to remove most of the solvent. The residue was dissolved in water (750 ml) and enough potassium carbonate was added to neutralize and saturate the solution. The separated material was dissolved in 1.5 l. of methylene chloride and the solution was dried over potassium carbonate, filtered, and concentrated. Ether (300 ml) was added to generate 130 g (66%) of solid **5a**, mp 110–115°. Recrystallization was effected by dissolution in a minimum volume of hot methylene chloride, concentration to about $^1/_2$ volume, and addition of an equal volume of ethyl acetate: mp 120–122°; nmr δ 6.82 (m, 3, aromatics), 4.18–4.5 (m, 2), 3.9 (s, 3, OCH_3), 2.9–3.7 (m, 3), 1–2.3 (m, 8, methylene envelope).

Anal. Calcd for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.33; N, 5.36. Found: C, 68.69; H, 7.35; N, 5.36.

Alternate Preparation of 5a.—A solution of 0.54 g (0.01 mol) of ammonium chloride in 15 ml of water was added to a solution of 3.6 g (0.01 mol) in **2a** in 75 ml of THF. With vigorous stirring, under nitrogen, zinc powder (7 g) was added over a 2-min period. The mixture was stirred for 45 min and filtered and the filtrate was treated with 50 ml of 1 *N* hydrochloric acid. After 15 min this solution was neutralized with solid potassium carbonate excess and the THF phase was dried further with anhydrous potassium carbonate, filtered, and concentrated. Upon addition of ether to the viscous residue, 2.2 g (85%) of solid **5a** developed, mp 105–110°. Recrystallization was effected as above, mp 118–121°.

2-Hydroxy-5-methoxyphenyl Isomer of 5a (5b).—This compound was prepared from **2b** by the above alternate zinc–NH_4Cl method: yield 78%, mp 180–182°.

Anal. Calcd for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.33; N, 5.36. Found: C, 69.19; H, 7.44; N, 5.24.

2-Ethyl-4-(2-hydroxy-3-methoxyphenyl)-3-methyl-1-pyrroline 1-Oxide (5c).—A solution of 5.4 g of ammonium chloride in 150 ml of water was added to a warm solution (35°) of 35 g (0.1 mol) of **2c** in 750 mol of tetrahydrofuran. The vigorously stirred mixture was treated with 70 g of zinc powder over the next several minutes. In 15 min, the zinc paste developed into a suspended solid. After $^1/_2$ hr the reaction was worked up in a fashion similar to that for the alternate preparation of **5a** to give 20.5 g (82.3%) of crude **5c**, mp 101–103°. Recrystallization from EtOAc gave pure nitrone, mp 107–109°.

Anal. Calcd for $C_{14}H_{19}NO_3$: C, 67.44; H, 7.68; N, 5.62. Found: C, 67.30; H, 7.82; N, 5.57.

3,3a,4,5,6,7-Hexahydro-3-(2-hydroxy-3-methoxyphenyl)-2*H*-indole (6).—A mixture of 108.6 g (0.3 mol) of **2a**, 3 l. of methanol, and 30 g of Raney nickel was hydrogenated at low pressure at a temperature of 50° for 16 hr. After filtration of the catalyst, the solution was concentrated to 1-l. volume. A volume of 350 ml of 2 *N* hydrochloric acid was added and the solution was heated on the steam bath for 10 min. Ice water was added to precipitate some red solid. After filtration, concentrated ammonium hydroxide was added to precipitate the tacky base. Recrystallization was effected by dissolution in 200 ml of hot methanol and addition of 100 ml of water to give 25 g (34%) of **6**, mp 135–140°. Recrystallization from absolute ethanol gave pure **6**: mp 140–145°; ir (Nujol) 1655 (C=N), 2500 cm^{-1} (C=NH$^+$); ir ($CHCl_3$) 1650 (C=N), 3550 cm^{-1} (OH).

Anal. Calcd for $C_{15}H_{19}NO_2$: C, 73.44; H, 7.81; N, 5.71. Found: C, 73.46; H, 7.77; N, 5.89.

Acknowledgment.—The authors are indebted to the Analytical and Physical Chemistry Department under the supervision of Mr. A. D. Lewis. In particular, we wish to thank Dr. C. Greenough for the spectral data and Mrs. U. Zeek for analytical determinations. We also wish to thank the Chemical Development Department under the supervision of Dr. A. W. Ruddy for the large-scale preparation of intermediates.

Registry No.—**2a**, 36848-01-8; **2b**, 40697-22-1; **2c**, 40697-23-2; **5a**, 40697-85-6; **5b**, 40697-86-7; **5c**, 40697-87-8; **6**, 40697-88-9; 2-hydroxy-3-methoxy-ω-nitrostyrene, 1986-06-7; cyclohexanone morpholine enamine, 670-80-4; 2-hydroxy-5-methoxy-ω-nitrostyrene, 35467-98-2; diethyl ketone morpholine enamine, 13654-48-3.

Synthesis of 1,7- and 1,11-Dihydrobenzo[1,2:4,5]dicycloheptene and 1*H*-Benzo[1,2:4,5]dicycloheptenium Tetrafluoroborate(1−)

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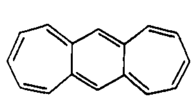
The dihydrobenzo[1,2:4,5]dicycloheptenes (*e.g.*, **3** and **4**) are molecules of considerable synthetic interest, since, in principle, these compounds can act as precursors to a variety of novel conjugated systems. Thus, removal of hydride could provide the monocation **5** and the 14-π-electron dication, proton removal the 18-π-electron dianion, and loss of hydrogen the 16-π-electron hydrocarbon **1**. We now report the synthesis of 1,7- (**3**) and 1,11-dihydrobenzo[1,2:4,5]dicycloheptene (**4**), and the conversion of these isomers into 1*H*-benzo[1,2:4,5]dicycloheptenium tetrafluoroborate(1−) (**5**).[1]



1

1,2,3,4,5,7,8,9,10,11-Decahydrobenzo[1,2:4,5]dicycloheptene (**2**), prepared by a known route,[2,3] was treated with 4 molar equiv of *N*-bromosuccinimide, and a complex mixture of bromides was formed. The total mixture was dehydrobrominated with 1,5-diazabicyclo[5.4.0]undec-5-ene in dimethylformamide, and the resulting mixture was chromatographed on silica, eluting with petroleum ether (bp 40–60°). A crystalline material was obtained, which on fractional crystallization or chromatography gave mixtures of varying composition of the isomers **3** and **4** (see Experimental Section). Attempts to separate these isomers completely proved unsuccessful, but the mixtures gave satisfactory mass spectral and analytical data. The nmr spectrum of the mixtures showed a singlet in the aromatic region at τ 2.92, assigned to the equivalent aromatic protons of **3**, and singlets at τ 2.75 and 3.06, assigned to the nonidentical aromatic protons of **4**. The allylic protons of **3** and **4** appeared as a doublet (τ 6.97) and the chemical shifts and coupling pattern of the olefinic protons was consistent with structures **3** and **4**.

A mixture (1:2) of the isomers **3** and **4** was treated with trityl fluoroborate in dry acetonitrile under nitrogen, and 1*H*-benzo[1,2:4,5]dicycloheptenium tetrafluoroborate(1−) (**5**) was formed as dark red needles. The nmr spectrum (CD_3CN) was complex [τ 6.49 (H^A, d, $J \approx 6$ Hz), 3.97 (dd, H^B, $J \approx 6, 10$ Hz), 3.68 (H^C, dd, $J \approx 6, 10$ Hz) 3.07 (H^D, dd, $J \approx 6, 12$ Hz), 2.52 (H^E, d, $J \approx 12$ Hz), 1.18–1.46 (H^H, $H^{H'}$, H^F, H^J, m), 0.92 (H^I, dd, $J \approx 10$ Hz), 0.47 (H^G, $H^{G'}$, d, $J \approx 10$

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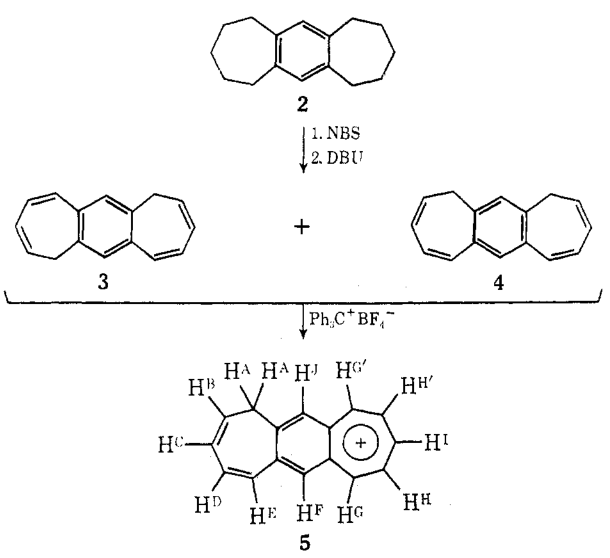
[1] We thank Dr. K. L. Loening, Director of Nomenclature, Chemical Abstracts Service, for helpful discussions concerning the correct name for the cation.

[2] R. Legros and P. Cagniant, *C. R. Acad. Sci.*, **252**, 2733 (1961).

[3] For a second method of preparation, see R. H. Wightman, R. J. Wain, and D. H. Lake, *Can. J. Chem.*, **49**, 1360 (1971).



Hz)] but entirely consistent with the assigned structure. The electronic spectrum [$\lambda_{max}^{CH_3CN}$ 228 nm (ϵ 14,000), 256 (13,700), 261 (12,900), 293 (11,100), 317 (8800), 550 (1800)] resembled that of other annelated tropylium ions.[4]

Attempts to convert **5** into **1** by treatment with trimethylamine according to the method of Dauben and Bertelli[5] gave a complex mixture of products, but no evidence for the production of **1** could be adduced. Reaction of **5** with a second mole of trityl fluoroborate did not lead to the dication, the nmr spectrum remaining virtually unchanged.

Experimental Section

The nmr spectra were run on a Varian HA-100 spectrometer with TMS as internal standard and are reported in τ units. Electronic spectra were recorded on a Unicam SP 800 spectrophotometer. Ir spectra were recorded on a Unicam SP 200 spectrometer. Mass spectra were taken with an AEI MS12 spectrometer at 70 eV.

Preparation of Mixtures of 1,7- (3) and 1,11-Dihydrobenzo[1,2:4,5]dicycloheptene (4).—The hydrocarbon **2** (4.28 g, 20 mmol) and *N*-bromosuccinimide (12.24 g, 80 mmol) were suspended in CCl_4 (300 ml), benzoyl peroxide (20 mg) was added, and the mixture heated under reflux until all of the *N*-bromosuccinimide had reacted (~3 hr). The resulting mixture was filtered to remove the succinimide, and evaporation of the solvent from the filtrate gave a glass (13.4 g). The nmr spectrum (CCl_4) showed signals at τ 2.4–2.6 (m, aromatic), 4.3–4.7 (b, s, benzylic), and 7.2–8.4 (aliphatic). The glass was dissolved in dimethylformamide (40 ml), 1,5-diazabicyclo[5.4.0]undeca-5-ene (10 ml), was added, and the mixture stirred at 80° for 3 hr. The mixture was then poured into water, 50 ml of 5 *N* HCl was added, and the mixture was extracted with ether (3 × 100 ml). The ethereal extracts were washed with water (3 × 50 ml), saturated NaCl solution (1 × 50 ml), and dried (Na_2SO_4). The solvent was removed by evaporation and the resulting dark solid was chromatographed on silica gel (90 g), eluting with petroleum ether. A white crystalline material was obtained (1.75 g) which slowly turned yellow on standing. A number of purification procedures were investigated. Six recrystallizations of the material from ethanol gave white plates (45 mg) which consisted of a 4:1 mixture of **3** and **4**: mass spectra *m/e* 206; ir (KBr) 1500, 1430, 1370, 910, 800, 690 cm^{-1}; nmr ($CDCl_3$) 6.98 (d, $J \approx 7$ Hz), 4.25 (m, $J \approx 7$, 9.5 Hz), 3.96 (dd, $J \approx 5.5$, 9.5 Hz), 3.58 (dd, $J \approx 5.5$, 12 Hz), 3.06 (s), 2.96 (d, $J \approx 12$ Hz), 2.92 (s), 2.15 (s); λ_{max}^{EtOH} 240 nm (ϵ 8000), 311 (14,000).

Anal. Calcd for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 93.09; H, 6.83.

Glc (Carbowax 20M, 256°) of the crystalline material (500 mg) gave a 1:1 mixture (55 mg) of **3** and **4**. Column chromatography on 20% $AgNO_3$-impregnated alumina (80 g)[6] of the crystalline material (800 mg), eluting with ether–benzene, gave a 1:2 mixture (85 mg) of **3** and **4**. A crystalline tetrahydrobenzo[1,2:3,4]dicycloheptene fraction (180 mg) was also isolated in this separation.

Preparation of 1*H*-Benzo[1,2:4,5]dicycloheptenium Tetrafluoroborate(1−) (5).—A mixture (1:2) of the olefins **3** and **4** (25 mg, 0.12 mmol) was added to a solution of trityl fluoroborate (40 mg) in dry acetonitrile (10 ml) under dry N_2. The mixture was stirred until all of the olefin had dissolved (~1 hr), the solvent was removed *in vacuo*, and the residue was washed with dry ether (3 × 5 ml) to give **5** (30 mg, 0.10 mmol, 83%) as dark red needles, which decomposed on attempted mp determination: for nmr see discussion; for electronic spectrum, see discussion; ir (KBr), 1500, 1060, 920, 700 cm^{-1}.

Anal. Calcd for $C_{16}H_{13}BF_4$: C, 65.75; H, 4.78. Found: C, 65.77; H, 4.48.

Registry No.—**2**, 14314-88-6; **3**, 40682-46-0; **4**, 40682-47-1; **5**, 40674-83-7; *N*-bromosuccinimide, 128-08-5; trityl tetrafluoroborate, 340-02-6.

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[4] See G. Naville, H. Strauss, and E. Heilbronner, *Helv. Chim. Acta*, **43**, 1221 (1960).

[5] H. J. Dauben and D. J. Bertelli, *J. Amer. Chem. Soc.*, **83**, 4659 (1961).

[6] See R. Wolovsky, *J. Amer. Chem. Soc.*, **87**, 3638 (1965).

Thermally Induced Side Chain to Ring Migrations in Aromatic Systems

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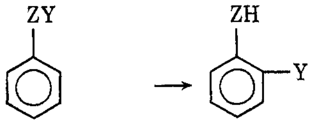
A number of organic molecules undergo rearrangements, by a variety of mechanistic pathways in which a group migrates from a side chain in an aromatic system to a ring position.[1] These migrations may be thermally induced, or acid[1] or base catalyzed.[2]



Z = N, O, C

The purpose of this report is to call attention to the rather general existence of this kind of thermally induced migration which arises during the high-temperature pyrolyses of appropriately substituted aromatic compounds. The recently reported conversion of phenylacetonitrile to *o*-tolunitrile by our laboratories[3] and by Wentrup and Crow[4] is an example of such a migration (see Table I). The relatively high yield of ortho isomer relative to meta and para isomers (tolunitrile) suggests the participation of an intramolecular migration.[1] On the other hand, competitive cleavage also occurs, as shown from the formation of benzene, toluene, and the isomeric cyanophenylacetonitriles.

Many of these side chain to ring migrations are obscured because the initially formed rearrangement

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[1] M. J. S. Dewar in "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience, New York, N. Y., 1963, Chapter 5.

[2] W. von E. Doering and R. A. Bragole, *Tetrahedron*, **22**, 385 (1966).

[3] N. F. Haidar, Ph.D. Thesis, University of Kentucky, Lexington, Ky., 1970.

[4] C. Wentrup and W. D. Crow, *Tetrahedron*, **26**, 3965 (1970).