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

Temp, °C	Hydrogen content $H_{3,8}$	Hydrogen content $H_{4,7}$	Hydrogen content $H_{5,6}$	Recovery, %	**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 C_8 ring in these polyolefins facilitates positional isomerization. These points are currently receiving attention.

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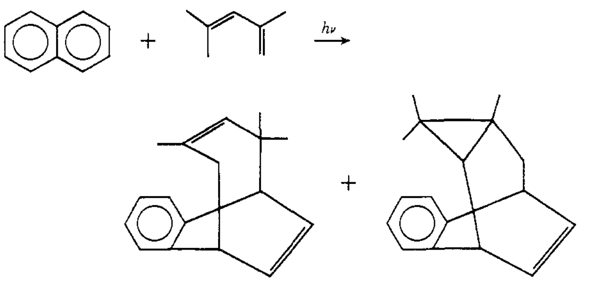
Photochemical Additions of Acyclic 1,3-Dienes to Naphthalene

Sir:

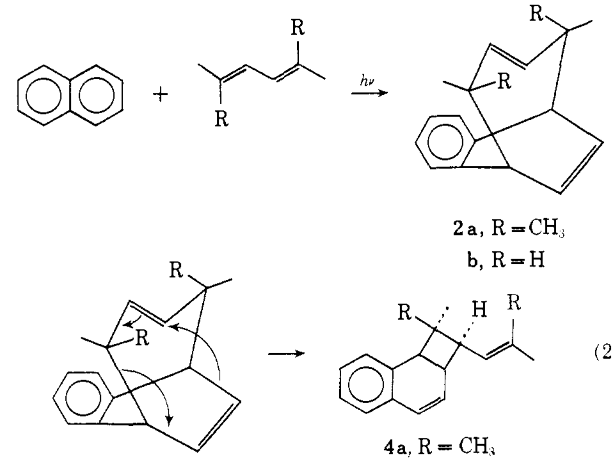
Recent contributions by Hammond,[1] Taylor,[2] and Evans[3] provided spectroscopic and kinetic evidence that exciplexes are the intermediates in the quenching of fluorescence of naphthalene by 1,3-dienes. The major pathway of decay of these exciplexes has been suggested to be the nonradiative decay to 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 ${}_{\pi}4_s + {}_{\pi}4_s$ 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 tricyclodecadiene (**3**) as the minor product.



1a 3

(1)

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 (cyclohexane) 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, $C{=}CCH_3$), 2.58 (m, 2, CH_2), 3.10 (m, 1, ArC*H*), 3.43 (m, 1, ArC*H*), 4.55 (s, 1, C=C*H*), 6.22 (m, 2, C*H*=C*H*), and 7.04 ppm (s, 4, Ar*H*).[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, ArC*H*), 3.78 (3 d, 1, J = 1.0 and 6.0 Hz, ArC*H*), 6.20 (4 d, 1, J = 1.0, 6.0, and 8.5 Hz, C=C*H*), 6.67 (4 d, 1, J = 1.0, 6.0, and 8.5 Hz, C=C*H*), and 6.97 ppm (s, 4, Ar*H*). 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.



2a, R = CH_3
b, R = H

4a, R = CH_3
b, R = H

(2)

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, ArC*H*), 4.98 d, 1, J = 18 Hz, *trans*-CH=CH),[6] 6.06 (d, 1, J = 18 Hz, *trans*-CH=CH), 6.23 (m, 2, CH=CH), and 6.95 ppm (m, 4, Ar*H*). Compound **2a** has not been isolated

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(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).

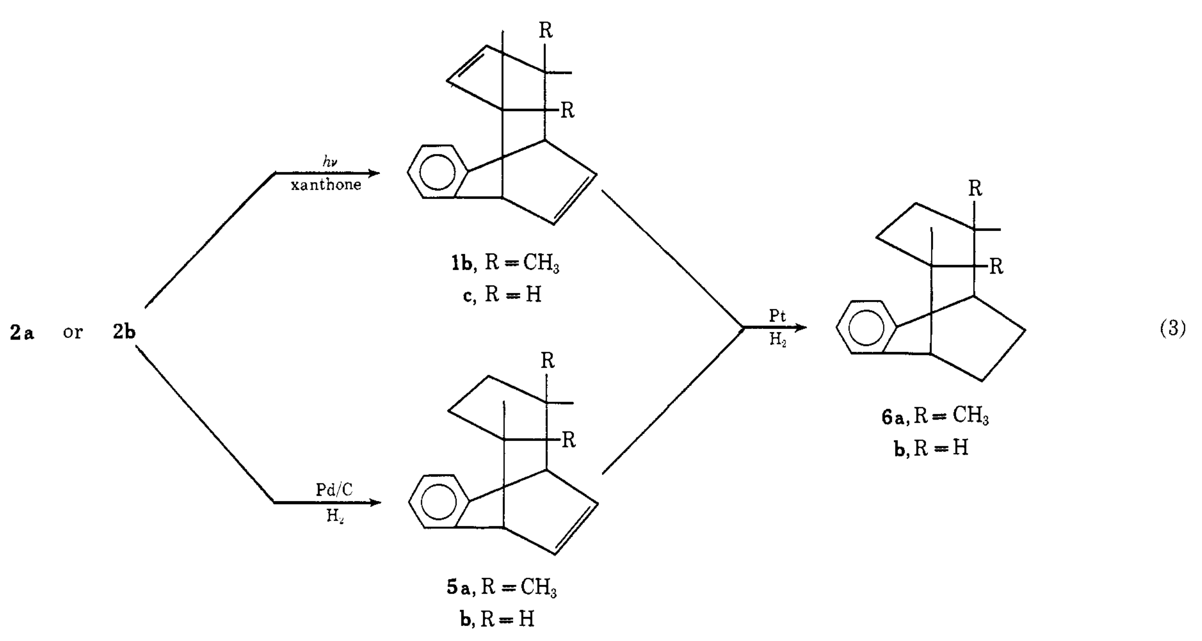
(2) G. N. Taylor, *Chem. Phys. Lett.*, **10**, 355 (1971).

(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).

(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.



(3)

in pure form. It rearranges quantitatively to **4a** within 15 min at 35° *via* a [3,3]-sigmatropic shift. Compound **4a**, which may be isolated directly from the irradiation at 22° in 75% yield, exhibits: mp 50–51°; uv max (cyclohexane) 275 nm (ε 7070); ir (KBr) 1650, 800, and 750 cm^{-1}; nmr (CCl_4) δ 0.78 (s, 3, CH_3), 1.14 (s, 3, CH_3), 1.62 (d, 3, J = 1.0 Hz, $C{=}CCH_3$), 1.75 (d, 3, J = 1.0 Hz, $C{=}CCH_3$), 3.33 (m, 3, CH), 5.45 (m, 1, $CH{=}CR_2$), 5.75 (2 m, 1, J = 10 Hz, $ArCH{=}CH$), 6.26 (d, 1, J = 10 Hz, $ArCH{=}CH$), and 6.90 ppm (m, 4, ArH). The quantum yield for the consumption of naphthalene at 313 nm and 22° in the presence of 1 M 2,5-dimethyl-2,4-hexadiene is 0.42 ± 0.02. Conclusive proof for the formation of **2a** as the primary photoproduct has been obtained (1) by the photosensitized conversion of **2a** *in situ* to its cis isomer **1b** [mp 63–64°; uv max (cyclohexane) 269 (ε 290) and 261 nm (ε 300); ir (KBr) 790 and 758 cm^{-1}; nmr (CCl_4) δ 1.09 and 1.18 (s, 6 each, CH_3), 3.08 (A_2B_2 sextet, 2, $ArCH$),[7] 4.35 (s, 2, $CH{=}CH$), 6.16 (A_2B_2 sextet, 2, $CH{=}CH$) and 6.93 ppm (s, 4, ArH)] and (2) by partial hydrogenation of **2a** *in situ* with Pd/C to the dihydro derivative **5a** [mp 62.5–63.5°; ir (KBr) 760 cm^{-1}; uv max (cyclohexane) 270 (ε 270) and 262 nm (ε 280); nmr (CCl_4) δ 0.72–1.15 (m, 4, CH_2), 0.92 (s, 6, CH_3), 1.08 (s, 6, CH_3), 2.96 (A_2B_2 sextet, 2, $ArCH$), 6.08 (A_2B_2 sextet, 2, $CH{=}CH$), and 6.91 ppm (s, 4, ArH)]. Both **1b** and **5a** may be further hydrogenated with Adams catalyst to the tetrahydro derivative **6a** (eq 3). Naphthalene reacted photochemically with *trans,trans*-2,4-hexadiene to give **2b** (R = H) as the major product: nmr (CCl_4) δ 1.12 and 1.22 (d, 3 each, J = 7 Hz, $CHCH_3$), 2.00 (m, 2, CH), 2.90 (m, 1, $ArCH$), 3.20 (m, 1, $ArCH$), 4.87 and 5.96 (2 d, 1 each, J = 9 and 18 Hz, *trans*-$CH{=}CH$), 6.21 (m, 2, $CH{=}CH$), and 7.00 ppm (m, 4, ArH). Compound **2b** underwent a similar series of transformations to give **4b**, **1c**, **5b**, and **6b**. Its rearrangement to **4b** was, however, insignificant at 22°, but occurred smoothly at 80°.

The formation of primary photoproducts **1–2** may be rationalized as ${}_{\pi}4_{s} + {}_{\pi}4_{s}$ photocycloaddition between excited naphthalene and 1,3-dienes.[8] The preference of such additions over the corresponding ${}_{\pi}2_{s} + {}_{\pi}2_{s}$ additions which would lead to the formation of **4** as the primary products may be attributed to the more extensive overlap between the π systems of reacting components at the transition state of ${}_{\pi}4_{s} + {}_{\pi}4_{s}$ additions.[9] The importance of overlapping between reactants is also reflected in the stereoselective formation of **3** as the only 1,3-addition product. The major adduct in these reactions may be either a 3-*cis*- or a 3-*trans*-benzobicyclodecatriene (**1** or **2**) depending upon the ground-state conformation of 1,3-dienes. Dienes such as 2,5-dimethyl-2,4-hexadiene (λ_{max} 244 nm (ε 24,000))[10] and *trans,trans*-2,4-hexadiene (λ_{max} 226.5 nm (ε 24,000))[10] which exist mainly in the s-transoid conformation give the trans adducts **2**, while 2,4-dimethyl-1,3-pentadiene (λ_{max} 230 nm (ε 9900)),[10] which exists mainly in the s-cisoid conformation,[11] gives the cis adduct **1a**. Since exciplexes are likely to be the precursors of these photoproducts, our results imply that one of the main factors determining the configuration of exciplexes is the ground-state conformation of the 1,3-diene. Although the quantum yields of adduct formation are excellent in some dienes, they do vary substantially with different dienes studied.[12] The detailed mechanism and structural dependence of these reactions are being investigated.

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[7] K. Tori, Y. Takano, and K. Kitahonoki, *Chem. Ber.*, **97**, 2798 (1964); J. A. Pople, W. G. Schneider, and J. H. Bernstein, *Can. J. Chem.*, **35**, 1060 (1957).

[8] R. G. Woodward and R. Hoffmann, "Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1971.

[9] L. Salem, *J. Amer. Chem. Soc.*, **90**, 543, 553 (1968).

[10] W. F. Forbes, R. Shilton, and A. Balasubramanian, *J. Org. Chem.*, **29**, 3527 (1964).

[11] R. S. Mulliken, *J. Chem. Phys.*, **7**, 121 (1939); *Rev. Mod. Phys.*, **14**, 265 (1942).

[12] M. F. Savitzky and J. Libman, unpublished results.

[13] National Science Foundation Undergraduate Research Participant, 1972.