Table I

No.	[*cis*-I][a]	[Ph_2CO][a]	[Quencher][a] or [Q]	[Quencher]/[*cis*-I]	Statistical[b] Φ/Φ_0	Obsd Φ/Φ_0	Φ/Φ_0(obsd)/ Φ/Φ_0(stat)
1	3.60	5.56					
2	3.80	5.48	3.18[c]	0.84	0.54	0.71	1.3
3	3.77	5.48	4.28[c]	1.14	0.47	0.68	1.4
4	3.66	5.48	8.34[c]	2.28	0.31	0.55	1.8
5	3.89	5.44	14.80[c]	3.81	0.21	0.37	1.8
6	3.56	5.65	2.04[d]	0.57	0.64	0.73	1.1
7	3.53	5.48	3.90[d]	1.11	0.48	0.54	1.1
8	3.46	5.63	7.70[d]	2.23	0.31	0.37	1.2

[a] Concentration $\times 10^{-2}$ *M*. [b] Φ/Φ_0 = [*cis*-I]/[*cis*-I] + [Q]). [c] *cis*-Piperylene. [d] 1,3-Cyclohexadiene.

ketone II was the sole product of reaction, and no evidence for an intermediate was observed. Thus, the two-quantum process (mechanism 2) would seem to be ruled out since the presence of a quencher should result in the increase of intermediate at the expense of product. Therefore the one-quantum mechanism shown below most adequately accounts for all of the above observations.

$$Ph_2CO + h\nu \longrightarrow Ph_2CO^{*3} \quad (1)$$

$$Ph_2CO^{*3} + Q \longrightarrow Ph_2CO + Q^{*3}\ (Q = \text{quencher}) \quad (2)$$

$$Ph_2CO^{*3} + I \longrightarrow I^* + Ph_2CO$$
$$(I^* = \text{excited nonquenchable state of I}) \quad (3)$$

$$I^* + Q \not\longrightarrow \quad (4)$$

$$I^* \longrightarrow I \quad (5)$$

$$I^* \longrightarrow [IV] \longrightarrow II \quad (6)$$

The absence of quenching (reaction 4) implies that the initially formed triplet state of I (E_T = 58.5 kcal/mol) undergoes rapid relaxation to a lower triplet state which cannot be effectively quenched by piperylene or cyclohexadiene. Relaxation of this type is known for the stilbenes.[11]

The detailed pathway by which ketone II is formed from the diradical IV has not been determined. However, it is felt that the reaction probably goes through a short-lived intermediate species. One possible intermediate of this type would be the heterocycle V. A reaction path involving V does not appear to be favorable since it could decompose in a dark reaction to both ketone II (hydrogen transfer followed by loss of sulfur) and oxide VI[13] (loss of sulfur). Oxide VI has been found to be completely inert to both sensitized and direct irradiation and can be readily detected in very small quantities. No oxide has been found in the photoreactions of I.

The sulfine VII could be an intermediate in the reaction of I also. Sulfines are known to thermally decompose to give olefins[14] and photochemically to undergo loss of sulfur to give carbonyl compounds.[15] Assuming its thermal behavior is similar to previously reported examples, VII would not appear to be an intermediate either.

We feel that the most viable intermediate in this reaction is the three-membered-ring heterocycle VIII which may be formed directly from the diradical IV. Loss of sulfur from VIII in a dark reaction would be expected to be facile even at room temperature.

Several other experiments including flash photolysis and direct irradiation of I are being carried out to test these hypotheses. In addition, the scope and utility of this reaction are being investigated with several other sulfoxides.

Acknowledgments. This work was supported by a Frederick Gardner Cottrell grant from the Research Corporation and by the Petroleum Research Fund (Grant No. 756-G).

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Received June 20, 1968

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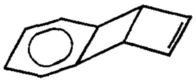
(16) Author to whom inquiries should be addressed.

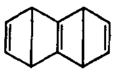
Strained Ring Systems. VII.[1] Benzobicyclo[2.2.0]hexa-2,5-diene (Hemi Dewar Naphthalene)

Sir:

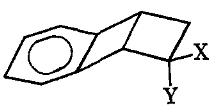
Benzobicyclo[2.2.0]hexa-2,5-diene ("hemi Dewar naphthalene") (**1**) has been of interest to us in that it is a simple entry into a family of compounds which incorporate two of the classically proposed structures of benzene fused in a single molecule.[2] It is half-way to "Dewar naphthalene" (**2**), and offers a convenient route to the synthesis of substituted benzobicyclo[2.2.0]hex-2-enes (**3**) for other studies.



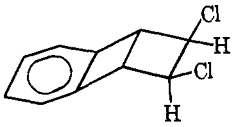
1



2



3



4

Our synthesis of **1** began with the reaction of benzyne and *cis*-3,4-dichlorocyclobutene.[3] The adduct **4**, mp 79–79.5° (sealed tube), is assigned the *cis-exo* structure on the basis of its nmr spectrum[4] which exhibits absorptions centered at τ 2.80 (aromatic, multiplet, J =

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(1) For paper VI in this series see R. N. McDonald and G. E. Davis, *Tetrahedron Letters*, 1449 (1968).

(2) D. E. Applequist and R. Searle, *J. Am. Chem. Soc.*, **86**, 1389 (1964), have reported the synthesis of a "Dewar anthracene." The preparation of "hemi Dewar biphenyl," a compound in which the moieties are joined but not fused, has been described by G. D. Burt and R. Pettit, *Chem. Commun.*, 517 (1965).

(3) M. Avram, I. Dinulescu, M. Elian, M. Farcasiu, E. Marcia, G. Mateescu, and C. D. Nenitzescu, *Ber.*, **97**, 372 (1964).

(4) Carbon tetrachloride solution with internal TMS.

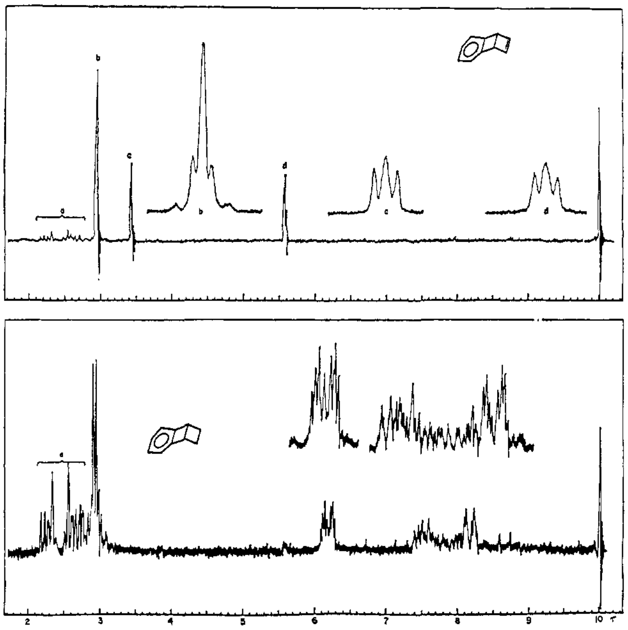

Figure 1. Nmr spectrum[4] (upper) of **1** containing 12% naphthalene (a) with the blow-ups at a sweep width of 50 cps. Nmr spectrum[4] (lower) of benzobicyclo[2.2.0]hex-2-ene (**3**, X = Y = H) containing naphthalene (a) with the blow-ups at a sweep width of 250 cps.

6.5 Hz, 4), 5.55 (bridgehead, multiplet, $J = 0.9$ Hz, 2), and 5.92 (C_5 and C_6, multiplet, $J = 0.9$ Hz, 2). The mass spectrum[5] (70 eV, direct inlet) of **4** showed the expected weak M^+ ions at m/e 198 (0.4),[6] 200 (0.25),[6] and 202 (0.1),[6] the $M^+ - Cl$ ions at m/e 163 (31.5)[6] and 165 (11.5),[6] and the $M^+ - 2Cl$ ion at m/e 128 (100).[6] Treatment of **4** with potassium *t*-butoxide in *t*-butyl alcohol afforded 2-chloronaphthalene in 69% yield.

A number of attempts to reductively dechlorinate **4** to the saturated hydrocarbon **3** (X = Y = H) failed, but did lead to mixtures of tetralin and 1,4-dihydronaphthalene. Several of these reduction products exhibited triplets in the nmr spectrum[4] at τ 3.42 and 5.58, suggesting the presence of **1**.

This was confirmed when **4** was allowed to react with disodium phenanthrene ($C_{14}H_{10}Na_2$) in dimethoxyethane. The product was isolated by trap-to-trap distillation (27% yield), and its nmr spectrum[4] (Figure 1) demonstrated that it consisted of 88% **1** and 12% naphthalene. The half-life of **1** in carbon tetrachloride was determined to be 3.96 hr at 38° (ambient probe temperature of the nmr spectrometer). The ultraviolet absorption spectrum of **1**[7] (in cyclohexane) exhibits absorptions at 257.8 (sh) (log ε 2.75), 263.4 (log ε 2.97), 270 (log ε 3.12), and 276.5 mμ (log ε 2.15) and is very similar to that reported for benzocyclobutene[8] with about a 5-mμ bathochromic shift. It therefore appears that "homoconjugation" does not exist in **1**.

Diimide reductions[9] of samples of **1** (contaminated with naphthalene and **4**) yield products containing **3** (X = Y = H). Attempted glpc separation of these components showed two major components to be present. Collection of these allowed the second component to be identified as naphthalene and the first as 1,2-dihydronaphthalene (**5**), characterized by comparison of its ultraviolet spectrum with that reported.[10] Hydrocarbon **5** undoubtedly arises by thermal ring opening of **3** (X = Y = H) to an *o*-xylylene which tautomerizes to **5**, similar to the glpc thermal rearrangement of bicyclo[2.2.0]hex-2-ene to cyclohexadiene.[11]

Separation of **3** (X = Y = H) from naphthalene can be accomplished on thin and thick layer chromatography with hexane as developer. The fastest moving material is **3** (X = Y = H) which has been characterized by its nmr spectrum[4] (Figure 1) and ultraviolet absorption spectrum (in cyclohexane) exhibiting absorptions at 262 (OD_{max} 0.94), 268 (OD_{max} 1.17), 274 (OD_{max} 1.28), and 285 mμ (OD_{max} 0.89).[12] This latter spectrum is very similar in position of absorptions and shape to those of **1** and benzocyclobutene.[8]

Acknowledgment. The authors are grateful to the National Science Foundation for their support of this research.

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(5) We thank Professor R. W. Kiser, University of Kentucky, for determination of this mass spectrum on an RMU-6E mass spectrometer.

(6) Relative abundance.

(7) The sample used contained about 5% of naphthalene (calculated from its absorption at 310 mμ), and the log ε values are *not* corrected for this impurity.

(8) M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, 80, 2255 (1958), report the spectrum of benzocyclobutene in 95% alcohol.

(9) Catalytic reductions of "Dewar benzenes" have not proven successful with aromatization preceding reduction: R. N. McDonald and G. E. Davis, unpublished results.

(10) R. A. Freidel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley & Sons, Inc., New York, N. Y., 1951, spectrum no. 29.

(11) R. N. McDonald and C. E. Reineke, *J. Org. Chem.*, 32, 1878 (1967).

(12) Extinction coefficients were not determined for this spectrum due to an unknown degree of contamination by naphthalene and binder from the tlc.

(13) Taken from the M.S. Thesis of D. G. Frickey.

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The Relative Fluoride Ion Donor Abilities of XeF_2, XeF_4, and XeF_6 and a Chemical Purification of XeF_4

Sir:

A number of adducts of XeF_6 with strong fluoride ion acceptors have been reported,[1-3] and the crystal structure[4] of the 1:1 adduct with platinum pentafluoride has established it as the salt $XeF_5^+[PtF_6]^-$. Recently, with others,[5,6] we have shown that xenon difluoride is also a fluoride ion donor, since the crystal structure of the 2:1 adduct with AsF_5, together with vibrational spectroscopic evidence, demonstrates that that $2XeF_2 \cdot MF_5$ adducts (M = As, Os, Ir, Pt, Ru) are the salts $Xe_2F_3^+[MF_6]^-$ and the 1:1 adducts are $XeF^+[MF_6]^-$ salts. The 1:2 adducts (M = Ir, Pt, Ru) are the salts $XeF^+[M_2F_{11}]^-$. Although it has been reported[7] that XeF_4 forms an adduct with SbF_5, this has not been properly

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(1) (a) H. Selig, *Science*, **144**, 537 (1964); (b) N. Bartlett, S. Beaton, and N. K. Jha, Abstracts, 148th National Meeting of the American Chemical Society, Chicago, Ill., Aug–Sept 1964, No. K3.

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(4) N. Bartlett, F. Einstein, D. F. Stewart, and J. Trotter, *J. Chem. Soc., A*, 1190 (1967).

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(7) B. Cohen and R. D. Peacock, *J. Inorg. Nucl. Chem.*, **28**, 3056 (1966).