the blue color changed to yellow. The yellow solid that remained after solvent removal was recrystallized from chloroform–acetone to give 300 mg (67%) of the bis-TCNE adduct **16**: mp 160 °C dec; ^{1}H NMR (250 MHz, acetone-d_6) δ 7.79 (s, 2 H), 6.62 (d, J = 1.9 Hz, 2 H), 6.30 (d, J = 1.9 Hz, 2 H); ^{13}C NMR (20 MHz, acetone-d_6) δ 151.09, 144.90, 133.95, 121.38, 120.30, 120.11, 73.17, 71.20, 61.94, 61.80; IR (KBr) 3010 (m), 2940 (w), 2260 (w), 1500 (w), 810 cm^{-1} (s); mass spectrum, m/e (relative intensity) 190 (100), 158 (4), 145 (14), 128 (57). Anal. Calcd for $C_{22}H_6N_8S_2$: C, 59.18; H, 1.36; N, 25.10; S, 14.36. Found: C, 59.52; H, 1.48; N, 24.82; S, 14.14.

Acknowledgment. We are indebted to the National Institutes of Health (GM 15997) for financial support of this research.

Registry No. **6**, 23062-31-9; **6**·2TCNE, 88703-12-2; **6**·2TCNQ, 88687-09-6; **7**, 63458-32-2; **8**, 88686-98-0; **9**, 88686-99-1; **10**, 88687-00-7; 11, 88687-01-8; **12**, 88687-02-9; **13**, 88687-03-0; **16**, 88687-04-1; NBS, 128-08-5; TCNE, 670-54-2; TCNQ, 1518-16-7; 4,5-dibromobenzo[1,2-*c*:3,4-*c*′]dithiophene, 88687-07-4; dibromoprehnitrene, 36321-73-0; 1,2-dibromo-3,4,5,6-tetrakis(bromomethyl)benzene, 88687-05-2; 1,3,4,5,6-pentabromobenzo[1,2-*c*:3,4-*c*′]dithiophene, 88687-08-5; 1,3,6,8-tetrahydro-4,5-dibromobenzo[1,2-*c*:3,4-*c*′]dithiophene, 88687-06-3; sodium disulfide, 1313-82-2.

Acid-Catalyzed Cyclization of 3,3′,4,4′-Tetrahydro-1,1′-binaphthyl and Single-Crystal X-ray Structure Determination of a Polycyclic Stable Ozonide

Thomas K. Dobbs,[1] Arnold R. Taylor, Julie A. Barnes, Belma D. Iscimenler, Elizabeth M. Holt,* and Edmund J. Eisenbraun*

Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078

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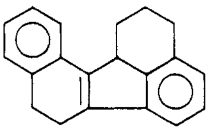
Amberlyst-15 (A-15) catalyzed cyclization of 3,3′,4,4′-tetrahydro-1,1′-binaphthyl (**1**) in refluxing toluene during 12 h provided, as the major product, (±)-1,2,3,6b,7,8-hexahydrobenzo[*j*]fluoranthene (**2a**). Ozonization of **2a** gave a stable ozonide (**3**), mp 159–161 °C. The structure of this ozonide was established by single-crystal X-ray analysis: monoclinic unit cell $P2_1/c$, a = 10.616 (1) Å, b = 9.607 (3) Å, c = 15.052 (4) Å, β = 105.06 (2)°, D_{calcd} 1.372 g cm^{-1}, Z = 4, final agreement factor 6.3%. Prolonged treatment (12–100 h) of **1** or **2a** with A-15 in refluxing toluene yielded a mixture of three 1,2,3,6b,7,8,12b,12c-octahydrobenzo[*j*]fluoranthenes (**4a**, **4b**, **4c**) and 1,2,3,12c-tetrahydrobenzo[*j*]fluoranthene (**5**). Hydrocarbon **2a** was readily dehydrogenated in the presence of hot Pd/C to benzo[*j*]fluoranthene (**6**).

Acid-catalyzed cyclization of 3,3′,4,4′-tetrahydro-1,1′-binapthyl (**1**, Scheme I) for 12 h using Amberlyst-15 (A-15)[2] in refluxing toluene provided, as the major product, a $C_{20}H_{28}$ olefin which was thought to be 1,2,3,6b,7,8-hexahydrobenzo[*j*]fluoranthene (**2a**) or 1,2,3,7,8,12c-hexahydrobenzo[*j*]fluoranthene (**2b**).



2b

Since ^{1}H and ^{13}C NMR failed to provide a distinction between **2a** and **2b**, an ozonization was carried out. This ozonolysis did not proceed as expected. Treatment of the olefin **2a** with ozone in dichloromethane until a blue color appeared, followed by addition of dimethyl sulfide[3a] to the reaction mixture, and removal of the solvent afforded a white crystalline solid which melted with decomposition at 150–160 °C. In a separate experiment, treatment of the ozonization reaction mixture with $NaBH_4$ in isopropyl alcohol also gave this unknown compound. Its IR spectrum showed that carbonyl and hydroxyl functions were absent, but, a weak C–O stretching absorbance[3b] was observed at 1250 cm^{-1}. An epoxide group seemed unlikely since the mass spectrum showed fragments at 32 and 306 amu. These data and a C,H elemental analysis are consistent with an ozonide structure. That a stable secondary ozonide had formed was established by single-crystal X-ray crystallographic analysis which showed the unknown compound to be the ozonide **3**.[3c] Therefore, 1,2,3,6b,7,8-hexahydrobenzo[*j*]fluoranthene (**2a**) is the structure of the initial acid-catalyzed cyclization product.

Table I. Cyclization Products of 1 with A-15 in Refluxing Toluene[a]

	%				
h	4a	4b	4c	1	5
24	9	3	2	76	10
48	27	15	8	5	45
72	31	19	8	2	40
96	30	19	8	2	41

[a] These ratios were determined by GC analysis[5] with the order of emergence from the GC column found to be 4a, 4b, 4c, 1, and 5.

Whereas **2a** readily formed from **1** by heating in the presence of A-15 during a 12 h reflux period in toluene, additional reflux caused slow disproportionation of **2a** to

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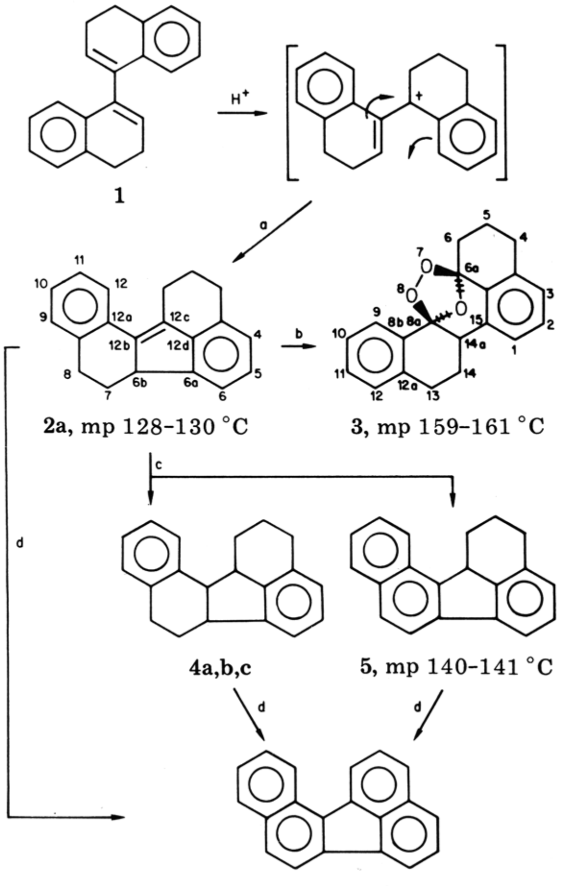
(1) Dobbs, T. K., M.S. Thesis, Oklahoma State University, 1978.

(2) We thank Rohm and Haas Co., Philadelphia, Pennsylvania 19105, for a generous sample of A-15. Literature describing the use and properties of A-15 is available from Rohm and Haas Co.

(3) (a) Pappas, J. J.; Keaveney, W. P.; Gancher, E.; Berger, M. *Tetrahedron Lett.* **1966**, 4273. (b) Bailey, P. S. "Ozonization in Organic Chemistry"; Academic Press: New York, 1978, Vol I, p 32. (c) The systematic name for structure **3** is (6a*S*,8a*S*,14a*S*)-5,6,14,14a-tetrahydro-4*H*,13*H*-6a,8a-epoxydinaphtho[1,8-*cd*:2′,1′-*f*][1,2]dioxepin. We thank Dr. K. Loening, Chemical Abstracts Services, for kindly supplying this information.

Scheme I[a]



[a] a, Amberlyst-15, toluene, Δ, 12 h; b, O_3, CH_2Cl_2; CH_3SCH_3 or $NaBH_4$ in 2-propanol, Δ; c, A-15, toluene, Δ, 12-100 h; d, Pd/C, Δ.

1,2,3,12c-tetrahydrobenzo[*j*]fluoranthene (**5**) and a mixture of three 1,2,3,6b,7,8,12b,12c-octahydrobenzo[*j*]fluoranthenes represented by **4a**, **4b**, and **4c** as shown in Table I. The structure of **5** is based on elemental analysis, the similarity of the UV spectrum with that of benzo[*j*]fluorene, and the presence of a quartet at δ 3.4 in the ^1H NMR spectrum.

The stereochemical assignments of the octahydrobenzo[*j*]fluoranthenes **4a**, **4b**, and **4c** could not be unambiguously determined. However, GC/MS studies show m/z 260 ($C_{20}H_{20}$) and our ^1H NMR and GC studies show that these hydrocarbons differ from the $C_{20}H_{20}$ hydrocarbons which arise from acid-catalyzed dimerizations of 1,2-dihydronaphthalene.[4a,4b,5]

Aromatization of **2a** in the presence of hot Pd/C,[4a] provided benzo[*j*]fluoranthene **6** in good yield. This synthesis, in our opinion, for the preparation of **6** via **1** and **2a** is comparable to or more efficient than earlier syntheses[4a] of **6**.

The ozonide **3** forms, from the racemic hydrocarbon **2a** with the peroxide bridge of the ozonide and the hydrogen at C-14a cis to each other, in a stereoselective reaction. Both the molecule shown in Figure 1 and its enantiomer are present in the unit cell. This single-crystal X-ray examination of the ozonide **3** provides the fifth reported structural examination of an organic ozonide. Reports of the single-crystal, X-ray structure determinations of 1,4-epoxy-4-(4-nitrophenylmethyl)-1-phenyl-1*H*-2,3-benzodioxepin-5(4*H*)-one (**7**)[6] and 3-methoxycarbonyl-5-anisyl-1,2,4-trioxacyclopentane (**8**)[7a] have already appeared. The latter structure shows disorder of the peroxide and ether bridges and thus does not provide reliable comparison values for bond angles and interatomic distances in that portion of the structure. Recently, McCollough[7b] et al. determined the structures of *endo*-1-methyl-3-phenylindene ozonide (**9a**) and *exo*-1-methyl-2,3-diphenylindene ozonide (**9b**) through single-crystal X-ray analysis. The stability of ozonides of this type permitted isolation of endo and exo forms. These five structures **3**, **7**, **8**, **9a**, and **9b** exhibit, as a common structural feature, an aromatic ring substituted on one or more of the carbons of the five-membered ozonide ring. In ozonides **3**, **7**, **9a**, and **9b** the C(ozonide)–C(aromatic ring) distances [1.505 (5), 1.504 (11), 1.501 (4), 1.51 (1) Å, respectively] do not indicate any significant delocalization of electron density about this bond. These ozonides show an additional similarity—the incorporation of ozone into a five-membered cyclopentene ring, two carbons of which are also part of an aromatic ring. However, structure **7** also includes a carbonyl function on the original cyclopentene ring and thus direct comparisons between the structural details of **3** and **7** are precluded.

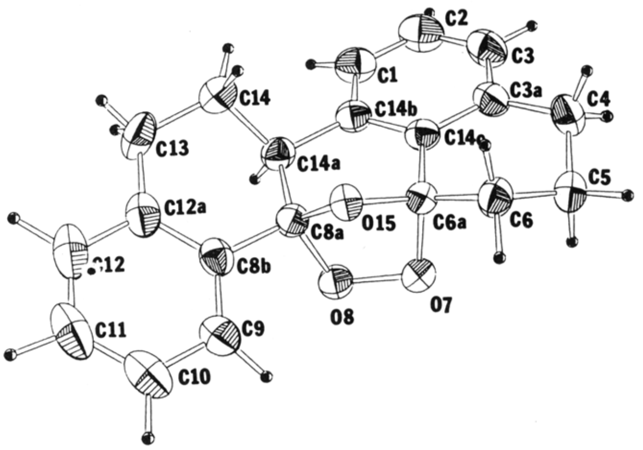
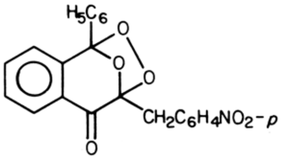
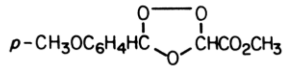


Figure 1. Projection view of **3**, $C_{20}H_{18}O_3$.

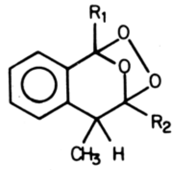


7



$$p\text{-}CH_3OC_6H_4HC\overset{O-O}{\underset{O}{}}CHCO_2CH_3$$

8



9a, R^1 = Ph; R^2 = H
9b, R^1 = R^2 = Ph

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(4) (a) Dobbs, T. K.; Hertzler, D. V.; Keen, G. K.; Eisenbraun, E. J.; Fink, R.; Hossain, M. B.; van der Helm, D. *J. Org. Chem.* **1980**, *45*, 4769. (b) Hertzler, D. V.; Eisenbraun, E. J.; Flanagan, P. W. *Chem. Ind. (London)* **1969**, 877–878.

(5) Gas chromatographic analyses were carried out on a 6 ft × 1/4 in. O.D. column containing 7% of UC W-98 on 80–100 mesh DCMS-treated Chromosorb G with a Hewlett-Packard 5750 instrument isothermally at 250 °C.

(6) Mullica, D. F.; Korp, J. D.; Milligan, W. O.; Belew, J. S.; McAtee, J. L., Jr.; Karban, J. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1703.

(7) (a) Groth, P. *Acta Chem. Scand.* **1970**, *24*, 2137. (b) Miura, M.; Ikegami, A.; Nojima, M.; Kusabayashi, S.; McCullough, K.; Nagase, S. *J. Am. Chem. Soc.* **1983**, *105*, 2414–2426.

In **3**, **9a**, and **9b**, the ether bridge appears symmetric [C–O distance: **3**, 1.417 (4), 1.417 (4) Å; **9a**, 1.427 (3), 1.407 (4) Å; **9b**, 1.43 (1), 1.42 (1) Å], whereas in **7**, the corresponding distances are 1.406 (9) and 1.434 (9) Å showing an asymmetry of the ether bridge. The peroxide bridge also exhibits different bonding characteristics in these structures [C–O distances 1.443 (4), 1.460 (4) Å and O–O 1.471 (3) Å in **3**; C–O 1.473 (9), 1.466 (9) Å and O–O 1.459 (7) Å in structure **7**]. Distances reported for **9a** and **9b** are similar. The torsional angles obtained for **3** from the single-crystal X-ray determinations are presented in Table VI (supplementary material).

The structure of **3** and that of **7** are similar in conformation of the ozonide ring, both showing ether oxygen envelope conformation and not the carbon–epoxide half-chair conformation predicted to be more stable on the basis of theoretical mechanistic studies[8] or the oxygen half-chair conformation predicted by Rouse[9] to be more stable from LCAO–MO studies of *cis*- and *trans*-2-butene ozonides and supported by microwave studies of gas-phase ozonides of propylene and *trans*-2-butene.[10] The high melting point of **3** and its resistance to attack by sodium borohydride suggests that ozonides can show considerable chemical stability and that this stability comes from structural factors which are not as yet well understood.

Experimental Section

3,3′,4,4′-Tetrahydro-1,1′-binaphthyl (1). The diene **1** was prepared as described[11] by pinacol condensation of α-tetralone, in the presence of aluminum foil activated with $HgCl_2$ in anhydrous ethanol–benzene, and dehydration of the resulting diol in refluxing acetic acid/acetic anhydride (1:1). The overall yield was 80%. Recrystallization from ethanol gave **1**: mp 140 °C (lit.[11] 141 °C); ^1H NMR ($CDCl_3$) δ 7.2–6.8 (m, 8 H, Ar H), 6.05 (t, 2 H, vinylic), 2.85 (t, 4 H, benzylic), 2.4–2.1 (m, 4 H, methylene).

Cyclization of 1 to 1,2,3,6b,7,8-Hexahydrobenzo[*j*]fluoranthene (2a).[12] A solution containing 15.0 g (0.06 mol) of diene **1** in 500 mL of toluene was added to 15.0 g of A-15.[2] The suspension was heated at reflux for 12 h and then filtered through Dicalite. The Dicalite cake was rinsed with an additional 200 mL of warm toluene. Concentration by rotary evaporation gave 13.7 g (91%) of yellowish-white crystals, mp 127–130 °C. These crystals were dissolved in a minimum amount of hot benzene and 95% ethanol was added until the solution became turbid. Scratching caused formation of 7.3 g of white crystals, mp 128–129.5 °C. Cooling the solution produced an additional 4.3 g of material, mp 128–130 °C, essentially identical with the first crop. Concentration of the mother liquor gave 1.9 g of crystalline **2a**, mp 127–128 °C. The first crop showed UV (95% ethanol) λ_{max} 305 nm (log ϵ 4.37), 314 nm (log ϵ 4.45); mass spectrum (8 eV), m/z (relative intensity) 258 ($M^{+}\cdot$, 100), 257 (17.6), 230 (19.0), 229 (19.7), 215 (21.6), 114 (25.7); ^1H NMR ($CDCl_3$) δ 6.9–7.6 (m, 7 H, Ar H), 3.46 (dd, 1 H, C-12c), 3.2–2.4 (m, 7 H, overlapping), 2.2–1.18 (m, 3 H, overlapping); ^{13}C NMR ($CDCl_3$) ppm 144.4, 143.4, 137.3, 136.7, 133.4, 132.7, 132.3, 128.8, 126.2, 125.7, 124.9, 124.5, 120.0, 49.5, 30.7, 28.2, 25.4, 23.7.

Anal. Calcd for $C_{20}H_{18}$: C, 92.98; H, 7.02. Found: C, 92.70; H, 7.17.

Conversion of 2a to 3.[3c] **A.** An ozonization tube containing 50 mL of CH_2Cl_2 and 1.0 g (0.004 mol) of **2a** was chilled in a dry ice–acetone bath and oxygen containing ozone was passed through the solution until a faint blue color appeared. The ozone flow was discontinued and 10 mL of dimethyl sulfide[3a] was added. The organic solution was washed three times with 100-mL portions of water, dried ($MgSO_4$), and concentrated by rotary evaporation to give 0.7 g of yellowish-white crystals of **3**, mp 156–160 °C. The crystals became dark and decomposed (nonexplosively) when an attempt was made to sublime a small sample at 100 °C (0.05 mmHg).

Table II. Crystal Data

formula	$C_{20}H_{18}O_3$
M_r	306.4
a	10.616 (1) Å
b	9.607 (3) Å
c	15.052 (4) Å
β	105.06 (2)°
V	1482.5 (6) Å^3
$F(000)$	648
λ Mo K_α	0.71069 Å
scan mode	$\theta-2\theta$
$2\theta_{max}$	116°
max scan rate	29.3°/min
min scan rate	15.0°/min
μ Mo K_α	1.07 cm^{-1}
D_{calcd}	1.372 g cm^{-3}
Z	4
space group	$P2_1/c$
total number of reflexions	4891
obsd reflexions	2385
R	6.3%

When the ozonization experiment was repeated using 10% methanol/methylene chloride solution as the solvent, the same product was obtained in comparable yields: IR (KBr) 1258, 1124 (C–O stretch) cm^{-1}; mass spectrum (70 eV), m/z (relative intensity) 306 ($M^{+}\cdot$, 10.7), 274 (100), 273 (50.0), 272 (72.6), 271 (68.4), 256 (62.1); ^1H NMR ($CDCl_3$) δ 7.9–7.72 (m, 1 H, Ar H), 7.42–6.94 (m, 6 H, Ar H), 2.25 and 3.23 (dd, 1 H, C-12c), 3.2–3.74 (m, 4 H, Ar CH), 2.5–1.8 (m, 6 H, CH_2); ^{13}C NMR ($CDCl_3$) ppm 139.6, 135.5, 135.1, 131.1, 130.6, 129.7, 128.2, 128.1, 126.7, 107.3, 105.0, 44.8, 30.3, 29.4, 28.5, 28.5, 20.7.

Anal. Calcd for $C_{20}H_{18}O_3$: C, 78.41; H, 5.92. Found: C, 77.13; H, 6.01.

B. A 2.0-g (0.008 mol) sample of **2a** in 50 mL of CH_2Cl_2 was chilled in a dry ice–acetone bath and treated with ozone until a faint blue color appeared. The solution was poured into a 250-mL round-bottomed flask which contained 4.0 g (0.11 mol) of $NaBH_4$ and 100 mL of 2-propanol. This solution was stirred overnight and then refluxed for 1 h. The solution was then concentrated and 250 mL of H_2O were added. The aqueous mixture was stirred for 6 h, then extracted (3 × 100 mL) with ethyl ether. The ether layer was dried ($MgSO_4$) and concentrated to give 2.3 g of a clear yellow oil. Crystallization from 95% ethanol gave 1.4 g of white crystals, mp 159–161 °C. The ^1H NMR spectrum of this product was identical with that of the product obtained by method A.

Single-Crystal X-ray Data for 3.[3c] A crystal of **3** was mounted on a Syntex automated P3 diffractometer using graphite monochromated Mo K_α radiation. Unit cell dimensions (Table II) were determined during normal instrument alignment procedures. The racemic mixture of molecules (three chiral centers) crystallizes in a centrosymmetric space group ($P2_1/c$) with four molecules per unit cell. Data were collected at room temperature with a θ–2θ scan mode and corrected for Lorentz, polarization, and background effects. The structure was solved by using MULTAN80[13] and refined[14] by using full-matrix least-squares procedures. Hydrogen positions were determined from a difference Fourier synthesis but these positions were unstable to refinement and were held fixed with isotropic thermal parameters (u = 3.79) during all further refinement. Refinement of scale factor and positional and anisotropic thermal parameters for all non-hydrogen atoms led to a final R factor of 6.3% [$R = (\sum||F_o| - |F_c||)/\sum|F_o|$]. A projection view of one of the enantiomers present in the unit cell is shown in Figure 1 based on the final positional and thermal parameters of Tables III and IV (supplementary material).

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[10] Lattimer, R. P.; Kuczkowski, R. L.; Gillies, C. W. *J. Am. Chem. Soc.* **1974**, *96*, 348.

[11] Altman, Y.; Ginsburgh, D. *J. Chem. Soc.* **1959**, 466.

[12] (a) Crawford, M.; Supanaker, V. *J. Chem. Soc.* **1968**, 2328. (b) Crawford, M.; Supanaker, V. *Ibid.* 1969, 832.

[13] Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; DeClerq, J. P.; Woolfson, M. M., University of York, England, 1980.

[14] Stewart, J. M., Ed. "The XRAY System-Version of 1980"; Technical Report TR446 of the Computer Center, University of Maryland, College Park, Maryland.

Cyclization of 1 to 1,2,3,12c-Tetrahydrobenzo[*j*]fluoranthene (5). In a 2-neck flask equipped with magnetic stirrer, condenser, and drying tube were combined 5.0 g (0.019 mol) of diene 1, 5.0 g A-15, and 200 mL of toluene. The mixture was heated at reflux for a total of 100 h with 2.0-mL aliquots removed at 24-h intervals. The samples were filtered through glass wool and the solvent removed under N_2. The oily residues were diluted with 2.0 mL of acetonitrile and analyzed by GC[5] with retention times at 15.0, 15.4, 17.2, 23.2, and 27.2 min for **4a**, **4b**, **4c**, 1, and 5, respectively. The ratios of these components are given in Table I. No starting material could be detected after 24 h. After 110 h of heating, the warm solution was filtered through Dicalite and concentrated by rotary evaporation to 1.7 g yellow crystals, mp 135–140 °C. Recrystallization from 95% ethanol gave yellow crystals, mp 139–140 °C. These crystals were sublimed at 120 °C (0.05 mm) to give 5: mp 140.5–141 °C; UV (95% ethanol) λ_{max} 274 nm (log ϵ 4.84); mass spectrum (9 eV), *m/z* (relative intensity) 257 (22.3), 256 ($M^{+\cdot}$, 100), 255 (25.3), 252 (22.3), 228 (65.9); ^{1}H NMR δ 7.0–8.1 (m, 8 H, Ar H), 3.69 (dd, 1 H, $CH(Ar)_3$), 2.6–3.2 (m, 3 H, overlapping), 2.04–2.4 (m, 2 H, overlapping), 1.04–1.52 (m, 1 H, overlapping); ^{13}C NMR ($CDCl_3$) δ 145.9, 143.4, 139.6, 138.8, 134.8, 132.8, 131.2, 128.8, 127.7, 127.2, 125.9, 125.2, 124.7, 124.0, 119.0, 116.5, 45.2, 26.4, 25.8, 23.4.

Anal. Calcd for $C_{20}H_{16}$: C, 93.71; H, 6.29. Found: C, 93.62; H, 6.31.

Dehydrogenation of 2a to Benzo[*j*]fluoranthene (6). In a 100-mL, round-bottomed flask equipped with a magnetic stirrer, condenser, and argon purge were combined 500 mg (2.0 mmol) of alkene **2a**, 100 mg of 10% Pd/C, and 50 mL of 1-methylnaphthalene. The mixture was heated at reflux for 5 h, cooled, and filtered through Dicalite, and the Dicalite cake was rinsed with warm toluene. Removal of the solvents by distillation followed by trituration of the residue with isohexane afforded 452 mg (1.8 mmol, 92%) of benzo[*j*]fluoranthene: mp 163–164 °C; picrate, mp 193–195 °C (lit.[4a] mp 165 °C; picrate mp 195 °C); mass spectrum of 6 (8 eV), *m/e* (relative intensity) 252 (100), 251 (7), 250 (20), 2126 (7), 57 (8), 43 (8); ^{1}H NMR (C_6D_6) δ 8.54 (d, 2 H, Ar H), 8.08 (d, 2 H, Ar H), 7.12–7.88 (m, 8 H, Ar H).

Acknowledgment. We thank the American Petroleum Institute for support in the early part of this work. We also thank Dr. O. C. Dermer for reading the manuscript.

Registry No. 1, 5405-96-9; **2a**, 18522-48-0; **3**, 88730-13-6; **5**, 20162-56-5; **6**, 205-82-3.

Supplementary Material Available: Tables III–VI, listing positional parameters, final anisotropic thermal parameters, bond angles and lengths for hydrocarbon 3, and a list of calculated and observed structure factors (22 pages). Ordering information is given on any current masthead page.

Reversible Retro-Diels–Alder Reactions of Bicyclo[4.1.0]hept-2-ene Systems

Simon F. Sellers, William R. Dolbier, Jr.,* Henryk Koroniak, and Dheya M. Al-Fekri

Department of Chemistry, University of Florida, Gainesville, Florida 32611

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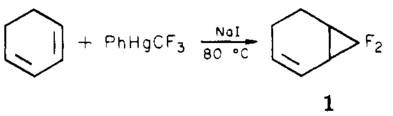
The synthesis and thermal isomerizations of 7,7-difluorobicyclo[4.1.0]hept-2-ene (1) and spiro[bicyclo-[4.1.0]hept-2-ene-7,1′-cyclopropane] (12) are described. 1 and 12 undergo reversible formal retro-Diels–Alder reactions with activation parameters which uniquely describe the highly ordered transition state for the Diels–Alder reaction. The relationship of the inherent strain of these bicyclic systems to the ability to observe such isomerizations is discussed.

The first to comment on the unusual effects of fluorine substitution on cyclopropane were O'Neal and Benson[1] who estimated that an increase in ring strain of 4.5–5 kcal/mol per fluorine substituent was produced. Hoffman predicted that fluorine should weaken the bond opposite the carbon bearing the fluorine substituent whereas the adjacent bonds should be slightly strengthened.[2] In a series of studies to obtain quantitative data on the kinetic and thermodynamic consequences of geminal fluorine substitution, we have found that the bond opposite to the CF_2 group is weakened by 8–10 kcal/mol[3] while there is a much less significant weakening of the adjacent bond of 0–2 kcal/mol,[4] results largely in keeping with these early predictions.

A study of the thermal rearrangements of 2,2-difluoro-1-vinylcyclopropanes[5] demonstrated a facile [1,3]-sigmatropic process involving the preferential initial homolytic cleavage of the C_1–C_3 bond of these molecules. We wish to report in this paper a detailed analysis of the thermal isomerization of a cis-fused difluorovinylcyclopropane, 7,7-difluorobicyclo[4.1.0]hept-2-ene (1). We compare its interesting thermal behavior with that of its hydrocarbon analogue and describe the preparation and thermal rearrangement of a hydrocarbon of similar ring strain.

Table I. Rate and Equilibrium Data for 1 ⇄ 2

temp, °C	$k_1 + k_{-1}$ ($\times 10^5$ s)	k_1	k_{-1}	K_{eq}
160.1	1.55	0.84	0.71	1.132
167.5	2.86	1.64	1.22	1.346
171.8	4.06	2.39	1.67	1.437
179.25	7.38	4.70	2.68	1.752
185.0	13.22	8.73	4.49	1.948
196.8	31.53	22.17	9.36	2.368



1

Results and Discussion

7,7-Difluorobicyclo[4.1.0]hept-2-ene (1) was prepared via Seyferth's[6] method of difluorocarbene addition to cyclohexa-1,3-diene in 56% yield. 1 was unambiguously char-

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