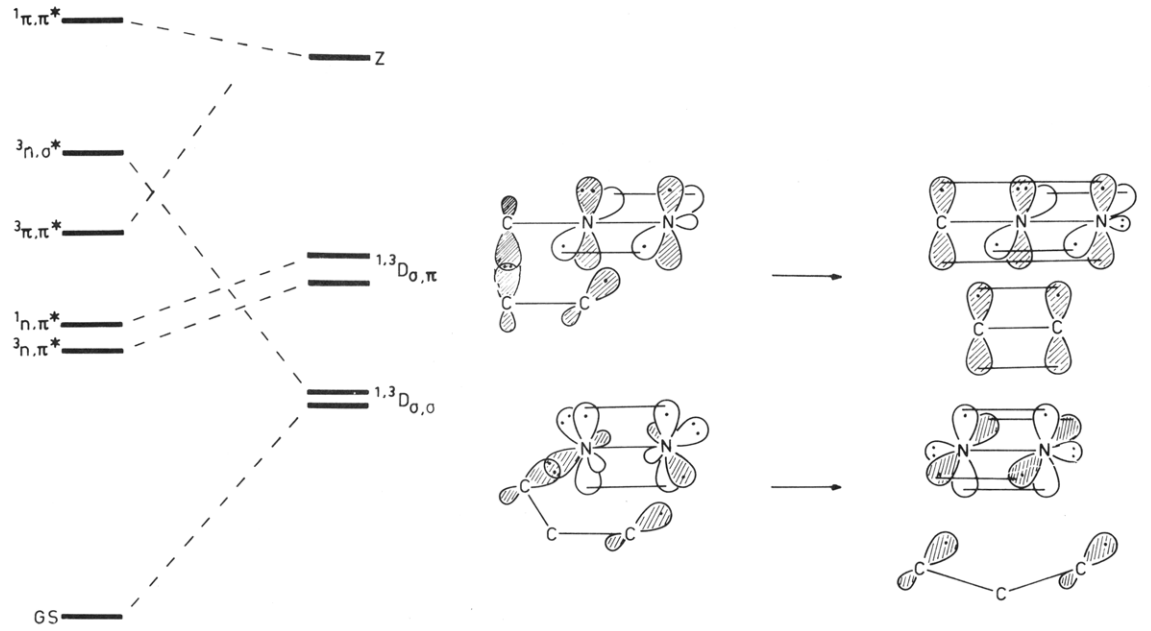
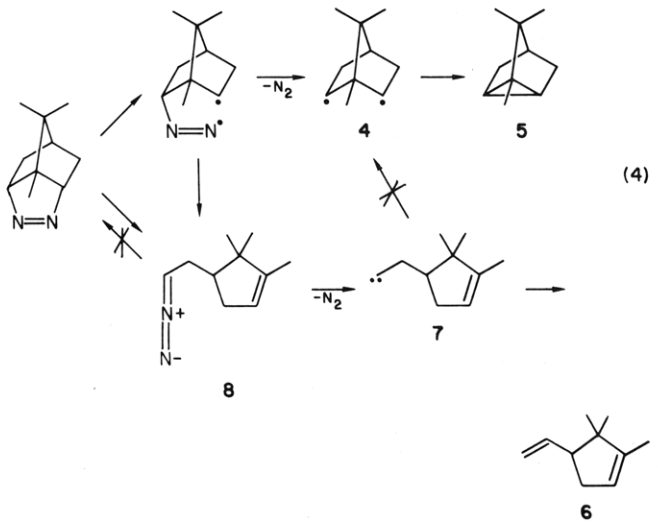


Figure 1. Salem diagram for the tritopic retrocyclization of azoalkanes and electron configurations of the intermediary $D_{\sigma,\sigma}$ and $D_{\sigma,\pi}$ diazenyl diradicals. Hatched orbitals are those involved directly in the fragmentations.

cursor to the vinylcyclopentene **6**. A reasonable mechanism explaining these facts is given in eq 4. The key



(4)

intermediate in this mechanism is the diazenyl diradical, which provides the required branching point in the observed product composition. The latter depends on the mode of activation, i.e., triplet-sensitized and direct photolyses and thermolysis. Of course, the mechanistic option may be entertained that the 1,3-diradical **4** is formed directly via simultanous two-bond cleavage of the azoalkane **3** without trespassing the diazenyl diradical. However, this notion would not rationalize the formation of the diazoalkane **8** because the direct photochemical retrocyclization **3** → **8** is forbidden on orbital symmetry grounds and requires a stepwise process.[6a] Furthermore, both experimental[10] and theoretical[11] work suggest that the thermolysis proceeds via stepwise one-bond cleavages. Thus, we find it more effective to engage one common intermediate for all three modes of activation, namely the diazenyl diradical (eq 4), and differentiate between them on the basis of spin multiplicity and electronic configuration.

Within this mechanistic framework, in the triplet-sensitized photolysis the triplet diazenyl diradical denitrogenates faster to the triplet 1,3-diradical **4** than it cleaves to diazoalkane **8**. That denitrogenation should be preferred over retrocleavage can be justified on the grounds that triplet diazoalkane **8** would have to result. This adiabatic photochemical process is energetically not feasible. Besides, the triplet 1,3-diradical **4** is expected[12] to cyclize readily into the tricycloalkane **5** since it is favorably disposed toward rapid intersystem crossing. In view of the norbornane geometry the radical lobes necessarily point toward each other, which promotes cyclization.[12]

In contrast, for the thermolysis and direct photolysis the single-excited azoalkane **3** leads to the singlet diazenyl diradical, which either loses nitrogen to give the singlet 1,3-diradical **4** and subsequently the tricycloalkane **5** or cleaves to afford the diazoalkane **8** and eventually the vinylcyclopentene **6** via carbene **7**. Intersystem crossing of the single-excited azoalkane **3** to its triplet state as product branching point, i.e., the triplet gives rise to tricycloalkane **5** and the singlet to the vinylcyclopentene **6**, is unlikely in view of the fact (entry 8 in Table I) that the 1,3-cyclohexadiene triplet quencher does not appreciably alter the product distribution between tricycloalkane **5** and vinylcyclopentane **6**. Besides, the small change in the proportion of these products goes in the wrong direction since less vinylcyclopentene **6** is formed in the presence of the 1,3-cyclohexadiene triplet quencher.

Why then does the singlet diazenyl diradical behave distinctly in the thermolysis and direct photolysis of azoalkane **3**? To postulate that for the latter vibrationally excited or "hot" precursors are involved is not reasonable because with increasing temperature of the direct photolysis the fragmentation to the diazoalkane is enhanced. This fact demands that thermally equilibrated intermediates intervene also in the direct photolysis. Consequently, we postulate that different electronic configura-

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tions of the singlet diazenyl diradical are produced in the thermolysis vs. direct photolysis.

As the Salem diagram[13] shows (Figure 1) for this typical tritopic process,[14] the ground-state reaction (thermolysis) generates the energetically preferred $D_{\sigma,\sigma}$-type diazenyl diradical, which fragments into nitrogen and the 1,3-diradical **4**. On the other hand, via singlet n,π^*-excitation (direct photolysis) the $D_{\sigma,\pi}$-type diazenyl diradical is produced, which cleaves into the diazoalkane **8**. At the intersection with the triplet n,σ^*-surface an avoided crossing and effective spin orbital coupling leads to the $D_{\sigma,\sigma}$-type diazenyl diradical.[13] The latter denitrogenates to give the tricycloalkane **5** via the 1,3-diradical **4**. Furthermore, on triplet n,π^*-excitation (triplet sensitized photolysis) also the $D_{\sigma,\sigma}$-type diazenyl diradical is formed through forbidden surface crossing with the triplet n,σ^*-surface. This path accounts for the efficient tricycloalkane **5** formation.

It remains still to rationalize why the $D_{\sigma,\sigma}$-configuration of the diazenyl diradical prefers to denitrogenate into the 1,3-diradical **4** while its $D_{\sigma,\pi}$-configuration fragments into the diazoalkane **8**. The orbital pictures for the $D_{\sigma,\sigma}$- and $D_{\sigma,\pi}$-configurations (Figure 1) seem to provide a plausible answer. The $D_{\sigma,\sigma}$-type diradical is aligned optimally for cleavage of the second C–N bond, affording a ground-state nitrogen molecule and the 1,3-diradical **4**. In contrast, for the $D_{\sigma,\pi}$-type diradical cleavage of the second C–N bond would lead to an electronically excited nitrogen molecule and the 1,3-diradical **4**. Instead, alignment of the adjacent C–C bond in parallel with the incipient allyl π-system of the diazo linkage results in fragmentation to the diazoalkane **8**. In view of the additional energy required to cleave the C–C bond, the observed activation energy for the latter process is reasonable.

In summary, a diazenyl diradical (eq 4) is postulated as the initial intermediate in the thermolysis and triplet-sensitized and direct photolysis of azoalkane **3**. The diazenyl diradical has the option of denitrogenating into the 1,3-diradical **4**, which affords the tricycloalkane **5**, or fragmenting into the diazoalkane **8**, which leads to the vinylcyclopentene **6** via the carbene **7**. A Salem diagram of this tritopic process (Figure 1) allows us to rationalize the divergent chemical behavior of the diazenyl diradical in terms of differences in the spin multiplicities, i.e., singlet vs. triplet states, and differences in the electronic configurations, i.e., $D_{\sigma,\sigma}$ vs. $D_{\sigma,\pi}$, of the diazenyl diradical. Therefore, the singlet $D_{\sigma,\sigma}$ diradical intervenes in the thermolysis and the singlet $D_{\sigma,\pi}$ diradical in the direct photolysis. The triplet-sensitized photolysis engages efficient surface jump from the ^{3}n,π^*–$^3D_{\sigma,\pi}$ to the ^{3}n,σ^*–$^3D_{\sigma,\sigma}$ energy surface leading to the $^3D_{\sigma,\sigma}$ diradical, which via intersystem crossing affords tricycloheptane **5**.

Experimental Section

General Methods. Melting and boiling points are uncorrected. Quantitative GC was performed on a Carlo Erba Fractovap 2900 (FID) with a 50-m OV-101 capillary column. Electronic integrations were carried out by means of a Spectra Physics System I. Preparative GC was performed either on a Varian 920 (TC) or on a Carlo Erba 420 (FID) instrument. Column A was a 3-m × $^3/_8$-in. steel column packed with 20% Apiezon M on 60/80 mesh Chromosorb W/AW-DMCS, column B a 6-m × $^3/_8$-in. steel column packed with 25% SE30 on 60/80 mesh Chromosorb W/AW-DMCS, and column C a 1.5-m × $^3/_8$-in. glass column packed with 20% Apiezon L on 60/80 mesh Chromosorb W-HP.

Elemental analyses were run for us either in-house or by Professor Dr. G. Maier's staff of the Universität Giessen.

The 60-MHz ^{1}H NMR spectra were run on a Perkin-Elmer-Hitachi R-24B, the 90-MHz ^{1}H NMR spectra on a Varian EM-390, the 400-MHz ^{1}H NMR and 100-MHz ^{13}C NMR spectra on a Bruker WP-400, and the 22.6-MHz ^{13}C NMR spectra on a Bruker WM-90. For the IR spectra a Beckman Acculab 4 was used and the UV–vis spectra were measured on a Cary Model 17 spectrophotometer. The MS were determined on a Varian CH-7 and the GC–MS experiments were kindly run for us by Dr. D. Henneberg, Max-Planck-institut für Strahlenchemie (Mülheim/Ruhr) and Professor Dr. H. Schwarz, Technische Universität Berlin.

All known compounds used here were prepared according to literature procedures and purified to match reported physical and spectral data. Unless otherwise stated, rotoevaporation of the solvent was carried out at ca. 20 °C (10–20 torr), room temperature was ca. 20 °C, drying was carried out over anhydrous $MgSO_4$, the adsorbant for column chromatography (CC) was silica gel (60–230 mesh) with a substrate–adsorbant ratio of ca. 1:20, and column length to width dimensions of ca. 16:1. Stirring was carried out magnetically by means of a spinbar.

Conventional photolyses were carried out in a Rayonet Photoreactor RP-100 equipped with 350-nm black phosphor lamps. For the laser irradiations a Coherent Supergraphite CR-18 argon ion laser with ca. 1-W output at the 333.6-nm line was used.

4,5-Diaza-*N*-phenyl-7,8,8-trimethyltricyclo[4.2.1.0^{3,7}]nonane-4,5-dicarboximide (2). When the starting material was 640 mg (3.68 mmol) of 4-phenyl-1,2,4-4H-triazole-3,5-dione (PTAD) and 500 mg (3.68 mmol) of α-pinene, 150 mg (14%) of the urazole **2** was obtained as colorless needles: mp 187–188 °C (lit.[1] mp 187–188 °C); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.97 (s, 6 H), 0.98 (s, 3 H), 1.48 (d, J = 13.5 Hz, 2 H), 1.92 (pseudo t, J = 3.8 Hz, 1 H), 2.39–2.46 (m, 2 H), 4.20 (d, J = 8.5 Hz, 2 H), 7.34–7.40 (m, 1 H), 7.44–7.50 (m, 4 H).

X-ray Crystallography of Urazole 2. The orientation matrix and the cell parameters were determined from a clear colorless crystal of dimensions 0.08 × 0.10 × 0.44 mm on a Syntex-P3 four-circle diffractometer. Measurement of intensities: ω scan, 1° range Mo Kα, 2θ maximum = 55°. The intensities of 7348 reflections were measured, 4313 of them with $F > 3(F)$ were applied for the structure determination. The structure was solved by direct phase determination. The phases of 460 strong reflections were determined and on the resulting E map approximate positions of all non-hydrogen atoms could be refined by anisotropic least-squares cycles to R = 0.071. The positions of the hydrogen atoms were calculated geometrically and considered isotropically in all refinements. Urazole **2** crystallizes triclinically in the space group $P\bar{1}$ (no. 2) with a = 1020.6 (4) pm, b = 2279.9 (8) pm, c = 709.2 (2) pm, α = 94.05 (2)°, β = 98.54 (2)°, γ = 99.85 (3)°. The unit cell contains Z = 4 formula units; the density was calculated to be 1.292 g cm^{-3}. See paragraph at the end of paper about supplementary material.

4,5-Diaza-7,8,8-trimethyltricyclo[4.2.1.0^{3,7}]non-4-ene (3). When the starting material was 311 mg (1.00 mmol) of urazole **2** and the established procedure[2] was followed, 146 mg (89%) of the azoalkane **3** was obtained as a colorless solid after slow sublimation at 60–65 °C (18 torr): IR (CCl_4) 2960, 2870, 1530, 1460, 1380, 1370, 1360, 1290, 1040, 960 cm^{-1}; UV (pentane) λ_{max} (log ϵ) 337 nm (2.47); ^{1}H NMR ($CDCl_3$, 60 MHz) δ 0.90 (s, 3 H), 1.00 (s, 6 H), 1.1 (m, 2 H), 1.7–2.2 (m, 3 H), 4.55 (br d, J = 8 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 10.98 (q, Me), 20.96 (q, two Me), 30.58 (t, C-2,9), 49.47 (d, C-1), 49.98 (s, C-8), 60.73 (s, C-7), 88.05 (d, C-3,6); MS (70 eV), m/e 136 (1, $M^+ - N_2$), 121 (10), 105 (8), 93 (100), 77 (22). Anal. $C_{10}H_{16}N_2$ (164.2). Calcd: C, 73.13; H, 9.82; N, 17.06. Found: C, 73.33; H, 9.84; N, 17.27.

2,3,3-Trimethyl-4-vinylcyclopentene (6).[7] Pyrolysis of 863 mg (4.40 mmol) of 2-(2,3,3-trimethylcyclopenten-4-yl)ethyl acetate (**12**) while passing through a hot quartz tube at 510 °C (18 torr) afforded 150 mg (25%) of vinylcyclopentene **6** after the usual workup. Preparative GC on column A at injector and column temperatures of 150 and 130 °C, respectively, and a nitrogen flow rate of 120 mL/min gave the pure product: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.77 (s, 3 H), 0.98 (s, 3 H), 1.62 (dt, J = 3.0, 1.5 Hz, 3 H), 2.14 (ddq, J = 15.8, 10.0, 2.6 Hz, 1 H), 2.37 (ddq, J = 15.8

(13) Bigot, B.; Sevin, A.; Devaquet, A. *J. Am. Chem. Soc.* **1978**, *100*, 2639. Although their analysis pertains to the dissociation of diimide, the qualitative features can be used for azoalkanes in general.

(14) (a) Salem, L. *J. Am. Chem. Soc.* **1974**, *96*, 3486. (b) Dauben, W. G.; Salem, L.; Turro, N. J. *Acc. Chem. Res.* **1975**, *8*, 41. (c) Devaquet, A. *Pure Appl. Chem.* **1975**, *41*, 455. (d) Devaquet, A. *Topics Curr. Chem.* **1975**, *54*, 1. (e) Michl, J. *Pure Appl. Chem.* **1975**, *41*, 507.

7.7, 1.5 Hz, 1 H), 2.40 (br dd, J = 10.0, 7.7 Hz, 1 H), 5.02 (d, J = 0.85 Hz, 1 H), 5.04–5.08 (m, 1 H), 5.16 (br ddq, J = 3.0, 2.6, 1.5 Hz, 1 H), 5.82–5.94 (m, 1 H).

***N*-Tosyl-2-(2,3,3-trimethylcyclopenten-4-yl)ethylamine (18).** To a solution of 640 mg (4.17 mmol) of 2-(2,3,3-trimethylcyclopenten-4-yl)ethylamine (17) in 4 mL of dry pyridine was added while cooling and stirring 1.00 g (5.25 mmol) of toluenesulfonyl chloride. After complete addition, the ice bath was removed, the mixture allowed to stir at room temperature for 5 h and poured onto ca. 25 mL of an ice/water mixture, and 15 mL CH_2Cl_2 was added. The CH_2Cl_2 was separated and washed with 1 × 15 mL of 5% aqueous HCl solution and with 1 × 5 mL of saturated aqueous NaCl. After the solvent was dried and removed, 717 mg (56%) of yellow solid was isolated, which was purified by two recrystallizations from 95% ethanol: mp 87.0–87.5 °C, white plates; IR ($CDCl_3$) 3400, 3300, 3170, 3060, 2980, 2940, 2910, 2880, 1610, 1410, 1330, 1160, 1090, 810 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 0.70 (s, 3 H), 0.90 (s, 3 H), 1.6 (br s, 3 H), 1.3–2.3 (m, 5 H), 2.40 (s, 3 H), 2.9 (m, 2 H), 4.7 (m, 1 H), 5.1 (br s, 1 H), AB pattern (δ_A 7.1, δ_B 7.6, J = 8 Hz); MS (70 eV), m/e 307 (2, M^+), 184 (8), 155 (38), 152 (80), 135 (78), 121 (16), 109 (63), 91 (92), 79 (19), 65 (21), 57 (20), 41 (22), 30 (100). Anal. $C_{17}H_{25}NO_2S$ (307.4). Calcd: C, 66.41; H, 8.20; N, 4.56. Found: C, 66.39; H, 8.18; N, 4.60.

***N*-Nitroso-*N*-tosyl-2-(2,3,3-trimethylcyclopenten-4-yl)-ethylamine (19).** To a suspension of 690 mg (2.20 mmol) of tosylamine 18 in 20 mL of CCl_4 and ca. 5 g of NaOAc was added ca. 2 g of N_2O_4 (condensed at −78 °C) while cooling at −10 °C and stirring over a period of 20 min. After stirring for an additional 30 min, the reaction mixture was poured into a solution of ca. 5.8 g of K_2CO_3 in 10 mL water. The layers were separated, the aqueous layer was extracted with 2 × 5 mL CH_2Cl_2, and the combined organic layers were washed with 1 × 15 mL saturated aqueous NH_4Cl and 1 × 10 mL saturated aqueous NaCl. After drying and solvent removal the crude product was purified by CC, eluting with CH_2Cl_2, resulting in 430 mg (61%) yellow oil, which resisted all attempts to crystallize: IR (film) 3040, 2950, 2890, 2860, 1600, 1510, 1500, 1375, 1195, 1160, 1155, 1090, 955, 870, 850, 815, 790, 765, 670 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 0.70 (s, 3 H), 0.90 (s, 3 H), 1.0–2.4 (m, 5 H), 1.5 (br s, 3 H), 2.4 (s, 3 H), 3.65 (t, J = 7 Hz, 2 H), 5.1 (br s, 1 H), AB pattern (δ_A = 7.1, δ_B = 7.6, J = 8 Hz).

***N*-[2-(2,3,3-Trimethylcyclopenten-4-yl)ethyl]urea (20).** To a solution of 2.04 g (13.3 mmol) of amine 17 in 6.65 g of 2 N aqueous HCl were added while stirring ca. 1.9 g of KOCN at 10 °C within 15 min. While stirring the mixture was allowed to warm to room temperature and stirred for 19 h. The reaction mixture was extracted with 4 × 50 mL of ethyl acetate and the combined extracts were washed with 3 × 20 mL of saturated aqueous NaCl. After the solution was dried and the solvent removed, 2.30 g (88%) of urea 20, colorless oil, was obtained, which crystallized on standing: mp 66–68 °C; IR (KBr) 3420, 3340, 3200, 3025, 2950, 2920, 2880, 2850, 2820, 1650, 1600, 1560, 1455, 1435, 1360, 1340, 790 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ (s, 3 H), 0.95 (s, 3 H), 1.4–2.5 (m, 5 H), 1.6 (br s, 3 H), 3.1 (m, 2 H), 4.6 (br s, 2 H), 5.0 (br s, 2 H); MS (70 eV), m/e 196 (6, M^+), 195 (38), 135 (100), 121 (44), 120 (55), 109 (98), 107 (54), 93 (86), 91 (40), 79 (43), 73 (48), 67 (32), 55 (33), 44 (36). Anal. $C_{11}H_{20}N_2O$ (196.3). Calcd: C, 67.31; H, 10.27; N, 14.27. Found: C, 66.97; H, 10.38; N, 13.53.

***N*-Nitroso-*N*-[2-(2,3,3-trimethylcyclopenten-4-yl)ethyl]-urea (22).** To a suspension of 1.22 g (6.21 mmol) of urea 20 and 890 mg (10.8 mmol) of NaOAc in 20 mL of dry ether under a nitrogen atmosphere was added while stirring at −15 °C ca. 1.0 g of N_2O_4 (condensed at −78 °C). After stirring for 2.5 h, the reaction mixture was poured into 20 mL of 5% aqueous $NaHCO_3$ and the ether layer separated. The aqueous layer was extracted with 3 × 5 mL of CH_2Cl_2, the combined organic layers were washed with 1 × 20 mL of 5% aqueous $NaHCO_3$ and with 1 × 20 mL of saturated aqueous NaCl and dried, and the solvent was removed. Purification was achieved by CC with CH_2Cl_2 as eluant, resulting in 650 mg (46%) of a colorless oil as second fraction, which resisted all attempts to crystallize: IR ($CDCl_3$) 3540, 3490, 3420, 3320, 3260, 3040, 2960, 2900, 2870, 2840, 1730, 1575, 1500, 1430, 1410, 1370, 1190, 1025, 800 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 0.80 (s, 3 H), 0.95 (s, 3 H), 1.2–2.4 (m, 5 H), 1.5 (br s, 3 H), 3.8 (t, J = 7 Hz, 2 H), 5.1 (br s, 1 H), 6.3 (br s, 2 H).

2-(2,3,3-Trimethylcyclopenten-4-yl)ethyl Isocyanate (21). In the above experiment 220 mg (20%) of isocyanate 21 was isolated as a first fraction: colorless oil; IR (film) 3040, 2960, 2920, 2860, 2270, 1470, 1450, 1380, 1370, 1270, 1100, 1020, 810 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 0.7 (s, 3 H), 0.9 (s, 3 H), 1.4–2.4 (m, 5 H), 1.6 (br s, 3 H), 3.1 (t, J = 7 Hz, 2 H), 5.0 (br s, 1 H).

1-Diazo-2-(2,3,3-trimethylcyclopenten-4-yl)ethane (8). To a mixture of 150 mg (0.660 mmol) of *N*-nitrosourea 22 in 20 mL of hexane was added while cooling at 0 °C and stirring 10 mL of 10% aqueous KOH. After stirring in the dark at 0 °C for 2 h, the layers were separated, the aqueous layer was washed with 2 × 5 mL of hexane, the combined hexane solutions were washed with 2 × 5 mL of 2 N NaOH and dried over KOH pellets, and the solvent was removed, resulting in a yellow oil that was used without further purification: IR (film) 3080, 3040, 2960, 2930, 2900, 2870, 2840, 2060, 1465, 1450, 1390, 1380, 1360, 1060, 1020, 800 cm^{-1}; UV (hexane) λ_{max} 370, 383, 398, 417, 460, 490 (sh) nm; ^1H NMR ($CDCl_3$, 60 MHz) δ 0.8 (s, 3 H), 1.0 (s, 3 H), 1.5–2.5 (m, 3 H), 1.6 (br s, 3 H), 3.3–3.8 (m, 3 H), 5.1 (br s, 1 H).

Phenyl 2-(2,3,3-Trimethylcyclopenten-4-yl)methyl Ketone Tosylhydrazone (14). To a solution of 270 mg (1.45 mmol) of tosyl hydrazide in 2.1 mL of MeOH at ca. 40 °C was added 300 mg (1.31 mmol) of phenyl 2-(2,3,3-trimethylcyclopenten-4-yl)-methyl ketone (13). After refluxing for 5 min, the mixture was allowed to cool to room temperature and on standing ca. 12 h the crystalline hydrazone separated out. Recrystallization from MeOH gave 450 mg (86%) of a white solid: mp 151.5–152.5 °C; IR (Nujol) 3200, 3060, 3020, 1600, 1350, 1170, 1070, 1040, 800, 760, 690 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ (s, 3 H), 0.95 (s, 3 H), 1.6 (s, 3 H), 1.6–2.0 (m, 3 H), 2.3 (s, 3 H), 2.4–2.7 (m, 2 H), 5.0 (s, 1 H), 7.0–7.8 (m, 10 H). MS (70 eV), m/e 396 (0.1, M^+), 288 (5), 212 (16), 197 (11), 169 (46), 155 (14), 133 (31), 124 (20), 108 (52), 91 (100), 77 (26). Anal. $C_{23}H_{28}N_2O_2S$ (396.6). Calcd: C, 69.67; H, 7.12; N, 7.06. Found: C, 69.81; H, 7.20; N, 7.09.

1-Diazo-1-phenyl-2-(2,3,3-trimethylcyclopenten-4-yl)-ethane (15). To a suspension of 305 mg (0.769 mmol) of tosylhydrazone 14 in 2.5 mL of dry diglyme and ca. 23 mg of NaH (80% oil dispersion) was added after 5 min 40 mL of dry petroleum ether (30–50 °C) and the sodium salt collected, dried, and resuspended in 5 mL of dry diglyme. After heating for 30 min at 110 °C the red color ceased to intensify and the reaction mixture was worked up by addition of 10 mL of petroleum ether (30–50 °C) and 10 mL of 2% aqueous NaOH. The organic layer was separated, washed with 2 × 10 mL of 2% aqueous NaOH, and dried over KOH pellets. On removal of the solvent a red oil remained, which was not further purified: IR (film) 3080, 3060, 3030, 2040, 1600, 1500, 1265, 800, 750, 690 cm^{-1}; UV (petroleum ether) λ_{max} 508 nm.

***cis*- and *trans*-1-Phenyl-2-(2,3,3-trimethylcyclopenten-4-yl)ethene (16a,b).** To a mixture of 400 mg (1.01 mmol) of tosylhydrazone 14 in 4.5 mL of *tert*-butyl methyl ether were added while stirring at 0 °C 2.3 mL of a 1.0 M solution of methyllithium within 10 min. After the mixture had stirred for 1 h, 2 mL of water and 2 mL of 5% aqueous NH_4Cl were added, the organic layer was separated, and the aqueous layer was extracted with 2 × 5 mL of ether. The combined organic layers were washed with 1 × 10 mL of saturated aqueous NH_4Cl and 1 × 15 mL of saturated aqueous NaCl and dried and the solvent was removed. By preparative GC on column C at a column temperature of 230 °C and a nitrogen flow of ca. 120 mL/min 510 mg (23%) of cis and 24.0 mg (11%) of trans isomers were collected as colorless oils.

Cis isomer **16b** (t_R 1033 s). IR (film) 3080, 3060, 3030, 3010, 2960, 2930, 2870, 2840, 1600, 1490, 1465, 1450, 1385, 1380, 1365, 1030, 920, 845, 800, 770, 695 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.85 (s, 6 H), 1.65 (br s, 3 H), 2.0–2.3 (m, 2 H), 3.1 (m, 1 H), 5.1 (br s, 1 H), 5.55 (dd, J = 11 Hz, 11 Hz, 1 H), 6.45 (d, J = 11 Hz, 1 H), 7.25 (br s, 5 H); MS (70 eV), m/e 213 (4, $M^+ + 1$), 212 (24, M^+), 197 (15), 169 (23), 155 (15), 121 (22), 108 (100), 91 (57), 77 (12).

Trans isomer **16a** (t_R 1143 s). IR (film) 3070, 3050, 3010, 2940, 2920, 2880, 2850, 2830, 1650, 1600, 1495, 1460, 1450, 1385, 1380, 1365, 970, 800, 750, 695 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.80 (s, 3 H), 1.00 (s, 3 H), 1.65 (br s, 3 H), 2.0–2.4 (m, 2 H), 2.4–2.7 (m, 1 H), 5.25 (br s, 1 H), 6.1–6.5 (m, 2 H), 7.1–7.4 (m, 5 H); MS (70 eV), m/e 213 (4, $M^+ + 1$), 212 (23, M^+), 197 (12), 169 (23),

155 (16), 141 (12), 128 (17), 121 (26), 115 (19), 108 (100), 93 (34), 91 (60), 77 (14).

Vacuum Flash Thermolysis (VFT) of Azoalkane 3. A 10-mL round-bottomed flask was charged with 32.0 mg (0.195 mmol) of azoalkane **3** and heated at ca. 120 °C (18 torr) through a hot 220 × 12 mm Pyrex tube heated externally to ca. 450 °C by means of a Nichrome wire, collecting the pyrolysate in a liquid nitrogen cold trap. Capillary GC showed that the tricycloheptane **5** (t_R 831 s) was formed essentially quantitatively with only traces of vinylcyclopentene **6** (t_R 721 s). The results are summarized in Table I. Both the tricycloheptane **5** and the vinylcyclopentene **6** were stable toward the above VFT conditions.

Direct Photolyses of Azoalkane 3. Into a 150 × 15 mm Pyrex test tube was placed ca. 5 mL of a 0.01–0.1 M solution of the azoalkane **3** in the appropriate solvent (benzene, tetrahydrofuran, etc.); the solution was deaerated by passing a slow stream of pure nitrogen gas for ca. 15 min, sealed, placed into the Rayonet photoreactor, and irradiated at the appropriate temperature, while monitoring the reaction progress by means of capillary GC. The volatile products were tricycloheptane **5** (t_R 823 s), vinylcyclopentene **6** (t_R 782 s), and unreacted azoalkane **3** (t_R 1582 s). The quantitative results for the individual experiments are collected in Table I. By means of preparative GC on column A, operated at injector and column temperatures of 250 and 130–230 °C (programmed at 5 °C/min), respectively, and a nitrogen gas flow of 150 mL/min, samples of tricycloheptane **5** and vinylcyclopentene **6** were collected and shown to be identical with authentic materials.

Direct Photolysis of Azoalkane 3 in the Presence of Acetic Acid. A 180 × 20 mm Pyrex test tube was charged with a 10 mL solution of 0.014 M azoalkane **3** and 0.35 M acetic acid in benzene, deaerated by passing a stream of pure nitrogen gas for 10 min, sealed, and irradiated for 20 min at 70 °C in the Rayonet photoreactor, equipped with 350-nm black phosphor lamps. By means of capillary GC, besides the tricycloheptane **5** and the vinylcyclopentene **6**, the cyclopentenyl acetate **12** (t_R 1749 s) was detected, identical with the authentic material. The quantitative GC results are given in Table I.

Sensitized and Quenched Photolyses of Azoalkane 3. Into a 150 × 15 mm Pyrex test tube were placed ca. 3 mL of a solution of the azoalkane **3** and the sensitizer (benzophenone, triphenylene, etc.) or quencher (cyclohexadiene) at the appropriate concentrations and in the appropriate solvent (pentane, THF, benzene, etc.), deaerated by passing a slow stream of pure nitrogen for 15 min, and the tube was sealed. The tube was placed into the Rayonet photoreactor and irradiated at the appropriate wavelength (254 or 350 nm) at the specified temperature. The reaction progress was monitored by capillary GC and the quantitative results are collected in Table I.

Laser Photolyses of Azoalkanes. A 5-mL aliquot of a ca. 0.1 M solution of azoalkane **3** in benzene was transferred into a 150 × 15 mm Pyrex test tube, degassed by passing a slow stream of pure nitrogen gas for ca. 15 min, sealed, and placed into the beam of the argon ion laser, irradiating with the 334-nm line at room temperature. Immediate yellow coloration of the photolysate ensued, attaining maximum intensity at ca. 8 min. IR and UV analyses of the photolysate confirmed the presence of diazoalkane **8**, exhibiting the characteristic azo bond at 2060 cm^{-1} and visible absorption at 400–500 nm. On prolonged laser irradiation and standing in the dark the yellow coloration disappeared and capillary GC analysis of the colorless photolysate confirmed the presence of the tricycloheptane **5** and the vinylcyclopentene **6**.

The same procedure was employed for the azoalkanes **23–30**. IR and UV monitoring showed that only for the azoalkanes **23–27** some diazoalkane was produced.

Photolysis and Thermolysis of Diazoalkane 8. A 5-mL aliquot of a ca. 0.1 M solution of diazoalkane **8**, as prepared from the *N*-nitrosourea (cf. above), in hexane was placed into the Rayonet photoreactor, equipped with 350-nm black phosphor lamps, and irradiated at room temperature until complete discoloration. Capillary GC analysis of the photolysate showed among other products, mainly the vinylcyclopentene **6** (t_R 782 s) but not even traces of tricycloheptane **5** (t_R 823 s). Similarly, heating of an aliquot of the above solution in a sealed tube at ca. 100–120 °C until complete consumption of the diazoalkane **8** gave a complex product mixture which contained vinylcyclopentene **6** but not tricycloheptane **5**, as confirmed by capillary GC analysis.

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Registry No. **2**, 82934-23-4; **3**, 87143-58-6; **5**, 508-32-7; **6**, 1727-69-1; **8**, 87143-59-7; **9**, 15373-31-6; **10**, 4501-58-0; **12**, 1727-68-0; **13**, 39692-51-8; **14**, 94235-37-7; **15**, 94235-38-8; **16a**, 94235-39-9; **16b**, 94235-40-2; **17**, 2051-45-8; **18**, 94235-32-2; **19**, 94235-33-3; **20**, 94235-34-4; **21**, 94235-36-6; **22**, 94235-35-5; $TsNHNH_2$, 1576-35-8.

Supplementary Material Available: X-ray (Figure 2) and structural data (Tables II and III) of urazole **2** and ^{13}C NMR data of compounds **6**, **9**, **10**, **12**, **13**, **16a,b**–**21** (Table IV) (4 pages). Ordering information is given on any current masthead page.