ments again confirmed less than ~0.01% bicycloalkadiene **1** formation as upper limit. Thus, the triplet-state acetone, which is formed in the thermolysis of TMD, sensitizes the decomposition of azoalkane **5** affording only tricycloalkene **2** via the triplet diradical **4**. This is in complete concordance with the benzophenone-sensitized photolysis of azoalkane **5**.

In Figure 1 we attempt to summarize the thermal, direct, and triplet-sensitized photolytic and the TMD-chemienergized denitrogenation of azoalkane **5** and the direct and triplet-sensitized photolytic di-π-methane reaction of bicycloalkadiene **1** in terms of a composite energy diagram. The key features of this qualitative picture are the interconverting cyclopropyldicarbinyl diradical **3** and the bicyclo[2.2.2]octenediyl diradical **4**, which provide a useful mechanistic interconnection between the di-π-methane process **1** → **2** and the denitrogenation process **5** → **1** + **2**.

Work is in process to acquire the essential activation parameters and photophysical data to place this mechanistic diagram on a quantitative basis. In the accompanying communication we describe a similar study on the di-π-methane rearrangement of benzonorbornadiene, using the corresponding azoalkane as source for the postulated diradicals,

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References and Notes

(1) (a) Hixson, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1973,** *73*, 531. (b) Zimmerman, H. E.; Binkley, R. W.; Givens, R. S.; Sherwin, M. A. *J. Am. Chem. Soc.* **1967,** *89*, 3932.

(2) (a) Hahn, R. C.; Rothman, L. J. *J. Am. Chem. Soc.* **1969,** *91*, 2409. (b) Goldschmidt, Z.; Gutman, U. *Tetrahedron* **1974,** *30*, 3331. (c) Hahn, R. C.; Johnson, R. P. *J. Am. Chem. Soc.* **1977,** *99*, 1508.

(3) (a) Zimmerman, H. E.; Boettcher, R. J.; Buehler, N. E.; Keck, G. E.; Steinmetz, M. G. *J. Am. Chem. Soc.* **1976,** *98*, 7680. (b) Turro, N. J.; Renner, C. A.; Waddell, W. H.; Katz, T. J. *Ibid.* **1976,** *98*, 4320. (c) Turro, N. J.; Cherry, W. R.; Mirbach, M. F.; Mirbach, M. J., *Ibid.* **1977,** *99*, 7388.

(4) (a) Adam, W.; De Lucchi, O.; Erden, I. *Angew. Chem.* **1979,** *91*, 4735. (b) Adam, W.; De Lucchi, O. *Tetrahedron Lett.* **1979,** 4367.

(5) The details for the preparation of azoalkane **5** will be reported separately as part of a general procedure on this novel rearrangement.

(6) (a) Michl, J. *Photochem. Photobiol.* **1977,** *25*, 141. (b) Zimmerman, H. E.; Binkley, R. W.; Givens, R. S.; Grunewald, G. L.; Sherwin, M. A. *J. Am. Chem. Soc.* **1969,** *91*, 3316. (c) Zimmerman, H. E. *Ibid.* **1966,** *88*, 1566.

(7) Adam, W.; Cheng, C.-C.; Cueto, O.; Sakanishi, K.; Zinner, K. *J. Am. Chem. Soc.* **1979,** *101*, 1324.

(8) NIH Career Development Awardee, 1975–1980.

(9) Graduate Research Fellow in the Support for University Biomedical Education (SUBE) Program sponsored by MBS–NIH.

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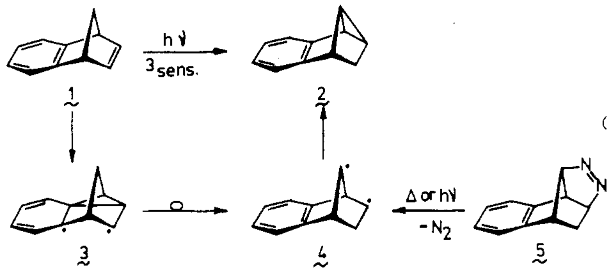
Unusual Thermal and Photochemical Transformations of the Azoalkane 2,3-Diaza-7,8-benzotricyclo[4.3.0.0^{4,9}]nona-2,7-diene

Sir:

The use of cyclic azoalkanes for the thermal and photolytic generation of diradicals is well documented.[1] Recent fascinating examples include the formation of the prismanyl,[2] the norbornadienyl and quadricyclenyl,[3] and the barrelenyl diradicals[4] via denitrogenation of the respective azoalkane precursors. The chemical behavior of these diradicals, some of which have been postulated as reaction intermediates in the general di-π-methane rearrangement of the corresponding hydrocarbons, has provided in-depth understanding of the mechanistic details of this ubiquitous photorearrangement. The preceding communication reports such a study.

An exhaustively studied di-π-methane rearrangement is the triplet-sensitized photocyclization of benzonorbornadiene (**1**) into 2,3-benzotricyclo[2.2.1.0^{5,7}]hept-2-ene (**2**), formed by the collapse of the ultimate diradical **4**, which results from the initial diradical **3** (eq 1).[5,6] For mechanistic conformation, the diradical **4** has so far not been generated by an independent route.



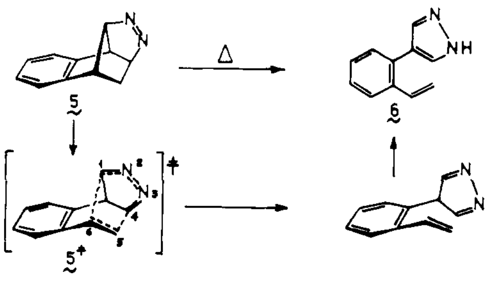
(1)

Recently[7] we succeeded in preparing the tricyclic azoalkane **5**, which on thermal or photochemical extrusion of molecular nitrogen, should provide a convenient entry into the diradical manifold of this di-π-methane rearrangement. Therefore, we have investigated the thermolysis and photolysis of azoalkane **5**, following the modus operandi outlined in the preceding communication, but uncovered some unprecedented chemical behavior of this unusual azoalkane. The highlights of our results are (i) on thermolysis (eq 2) **5** isomerizes quantitatively into 4-(2′-styryl)pyrazole (**6**); (ii) on direct photolysis (eq 1) **5** extrudes N_2 quantitatively, affording mainly the tricycloalkane **2** and some norbornadiene (**1**); (iii) on benzophenone-sensitized photolysis (eq 3) **5** rearranges into 2,3-diaza-7,8-benzotricyclo[4.3.0.0^{2,9}]nona-3,7-diene (**7**).

This unusual thermal and photochemical behavior of azoalkane **5**, especially if contrasted with the more normal comportment of the next higher azoalkane homologue reported in the previous communication, provides a unique opportunity for broadening the scope and understanding of the chemistry of azoalkanes. Below we summarize the experimental evidence and their mechanistic interpretations on this study.

On vacuum flash pyrolysis of the azoalkane **5** by sublimation at 60 °C and 0.2–0.3 Torr through a hot tube maintained at ~400 °C and collection of the affluent in an ice-cooled trap afforded a quantitative yield of the pyrazole **6**, mp 114 °C, $C_{11}H_{10}N_2$ elemental composition by combustion analysis, *m/e* 170. The following spectral data[8] confirm the structural assignment: ^{1}H NMR (CCl_4, Me_4Si) δ (ppm) 5.10–7.15 (3 H, $CHCH_2$, ABC pattern, $J_{AB} = 1.5$, $J_{BC} = 10.06$, $J_{AC} = 16.15$ Hz), 7.65 (2 H, pyrazole, s), 7.1–7.7 (4 H, C_6H_4, m), 10.4 (1 H, N–H, br s); ^{13}C NMR ($CDCl_3$, Me_4Si) δ (ppm) 115.34, 120.80, 126.38, 127.08, 127.81, 129.52, 131.23, 133.56, 136.22; IR (KBr) ν (cm^{-1}) 3150, 3080, 2980, 1480, 1380, 1150, 1040, 1000, 960, 920, 875. On catalytic hydrogenation over Pd/C, 1 mol of H_2 was absorbed, resulting quantitatively in 4-(2′-ethylphenyl)pyrazole, mp 102.5 °C, $C_{11}H_{12}N_2$ elemental composition by combustion analysis; the ^{1}H NMR confirmed the replacement of the vinyl for the ethyl pattern.

We interpret this unexpected thermal behavior of the azoalkane **5** in terms of the retro-Diels–Alder process, followed by tautomerization, as shown in eq 2. Apparently the C_1–C_6



(2)

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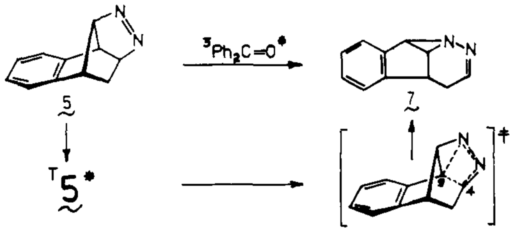
and C_4–C_5 σ bonds are sufficiently weakened compared with the C_1–N_2 and N_3–C_4 σ bonds in this strained azoalkane that the retrocyclic process via $5^{\ddagger}$ is prefered over N_2 extrusion to afford the expected diradical **4** (eq 1). Of course, instead of the concerted process via $5^{\ddagger}$, a stepwise mechanism involving first C_1–C_6 σ bond rupture to yield a diradical is also likely. Whichever the mechanistic course, the thermal behavior of the azoalkane **6** is unusual; however, a few examples have been reported[9] in which azoalkanes transform into pyrazoles instead of expelling molecular nitrogen on heating.

In contrast to the thermolysis, direct photolysis of the azoalkane **5** in $\sim 10^{-4}$ M pentane (Spectroquality) at 254 (quartz vessel) and 350 nm (Pyrex vessel) in a Rayonet reactor gave the expected tricycloalkene **2** (99.0 ± 0.3% at 350 nm and 96.0 ± 0.3% at 254 nm) and the bicycloalkadiene **1** (1.0 ± 0.3% at 350 nm and 4.0 ± 0.3% at 254 nm). Control experiments confirmed that under our photolysis conditions **1** is not transformed into **2**.[10] Consequently, the low yield of **1** suggests that the diradical **4**, formed on photoextrusion of N_2 from the singlet excited azoalkane **5**, efficiently cyclizes into **2** rather than rearranging into diradical **3** to give **1** (eq 1). Apparently, the diradical **4** represents an energy minimum on the singlet excited-state energy surface of the azoalkane.

The most surprising result was observed in the benzophenone-sensitized photolysis of azoalkane **5**, which was carried out in a Rayonet reactor, equipped with 300-nm lamps and employing solutions $\sim 10^{-4}$ M **5** and $\sim 10^{-3}$ M benzophenone in deaerated C_6D_6. Only 300–330-nm light was allowed to irradiate the sample by utilizing an appropriate $K_2Cr_2O_7$/K_2CO_3 aqueous filter.[4] The only product that was detected by ^{1}H NMR was the novel diazavinylcyclopropane derivative **7**, mp 140 °C dec, $C_{11}H_{10}N_2$ elemental composition by combustion analysis, *m/e* 170. The following spectral data[8] confirm the structural assignment: ^{1}H NMR ($CDCl_3$, Me_4Si) δ (ppm) 1.7–1.85 (2 H, H_5, m), 3.3–3.8 (2 H, $H_{1,6}$, m), 3.9 (1 H, H_9, d, $J_{19} = 2.9$ Hz), 6.7–7.2 (4 H, C_6H_4, m), 7.5 (1 H, H_4, m); ^{13}C NMR ($CDCl_3$, Me_4Si) δ (ppm) 27.24, 33.24, 46.96, 51.47, 123.01, 125.84, 127.30, 127.87, 137.27, 147.02, 156.99; IR (KBr) ν (cm^{-1}) 3050, 3030, 3025, 2955, 2921, 1600, 1480, 1460, 1442, 1345, 1330, 1310, 1230, 1200, 1160, 1070, 1005, 935, 920. This substance is thermally labile, leading to a complex product mixture, but the pyrazole **6** is not produced.

This novel photorearrangement of the azoalkane **5** into **7** is mechanistically rationalized in eq 3. Again, the triplet-sensitized behavior of azoalkane **5** is unusual; however, a few examples have been reported[11] in which azoalkanes undergo related rearrangements rather than extruding molecular nitrogen on photolysis. As an analogy from hydrocarbon chemistry, we offer the photochemical conversion of norbornene into norcarene-2.[12] Similar to the mechanism in the hydrocarbon system, instead of the proposed concerted pathway, a suitable diradical mechanism can be envisaged, involving initial C_4–C_9 σ-bond rupture in the triplet excited $^T5^*$.



(3)

Each energization mode of azoalkane **5** has led to distinct products. Such divergent chemical behavior makes the tricyclic azoalkane **5** a unique case and underscores its novelty. Although these disconnected product channels of azoalkane **5** have severely limited the opportunities for elucidating the mechanistic details of the di-π-methane rearrangement of norbornadiene (**1**), the unprecedented observations reported herein provide new challenges for mechanistic investigation and synthetic utilization. For example, in view of the spin-state-specific behavior of azoalkane **5**, we intend to exploit it for single and triplet titration of chemienergized excited states.[10]

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References and Notes

(1) (a) Berson, J. A. *Acc. Chem. Res.* **1978,** *11*, 446. (b) Meier, H.; Zeller, K.-P. *Angew. Chem.* **1977,** *89*, 876. (c) Dürr, H.; Ruge, B. *Top. Curr. Chem.* **1976,** *66*, 53. (d) Engel, P. S.; Steel, C. *Acc. Chem. Res.* **1973,** *6*, 275.
(2) Turro, N. J.; Renner, C. A.; Waddell, W. H.; Katz, T. J. *J. Am. Chem. Soc.* **1976,** *98*, 4322.
(3) Turro, N. J.; Cherry, W. R.; Mirbach, M. F.; Mirbach, M. J. *J. Am. Chem. Soc.* **1977,** *99*, 7388.
(4) Zimmerman, H. E.; Boettcher, R. J.; Buchler, N. E.; Keck, G. E.; Steinmetz, M. G. *J. Am. Chem. Soc.* **1978,** *100*, 7680.
(5) (a) Paquette, L. A.; Yeh Ku, A.; Santiago, C.; Rozeboom, M. D.; Houk, K. N. *J. Am. Chem. Soc.* **1979,** *101*, 5972. (b) Yeh Ku, A.; Paquette, L. A.; Rozeboom, M. D.; Houk, K. N. *Ibid.* **1979,** *101*, 5972. (c) Santiago, C.; McAlduff, E. J.; Houk, K. N.; Snow, R. A.; Paquette, L. A. *Ibid.* **1978,** *100*, 6149. (d) Paquette, L. A.; Cottrell, D. M.; Snow, R. A. *Ibid.*, **1977,** *99*, 3723. (e) Snow, R. A.; Cottrell, D. M.; Paquette, L. A. *Ibid.* **1977,** *99*, 3734.
(6) Hahn, R. C.; Johnson, P. R. *J. Am. Chem. Soc.* **1977,** *99*, 1508.
(7) Adam, W.; De Lucchi, O.; Erden, I. *Angew. Chem.* **1979,** *91*, 512.
(8) A detailed discussion of the NMR spectral data is reserved for a full paper on this subject. We thank Dr. M. Balci for recording and interpreting the ^{13}C NMR spectra and Dr. I. Erden for helping us to get started in this field of research.
(9) (a) Tsuruta, H.; Kurabayashi, K.; Mukai, T. *J. Am. Chem. Soc.*, **1968,** *90*, 7168. (b) Hinshaw, J. C.; Allred, E. L. *Chem. Commun.* **1969,** 72. (c) Paquette, L. A.; Wyvratt, M. J.; Berk, H. C.; Moerck, R. E. *J. Am. Chem. Soc.* **1978,** *100*, 5845.
(10) Adam, W.; Cheng, C.-C., Cueto, O.; Sakanishi, K.; Zinner, K. *J. Am. Chem. Soc.* **1978,** *100*, 1324.
(11) (a) Closs, G. L.; Boll, W. A.; Heyn, H.; Dev, V. *J. Am. Chem. Soc.* **1968,** *90*, 173. (b) Franck-Neumann, M.; Martina, D.; Dietrich-Buchecker, C. *Tetrahedron Lett.* **1975,** 1763. (c) Miyashi, T.; Nishizawa, Y.; Sugiyama, T.; Mukai, T. *J. Am. Chem. Soc.* **1977,** *99*, 6109.
(12) Arnold, D. R.; Abraitys, V. Y. *Mol. Photochem.* **1970,** *2*, 27.
(13) NIH Career Development Awardee, 1975–1980.

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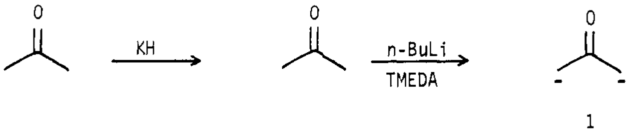
α,α' Dianions of Aliphatic Ketones and the 1,3,5 Trianion of 2,4-Pentanedione: Strongly Nucleophilic Carbonyl Synthons

Sir:

We report here the twofold ionization of unactivated ketones by treatment with strong bases to give highly nucleophilic α,α' dianions. Previous reports of α,α' dianions of unfunctionalized ketones have involved cases in which aromatic rings participated in delocalization of negative charge[1-4] or in which formation of the dianion created an aromatic ring.[5]

Potassioacetone, prepared from the ketone and excess KH (25 °C, 20 min) in ethyl ether,[6] was treated with equivalent amounts of *n*-butyllithium and tetramethylethylenediamine (0 °C, 5 min) to give the dianion salt as a yellow precipitate (Scheme I). Treatment of the dianion **1** with 1 equiv of methyl

Scheme I



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