mechanism is provided by the apparent absence of reaction products derived from dimethyl sulfoxide, which is known to react with nitrenes.[21] A concerted mechanism should involve some degree of charge separation in the transition state, which is consistent with the observed increase in rate on changing from xylene to dimethyl sulfoxide.

Experimental Section

Melting points were taken on a Büchi apparatus and are uncorrected. NMR and infrared spectra were recorded, respectively, on a Varian HA-100 instrument and on a Perkin-Elmer 377 spectrophotometer. Chemical shifts are given in parts per million from internal Me_4Si and refer to deuteriochloroform solutions.

Compounds **5a**[10] and **1b**[9] were prepared according to known methods.

(*Z*)-*o*-Nitrocinnamonitrile. Sodium hydride (1.2 g, 0.05 mol) was added in portions to a solution of diethyl cyanomethylphosphonate[22] (8.85 g, 0.05 mol) in anhydrous dimethylformamide (100 mL) under stirring and ice cooling. A solution of *o*-nitrobenzaldehyde (7.55 g 0.05 mol) in dimethylformamide (20 mL) was then added dropwise during 10 min. After being stirred for 5 min, the reaction mixture was poured in ice water, neutralized with ammonium chloride, and extracted with ether. The organic solution was dried over sodium sulfate and evaporated. The residue was chromatographed on a silica gel column with hexane–diethyl ether (1:1) as eluent to give the title compound:[23] 1.6 g; mp 87 °C (from diisopropyl ether); NMR δ 5.73 (1 H, d, J = 12 Hz), 7.5–8.4 (5 H, m); IR (Nujol) 2220 cm^{-1}. Subsequent fractions gave a mixture (2.3 g) of the title compound and its *E* isomer in the approximate ratio of 3:2.

Amine 1a. A solution of (*Z*)-*o*-nitrocinnamonitrile (1.2 g) in methyl acetate (100 mL) was hydrogenated in the presence of 10% palladium/charcoal (0.25 g). After 500 mL of hydrogen was absorbed, the catalyst was filtered off, and the solvent was removed in vacuo at room temperature. The oily residue (0.90 g) was a mixture of **1a** (80%) and 3-(2-aminophenyl)propionitrile[3] (20%): NMR δ 3.8 (br s), 5.26 (d, J = 12 Hz), 6.5–7.9 (m); IR (Nujol) 2220 cm^{-1}.

Amine 1c. *o*-Nitro-α-methylcinnamonitrile[24] (5.0 g) was hydrogenated according to the above procedure. The crude product was dissolved in anhydrous ether and treated with ethereal hydrogen chloride to give the hydrochloride of **1c**: 2.2 g; mp 240–242 °C; NMR (D_2O) δ 2.20 (3 H, d, J = 1.8 Hz), 7.3–7.9 (5 H, m); IR (Nujol) 2225 cm^{-1}.

A sample of **1c** (0.10 g) in ethanol (20 mL) was refluxed for 30 min. Evaporation of the solvent and recrystallization of the residue from methanol gave **4c**: 0.075 g; mp 228–230 °C; NMR (CD_3SOCD_3) δ 2.38 (3 H, s), 7.0–7.8 (4 H, m), 8.3–8.5 (1 H, m).

Amine 5b. Sodium hydride (0.65 g) was added in portions to a solution of diethyl cyanomethylphosphonate (5.94 g) in anhdrous dimethylformamide (60 mL) under stirring and ice cooling. A solution of 2-amino-5-chlorobenzophenone (5.2 g) in dimethylformamide (15 mL) was added dropwise, and the mixture was stirred for 16 h at room temperature. The solvent was partly removed in vacuo, and the residue was pured in ice–water, neutralized with ammonium chloride, and extracted with ether. The organic solution was dried over sodium sulfate and evaporated.

Chromatography of the residue on a silica gel column with hexane–diethyl ether (1:1) as eluent gave **5b**: 4.3 g; mp 92–93 °C (from diisopropyl ether); NMR δ 3.5 (2 H, br s), 5.58 (1H, s), 6.4–7.6 (8 H, m); IR (Nujol) 2220 cm^{-1}. A sample of **5b** was recovered unchanged after 24 h of refluxing in ethanol.

Amine 5c. This compound[9] was prepared from *o*-aminoacetophenone according to the procedure described for **5b** (3 h; 54% yield). A sample of **5c** was recovered unchanged after 24 h of refluxing in ethanol.

Cyclization of 1b. A solution of **1b** (0.20 g) in ethanol (30 mL) was refluxed for 7 h. Evaporation of the solvent and recrystallization of the residue from methanol gave **4b** (0.12 g).[25]

Preparation of Azides 2 and 6. General Procedure. Sodium nitrite (5 mmol) in water (5 mL) was added to a solution of amine **1** or **5** (5 mmol) in 1 N aqueous hydrochloric acid (20 mL) under stirring and ice cooling. The solution was adjusted to pH 5 with sodium acetate; sodium azide (5 mmol) was then added in portions with vigorous stirring. After 30 min, the mixture was extracted with ether, and the organic layer was dried over sodium sulfate. Evaporation of the solvent under reduced pressure gave practically pure azide **2** or **6**, with the exception of **2a** which was isolated by chromatography on a silica gel column (diethyl ether as eluent). Samples of analytical purity were obtained upon recrystallization from pentane–diisopropyl ether (see Table I).

Thermal Reaction of Azides 2. General Procedure. A solution of **2** (3 mmol) in anhydrous toluene (150 mL) was refluxed for 30 min. Evaporation of the solvent and recrystallization of the residue from methanol gave **3** (see Table II).

Thermal Reaction of Azides 6. General Procedure. A solution of **6** (5 mmol) in anhydrous dimethyl sulfoxide (250 mL) was heated at 140 °C for the time indicated in Table II. After the solvent was partly removed under reduced pressure, the mixture was treated with water and extracted with chloroform. The organic layer was dried over sodium sulfate and evaporated. The residue was chromatographed on a silica gel column with hexane–diethyl ether (1:1) as eluent to give **6** (see Table II).

Registry No. 1a, 72119-96-1; **1c**, 74844-95-4; **2a**, 74844-96-5; **2b**, 74844-97-6; **2c**, 74844-98-7; **3a**, 235-25-6; **3b**, 27537-94-6; **3c**, 72716-16-6; **4b**, 51478-40-1; **4c**, 74844-99-8; **5b**, 74868-71-6; **5c**, 74845-00-4; **6a**, 74845-01-5; **6b**, 74845-02-6; **6c**, 74845-03-7; **7a**, 36193-65-4; **7b**, 24139-17-1; **7c**, 13006-59-2; (*Z*)-*o*-nitrocinnamonitrile, 74845-04-8; *o*-nitro-α-methylcinnamonitrile, 74845-05-9; diethyl cyanomethylphosphonate, 2537-48-6; *o*-nitrobenzaldehyde, 552-89-6; 3-(2-aminophenyl)propionitrile, 55000-16-3; 2-amino-5-chlorobenzophenone, 719-59-5; *o*-aminoacetophenone, 551-93-9; **5a**, 58106-57-3.

(21) See ref 1, p 315.
(22) Fiszer, B.; Michalski, J. *Rocz. Chem.* **1954**, *28*, 185; *Chem. Abstr.* **1955**, *49*, 9493.
(23) Haruyuki, I. *Chem. Pharm. Bull.* **1964**, *12*, 350.
(24) Pastushak, N. O.; Dombrovskii, A. V. *Zh. Obshch. Khim.* **1964**, *34*, 3110; *Chem. Abstr.* **1965**, *62*, 1594.
(25) Kwon, S.; Tanaka, S.; Isagawa, K. *Yuki Gosei Kagaku Kyokaishi* **1973**, *31*, 328; *Chem. Abstr.* **1974**, *80*, 82599.

Regioselective Acid-Catalyzed Cyclodimerization of 1,2-Dihydronaphthalene. Mechanism of Formation and Single-Crystal X-ray Analysis of Two Octahydrobenzo[*j*]fluoranthenes

Thomas K. Dobbs,[1a] Donald V. Hertzler,[1b] Gary W. Keen,[1c] and Edmund J. Eisenbraun*

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

Robert Fink, M. Bilayet Hossain, and Dick van der Helm*

Department of Chemistry, University of Oklahoma, Norman, Oklahoma 73019

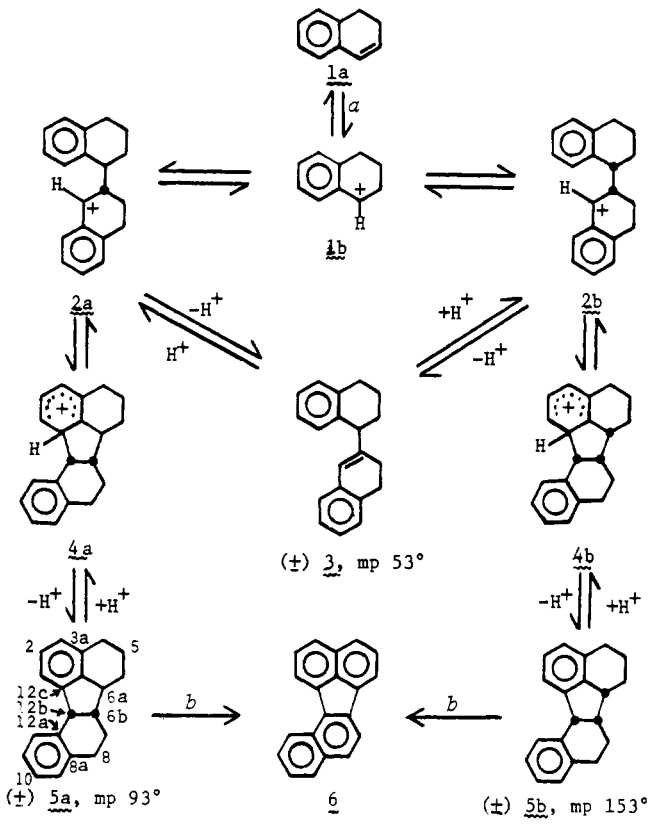
Received May 9, 1980

Treatment of 1,2-dihydronaphthalene (**1a**) with sulfuric acid gives a $C_{20}H_{20}$ hydrocarbon,[2] mp 92–93 °C, whereas with P_2O_2 in the presence of tetralin a diastereomer,[3] mp 151–153 °C, is formed. Both were readily dehydrogenated to benzo[*j*]fluoroanthene which established their gross structure.[3] Earlier ^1H NMR studies and use of Dreiding models suggested (±)-*cis,anti*- and (±)-*cis,syn*-4,5,6,6a,6b,7,8,12b-octahydrobenzo[*j*]fluoranthenes, **5a** and

(1) (a) T. K. Dobbs, M.S. Thesis, Oklahoma State University, Stillwater, July 1978. (b) Department of Chemistry, Southwestern Oklahoma State University, Weatherford, OK 73096. (c) Conoco Inc., Ponca City, OK 74601.
(2) J. Von Braun and G. Kirschbaum, *Chem. Ber.*, **54**, 597 (1921).
(3) C. D. Nenitzescu and M. Avram, *J. Am. Chem. Soc.*, **72**, 3486 (1950).

0022-3263/80/1945-4769$01.00/0

Scheme I



[a] Amberlyst 15, solvent, Δ. [b] Pd/C, Δ.

5b, respectively, as structures for these hydrocarbons.[4] These structures have now been conclusively verified through single-crystal X-ray analysis and this will be described later in the paper. These studies show that the formation of **5a** and **5b** from **1a** is regioselective. The structure proof for these hydrocarbons and a study of their formation was prompted by our earlier interest in acid-catalyzed reactions of unsaturated hydrocarbons[4,5] as well as the need for developing an effective and direct synthesis of the carcinogenic benzo[*j*]fluoranthene (**6**). The important intermediate (±)-1,2,3,3′,4,4′-hexahydro-1,2′-binaphthyl (**3**), mp 52–53.5 °C, shown in Scheme I, was isolated and identified. Hydrocarbon **3** is probably the product obtained by Scott and Walker[6] in their sulfuric acid catalyzed polymerization of **1a**. There was insufficient information to repeat their work but fortunately Amberlyst-15 (A-15)[7] provides sufficiently mild conditions to permit preparation of **3** in 51% yield without extensive conversion to **5a** and/or **5b**.

The carbon skeleton of **3** was determined readily through Pd/C-catalyzed dehydrogenation to 1,2-binaphthyl, mp 79–81 °C. Mass spectrometric studies established the molecular weight of **3** as 260 and the location of the conjugated double bond followed from the ^1H and ^{13}C NMR spectra. Of particular significance is the singlet absorption at δ 6.2 (vinylic proton) in the ^1H NMR spectrum. The ^{13}C NMR spectrum also supports the structural assignment for **3** since 5 sp^2 carbon resonances are observed as singlets in the fully decoupled off-resonance spectrum. The isolation of **3** as a product from the A-15-catalyzed dimerization of **1a** pointed to its role as an intermediate in forming **5a** and **5b** and prompted its trial as such.

Table I. Cyclization Products of 1a with A-15 in Refluxing Solvent

time, h	relative % (benzene solvent)[a] 3	5a	5b
24	97	-	-
48	32	68	-
72	21	79	-
96	7	93	trace
120	5	83	12
144	1	81	18
	relative % (toluene solvent)[b]		
24	2	13	85
48	0	11	89
72	0	4	96
96	0	4	96
110	0	4	96

[a] Relative percent of dimeric components only. The order of emergence from a C-18 LC column, [8b] using 80% CH_3CN/H_2O, was **3**, **5a**, and **5b**. These are corrected for differences in absorbance at 254 nm. [b] These relative percentages were obtained from GC analysis. An unknown compound, believed to be a 1:1 reaction product of **1a** and toluene, appeared at an earlier GC retention time (5 min) than that of **3** (13.7 min). Its ratio to the total dimeric product was 1:5.3 for the 24-h experiment and remained essentially constant for the remainder of the experiment.

Refluxing cyclohexane is a suitable reaction solvent for A-15-catalyzed dimerization of **1a** to **3** in yields up to 80%. Some **5a** and **5b** are formed but they can be removed through their preferential crystallization from acetone. After 24 h the GC ratio of **3**:**5a**:**5b** was 22:2:1 and this did not change appreciably for an additional 48 h. The emergence of **3**, **5a**, and **5b** from a UC W98 GC column[8a] was in that order with retention times of 13.7, 14.5, and 15.7 min, respectively. In refluxing benzene and toluene, the reaction is driven beyond **3** and as shown in Table I, **3** is formed initially and is then converted to **5a**. In refluxing toluene, **5a** is consumed with simultaneous formation of **5b**. However, an unknown product (ca. 20%) having a lower boiling point and shorter retention time (5 min vs. 13.7 min for **3**) was observed. This material, presumed to be a 1:1 alkylation product with toluene, is readily separated from the dimers of **1a** by vacuum distillation. Its presence interfered with the high-pressure

(4) D. V. Hertzler, E. J. Eisenbraun, and P. W. K. Flanagan, *Chem. Ind. (London)*, 877 (1969).

(5) E. J. Eisenbraun, W. M. Harms, J. W. Burnham, O. C. Dermer, R. E. Laramy, M. C. Hamming, G. W. Keen, and P. W. Flanagan, *J. Org. Chem.*, **42**, 1967 (1977).

(6) N. D. Scott and J. F. Walker, *Ind. Eng. Chem.*, **32**, 312 (1940).

(7) Amberlyst-15 and Amberlyst-XN1011 are macroreticular sulfonated styrene–divinylbenzene copolymer resins. These catalysts were a gift from Rohm and Haas Co., Philadelphia, PA 19105, and literature describing their use and properties may be obtained from this source. The greater thermal stability of Amberlyst XN-1011 compared to A-15 suggested its trial in the dimerization of **1a**. Amberlyst XN-1011 in refluxing benzene or toluene causes cyclization of **1a** in the same manner as described for A-15 (**1a** → **3** → **5a** and **5b**), but the rate of reaction is much slower. This is probably a reflection of the decreased porosity (24%) of XN-1011 as compared with 32% for A-15.

(8) (a) GC studies were performed with a Hewlett-Packard 5750 chromatography apparatus equipped with dual FID detectors. An 8 ft × 0.25 in. column of 80–100-mesh Chromosorb G coated with 7% UC W-98 at 230 °C was used. (b) High-pressure liquid chromatographic analyses were performed with an M6000 pump, U6K injector, a 440 dual-wavelength UV detector, and a reversed-phase C_{18} analytical column, all purchased from Waters Associates, Milford, MA. (c) ^{13}C NMR spectra were recorded at 25.2 MHz in the FT mode on a Varian XL-100A interfaced with a 12K Nicolet 1080 computer system. Spectra were run in $CDCl_3$, using a deuterium lock, and are reported in parts per million downfield from Me_4Si (δ $CDCl_3$ = 76.9 ppm). ^1H NMR spectra were recorded on the same instrument and are reported in terms of δ relative to internal Me_4Si. We thank the NSF for Grants GP17641 and CHE76-5571 which enabled purchase of this instrument. (d) Beckman IR-5A instrument. (e) Cary 14 spectrophotometer. (f) CEC 21-110B instrument.

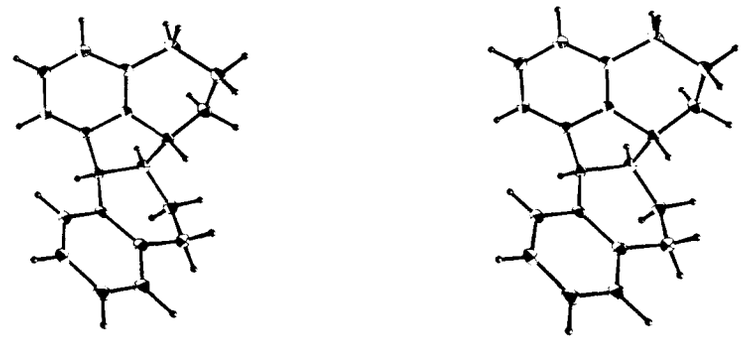


Figure 1. Stereoscopic view of **5a**.

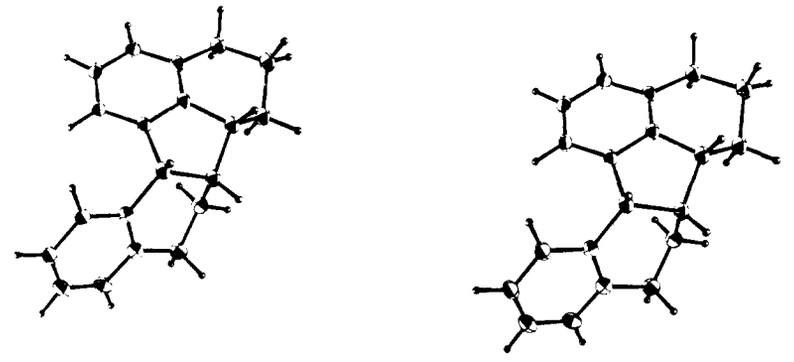


Figure 2. Stereoscopic view of **5b**.

LC[8b] studies of crude reaction products and hence GC studies[8a] were used to obtain the product ratios reported in Table I.

Scheme I shows that the olefin dimer **3** is a common intermediate to both cyclized dimers **5a** and **5b** as was demonstrated by reacting pure **3** with A-15 in refluxing benzene for 72 h. Since **1a** was detected, the reversibility of **1a** $\rightleftarrows$ **3** is considered established. Filtration, concentration, and vacuum distillation gave dimer **5a** in 81% yield accompanied by 3% **5b**. In refluxing toluene, good yields (70–80%) of **5b** were obtained. A sample of pure **3** was treated with P_2O_5 in tetralin at 140 °C for 1 h to demonstrate that dimer **3** is also a common intermediate in the formation of **5a** and **5b** in the reaction with P_2O_5. Subsequent workup gave a clear yellow oil, of which GLC analysis showed no detectable quantity of **3**, and the ratio of **5a** to **5b** was 1:9. This oil, dissolved in boiling acetone, upon cooling gave a 20% yield of white crystals of **5b** which showed no depression in melting point on admixture with authentic material. Similarly pure **5a** gave a 27% yield of **5a**:**5b** (1:14). The reaction of **1a** in tetralin with P_2O_5 at 140 °C for 1 h yields the crystalline dimer **5b** in 6% yield. These crystals were removed and GLC analysis of the mother liquor showed 58% of **5a** in addition to two other minor components. Tetralin was recovered unchanged with no formation of dimeric products when it was exposed in the absence of **3**, **5a**, or **5b** to acidic catalyst under identical conditions.

A higher yield (49%) of **5b** was obtained when refluxing chlorobenzene (1.5 h) was used as the solvent for the cyclodimerization of **1a** with P_2O_5. The crude reaction mixture was shown by GC to contain **5a**:**5b** (1:8). An unknown component was also detected along with 1% of benzo[*j*]fluoranthene (**6**). Cyclization of **1a** with P_2O_5 in the absence of solvents resulted in lower yields of **5b** (18% by GC).

Since the dimer **5b** is formed in the presence of A-15[7] and toluene, as well as with P_2O_5 in tetralin at different temperatures, we suggest that the specificity of the reaction

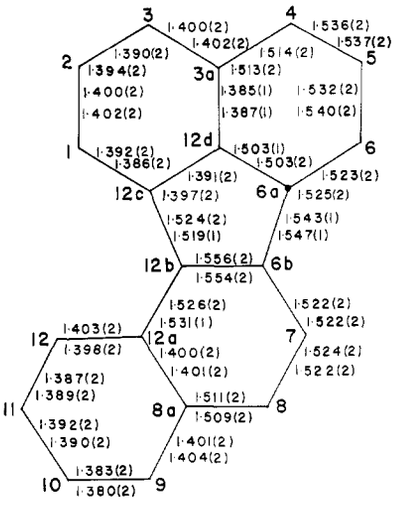


Figure 3. Bond distances in the two independent molecules of **5a**.

(absence of trans isomers and ultimate destruction of **5a** in favor of **5b**) is the result of a thermodynamic–kinetic control rather than a difference in acid catalysts.

Dehydrogenation of **5a** and **5b** with 10% Pd/C in refluxing 1-methylnaphthalene affords **6** in 94% and 92% yield, respectively. This synthesis of **6** is attractive since the yields of the dimers **5a** and **5b** have been improved from 6–18% to ca. 80% through use of A-15 in refluxing solvent.[7]

Because of the possible multiplicity of octahydrobenzo[*j*]fluoranthene isomers we chose single-crystal X-ray analysis of **5a** and **5b** to rigorously establish the structures of these cyclodimers.

Single-Crystal X-ray Analysis of 5a and 5b. A stereoscopic view of the crystal structure of **5a** is shown in Figure 1. This hydrocarbon crystallizes with two molecules in the asymmetric unit, but their conformation is essentially the same. The stereoscopic view of **5b**, is ob-

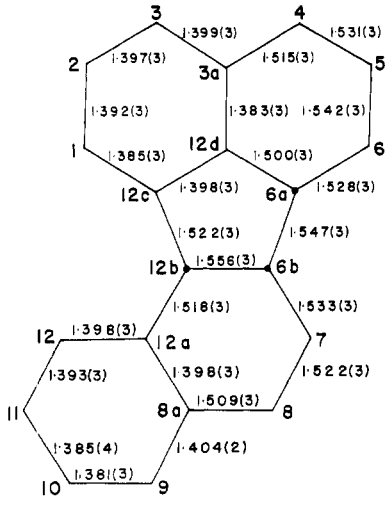


Figure 4. Bond distances in **5b**.

tained by single-crystal X-ray diffraction, is shown in Figure 2. These figures clearly show the differences in the diastereomers **5a** and **5b**. Formally this is also indicated in Figures 3 and 4 which show their bond distances. The C(6b)–C(12b) bond is strained in both diastereomers and this is reflected in the bond distances (1.554–1.556 Å). The difference in configuration between the two diastereomers can most easily be described by exocyclic conformational angles C(6a)–C(6b) (81.7° and 80.3° for **5a** and −37.5° for **5b**), C(12c)–C(12b) (−81.8° and −86.6° for **5a** and 29.6° for **5b**), and C(12b)–C(12a) (57.6° and 50.0° for **5a** and −73.2° for **5b**). All other conformational angles are similar in both compounds. The difference in configuration results in a short intramolecular distance of 2.27 Å between H(C6a) and H(2)(C8) in **5a**, which does not occur in **5b**, while in the latter compound there is an intramolecular contact of 2.30 Å between H(C6a) and H(C6b) which does not occur in the former. This is, however, not discernible in the ^{1}H NMR spectrum since the relevant absorptions were not resolved in our studies. The results of the single-crystal X-ray analysis do not allow a distinction of the relative stability of **5a** and **5b**. However, the data from Table I suggest that between **5a** and **5b** the former is the kinetic product and the latter is the thermodynamic product.

Experimental Section[8]

1,2-Dihydronaphthalene (1a). 1,2-Dihydronaphthalene (**1a**), bp 70 °C (0.3 mmHg), was prepared from 1-tetralone.[1a]

Cyclodimerization of 1a to (±)-1,2,3,3′,4,4′-Hexahydro-1,2′-binaphthyl (3). A mixture of 200 mL of cyclohexane, 36.0 g (0.3 mol) of **1a**, and 6.0 g of A-15 resin[7] was heated at reflux for 3 h. This mixture was cooled, filtered, concentrated, and distilled (Kugelrohr, 0.1 mmHg). The fraction with bp 80–90 °C gave 17.0 g of recovered **1a**. The fraction with bp 140–160 °C gave 18.2 (51%) of oil which crystallized from methanol to give 12.7 g of colorless crystals, mp 52–53.5 °C. A second crop, mp 48–50 °C, could not be further purified by recrystallization. GC analysis[8a] of the crude reaction mixture showed the presence of at least three dimers (22:3:1) whose retention times were 13.7, 14.5, and 15.7 min, respectively. Subsequently, mixed injections showed the peaks to be **3**, **5a**, and **5b**, respectively. Structural assignment of **3**, mp 52–53.5 °C, has not previously been reported: IR[8d] (KBr) 753, 745, 735, 1632, 1252, 1239, 1198 cm^{-1}; UV[8e] (95% ethanol) λ_{max} 265 (log ϵ 4.26); mass spectrum[8f] (70 eV), *m/e* (relative intensity) 260 (56), 131 (25), 130 (100), 129 (35), 128 (24), 115 (17); ^{1}H NMR (acetone-d_6) δ 1.6–2.2 (m, 6, CH_2), 2.6–2.9 (m, 4, $ArCH_2$), 2.7 (t, 1, ArCH), 6.2 (s, 1, ArCH=C), 6.8–7.2 (m, 8, Ar H); ^{13}C NMR ($CDCl_3$) 145.3, 137.6, 137.4, 134.6, 134.5, 129.0, 128.8, 126.9, 126.5, 126.2, 126.1, 125.8, 125.4, 124.9, 47.2, 29.8, 28.5, 25.1, 21.4 ppm.

Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.00; H, 7.63.

Dehydrogenation of 3 to 1,2′-Binaphthyl. To a mixture of 1.0 g (4 mmol) of **3** and 0.5 g of 10% Pd/C was added 100 g of 1-methylnaphthalene. A nitrogen inlet tube was placed below the surface and the mixture was heated at reflux until no further evolution of hydrogen was evident (1 h). The reaction mixture was cooled, 50 mL of toluene was added, the suspension was filtered through Dicalite and concentrated, and methylnaphthalene was removed by vacuum distillation. The residue, crystallized from isohexane,[10] gave 0.8 g of white crystals, mp 79–81 °C. The melting point of a mixture with an authentic sample of 1,2′-binaphthyl showed no depression.

Cyclodimerization of 1a to (±)-*cis,anti*-4,5,6,6a,6b,7,8,12b-Octahydrobenzo[*j*]fluoranthene (5a). A. A 108-g (0.83 mol) sample of **1a**, 20.0 g of A-15,[7] and 500 mL of benzene were heated at reflux for 96 h, cooled, filtered, and concentrated. The residue was distilled [Kugelrohr, 110–150 °C (0.1 mmHg)] to give 77.2 g (77%) of light yellow oil. Crystallization from ether/isohexane[10] (1:1) gave 58 g (0.22 mol) of white crystals **5a**: mp 92–93 °C (lit.[4] mp 91–93 °C); mass spectrum (70 eV), *m/e* (relative intensity) 260 (100), 259 (31), 232 (44), 217 (35), 169 (61), 78 (44); ^{1}H NMR[4]; (CCl_4) δ 6.7–7.4 (m, 6, Ar H), 4.06 (d, 1, $CH(Ar)_2$, J = 7.4 Hz), 2.2–2.9 (m, 6, overlapping), 1.0–2.10 (overlapping, m, 6); ^{13}C NMR ($CDCl_3$) 144.4, 143.7, 137.6, 136.7, 134.1, 128.2, 128.1, 126.3, 125.8, 125.7, 125.3, 122.3, 47.4, 46.7; 42.8, 27.6, 26.7, 26.4, 23.6, 23.5 ppm.

B. Smaller scale reactions are conveniently carried out by using magnetic stirring with a Teflon-coated bar. With 16.0 g of **1a**, 600 mL of refluxing benzene, and 10.0 g of A-15[7] an 80% yield of **5a** was obtained.

Cyclodimerization of 1a to (±)-*cis,syn*-4,5,6,6a,6b,7,8,12b-Octahydrobenzo[*j*]fluoranthene (5b). A. Toluene (300 mL), 5.0 g (0.19 mol) of **1a**, and 5.0 g of A-15[7] were heated at reflux for 48 h, filtered while warm, concentrated, and distilled [Kugelrohr, 110–140 °C (0.1 mmHg)]. Crystallization from 95% ethanol gave 3.7 g (74%) of white crystals, mp 149–151 °C.

A 50-g sample of **5b** was eluted through a picric acid column, using isohexane. This eluant was concentrated and the residue was recrystallized twice from a mixture of benzene and 95% ethanol (1:9), and then from ethyl acetate, dried, and sublimed (130 °C, 0.05 mmHg) to give 12.0 g of **5b**: mp 152.5–153 °C [lit.[4] mp 152.5–153 °C]; mass spectrum (70 eV), *m/e* (relative intensity) 260 (M_+, 100), 223 (49), 218 (32), 170 (20), 139 (21), 129 (27), 128 (27); ^{1}H NMR[4] (CCl_4) δ 6.7–7.4 (m, 7, Ar H), 4.2 (d, 1, $CH(Ar)_2$, J = 5.4 Hz), 2.85–3.28 (m, 1, ArCH in plane of Ar ring), 2.4–2.85 (m, 5), 0.8–2.35 (overlapping m, 6); ^{13}C NMR ($CDCl_3$) 144.3, 141.4, 136.7, 136.4, 134.6, 130.0, 128.8, 126.1, 125.7, 125.3, 125.2, 120.6, 47.8, 44.9, 44.4, 28.9, 26.7, 23.8, 23.7, 20.2 ppm.

B. A mixture of 20.0 g (0.154 mol) of **1a** and 30.00 g of P_2O_5[3,9] was diluted with 300 mL of chlorobenzene, heated at reflux for 1.5 h, cooled, and poured over 500 g of ice. The aqueous slurry was extracted (3 × 100 mL) with ethyl ether. The combined extracts were washed three times with H_2O, dried ($MgSO_4$), and concentrated by rotary evaporation. The residue was distilled [Kugelrohr, 140–170 °C (0.2 mmHg)] to give 13.3 g of yellow oil which did not crystallize. The oil was passed through a basic alumina (Merck, activity I) column (15 × 1.5 cm), using isohexane[10] as eluant. Concentration of this eluate gave 9.9 g (49%) of **5b**, mp 150–153 °C. The mother liquor was reprocessed as above to yield 0.56 g of colorless crystals, mp 89–93 °C, which were shown to be **5a** by ^{1}H NMR[4].

C. A mixture of 15 g of tetralin, 5.0 g (0.038 mol) of **1a**, and 63.0 g of PPA[1a] was heated at 140 °C for 15 min and then poured over 300 g of ice. Workup as in **B** gave 2.1 g (42%) of **5b**, mp 147–149 °C.

Conversion of 3 to 5a. A reaction mixture of benzene (700 mL), 16.0 g (0.12 mol) of **3**, and 10.0 g of A-15[7] was refluxed for 72 h, filtered, concentrated, and distilled [Kugelrohr, 130–160 °C (0.1 mmHg)] to give 14.8 g of **5a**. Crystallization from isohexane[10] gave 13.1 g (81%) of **5a**, mp 92–93 °C. The melting point of **5a**

(9) This experiment is difficult to reproduce. Scrupulously dry P_2O_5 produces dark tars. Previously opened bottles of P_2O_5 with the hydrated surface scum removed provided a powdery P_2O_5 which performed best.
(10) Phillips Chemical Co., isohexane, bp 52–61 °C.

when mixed with an authentic sample was undepressed.

Conversion of 3 to 5b. A mixture of 20 g of P_2O_5,[9] 9.9 g (0.038 mol) of **3**, and 15 g of tetralin was heated at 130–140 °C for 1 h in a three-necked, round-bottomed flask equipped with a drying tube, thermometer, and magnetic stirring bar. The cooled mixture was poured onto 500 g of ice and extracted three times with ethyl ether, and the combined extracts were washed twice with water, dried ($MgSO_4$), and concentrated by rotary evaporation. Vacuum distillation [Kugelrohr, 130–180 °C (0.1 mmHg)] gave 5.1 g of yellow oil which crystallized from ethyl ether to give 2.0 g (20%) of **5b**, mp 149–151 °C.

A mixture melting point of the product with that obtained from cyclodimerization of **1a** to **5b** was undepressed. The ^1H NMR spectra of these two products were also identical.

Conversion of 5a to 5b. A mixture of 300 mL of toluene, 5.0 g (0.019 mol) of **5a**, and 5.0 g of A-15[7] was refluxed for 48 h, filtered, concentrated, and distilled [Kugelrohr, 110–140 °C (0.1 mmHg)]. Crystallization from 95% ethanol gave 3.7 g (74%) of **5b**, mp 149–151 °C. The ^1H NMR spectrum[4] of this product is identical with that of an authentic sample of **5b**.

Formation of Cyclodimerization Products from 1a with Time. A. Amberlyst-15 in Benzene. To 200 mL of benzene were added 5.0 g (0.04 mol) of **1a** and 5.0 g of A-15 catalyst. The suspension was heated at reflux and 2.0-mL aliquots were removed at 24-h intervals. Filtering the sample through glass wool, rinsing with 2 mL of warm acetone, and evaporation under N_2 gave an oil. This was dissolved in 2 mL of acetonitrile and analyzed by high-pressure LC.[8b] The retention times for dimers **3**, **5a**, and **5b** were 21.5, 23.5, and 25.5 min, respectively, using 80% acetonitrile/water with a flow rate of 2.0 mL/min. Relative percentages of **3**, **5a**, and **5b** vs. time are presented in Table I. After 144 h the warm mixture was filtered through Dicalite, concentrated by rotary evaporation, and distilled [Kugelrohr, 135–160 °C (0.1 mmHg)] to give 3.2 g (64%) of light yellow oil which crystallized upon trituration with ethyl ether. Recrystallization from 95% ethanol afforded 2.2 g (0.008 mol) of crystalline dimer **5a**, mp 92–93 °C. The melting point of a mixture with an authentic sample was undepressed.

B. Amberlyst-15 in Toluene. The above procedure for the cyclization of **1a** was repeated, substituting toluene for benzene. The products were analyzed by GC.[8a] Changes in the **3**:**5a**:**5b** ratio with time are shown in Table I.

After 110 h, the warm solution was filtered and concentrated, and the brown oil was distilled to give 2.8 g (56%) of clear yellow liquid. Crystallization from methanol gave 1.9 g (0.007 mol) of **5b**, mp 150–152 °C. A mixture melting point with an authentic sample was undepressed, and the ^1H NMR spectrum[4] was identical with that of an authentic sample.

Preparation of Benzo[*j*]fluoranthene (6). A mixture of 10.0 g (0.038 mol) of **5a**, 1.0 g of 10% Pd/C, and 150 mL of 1-methylnaphthalene was heated at reflux in a 300-mL round-bottomed flask equipped with a magnetic stirrer, condenser, and nitrogen purge. GC[8a] analyses showed that after 24 h the ratio of **6** to **5a** was 1:7. After 84 h, the solution was cooled and filtered through Dicalite, and the Dicalite bed was rinsed with warm toluene. Removal of the solvents by distillation, followed by trituration of the residue with isohexane,[10] afforded 9.0 g (0.036 mol, 94%) of benzo[*j*]fluoranthene (**6**): mp 162–164 °C, picrate, mp 193–195 °C [lit.[11] mp 165 °C; picrate, mp 195 °C]; mass spectrum (8 eV), *m/e* (relative intensity 252 (M^+, 100), 251 (7), 250 (20), 126 (7), 57 (8), 43 (8); ^1H NMR (C_6D_6) δ 8.54 (d, 2, C-1, C-12), 8.08 (d, 2, C-6, C-7), 7.12-7.88 (m, 8, Ar H); ^{13}C NMR ($CDCl_3$) 137.5, 137.4, 136.8, 133.7, 131.7, 130.3, 129.3, 128.9, 128.0, 127.5, 127.0, 126.6, 126.6, 125.0, 124.9, 124.0, 123.8, 120.5, 119.5 ppm. The dimer **5b** behaves similarly, giving **6** in 92% yield when subjected to identical reaction conditions.

Optical Activity Studies. Hydrocarbons **3**, **5a**, and **5b** showed $[\alpha]^{25}_D$ 0.0° (*c* 2.5, $CHCl_3$).

Single-Crystal X-ray Analysis. Crystals of **5a** were formed by cooling a saturated solution of acetonitrile, whereas **5b** was crystallized from hot benzene by the addition of methanol. All diffraction data were taken on a Nonius-CAD-4 automatic diffractometer at −135 (3) °C. The data were corrected for Lorentz and polarization effects and individual weights were calculated for all reflections.[12] No absorption corrections were made; μ = 5.30 and 5.37 cm^{-1} for **5a** and **5b**, respectively. The crystal data and parameters for the intensity data are summarized in Table II.

Table II. Crystal and Structure Data for 5a and 5b

	5a	5b
formula	$C_{20}H_{20}$	$C_{20}H_{20}$
formula weight	260.38	260.38
space group	$P2_1/a$	$P\bar{1}$
molecules/unit cell (Z)	8	2
unit cell dimensions at −135 (3) °C		
a, Å	28.112 (8)	8.624 (6)
b, Å	8.021 (1)	10.618 (5)
c, Å	12.420 (2)	8.337 (4)
α, deg		99.44 (5)
β, deg	94.77 (2)	91.47 (6)
γ, deg		113.22 (4)
V, Å^3	2790.8	688.6
unit cell dimensions at 20 (2) °C		
a, Å	28.344 (11)	8.6588 (5)
b, Å	8.078 (2)	10.7277 (8)
c, Å	12.523 (3)	8.3634 (9)
α, deg		98.09 (1)
β, deg	94.69 (2)	91.32 (1)
γ, deg		112.92 (1)
V, Å^3	2857.7	705.8
D_c (at 20 °C), g cm^{-3}	1.21	1.23
D_m (at 20 °C), g cm^{-3}	1.20	1.21
radiation for unit cell dimentions,	Cu Kα_1 (Ni filtered)	Cu Kα_1 (Ni filtered)
λ, Å	1.54051	1.54051
radiation for intensity data	Cu K$\bar{\alpha}$ (Ni filtered)	Cu K$\bar{\alpha}$ (Ni filtered)
λ, Å	1.5418	1.5418
scan mode	Θ-2Θ	Θ-2Θ
Θ_{max}, deg	75	75
maximum scan time, s	60	90
crystal dimensions, mm	0.46 × 0.38 × 0.30	0.26 × 0.22 × 0.06
total number of reflections	5742	2845
number of unobserved reflections ($I < 2\sigma(I)$)	414	596
$R = \frac{\Sigma \lvert\lvert kF_o\rvert - \lvert F_c\rvert\rvert}{\Sigma \lvert kF_o\rvert}$ (observed data)	0.040	0.054
R value for all data	0.047	0.077

Both structures were solved by direct methods, using the program MULTAN,[13] and refined by block-diagonal least-squares methods. Scattering factors for the C atoms were taken from the International Tables for X-ray Crystallography[14] while values for the H atoms were taken from the work of Stewart, Davidson, and Simpson.[15] After the initial least-squares refinement, the positional parameters of all H atoms were calculated from geometric considerations, observed in difference Fouriers, and added as refinement variables. The lease-squares refinement was continued with anisotropic thermal parameters for the C atoms and isotropic temperature factors for the H atoms until the shifts in the positional parameters of the C atoms were less than one-third of the standard deviations. A final difference Fourier synthesis for each

(11) G. M. Badger, S. D. Jolad, and T. M. Spotswood, *Aust. J. Chem.*, **19**, 85 (1966).

(12) D. van der Helm, S. E. Ealick, and J. E. Burks, *Acta Crystallogr., Sect. B*, **31**, 1013 (1975).

(13) G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A*, **27**, 368 (1971).

(14) International Tables for X-Ray Crystallography, Vol IV, Kynoch Press, Birmingham, U.K., 1974, p 73.

(15) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

compound showed no peaks with magnitude greater than 0.3 e/Å^3.

Acknowledgment. We thank the Environmental Protection Agency (Grant R-805419) and the Department of Energy, Bartlesville Energy Technology Center (contract DE-AT19-78BC31001), for support. We are also grateful to the American Petroleum Institute (Research Project 58A) for support during the initial phase.

Registry No. **1a**, 447-53-0; **3**, 74929-95-6; **5a**, 74983-81-6; **5b**, 74983-82-7; **6**, 205-82-3; **6** picrate, 74929-96-7; 1,2′-binaphthyl, 4325-74-0.

Supplementary Material Available: Positional parameters, anisotropic thermal parameters, hydrogen atom parameters, bond angles, and conformational angles (13 pages). Ordering information is given on any current masthead page.

Mechanism of the Dimethyl Mesoxalate-Alkene Ene Reaction. Deuterium Kinetic Isotope Effects[1]

Osman Achmatowicz, Jr.,* and Jan Szymoniak

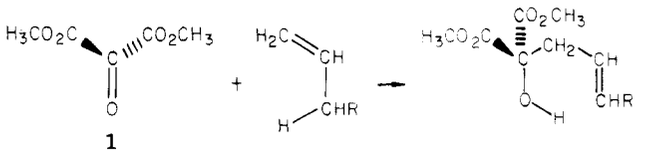
Institute of Chemistry and Agricultural Chemistry, Warsaw Agricultural University, Rakowiecka 26/30, 02-528 Warszawa, Poland

Received April 1, 1980

Our previous kinetic studies[2] of the addition of dimethyl mesoxalate (1) to alkenes furnished thermodynamic parameters ($\Delta H^{\ddagger}$ = 75 to 96 kJ mol^{-1} and $\Delta S^{\ddagger}$ = −120 to −170 J mol^{-1} K^{-1}) which strongly suggest that this ene reaction (see Scheme I) has a concerted mechanism with a late (product-like) transition state. In the present report we describe an extension of this work aimed at a more detailed elucidation of the structure of the transition state by the study of kinetic isotope effects.

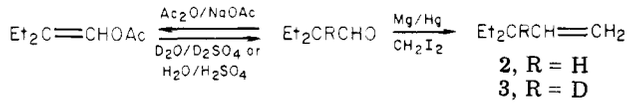
Kinetic isotope effects are a powerful diagnostic tool for the investigation of reaction mechanisms.[3] However, this approach has been used to study relatively few ene reactions.[4] The conclusions that can be drawn from the data can be summarized by two generalizations; viz., (i) a primary isotope effect $k_H'/k_D' \neq 1$ supports a concerted reaction mechanism and (ii) values that are clearly short[3] of the theoretical maximum (k_H'/k_D' = 7) are indicative of a nonsymmetrical transition state. On the other hand an example of such a primary isotope effect (k_H'/k_D' = 2.41) was observed recently[4d] for the reaction of allene with perfluorocyclobutanone and was ascribed to the nonlinear transfer of the hydrogen atom (C··H··O angle of ca. 100 °C). We conclude that isotope effects of this intermediate magnitude could also be due to a deviation from a symmetrical migration of the hydrogen atom or a combination of these effects, and in the absence of independent information on the degree of the C–H bond rupture in the transition state, the inference of its geometry from the value of the isotope effect appears inconclusive.

Scheme I



1

Scheme II



2, R = H
3, R = D

Table I. Primary Isotope Effects for the Reaction of 3-Ethyl-1-pentene with Dimethyl Mesoxalate

temp, °C	120	130	140	150
k_H'/k_D'	2.36 ± 0.16	2.37 ± 0.16	2.29 ± 0.15	2.09 ± 0.13

Results and Discussion

An alkene containing a tertiary allylic hydrogen atom is required to obtain a primary effect directly, free from secondary effects. For our experiments we chose 3-ethyl-1-pentene (**2**) and its deuterated derivative **3**. The alkenes were obtained by the route shown in Scheme II.

The kinetic isotope effect for the reaction of 3-ethyl-1-pentene with dimethyl mesoxalate (**1**) was determined at various temperatures (Table I) by an independent measurement of the ene reaction rate for deuterated **3** (k_D) and undeuterated (k_H) alkene **2**. However, the measured isotope effect for the ene reaction of the 1-heptenes, i.e., with hydrogen atoms at the secondary allylic carbon atom, is actually the resultant of primary (k_H'/k_D') and secondary k_H''/k_D'') effects. To separate these effects, it was necessary to examine the reactions of 1-heptene (**4**), 1-heptene-*3*-d_1 (**5**), and 1-heptene-*3,3*-d_2 (**6**).

The experimental values of the kinetic isotope effects were found from the ratios of the deuterated and protic adducts determined by mass spectrometry, i.e., by the competitive method which ensured an adequately high accuracy.

The reactions with monodeuterated heptene (**5**) were carried out for the intramolecular comparison and with dideuterated heptene (**6**) for the intermolecular comparison with **4**. The separate primary and secondary isotope effects were calculated by using eq 1 and 2 (see Experimental Section). The solution of these equations gave k_H'/k_D' = 2.16 ± 0.08 and k_H''/k_D'' = 1.05 ± 0.04 values, respectively. Very similar values for the primary isotope effect (Table I) were obtained from the reactions of 3-ethyl-1-pentene. The results also show that isotope differentiation takes place in the rate-determining step.[4e]

In a concerted ene reaction the magnitude of the secondary isotope effect depends on the extent of the $sp^3 \rightarrow sp^2$ rehybridization of the alkene C-3 carbon atom in the transition state. The value k_H''/k_D'' = 1.05 is consistent with our previous findings[2] which indicated a late transition state of the ene reaction of dimethyl mesoxalate with alkenes. On the one hand it is lower than the value (1.15) of the secondary isotope effect in a S_N1 solvolysis reaction in which the transition state has a structure resembling that of an sp^2 hybridized carbonium ion;[5] on the other hand it is close to the isotope effect for the retrodiene reaction of the tetracyanoethylene-9,10-dideuterio-

(1) This research was supported by the Polish Academy of Sciences through the Project MR-I.12.1.

(2) O. Achmatowicz, Jr., and J. Szymoniak, *J. Org. Chem.*, **45**, 1228 (1980).

(3) V. J. Shiner, Jr., "Isotope Effects in Chemical Reactions", C. J. Collins and N. S. Bowman, Eds., Van Nostrand Reinhold Co., New York, 1971.

(4) (a) R. Huisgen and H. Pohl, *Chem. Ber.*, **93**, 527 (1960); (b) W. R. Roth, *Chimia*, **20**, 229 (1966); (c) J. P. Schaefer, B. Horvath, and H. P. Klein, *J. Org. Chem.*, **33**, 2647 (1968); (d) Shong-Hong Dai, and H. R. Dolbier, Jr., *J. Am. Chem. Soc.*, **94**, 3953 (1972); (e) "Isotopes in Organic Chemistry", Vol. 1, E. Buncel and C. C. Lee, Eds., Elsevier, Amsterdam, New York, 1975, p 51-55.

(5) A. Streitwieser, Jr., H. A. Jajow, R. C. Fahey, and S. Suzuki, *J. Am. Chem. Soc.*, **80**, 2326 (1958).

0022-3263/80/1945-4774$01.00/0