

cycloheptadiene from **1a** by direct reaction with Ag^+ comprises only $\sim 1\%$ of the total reaction in methanol.

The change in product type exhibited by **5** on the one hand and **2**, **3**, and **7** on the other is fully consistent with established carbonium ion behavior and the relative stabilities of cyclopropylcarbanyl and homoallylic cations substituted to various degrees with alkyl groups.⁹ In addition, the foregoing results demonstrate that effective complexation of Ag^+ with methanol appreciably reduces its capability to promote skeletal isomerization.¹⁰ However, methanol and presumably other hydroxylic media appear unique in providing suitable conditions under which bicyclobutanes can react (at seemingly different rates depending upon substitution) with silver salts to form acid. Unlike the situation which perhaps prevails with rhodium(I) catalysts under certain conditions,¹¹ this acid is not introduced inadvertently on the catalyst or in the solvent, but arises from a chemical reaction of Ag^+ with methanol and the strained hydrocarbon. The mechanism of this uncommon process has not yet been established and remains currently an outstanding important question.

We caution, therefore, that the formation of cyclopropylcarbanyl ethers **2**, **3**, and **7** need not be the result of interception of intermediate silver cyclopropyl cations of type **10**.^{3,4,11,12} The present data suggest that direct proton-mediated opening of the bicyclobutane constitutes a real possibility.

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(9) For a leading reference, consult C. D. Poulter and S. Winstein, *J. Amer. Chem. Soc.*, **94**, 2297 (1972).

(10) A kinetic study of solvent effects on Ag^+ -catalyzed isomerization reactions of bicyclobutanes may be found in L. A. Paquette, S. E. Wilson, and R. P. Henzel, *ibid.*, **94**, 7771 (1972).

(11) W. G. Dauben and A. J. Kielbania, Jr., *ibid.*, **94**, 3669 (1972).

(12) The intermediacy of such cations in nonprotic solvents now appears well established with certain bicyclobutanes: ref 10; L. A. Paquette, R. P. Henzel, and S. E. Wilson, *J. Amer. Chem. Soc.*, **94**, 7780 (1972); relevant references cited in these papers.

(13) National Institutes of Health Postdoctoral Fellow, 1970–1971; National Science Foundation Postdoctoral Fellow, 1971–1972.

(14) National Institutes of Health Postdoctoral Fellow, 1972–1973.

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Degenerate Rearrangement and Isomerization of Disubstituted Cyclooctatetraenes under Conditions of Thermal Activation¹

Sir:

Of the $(\text{CH})_{10}$ hydrocarbons so far studied, six are presently recognized to exhibit a remarkable capability for degenerate bond reorganization at somewhat elevated temperatures.² In contrast, no substance of molecular formula $(\text{CH})_8$ has yet been reported capable of undergoing interchange of its constituent atoms and

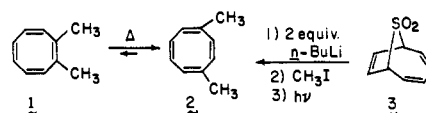
(1) This research was supported in part by the National Science Foundation (Grant No. GP-35344).

(2) For a current listing, see L. A. Paquette, M. J. Kukla, and J. C. Stowell, *J. Amer. Chem. Soc.*, **94**, 4920 (1972), footnote 3.

bonds with regeneration of the same gross structure.^{3,4} We now provide evidence which reveals that disubstituted cyclooctatetraenes can, in fact, partake of this same fascinating propensity for structural self-interconversion.

The thermal chemistry of cyclooctatetraene had its origins nearly 20 years ago when its fragmentation to styrene, benzene, ethylene, and acetylene was reported.⁵ More recently, pyrolytic rearrangement of the parent hydrocarbon to dihydropentalene⁶ and of the 1,3,5,7-tetramethyl⁷ and octamethyl derivatives⁸ to the corresponding semibullvalenes has been achieved. The latter reactions have been postulated to occur *via* bicyclo[3.3.0]octadienediyls,⁹ intermediate species apparently involved also in the thermal isomerization of 5,6- to 5,11-disubstituted dibenzocyclooctatetraenes.¹⁰ In the present study, this pathway has been found *not* to be of mechanistic significance.

To permit detection of the rearrangements, recourse was made to alkyl substitution. Thus, when **1**^{11,12} was pyrolyzed in a flow system at 405–590° under nitrogen at 20–30 mm (contact time ~ 1 sec) and the resulting mixture of cyclooctatetraenes analyzed by vpc, ir, and nmr methods,¹³ conversion to the 1,4-isomer **2** in proportion to the oven temperature was evidenced (Table I). Authentic **2** was prepared by dimethylation of **3**¹⁴



and subsequent photoinduced sulfur dioxide extrusion.^{15,16} Aromatic products were also formed in amounts paralleling the input of heat to the system. In a typical run involving **1** at 600°, for example, benzene (1.3%), toluene (96.2%), *p*-xylene (1.1%), and *o*-xylene (1.3%), but no *m*-xylene, were found in the volatile fraction.

Conditions analogous to those used above reconvert

(3) This field has been exhaustively reviewed by L. T. Scott and M. Jones, Jr., *Chem. Rev.*, **72**, 181 (1972).

(4) The Cope rearrangement of a tetrabromotetramethyltricyclo[4.2.0.0^{2,6}]octa-3,7-diene is, at least formally, an exception to this statement [R. Criegee and R. Huber, *Chem. Ber.*, **103**, 1855 (1970)].

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

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

(7) H. E. Zimmerman and H. Iwamura, *ibid.*, **92**, 2015 (1970).

(8) R. Criegee and R. Askani, *Angew. Chem., Int. Ed. Engl.*, **7**, 537 (1968).

(9) Such intermediates have also been invoked in the thermal rearrangement of tricyclo[3.3.0.0^{2,6}]octa-3,7-diene to semibullvalene: J. Meinwald, D. Schmidt, and H. Tsuruta, *J. Amer. Chem. Soc.*, **91**, 5877 (1969); H. E. Zimmerman, J. D. Robbins, and J. Schantl, *ibid.*, **91**, 5878 (1969). See also W. T. Borden and A. Gold, *ibid.*, **93**, 3830 (1971).

(10) M. Stiles and U. Burckhardt, *ibid.*, **86**, 3396 (1964); M. Stiles, 19th National Organic Chemistry Symposium, Tempe, Ariz., June 1965, p 62.

(11) A. C. Cope and H. C. Campbell, *J. Amer. Chem. Soc.*, **73**, 3536 (1951).

(12) Full details of an improved synthesis of this hydrocarbon will appear elsewhere.

(13) Dimethyl derivatives **1** and **2** were separated on a 24 ft \times $\frac{1}{8}$ in. Hi-Pac column at 60° and could easily be distinguished by the chemical shifts of their methyl signals (δ 1.68 and 1.82 for **1**; δ 1.75 for **2**). Their solution infrared spectra differ significantly in the fingerprint region.

(14) Obtained by *m*-chloroperbenzoic acid oxidation of the related sulfoxide [A. G. Anastassiou and Y.-H. Chao, *Chem. Commun.*, 979 (1971)]. See also J. Gasteiger and R. Huisgen, *J. Amer. Chem. Soc.*, **94**, 6541 (1972).

(15) L. A. Paquette, R. E. Wingard, Jr., and R. H. Meisinger, *ibid.*, **93**, 1047 (1971).

(16) W. E. Konz, W. Hechtel, and R. Huisgen [*ibid.*, **92**, 4104 (1970)] have prepared **2** by yet another route.

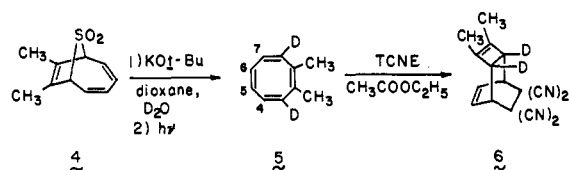
Table I. Product Composition Data from the Pyrolysis of **1** and **2**^a

Hydrocarbon	Temp, °C	Recovery, % ^b	Hydrogen content	
			1, %	2, %
1	405	67	99.9	0.1
	450	46	94	6
	500	25	71	29
	545	20	44	56
	590	7	12	88
2	500	38	1.5	98.5
	560	19	15.5	84.5
	585	10	16	84

^a Percentage compositions determined by manual integration of the methyl absorptions on expanded scale 100-MHz nmr spectra. ^b Values related to cyclooctatetraenes isolated upon vpc purification and do not include aromatic products.

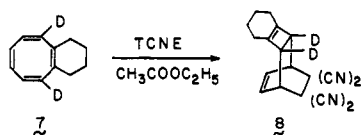
2 to **1** (Table I), but since **2** dominates this equilibrium, the quantitative aspects of this isomerization are less dramatic. In this case, the composition of the aromatic fraction produced at 600° was 2.6% benzene, 70.5% toluene, 21.6% *p*-xylene, and 5.4% *o*-xylene. These differences reflect expectedly the nonequivalent rates attending retro [2 + 2] cleavage of the various possible valence isomeric bicyclo[4.2.0]octatrienes derivable from **1** and **2**.

Experiments with isotopically labeled **5**, readily available from deuterium exchange and photolysis of **4**,¹⁵ were designed to assess the possible operation in **1** of degenerate skeletal rearrangement previously masked during its interconversion with **2**. Pyrolyses at 395° for short contact times did not result in scrambling of the isotope to other ring positions. At 510°, however, the recovered 1,2-dimethylcyclooctatetraene-*d*₂ gave a TCNE adduct (cf. **6**) in which 13% of the available



deuterium had migrated from its original C₃,C₈ position in **5** to C₄,C₇ as determined by quantitative integration of nmr spectra.^{17,18} No measurable change in protium content at C₃,C₆ could be detected.

Since the pyrolysis of annelated cyclooctatetraene **7**¹⁹ does not result in the formation of structural iso-



mers, this hydrocarbon serves as a more convenient substrate with which to examine such degenerate rearrangements. Gas-phase experiments with **7** (89% isotopically labeled) again provided immediate indication of nondestructive skeletal isomerization (Table II).¹⁸ Because higher temperatures were now utiliz-

(17) The well-separated chemical shifts of the several pairs of protons in unlabeled **6** lend themselves nicely to this purpose: $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 1.55 (s, 6), 3.08 (m, 2), 3.95 (m, 2), and 6.47 (m, 2).

(18) Mass spectral analysis of these substances indicated that no measurable loss of deuterium had occurred during the pyrolyses.

(19) L. A. Paquette and R. E. Wingard, Jr., *J. Amer. Chem. Soc.*, **94**, 4398 (1972).

Table II. Hydrogen Distribution in **8** Prepared from Samples of **7** Pyrolyzed at Various Temperatures^a

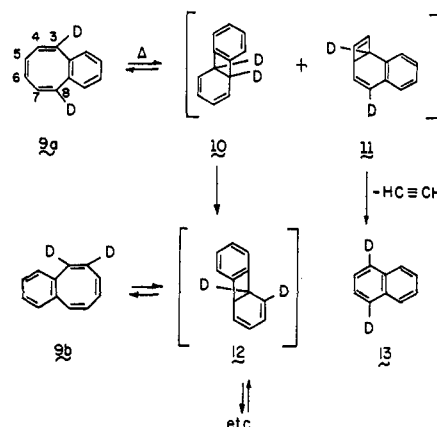
Temp, °C	Hydrogen content		
	Cyclobutene ring	Bridgehead	Olefinic
Before pyrolysis	0.21	1.99	2.00
545	0.31	1.85	2.03
575	0.70	1.70	1.80
610	0.94	1.66	1.60

^a Determined by careful integration of 100-MHz nmr spectra. The nmr spectrum of unlabeled **8** has been reported (ref 19).

able, the stepwise shift of deuterium first to C₄,C₇ and then to C₅,C₆ was made evident.

In terms of mechanistic detail, two possibilities suggest themselves. One involves intramolecular ($\pi 2_s + \pi 4_s$) bonding of isomeric bicyclo[4.2.0]octatrienes and results in the formation of tetracyclo[4.2.0.0^{2,8}.0^{5,7}]octene intermediates. The other requires [1,5]-sigmatropic rearrangement in these same bicyclics of a trigonal-cyclobutene carbon atom, followed by disrotatory ring opening of the newly formed triene.²⁰ The latter option has recently been shown not to be exercised by preformed bicyclo[4.2.0]octatriene derivatives,¹⁹ but the feasibility of its operation in nonconstrained systems is attested to by the degenerate behavior of benzocyclooctatetraene.

Thus, suitably labeled benzocyclooctatetraene **9a** of



quite acceptable isotopic purity was prepared according to the method of Barton, *et al.*,²¹ by taking advantage of the reported photobromination of biphenylene to give 3,8-dibromobenzocyclooctatetraene,²² halogen-metal interconversion, and deuteration. Owing to the well-separated chemical shifts of the olefinic protons in the parent hydrocarbon²³ direct quantitative integration of nmr spectra without recourse to the preparation of adducts was possible in this case. As revealed in Table III, gas-phase pyrolysis of **9a** at temperatures in excess of 565° results in the influx of deuterium first to C_{4,7} and subsequently to C_{5,6}. Loss of acetylene and formation of 1,4-dideuterionaphthalene (**13**) complete

(20) In this connection, [$\pi 2_s + \pi 2_a + \pi 2_a$] bond relocation involving the cyclobutene π bond of possible bicyclo[4.2.0]octatriene intermediates does not satisfactorily account for the distinctive degenerate isomerizations and must be considered a less than adequate mechanistic alternative.

(21) J. W. Barton, T. A. Chandri, P. Gaskin, and K. E. Whitaker, *J. Chem. Soc., Perkin Trans. 1*, 717 (1972).

(22) J. W. Barton and K. E. Whitaker, *J. Chem. Soc. C*, 1663 (1968).

(23) H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *J. Amer. Chem. Soc.*, **90**, 6096 (1968).

Table III. Hydrogen Distribution in Benzocyclooctatetraene Arising from Pyrolysis of 9a

Temp, °C	Hydrogen content			Recovery, %	
	H _{3,8}	H _{1,7}	H _{5,6}	%	13, %
Before pyrolysis	0.13	2.00	2.00		
565	0.13	2.00	2.00	46	
625	0.29	1.85	2.00	22	4 ^a
675	0.67	1.57	1.88	5	10 ^a

^a Uncharacterized higher boiling materials are also obtained (5–20%).

with the degenerate rearrangement. In an effort to bypass transient destruction of aromatic character in the benzenoid ring, [1,5]-sigmatropic migration (10 → 12 → etc.) is advanced as the likely mechanism.

Remaining unanswered by this work is the precise pathway followed by 1, 2, 5, and 7 and whether the disubstituted nature of the C₈ ring in these polyolefins facilitates positional isomerization. These points are currently receiving attention.

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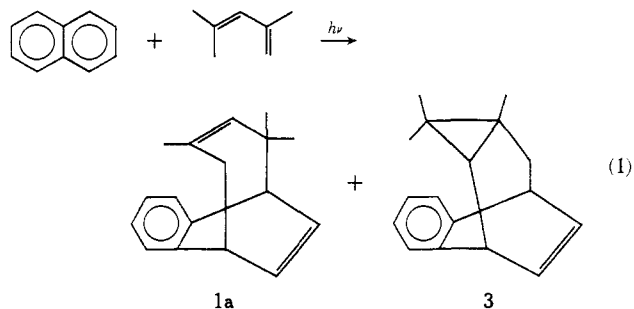
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Photochemical Additions of Acyclic 1,3-Dienes to Naphthalene

Sir:

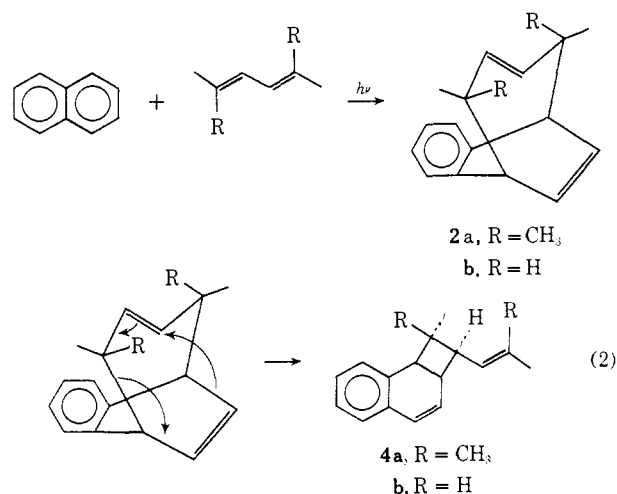
Recent contributions by Hammond,¹ Taylor,² and Evans³ provided spectroscopic and kinetic evidence that exciplexes are the intermediates in the quenching of fluorescence of naphthalene by 1,3-dienes. The major pathway of decay of these exciplexes has been suggested to be the nonradiative decay to their components in the ground state, although the possibility of product formation has not been excluded.^{1,4} In this communication, we wish to report that naphthalene undergoes highly efficient $\pi_4s + \pi_4s$ photocycloadditions with several 1,3-dienes demonstrating that chemical product formation may be a significant pathway for the decay of these exciplexes. The major product in these reactions may be either a 3-*cis*- or a 3-*trans*-9,10-benzobicyclo[4.2.2]deca-3,7,9-triene (1 or 2) depending on the ground-state conformation of the diene. Aromatic hydrocarbons undergo a novel 1,3 photocycloaddition with 2,4-dimethyl-1,3-pentadiene to give a tricyclicodecadiene (3) as the minor product.

Irradiation of naphthalene and 2,4-dimethyl-1,3-pentadiene in benzene with a Hanovia 450-W Hg arc through a Corex filter yielded a mixture of 1a and 3 in a 7:1 ratio as indicated by the nmr of the reaction mixture (eq 1). Compound 1a was isolated in 60% yield by chromatography: mp 60.5–61.5°; uv max (cyclo-



hexane) 270 (ϵ 370) and 262 nm (ϵ 360); ir (KBr) 753 cm^{-1} ; nmr (CCl_4) δ 1.03 (s, 3, CH_3), 1.17 (s, 3, CH_3), 1.53 (s, 3, $\text{C}=\text{CCH}_3$), 2.58 (m, 2, CH_2), 3.10 (m, 1, ArCH), 3.43 (m, 1, ArCH), 4.55 (s, 1, $\text{C}=\text{CH}$), 6.22 (m, 2, $\text{CH}=\text{CH}$), and 7.04 ppm (s, 4, ArH).⁵ Compound 3 was isolated in 11% yield as an oil: uv max (cyclohexane) 270 (ϵ 500) and 262 nm (ϵ 500); ir (neat) 760, 732, and 690 cm^{-1} ; nmr (CCl_4) δ -0.06 (s, 3, CH_3), 0.53 (d, 1, cyclopropyl H), 0.94 (s, 3, CH_3), 1.00 (s, 3, CH_3), 1.63 (m, 2, CH_2), 3.42 (m, 1, ArCH), 3.78 (3 d, 1, $J = 1.0$ and 6.0 Hz, ArCH), 6.20 (4 d, 1, $J = 1.0, 6.0,$ and 8.5 Hz, $\text{C}=\text{CH}$), 6.67 (4 d, 1, $J = 1.0, 6.0,$ and 8.5 Hz, $\text{C}=\text{CH}$), and 6.97 ppm (s, 4, ArH). The quantum yield for the consumption of naphthalene at 313 nm in the presence of 1 M 2,4-dimethyl-1,3-pentadiene was found to be 0.95 ± 0.05 . Analogous reactions occurred between anthracene and the diene to give the corresponding bicyclic and tricyclic derivatives. The photochemical 1,3 addition of a 1,3-diene to an aromatic hydrocarbon with simultaneous formation of a cyclopropane ring to give 3 and related compounds which is an allowed process according to the conservation of orbital symmetry has no precedent in the chemical literature.

Irradiation of a solution of naphthalene and 2,5-dimethyl-2,4-hexadiene in benzene-toluene (2:1) at -5° (eq 2) yielded mainly one adduct (2a, R = CH_3) as



demonstrated by the nmr at -5° : nmr (CCl_4) δ 0.37, 1.07, 1.22, 1.34 (s, 3 each, CH_3), 2.68 (m, 2, ArCH), 4.98 (d, 1, $J = 18$ Hz, *trans*- $\text{CH}=\text{CH}$), 6.06 (d, 1, $J = 18$ Hz, *trans*- $\text{CH}=\text{CH}$), 6.23 (m, 2, $\text{CH}=\text{CH}$), and 6.95 ppm (m, 4, ArH). Compound 2a has not been isolated

(5) Satisfactory elemental analyses have been obtained for all new compounds except 2.

(6) L. M. Jackman and S. Sternhell, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1969, p 301.

(1) D. A. Labianca, G. N. Taylor, and G. S. Hammond, *J. Amer. Chem. Soc.*, **94**, 3679 (1972); G. N. Taylor and G. S. Hammond, *ibid.*, **94**, 3684, 3687 (1972).

(2) G. N. Taylor, *Chem. Phys. Lett.*, **10**, 355 (1971).

(3) T. R. Evans, *J. Amer. Chem. Soc.*, **93**, 2081 (1971).

(4) L. M. Stephenson and G. S. Hammond, *Pure Appl. Chem.*, **16**, 125 (1968); *Angew. Chem., Int. Ed. Engl.*, **8**, 261 (1969); L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 3665, 3893 (1966).