and reactivity—will therefore be possible only at low temperatures, low substrate concentrations, and high levels of photon flux.

Nevertheless, efficient photoisomerization about the B–N bond of aminoboranes and homologs is clearly important as an effective, though virtually invisible, energy dissipation mechanism. Such "free rotor" effects are known to limit the photoreactivity of 1,4-dienes[11,12] and β,γ-unsaturated ketones.[13,14] Analogous photochemical boron–nitrogen free rotors are evidently partly responsible for the only moderately quantum-efficient boron–carbon cleavage reactions in aminoboranes such as **1**,[1,2] and may also play a role in photoreactions of B–N diene analogs.[3,15]

The parallel between aminoborane photoisomerizations and analogous transformations in olefins, imines, and β,γ-unsaturated ketones, however, is apparently only superficial. Whereas triplet states (mostly $\pi-\pi^*$) are the "free rotors" in most cis–trans photoisomerizations, photoinduced rotation about the boron–nitrogen bond in aminoborane **1** evidently occurs in an excited singlet state.[16] Conversion of **1** to **2** photochemically could not be quenched by piperylene, nor could the conversion be sensitized under a variety of conditions: in chlorobenzene (E_T = 82 kcal/mol) at 2537 Å; in toluene with 0.06 M xanthone (E_T = 74 kcal/mol) at 3500 Å; or in toluene with 0.25 M phenanthrene (E_T = 62 kcal/mol) at 3500 Å.

Photochemical cis–trans isomerization in aminoboranes appears to be general,[1] and additional experiments are in progress to probe in detail the electronic distribution of this apparently anomalous singlet-state[16] "free rotor."

Acknowledgment. Financial support by the Research Corporation and by the Petroleum Research Fund of the American Chemical Society (No. 5860-AC3) is gratefully acknowledged.

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[11] J. S. Swenton, A. R. Crummrine, and T. J. Walker, *J. Amer. Chem. Soc.*, **92**, 1406 (1970).

[12] H. E. Zimmerman and A. C. Pratt, *ibid.*, **92**, 1407, 1409 (1970); H. E. Zimmerman and G. A. Epling, *ibid.*, **92**, 1411 (1970).

[13] K. G. Hancock and R. O. Grider, *Tetrahedron Lett.*, 4281 (1971).

[14] K. G. Hancock and R. O. Grider, *ibid.*, 1367 (1972).

[15] K. G. Hancock and A. K. Uriarte, *J. Amer. Chem. Soc.*, **92**, 6374 (1970).

[16] The excitation could be either electronic or vibronic; the possible intermediacy of a vibrationally "hot" ground state either instead of or subsequent to involvement of the electronically excited singlet state is a detail still under study.

[17] Petroleum Research Fund Predoctoral Fellow, 1971–1973.

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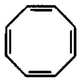
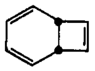
Received March 6, 1972

Pyrolytic Conversion of Bicyclo[4.2.0]octatrienes to Cyclooctatetraenes. The Tetracyclo[3.2.0.0^{2,8}.0^{5,7}]octene Pathway of Thermal Bond Reorganization

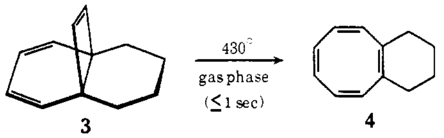
Sir:

Alicyclic molecules endowed with appreciable degrees of unsaturation usually possess the capability for thermal bond reorganization. In fact, pyrolytic interconversions, in tandem with photoisomerizations, have comprised the chief means for elucidation of the interrelationships of many (CH)$_n$ hydrocarbons, particularly those with the empirical formulas (CH)$_{10}$[1,2] and (CH)$_{12}$.[3] However, only scattered reports of thermal rearrangements in the (CH)$_8$ series have appeared.[4–7] Cyclooctatetraene (**1**), for example, affords styrene, benzene, ethylene, acetylene, and under suitable conditions, dihydropentalene at elevated temperatures.[4,6] Although the role played by bicyclo[4.2.0]octatriene (**2**)[8] in the thermal degradations of **1** remains elusive, we have concerned ourselves with the possibility that preformed derivatives of **2** might exhibit previously unrecognized thermal rearrangement by one or more low activation energy pathways which are inaccessible or invisible when starting from **1**.[9]

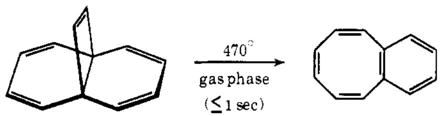

1


2

Gas-phase experiments with the readily accessible unsaturated propellanes **3** and **5**[10] provided immediate indication of skeletal rearrangement. Pyrolysis of **3** at 430° (2.5 mm) in a flow system[11] under nitrogen (contact time ≤1 sec) resulted in >95% conversion to cyclooctatetraene **4**[12] (60% isolated). Similar treatment of **5** gave benzocyclooctatetraene (**6**)[12,13] in 53% isolated yield as the only product. Leaving aside for the moment the question of mechanism, these observations assume particular significance when viewed as the pyrolytic isomerization of a 1,4-disubstituted cyclooctatetraene to the corresponding 1,2 isomer. The actual operation of such a skeletal rearrangement gains



3 **4**



5 **6**

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[1] (a) T. L. Burkoth and E. E. van Tamelen, "Nonbenzenoid Aromatics," Vol. I, Academic Press, New York, N. Y., 1969; (b) L. A. Paquette and J. C. Stowell, *J. Amer. Chem. Soc.*, **93**, 2459 (1971); (c) J. S. McKennis, L. Brenner, J. S. Ward, and R. Pettit, *ibid.*, **93**, 4957 (1971); (d) L. A. Paquette, *ibid.*, **93**, 7110 (1971).

[2] A leading reference to benzo (CH)$_{10}$ chemistry is: L. A. Paquette, M. J. Kukla, and J. C. Stowell, *ibid.*, in press.

[3] L. A. Paquette and J. C. Stowell, *ibid.*, **93**, 5735 (1971), and pertinent references therein.

[4] I. Tanaka, *J. Chem. Soc. Jap., Pure Chem. Soc.*, **75**, 212 (1954); *Chem. Abstr.*, **48**, 4984b (1954).

[5] R. Criegee and R. Askani, *Angew. Chem.*, **80**, 531 (1968); *Angew. Chem., Int. Ed. Engl.*, **7**, 537 (1968).

[6] M. Jones, Jr., and L. O. Schwab, *J. Amer. Chem. Soc.*, **90**, 6549 (1968).

[7] A leading reference is: H. E. Zimmerman and L. R. Sousa, *ibid.*, **94**, 834 (1972).

[8] The equilibrium position of the 1–2 valence tautomer pair has been found to reside substantially in favor of **1** at 100° (only 0.01% of **2**!): R. Huisgen, F. Mietzsch, G. Boche, and H. Seidl, *Chem. Soc., Spec. Publ.*, No. **19**, 3 (1964).

[9] The free-energy difference between **1** and **2** is 6.8 kcal mol.[8]

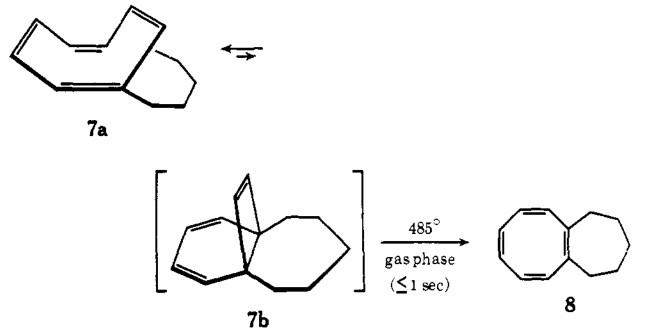
[10] L. A. Paquette, J. C. Philips, and R. E. Wingard, Jr., *J. Amer. Chem. Soc.*, **93**, 4516 (1971).

[11] The apparatus has been described previously.[1b,d,3]

[12] L. A. Paquette, R. E. Wingard, Jr., and R. H. Meisinger, *J. Amer. Chem. Soc.*, **93**, 1047 (1971).

[13] L. Friedman and D. F. Lindow, *ibid.*, **90**, 2329 (1968).

additional credence from the behavior of **7**. In this polyolefin, the pentamethylene "belt" is sufficiently "loose" to permit adoption by the molecule of valence tautomeric form **7a**.[10] No observable concentration of structure **7b** develops over a wide temperature range.[10] In any event, **7** likewise undergoes smooth thermal isomerization to **8**,[12] presumably *via* **7b** which is undoubtedly more energetically accessible to this system than **2** is to **1**.



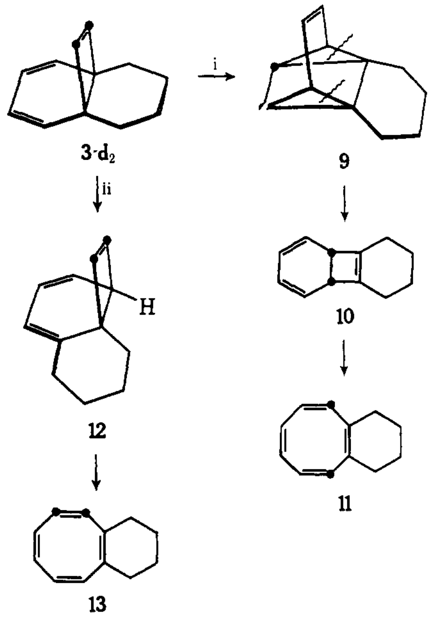
7a

7b

8

Two plausible hypothetical mechanisms for these reactions are: (i) intramolecular ($_\pi4_s + _\pi2_s$) cycloaddition leading to the annelated tetracyclo[3.2.0.0^{2,8}.0^{5,7}]octene, followed by valence isomerization[14] to the observed cyclooctatetraene; or (ii) a process initiated by [1,5]sigmatropic shift of a trigonal cyclobutene carbon atom and completed by disrotatory ring opening of the newly formed bicyclo[4.2.0]octatriene.[15] Scheme I illustrates how pyrolysis of **3**-*11,12-d*$_2$ would permit in principle a distinction between these two alternatives. Pathway i affords product with olefinically bound deuterium at C_3 and C_8 (**11**), whereas the isotopic labeling resulting from mechanism ii is located at C_3 and C_4 (**13**).

Scheme I



3-d$_2$

9

12

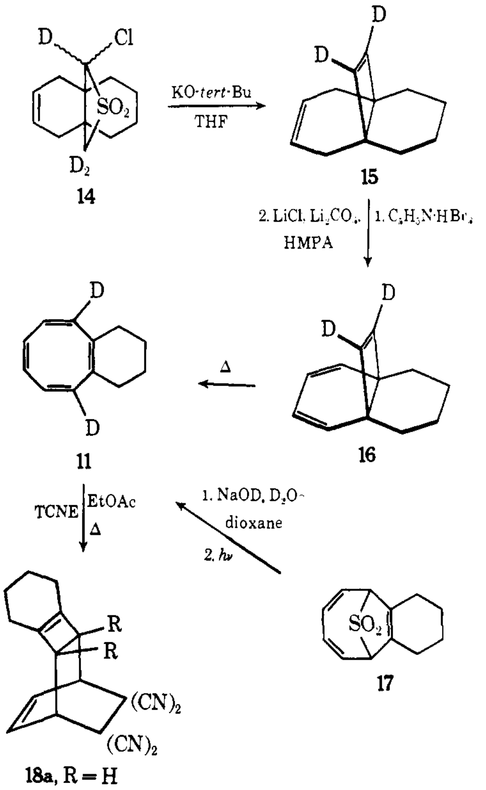
10

11

13

● denotes deuterium

Triene **3**-d_2 was prepared by a modification of our earlier synthesis.[10] α-Chloro sulfone **14**,[16] available from the protio analog by exchange with NaOD in dioxane–D_2O at reflux,[17] underwent ready Ramberg–Bäcklund rearrangement to **15**. Bromination–dehydrobromination of **15** gave **16** (calcd *m/e* 160.1223; found *m/e* 160.1221; 92% d_2) which on pyrolysis as before yielded only **11** (calcd *m/e* 160.1223; found *m/e* 160.1220; 91% d_2).[16] The positions of isotopic substitution in this tetraene were established by independent unequivocal synthesis of **11** from sulfone **17**[12] and by conversion of both **4** and **11** to their respective TCNE adducts (**18**). In **18a**, the three proton pairs of consequence exhibit distinctly different chemical shifts: $\delta_{\text{TMS}}^{\text{CD}_2\text{Cl}_2}$ 6.42 (m, 2, olefinic), 3.65 (m, 2, bridgehead), 3.33 (m, 2, cyclobutyl), and 1.5–1.8 (m, 8, methylene groups). In **18b** (calcd *m/e* 286.1218; found *m/e* 286.1216), the absorptions at δ 3.33 were essentially lacking except for the *ca.* 10% of protium impurity carried through from **14**.



14

15

11

16

17

18a, R = H
b, R = D

These results implicate the exclusive operation of the intramolecular Diels–Alder mechanism (path i). Clearly, the ease of initial conversion to the tetracyclo-

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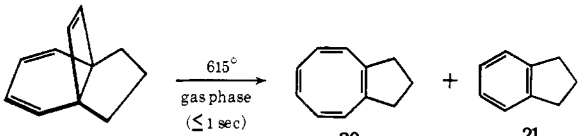
(14) Closely related parallels appear in: (a) ref 12; (b) L. A. Paquette, R. H. Meisinger, and R. E. Wingard, Jr., *ibid.*, **94**, 2155 (1972); (c) H. W. Whitlock, Jr., and P. F. Schatz, *ibid.*, **93**, 3837 (1971), and earlier references cited in these papers.

(15) Competitive Cope rearrangement (involving the cyclobutene double bond) or ($_\sigma2_s + _\pi2_a + _\pi2_a$) bond relocation appears prohibited in these annelated systems because of obvious Bredt's rule difficulties. The possible operation of such alternative pathways in structurally unencumbered analogs should not be discounted at this time.

(16) All deuterium-labeled substances gave nmr spectra fully compatible with the designated structures. Compounds **18a** and **20** which are new had the expected analytical and spectral properties.

(17) L. A. Paquette and J. C. Philips, *Tetrahedron Lett.*, 4645 (1967).

octene intermediate (*e.g.*, **9**) will depend upon the capability of the trigonal cyclobutene carbons to bend in the direction of the neighboring diene unit (or *vice versa*). Molecular models indicate that a trimethylene bridge substantially restricts this requisite motion. Not unexpectedly, therefore, the pyrolysis of **19**[18] required enhanced temperatures and gave only low yields of **20** and **21** in which the fragmentation product **21** predominated by a factor of 2.



19 **20** **21**

This work also raises the intriguing possibility that cyclooctatetraene and certain of its derivatives may be capable of skeletal rearrangement in their own right. We are currently exploring this question.

Acknowledgment. Appreciation is expressed to the National Cancer Institute for partial support of this research. The sample of **19** was kindly supplied by Mr. Ronald K. Russell whom we thank.

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[18] L. A. Paquette, R. E. Wingard, Jr., and R. K. Russell, *J. Amer. Chem. Soc.*, in press.

[19] National Institutes of Health Predoctoral Fellow, 1969–1971.

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Received March 24, 1972

Additions and Corrections

A Study of the Decay Processes in the Triplet Sulfur Dioxide Molecule Excited at 3828.8 Å [*J. Amer. Chem. Soc.*, **93,** 2587 (1971)]. By HOWARD W. SIDEBOTTOM, CHARLES C. BADCOCK, JACK G. CALVERT,* GEORGE W. REINHARDT, BLAINE R. RABE, and EDWARD K. DAMON, Department of Chemistry and the ElectroScience Laboratory, The Ohio State University, Columbus, Ohio 43210.

On page 2588, column 2, line 15, the length of the tube should read 88 cm. Also, on page 2592, column 1, line 8 and in the caption to Figure 6, the pathlength should read 88 cm.

On page 2592, the sentence beginning on line 20 should read: The slopes give: $\epsilon_{SO_2} = 0.11 \pm 0.02$ and $\epsilon_{Ac_2} = 8.3 \pm 0.8$ l./(mol cm) at 3828.8 Å.

An Equilibrium Centrifugation Study of the Self-Association of *N*-Methylacetamide in Carbon Tetrachloride Solutions at 25° [*J. Amer. Chem. Soc.*, **93,** 7075 (1971)]. By ROBERT J. ALBERS, ANNE B. SWANSON, and GORDON C. KRESHECK,* Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115.

The values given in line 5 of the abstract should read 73 g/mol, $2.68 \pm 0.15 \times 10^4$ ml/g, 0.00312 ± 0.00036 mol-ml/g^2, and 0.00970 ± 0.00201 mol-ml^2/g^3, respectively.

In the column headings of Table I, the units of BM_1 should read (g/ml)$^{-1}$ and those of CM_1 should read (g/ml)$^{-2}$.

Photolysis of Ortho-Substituted Aryl Azides in Diethylamine. Formation and Autoxidation of 2-Diethylamino-1*H*-azepine Intermediates [*J. Amer. Chem. Soc.*, **94,** 513 (1972)]. By RICHARD J. SUNDBERG,* STUART R. SUTER, and MARTIN BRENNER, Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901.

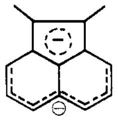
On page 518, column 1, the final sentence is in error. The structure under discussion, 2,7-dimethyl-4*H*-azepin-4-one, was later retracted: E. Bullock, B. Gregory, and A. W. Johnson, *J. Chem. Soc.*, 1632 (1964).

Structure and Reactivity of Organic Ions in Gas-Phase Radiolysis. V. The Structure and Formation Process of the $C_7H_7^+$ Ions from Toluene [*J. Amer. Chem. Soc.*, **94,** 661 (1972)]. By YUKIO YAMAMOTO,* SETSUO TAKAMUKU, and HIROSHI SAKURAI, The Institute of Scientific and Industrial Research, Osaka University, Suita, Osaka, Japan.

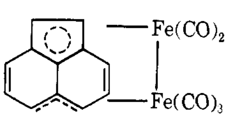
In footnote 13, the feature of the nmr spectrum is incorrect and should be H_{Ph}, τ 2.9~3.1; H_{CH_2}, τ 6.1; and H_{CH_3}, τ 7.8.

Deprotonation of Acenaphthene. The Acenaphthylene Dianion [*J. Amer. Chem. Soc.*, **94,** 985 (1972)]. By L. D. KERSHNER, J. M. GAIDIS, and H. H. FREEDMAN,* The Dow Chemical Company, Eastern Research Laboratory, Wayland, Massachusetts 01778.

Structures Ia and VII should be



IA



VII

Photoisomerization about the Carbon–Nitrogen Double Bond of an Oxime Ether [*J. Amer. Chem. Soc.*, **94,** 1000 (1972)]. By ALBERT PADWA* and FRED ALBRECHT, Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214.

Due to a mathematical error in the determination of the light intensity, the quantum yield reported in the last two lines of page 1000 should be $\Phi = 0.30$ and $\Phi = 0.36$ at 0.036 *M*.

On the Mechanism of Intermolecular Aromatic Substitution by Arylnitrenes [*J. Amer. Chem. Soc.*, **94,**