by preparative glpc (10 ft × 0.25 in. 10% SE-30 at 170°). The spectral properties of this material were identical in all respects to those of the material isolated from the acid-catalyzed rearrangement of tricyclic ketone **5** (*vide supra*).

Acid-Catalyzed Rearrangement of Octalone 21.—To 821.4 mg of octalone **21**[11] in a 10-ml Erlenmeyer flask was added 2 ml of concentrated sulfuric acid. The flask was stoppered and the brown mixture was stirred for 2 days at room temperature. The mixture was poured into 15 ml of ice-water and extracted with ether (2 × 15 ml). The combined extracts were washed with 20 ml of 1 *N* sodium hydroxide and dried over magnesium sulfate. The solvent was evaporated to afford 646.8 mg of yellow oil. Glpc analysis of the product (6 ft × 0.25 in. 10% FFAP at 180°) revealed the presence of two components in a ratio of 48:52. The two components were identified as the α,β-unsaturated ketones **8** and **9**, respectively, by comparison of their spectra with those of authentic samples.

Registry No.—**5**, 17159-66-9; **6**, 18503-74-7; **6** 2,4-DNP, 18503-75-8; **7**, 33830-72-7; **7** 2,4-DNP, 33830-73-8; **9**, 33835-42-6; **10**, 33835-43-7; **11**, 33835-44-8; **18**, 25826-87-3; **19**, 33835-46-0; **20**, 33835-47-1; **25**, 33835-48-2; **26**, 33835-49-3.

Acknowledgments.—We thank the National Science Foundation and the Alfred P. Sloan Foundation for financial support.

Strained Ring Systems. XI.[1a] The Synthesis of Benzobicyclo[2.2.0]hexa-2,5-diene, Benzobicyclo[2.2.0]hex-2-ene, and Benzobicyclo[2.2.0]hex-5-en-*exo*-2-ol[1b]

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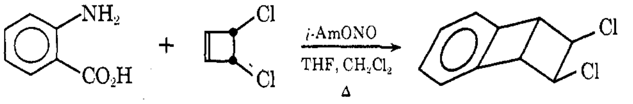
Received October 4, 1971

This paper describes the cycloaddition of benzyne with *cis*-3,4-dichlorocyclobutene to give *exo,cis*-5,6-dichlorobenzobicyclo[2.2.0]hex-2-ene (**4**), the disodium-phenanthrene dechlorination of **4** to benzobicyclo[2.2.0]-hexa-2,5-diene (**2**), the diimide reduction of **2** to benzobicyclo[2.2.0]hex-2-ene (**3**), and the hydroboration of **2** to benzobicyclo[2.2.0]hex-5-en-*exo*-2-ol (**8**). Some of the spectral features of these compounds are discussed.

When Dewar in 1867[2] reported his results from the oxidation of phenol, he suggested the use of a model by which he could construct the various structural isomers of a given molecular formula. For the formula C_6H_6, one of the structures written was that of bicyclo[2.2.0]-hexa-2,5-diene (**1**), which has become known as "Dewar benzene." Nearly 100 years later, van Tamelen and Pappas[3] reported the successful synthesis of **1**. Since that report various syntheses and studies of the chemistry of derivatives of **1** have been reported.

In our continuing program of the chemistry of molecules incorporating the [2.2.0] system, we felt that it would be most useful to develop a synthesis of benzobicyclo[2.2.0]hexa-1,5-diene ("hemi Dewar naphthalene")[4] (**2**) which might also be applicable to the preparation of 1-substituted derivatives of benzobicyclo[2.2.0]hex-2-ene (**3**). Since **2** should be convertible to 5-substituted derivatives of **3**, this approach would make available this set of compounds for further study. Such a synthetic approach has been achieved and is the subject of this paper.

Synthesis.—Conceptually, the approach was to prepare *cis*-5,6-dichlorobenzobicyclo[2.2.0]hex-2-ene (**4**) by the cycloaddition of benzyne and *cis*-3,4-dichlorocyclobutene[7] (**5**) and then to seek methods for dechlorination of **4** to **2**. Two methods were carried out for the cycloaddition reaction. One involved the *in situ* generation of the benzyne precursor and benzyne itself;[8a] only 0.1% of **4** was obtained. The second method involved isolation of the benzyne precursor, benzenediazonium-2-carboxylate (**6**),[8b] and allowing it to decompose thermally in the presence of **5**. Yields of **4** ranging from 2.4 to 11.3% were obtained depending on the ratio of **5**:**6** used. The impurities in the crude reaction mixture appeared to be largely aromatic from the nmr spectrum; one of these was benzoic acid. Chromatography on basic, activity I alumina and elution with carbon tetrachloride gave quite pure **4** in the first few fractions. The infrared spectrum of **4** was fairly simple, indicating a high degree of symmetry in the tricyclic structure.



5 **4**

The nmr spectrum (CCl_4, internal TMS) of **4** exhibited absorptions centered at τ 2.80 (m, 4), 5.55 (m, J = 0.9 Hz, 2), and 5.92 (m, J = 0.8 Hz, 2). The aromatic hydrogens were assigned to the finely split multiplet at τ 2.80 which is only 0.2 ppm lower field than the center of the aromatic proton multiplet of benzocyclobutene (τ 3.01).[9] Irrespective of how we wish to rationalize the assignments[10] of the latter two absorptions (C_1, C_4 bridgehead *vs.* C_5, C_6 methine protons), the fact that the coupling constants are so small

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[1] (a) Paper X: R. N. McDonald and E. P. Lyznicki, *J. Amer. Chem. Soc.*, **93**, 5920 (1971). (b) Part of this research was communicated in R. N. McDonald and D. G. Frickey, *ibid.*, **90**, 5315 (1968). (c) Taken from the M.S. thesis of D. G. Frickey, 1968, and the Ph.D. thesis of G. M. Muschik, 1972.

[2] (a) J. Dewar, *Proc. Roy. Soc. Edinburgh*, 84 (1866); (b) W. Baker, *Chem. Brit.*, **1**, 191 (1965), discusses Dewar's paper, and some of the efforts to synthesize **1** and its various derivatives.

[3] E. E. van Tamelen and S. P. Pappas, *J. Amer. Chem. Soc.*, **85**, 3297 (1963).

[4] We are aware of only two other literature entries into this family of compounds which incorporate two of the classically considered structures of benzene fused into a single molecule; one is a bridged "Dewar anthracene" reported by Applequist and Searle,[5a] and the second is a report of the 1,2-dimethyl and 1,2,3,4-tetramethyl derivatives of **2**.[5b] The preparation of "hemi Dewar biphenyl," a compound in which the moieties are joined but not fused, has been described by Burt and Pettit.[6]

[5] (a) D. E. Applequist and R. Searle, *J. Amer. Chem. Soc.*, **86**, 1389 (1964); (b) D. T. Carty, *Tetrahedron Lett.*, 4753 (1969).

[6] G. D. Burt and R. Pettit, *Chem. Commun.*, 517 (1965).

[7] M. Avram, I. Dinulescu, M. Elian, M. Farcasiu, E. Marica, G. Mateescu, and C. D. Nenitzescu, *Chem. Ber.*, **97**, 372 (1964).

[8] (a) L. Friedman and F. M. Logullo, *J. Amer. Chem. Soc.*, **85**, 1549 (1963); (b) M. Stiles, R. G. Miller, and U. Burkhardt, *ibid.*, **85**, 1792 (1963).

[9] G. Fraenkel, Y. Asahi, M. J. Mitchell, and M. P. Cava, *Tetrahedron*, **20**, 1179 (1965).

[10] See S. J. Cristol and G. W. Nachtigall, *J. Org. Chem.*, **32**, 3738 (1967), for the assigned nmr spectrum of the related *exo,cis*-5,6-dichlorobicyclo-[2.2.1]hept-2-ene.

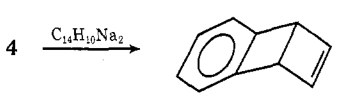
requires the cis,exo relationship of the chlorines in **4**.[11]

The mass spectrum[12] of **4** was correct for a dichloride with the $M^{+\cdot}$, $M^{+\cdot} + 2$, $M^{+\cdot} + 4$ peaks in a ratio of 1:0.625:0.25, which is well within experimental error of the expected ratio since the intensities of these peaks are very small. The base peak is *m/e* 128 and could correspond to the radical cations of naphthalene or "hemi Dewar naphthalene."

Chemical proof of the gross structure of **4** was given by its dehydrohalogenation with potassium *tert*-butylate in *tert*-butyl alcohol to 2-chloronaphthalene in 45% yield. This product was characterized by comparison of its nmr spectrum with that of authentic material.

The next step in this investigation was to examine methods for converting **4** into **2**. Reaction of **4** with methyllithium[13] did not take place and with sodium in 1,2-dimethoxyethane formation of only a small amount of **2** was observed. Treatment of **4** with lithium or sodium in *tert*-butyl alcohol and tetrahydrofuran[14] produced trace to small amounts of **2** along with varying amounts of tetralin, 1,4-dihydronaphthalene, and naphthalene, and, in the case using lithium, a small amount of benzobicyclo[2.2.0]hex-2-ene (**3**).[15]

Finally, it was found that disodium–phenanthrene,[16] a mild dehalogenating reagent, effected the dechlorination of **4** to **2** in 34% yield.[17]



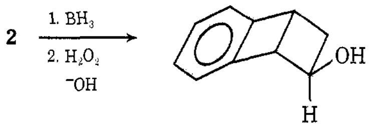
2

The nmr spectrum of **2** (the samples always contain trace to small amounts of naphthalene) exhibited three finely split multiplets at τ 2.95 (aromatic), 3.43 (olefinic), and 5.58 (bridgehead); this spectrum is reproduced in ref 1b. The chemical shift of the olefinic protons is virtually identical with the values reported for the analogous protons (τ 3.45) of bicyclo[2.2.0]hexa-2,5-diene (**1**)[3] and (τ 3.43) benzobicyclo[2.2.1]hepta-2,5-diene (**7**).[10] The bridgehead protons of **2** absorbed 0.58 ppm downfield from those of **1**[3] (τ 6.16) and over 0.8 ppm downfield from those in **7** (τ 6.41, neat).[10]

The ultraviolet spectrum of **2** was not sufficiently different from that of benzocyclobutene[18] to warrant postulation of homoconjugation of the olefinic double bond with the aromatic ring

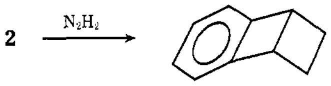
As was previously mentioned, **2** rearranges to naphthalene. The rate constant for this rearrangement was determined in carbon tetrachloride at 38 ± 0.2°, the ambient probe temperature of the nmr spectrometer. A half-life of 3.96 hr and a rate constant of $(4.85 \pm 0.48) \times 10^{-5}$ sec^{-1} were determined for this rearrangement under these conditions.

Hydroboration of **2** followed by reaction of the intermediate borane with basic hydrogen peroxide produced benzobicyclo[2.2.0]hex-5-en-*exo*-2-ol (**8**) in 15% yield (based on **4**). The exo configuration of the 2-hydroxy substituent in **8** is argued for by analogy with the specific exo hydroboration of bicyclo[2.2.0]hex-2-ene[19] and other bicyclic olefins, and the results of spin decoupling of the nmr spectrum of **8**.[20]

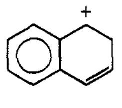


8

To further characterize **2**, it was reduced with diimide to **3**.[17] Attempted glpc of **3** led to rearrangement, with 1,2-dihydronaphthalene and naphthalene as the only observed products. The mass spectrum[22] of **3** showed a large $M^{+\cdot}$ ion (*m/e* 120, relative abundance 79%) with the $M^{+\cdot} - 1$ peak as the base peak. This may involve cleavage of the C_1–C_4 bridge bond with loss of a hydrogen atom to produce benzylic cation **9**. Further loss of a hydrogen atom then leads to *m/e* 128 (relative abundance 72%), the naphthalene or **2** cation radical. The second major process appears to be the loss of $\cdot CH_3$ to an ion *m/e* 115 (relative abundance 74%). A third path of electron impact fragmentation is the loss of ethylene from $M^{+\cdot}$, the product of which may be **10** (*m/e* 102, relative abundance 10%).



3



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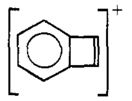

10

The nmr spectrum of **3** (reproduced in ref 1b) consists of an A_2B_2 multiplet for the aromatic protons centered at τ 2.93, a multiplet centered at τ 6.19 for the bridgehead protons, and a complex multiplet between τ 7.33 and 8.28 attributed to the methylene protons. The ultraviolet spectrum of **3** showed that the three large absorptions were shifted to somewhat lower wavelengths than those of **2** and gave a reasonable correspondence to those of benzocyclobutene.[18]

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(11) Cis vicinal coupling constants in four-membered rings are large (4–10 Hz); see F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N. Y., 1969, p 362.

(12) We thank Dr. R. W. Kiser, University of Kentucky, for determination of this mass spectrum on an RMU-6E mass spectrometer.

(13) G. Schroder and T. Martini, *Angew. Chem., Int. Ed. Engl.*, **6**, 806 (1967), reported a 70% yield of 2-chloro-3-fluorobicyclo[2.2.0]hexa-2,5-diene from the reaction of 5,5-dichloro-6,6-difluorobicyclo[2.2.0]hex-2-ene and methyllithium.

(14) P. G. Gassman and P. G. Pape, *J. Org. Chem.*, **29**, 160 (1964).

(15) The components were shown to be present from the nmr spectra of chromatographic fractions of the mixtures.

(16) E. Vogle, H. Kiefer, and W. R. Roth, *Angew. Chem., Int. Ed. Engl.*, **3**, 442 (1964), reported the use of this reagent in a debromination step to produce bicyclo[2.2.0]octa-2,4,7-triene.

(17) This is a minimum yield. The yield of **2** used in a diimide reduction to **3** was 58% assuming a 90% yield in the reduction step.

(18) M. P. Cava and D. R. Napier, *J. Amer. Chem. Soc.*, **80**, 2255 (1958).

(19) R. N. McDonald and C. E. Reineke, *J. Org. Chem.*, **32**, 1878 (1967).

(20) Saturating in the methylene proton (xH_3 and nH_3) region (τ 7.6–7.85) the original methine (nH_2) simplified to a broad singlet. The residual coupling was between H_1 and nH_2 and must be less than $J = 1$ Hz, which establishes the hydroxyl group as exo.[11,21] Saturation in the bridgehead proton (H_1 and H_4) region simplifies the methylene (xH_3 and nH_3) multiplet to a complex doublet due to the remaining germinal coupling, $J_{nH_3} - J_{xH_3}$, a chemical shift difference in xH_3 and nH_3, and cis ($J_{nH_2} - J_{nH_3}$) and trans ($J_{nH_2} - J_{xH_3}$) vicinal couplings. The triplet observed for nH_2 sharpened by saturating at the bridgehead proton region. n and x refer to endo and exo, respectively.

(21) (a) K. B. Wiberg, V. Z. Williams, and L. E. Friedrich, *J. Amer. Chem. Soc.*, **90**, 5338 (1968); (b) K. B. Wiberg and D. E. Barth, *ibid.*, **91**, 5124 (1969).

(22) We thank Dr. R. G. Cooks for determination of this mass spectrum on an MS-9 mass spectrometer.

Experimental Section[23]

Benzenediazonium-2-carboxylate.—This compound was prepared according to the published procedure.[8b] Yields of 33–61% of brown to light buff needles were obtained. The infrared spectrum compared well to that reported.[8b] *Caution:* This compound is explosive when subjected to friction, especially when scraped on hard surfaces.

***exo,cis*-5,6-Dichlorobenzobicyclo[2.2.0]hex-2-ene (4).**—To a solution of 13.2 g (107 mmol) of *cis*-3,4-dichlorocyclobutene[7] in 100 ml of dioxane (distilled from sodium) was added 3.14 g (21.2 mmol) of freshly prepared benzendiazonium-2-carboxylate. The resultant slurry was magnetically stirred at 48–52° under nitrogen until the mixture became homogeneous (3.25–4.5 hr depending on the purity of the benzyne precursor). The solution was dark brown at this point. The dioxane and the *cis*-3,4-dichlorocyclobutene were removed under vacuum using a 33-cm Vigreux column with a maximum pot temperature of 70°, leaving a dark brown viscous residue. This residue was dissolved in about 100 ml of ether and filtered to give a colored solution. The ether was evaporated in a molecular still, and the product was sublimed at room temperature and 0.05 mm from the residue as a white crystalline solid mixed with a light yellow oil. The oil was separated from the solid by rubbing the mixture on a piece of absorbent paper. This afforded 0.48 g (11.3% yield) of crude product. Further purification was effected by subliming half of the total yield at room temperature and 0.05 mm, cleaning the cold finger and continuing the sublimation. The second half of the sublimation was the purer sample (mp ~ 70–79°), which was purified further by repeated sublimations.

The first half was impure and was purified by column chromatography using neutral, activity I Woelm alumina with carbon tetrachloride as an eluent with a fairly fast elution rate. The first few fractions contained the purest product, mp 60–79°, from the chromatography. This was purified further by repeated sublimations. The melting point of the product was 79–79.5° (sealed tube). The nmr, infrared, mass, and ultraviolet [263 nm (log ε 3.19), 267 (shoulder) (3.23), 269 (3.42), and 275.3 (3.44) in cyclohexane] spectra all agreed with the assigned structure.

Anal. Calcd for $C_{10}H_8Cl_2$: C, 60.35; H, 4.02. Found: C, 60.39; H, 4.14.

In several runs of this preparation, various ratios of the *cis*-3,4-dichlorocyclobutene to benzenediazonium-2-carboxylate were used. Table I is a table of these ratios and their respective yields.

TABLE I

Cyclobutene: diazonium salt	Yield of 4, %
3.7:1	7.3
5.5:1	4.5
8.0:1	10.4
4.0:1	10.0
5.0:1	11.3
12.5:1	8.9
1.5:1	2.4

These yields are based on the product sublimed from the crude product mixture with the benzenediazonium-2-carboxylate as the limiting reagent as described in the above procedure.

Dehydrochlorination of *exo,cis*-5,6-Dichlorobenzobicyclo[2.2.0]hex-2-ene.—4 (30 mg, 0.15 mmol) was dissolved in 4.5 ml of *tert*-butyl alcohol (distilled from sodium). To this was added 24 mg (0.6 mg-atom) of potassium and the mixture was heated under reflux overnight. Water (25 ml) was then added and the mixture was extracted with three 25-ml portions of pentane. The pentane extracts were washed with three 100-ml portions of water, dried ($MgSO_4$), and distilled to near dryness. The rest of the solvent was evaporated on a rotary evaporator to give 11 mg (45% yield) of crude 2-chloronaphthalene, mp 35–58° (lit.[24] mp 58°). The nmr spectrum of the product was identical with that of an authentic sample.

Benzobicyclo[2.2.0]hexa-2,5-diene (2).—To a magnetically stirred solution of 2.021 g (11.79 mmol) of phenanthrene in 10 ml of freshly distilled glyme (distilled from calcium hydride and then from lithium aluminum hydride) in a 25-ml, dry, two-necked flask fitted with a rubber septum and a gas inlet was added 0.700 g (30.4 mg-atoms) of sodium at ice bath temperature. (The sodium was cut immediately prior to addition and added quickly so as to present a clean surface to the phenanthrene solution.) After a few minutes of stirring under nitrogen, the solution became very dark green. Thirty minutes was allowed for the reaction of the sodium with the phenanthrene.

The green solution was then recovered from the flask by means of a syringe and charged into a solution of 0.782 g (3.93 mmol) of 4 (75–90% pure) in 10 ml of anhydrous glyme under nitrogen at room temperature in a 50-ml two-necked flask fitted as above. The first few drops were decolorized and a white precipitate formed immediately. After 30 min of stirring under nitrogen, the mixture became brown and never lightened much more during the 1.25-hr reaction time.

The reaction mixture was dissolved in 100 ml of ether, which was washed with four 50-ml protions of water and dried ($MgSO_4$) in the freezer. Evaporation on a rotary evaorator to near dryness gave a yellow, solid residue. Any residual ether or glyme was evaporated by means of an oil pump and collected in a Dry Ice cooled trap. The product was distilled using a trap-to-trap apparatus at room temperature and 0.1–0.2 mm pressure and collected in a trap cooled in liquid nitrogen. The length of time of distillation was determined by stopping when a little of the starting material began to sublime onto the inside of the upper portion of the vacuum adaptor used for the distillation. The yield of the product as a clear, colorless liquid was 171 mg (34%). The unreacted starting material was recovered by subliming about one-fourth to one-third of the residual solid from the distillation and chromatographing the sublimate on basic, activity I alumina with carbon tetrachloride as the eluent.

The nmr and ultraviolet [257.8 nm (shoulder) (log ε 2.75), 263.4 (2.97), 270 (3.12), 276.5 (3.15), 284.5 (2.37), 287 (2.32) in cyclohexane containing *ca.* 5.6% naphthalene impurity] spectra were in agreement with the assigned structure of 2.

Determination of the Kinetics of the Isomerization of 2 to Naphthalene.—A sample of 5–10 mg of 2 was dissolved in 0.2 ml of carbon tetrachloride (distilled from phosphorus pentoxide) to give a 0.17–0.39 *M* solution. Using a capillary tube containing a 10% solution of methylene chloride in carbon tetrachloride as a standard, the amount of 2 present at various times was determined by integration. The nmr spectral absorption corresponding to the τ 3.42 absorption of 2 and the methylene chloride singlet were integrated and a ratio of the areas was obtained. The temperature at which the study was done was 38 ± 0.2°, the ambient probe temperature.

Benzobicyclo[2.2.0]hex-2-ene (3).—A 250-mg (1.26 mmol) sample of dichloride 4 was dechlorinated to 2 using the disodium–phenanthrene complex. Two trap-to-trap distillation fractions were obtained which contain 2 with no apparent naphthalene present. These fractions were dissolved in 5 ml of dry methanol and combined with a yellow, methanolic slurry of dipotassium azodicarboxylate [prepared from 0.630 g (5.43 mmol) of azodicarbonamide[25]] with stirring under nitrogen. To this was slowly added a solution of 0.90 ml of glacial acetic acid dissolved in 5 ml of dry methanol over a 2-hr period at room temperature. The yellow slurry changed to white after a portion of the acid had been added. After stirring under nitrogen for an additional 5 hr, the reaction mixture was transferred to a separatory funnel with 150 ml of ether. The ether layer was separated, washed with eight 60-ml portions of water and 10 ml of saturated, aqueous sodium bicarbonate solution, and dried ($MgSO_4$) in the refrigerator overnight. Evaporation of the ether left a yellow, liquid residue which was trap-to-trap distilled to give 85 mg of 3, bp 25° (0.5–0.8 mm). This represents a 52% overall yield of 3 from 4. The nmr and ultraviolet [262 nm (OD_{max} 0.94), 268 (1.17), 274 (1.28), and 285 (0.89)][26] spectra were in agreement with the assigned structure.

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[23] All melting points were determined on a Kofler hot stage and are corrected. Boiling points are uncorrected. Infrared and ultraviolet spectra were determined on a P-E 137 and Cary 11 spectrophotometer, respectively, while nmr spectra were obtained on a Varian A-60 spectrometer. Gas chromatographic analyses were performed using a F & M Model 500 temperature-programmed gas chromatograph. Microanalyses were done by Galbraith Laboratories.

[24] F. D. Chattaway and W. H. Lewis, *J. Chem. Soc.*, 875 (1894).

[25] J. Thiele, *Justus Liebigs Ann. Chem.*, **271**, 127 (1892).

[26] Extinction coefficients were not determined for this spectrum due to an unknown degree of contamination by naphthalene and binder from tlc from another preparation.

Another preparation of **3** produced enough pure compound by column chromatography for elemental analysis.

Anal. Calcd for $C_{10}H_{10}$: C, 92.26; H, 7.74. Found: C, 92.09; H, 7.74.

Benzobicyclo[2.2.0]hex-5-en-*exo*-2-ol (8).—**4** (150 mg) was converted to **2** as described above. Olefin **2** was immediately transferred to a reaction vessel containing 1 ml of tetrahydrofuran (distilled from $LiAlH_4$) at 5–10°. To this was added 0.45 ml of a 0.45 *M* diborane solution in tetrahydrofuran. After stirring for 1 hr, water was added dropwise to destroy excess diborane followed by 0.1 ml of 3 *N* aqueous sodium hydroxide and 0.1 ml of 30% hydrogen peroxide. Stirring was continued for 1 hr. The reaction mixture was extracted with 20 ml of ether, which was separated and washed with four 5-ml portions of saturated, aqueous brine. The organic layer was dried ($MgSO_4$) at 0°, the ether was removed on a rotatory evaporator, and the liquid residue was chromatographed on activity II, basic alumina to give 17 mg (15% based on **4**) of **8**: ir (neat) 3260, 2950, 1460, 1060, and 745 cm^{-1}; nmr (CCl_4, internal TMS) τ 2.85 (m center, aromatic A_2B_2, 4), 5.75 (t center, C_2H, 1), 6.15 (m center, bridgehead H's, 2), 6.87 (s, OH, 1), and 7.6–7.85 (m, CH_2, 2).

Anal. Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.90. Found: C, C, 81.98; H, 6.81.

Registry No.—**2**, 20847-82-9; **3**, 20847-83-0; **4**, 20902-25-4; **8**, 33905-59-8.

Acknowledgment.—We wish to thank the National Science Foundation (GP-7818, GP-10691) for support of the research and the U. S. Department of Health, Education, and Welfare for an NDEA Title IV Fellowship to G. M. M. (1966–1969).

Synthesis of Angularly Substituted Tetrahydro- and Hexahydrofluorenes[1]

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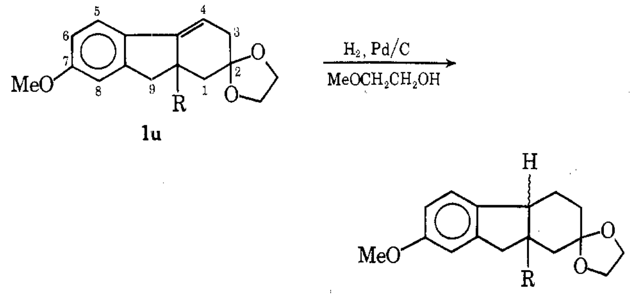
Received June 15, 1971

A series of 7-methoxy-2,2-ethylenedioxy-1,2,3,9a-tetrahydrofluorenes has been synthesized in which the 9a substituent has been transformed from COOEt into CHO, CHNOH, COOLi, COONa, $CONH_2$, CN, and COMe as well as into the previously reported groups COOMe, CH_2OH, and COOH. For each substituent the cis and trans compounds resulting from olefin reduction have been synthesized by routes which establish their stereochemistry. The influence of the stereochemistry at C-4a on the course of reactions at the group attached at C-9a is discussed.

In the hydrogenation of olefins over heterogeneous catalysts, the stereochemistry of reduction has been found to be influenced not only by the bulk of neighboring functional groups but by attractive interactions between certain of these groups and the catalyst surface.[3] These interactions, in contrast to steric effects, are responsible for addition of hydrogen cis with respect to the group involved. Our study of this phenomenon[3] required us to synthesize a series of compounds **1u**, in which the angular group R represented a variety of common functional groups, as well as requiring us to prepare authentic samples of the corresponding cis (**1c**) and trans (**1t**) reduction products.



1u

1c = cis; **1t** = trans

We report here these syntheses, which were accomplished by transformations of the unsaturated carboethoxy compound (**2u**) and which illustrate reactivities and limitations in a system which is both severely crowded and acid sensitive. The results are instructive as to the relative usefulness in such an environment of a number of the existing methods for functional group transformation.

The only cases for which we had already made entire sets consisting of all three compounds (**u**, **c**, and **t**) for a given functional group were carbomethoxy (**3**) and hydroxymethyl (**4**). Since the stereochemistry of each of these materials was unequivocally known,[3] they were in practice the starting or reference points for our synthetic sequences. As these sequences in many instances parallelled each other for our three series of compounds (Schemes I–III) we shall usually discuss the transformations in the unsaturated series as being typical of all three.

We had synthesized the previously reported cis aldehyde (and established its stereochemistry)[4] by oxidation of the *cis*-hydroxymethyl compound **4c** with CrO_3 in pyridine.[5] The same procedure was successful for preparation of **5u** and **5t**; however, yields were consistently poor and we found that greatly improved yields for the entire aldehyde set could be obtained with the procedure employing dicyclohexylcarbodiimide and dimethyl sulfoxide.[6] Treatment of the aldehyde **5u** with hydroxylamine in ethanol proceeded smoothly to give the oxime **6u**.[7]

The unsaturated carboxylic acid **7u** had been produced as previously described[3] from the corresponding ester by saponification. The trans acid could also be obtained by saponification, albeit under more drastic conditions than were required for **2u**, and the stereochemistry of **7t** was thus related unequivocally to the trans series. As none of the reduction methods tried on the unsaturated ester **3u** gave appreciable quantities of cis ester, we could not prepare the cis acid by an analogous saponification. However, metal–ammonia reduction of the acid **7u** provided **7c** in good yield and

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(1) Abstracted in part from the Ph.D. thesis of R. E. N.

(2) NASA Predoctoral Trainee, 1966–1967.

(3) H. W. Thompson, *J. Org. Chem.*, **36**, 2577 (1971).

(4) H. W. Thompson, *ibid.*, **32**, 3712 (1967).

(5) J. Schmidlin and A. Wettstein, *Helv. Chim. Acta*, **45**, 331 (1962).

(6) K. E. Pfitzner and J. G. Moffatt, *J. Amer. Chem. Soc.*, **87**, 5670 (1965).

(7) The same procedure was used to obtain the cis and trans isomers.