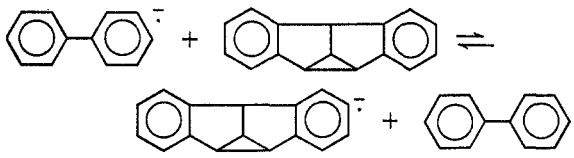
opening and further reduction (or *vice versa*) of the transient radical anion to the dianion **4a** must be extremely facile and irreversible. Thus, in the reaction of sodium biphenyl with **1**, the reaction (eq 1) is driven from left to right by the formation of **4a**. Jagur-

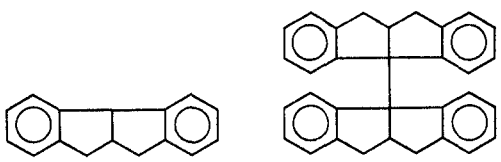


(1)

Grodzinski and Szwarc[19] have recently shown in related systems that equilibria, such as eq 1, greatly favor the radical anion of the hydrocarbon with the higher electron affinity. If biphenyl has a significantly higher electron affinity than **1**, the equilibrium (eq 1) should greatly favor biphenyl radical anion and no overall reaction would be observed in the absence of secondary processes (*e.g.*, formation of **4a**). At −78°, the ring opening must be extremely slow and overall electron transfer from sodium biphenyl to **1** cannot be detected. When an alkali metal mirror was used as the reductant, ring opening occurred even at −78° and must have taken place on the metal surface.

The dianion **4a** is very unstable (significant amounts of **4** were formed only if the reaction was quenched after very short reaction times), possibly because of the close proximity of the two negatively charged centers, and reacts very rapidly, either by proton abstraction from the solvent to give **5a** or by rearrangement to **6a**. Both **5a** and **6a** appear to be converted to **7a**, since quenching with deuterium oxide after long reaction times led to **7** as the only dibenzobicyclo[3.3.0]octadiene isolated. That **7a** is not only more stable than **5a**, but also more accessible kinetically, was demonstrated by the reaction of **2** with potassium *t*-butoxide in hexadeuteriodimethyl sulfoxide (DMSO-d_6), which gave **7** exclusively.

Oxidation of a solution of **7a** with iodine or molecular oxygen gave **2** and the symmetrical dimer **8**. The



7b **8**

dimer must arise by dimerization of the radical **7b**, a one-electron oxidation product of **7a**.

Experimental Section

General.—3,6-Dibenzotricyclo[3.3.0.$0^{2,8}$]octadiene (**1**) and 3,6 dibenzobicyclo[3.3.0]octadiene (**2**) were prepared by the method of Ciganek.[15] 1,2-Dimethoxyethane (DME) was distilled from sodium–potassium alloy and then from sodium benzophenone ketyl directly into the reaction flask. Sodium biphenyl radical anion was prepared by the method of Liggett.[20] Gas–liquid partition chromatographic (glpc) analyses and separations were accomplished with 15% diethylene glycol succinate (DEGS) on Chromosorb W columns.

Reduction of 1 with Sodium Biphenyl.—Dry, prepurified N_2 was bubbled through a solution of 204 mg (1.0 mmol) of **1** in 10 ml of DME in a 25-ml round-bottom flask sealed with a rubber serum stopper for 2 hr at 0°. The desired volume of a 0.3 *M* solution of sodium biphenyl in DME was added *via* a syringe. The solution was stirred at 0° for the desired period of time and then 0.3 ml of water (or D_2O) was added *via* a syringe. The solution was added to 100 ml of ether and the ethereal solution was extracted with 30-ml portions of saturated $NaHCO_3$ and NaCl solutions, dried ($MgSO_4$), and concentrated *in vacuo*. The pure components, **1** and **2**, were isolated by preparative glpc (7 ft × $^3/_8$ in. column packed with 15% DEGS on Chromosorb W, 175°, helium flow of about 600 cm³/min) and identified by comparison of their retention volumes (10,800 and 16,200 cm³, respectively), pmr spectra,[21] and melting points[17,18] with those of the authentic compounds; pmr of **2** (CCl_4) δ 2.6–3.5 (m, 5), 4.6 (d, 1, J = 7 Hz), 7.0–7.5 (m, 8).

Base-Catalyzed Hydrogen–Deuterium Exchange of 2.—To a deoxygenated solution of 103 mg (0.50 mmol) of **2** in 2 ml of DMSO-d_6 was added 66 mg (0.59 mmol) of freshly sublimed potassium *t*-butoxide. The solution was stirred at 25° for 4 hr and then 1.0 ml of D_2O was added. The mixture was extracted with 100 ml of ether. The ethereal solution was washed several times with water, dried ($MgSO_4$), and concentrated *in vacuo*. The pure dibenzobicyclo[3.3.0]octadiene was isolated by preparative glpc (same conditions as above). A pmr spectrum of the pure compound showed the complete disappearance of the hydrogen located at δ 4.6 (the hydrogen at C-5 in **2**). No deuterium incorporation at C-2 and C-8 could be detected by pmr.

Oxidation of 7a.—To a solution of **7a** (prepared from 278 mg (1.36 mmol) of **1** and 2.80 mmol of sodium biphenyl) in 15 ml of DME was added 169 mg (0.67 mmol) of iodine in 5 ml of DME. The solution was stirred at 0° for 20 min and then added to 100 ml of ether. The ethereal solution was extracted with saturated $NaHCO_3$, 10% NaS_2O_3, and saturated NaCl solutions, dried ($MgSO_4$), and concentrated *in vacuo*. The crude product mixture was passed over 40 g of Merck 71707 alumina. Elution with petroleum ether (bp 60–70°) yielded a mixture of **2**, biphenyl, and **8**. Recrystallization of this mixture from methanol gave 84 mg (0.21 mmol, 31%) of **8**: mp 233–235°; pmr ($CDCl_3$) δ 2.3–3.3 (m, 10), 6.8–7.4 (m, 16); mass spectrum *m/e* 205 was the major peak (one-half of that expected for the molecular ion).

Anal. Calcd for $C_{32}H_{26}$: C, 93.66; H, 6.34. Found: C, 93.50; H, 6.45.

Registry No.—**1**, 2199-28-2; **8**, 25244-21-7.

Acknowledgment.—The authors are indebted to Dr. Melvin Hanna of this department for use of his esr equipment.

(19) J. Jagur-Grodzinski and M. Szwarc, *J. Amer. Chem. Soc.*, **91**, 7594 (1969).

(20) L. M. Liggett, *Anal. Chem.*, **26**, 748 (1954).

(21) G. F. Emerson, L. Watts, and R. Pettit, *J. Amer. Chem. Soc.*, **87**, 131 (1965).

Condensation between Homophthalic Acid and *o*-Chlorobenzaldehydes

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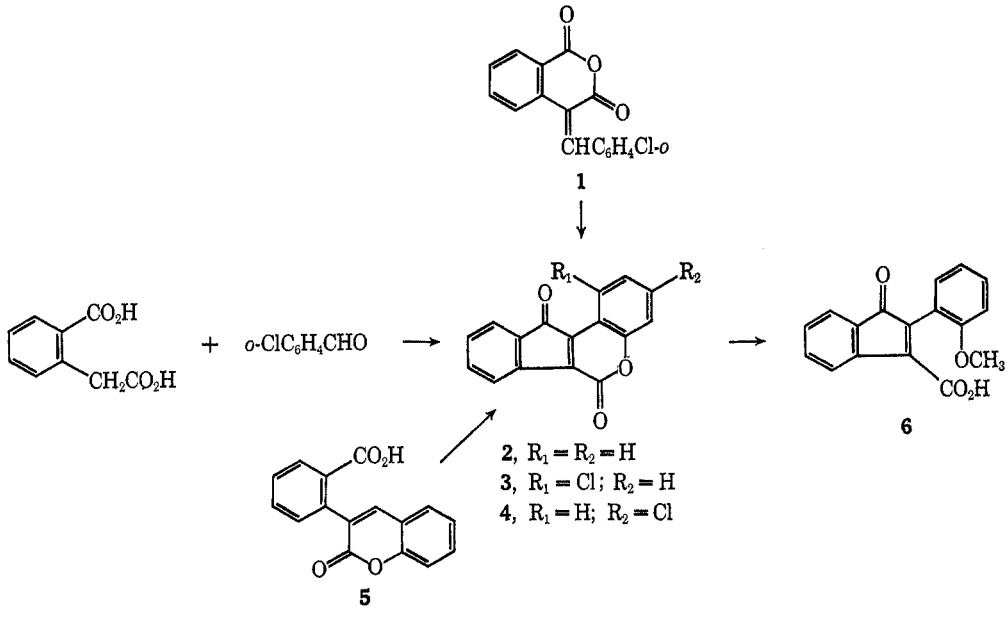
The reaction between homophthalic acid and aromatic aldehydes in the presence of an organic base leads to 4-arylidenehomophthalic anhydrides.[1] During studies of this reaction in these laboratories homophthalic acid and *o*-chlorobenzaldehyde (at 240–250°) in the presence of piperdine unexpectedly gave 2-(2-hydroxyphenyl)indenone-3-carboxylic acid lactone (**2**). Similarly, 2,6-dichlorobenzaldehyde and 2,4-dichlorobenzaldehyde gave **3** and **4**, respectively. Compounds **2**, **3**, and **4** are red crystalline substances subliming at 250–300° (1 atm).

(1) M. Buu-Hoi, *C. R. Acad. Sci.*, **211**, 330 (1940).

SCHEME I



Treatment of 2 with alcoholic potassium hydroxide followed by addition of dimethyl sulfate yielded 2-(2-methoxyphenyl)indenone-3-carboxylic acid (6). The ultraviolet spectra for 2, 3, 4, and 6 were very similar to that of 2-(2-methoxyphenyl)-1,3-indandione.[2] Mass spectral studies of 2 gave a parent peak at *m/e* 248.0471 and a peak at 163.0552 probably arising from destruction of 2 analogous to loss of CO from phenols and carbonyl compounds.[3]

Compound 2 also was formed when 1 or 3-(2-carboxyphenyl)coumarin (5)[4] was heated in the presence of piperidine (Scheme I).

Experimental Section[5]

2-(2-Hydroxyphenyl)indenone-3-carboxylic Acid Lactone (2).—A mixture of *o*-chlorobenzaldehyde (16.8 ml, 0.150 mol), homophthalic acid (18.0 g, 0.100 mol, freshly crystallized, mp 175–177°), and piperidine (4 drops) was heated for 15 min at 180° (internal temperature) and 3 hr at 250°. When the mixture had cooled to 70°, acetone was carefully added until the total volume was about 175 ml. When this mixture had cooled to room temperature, red needles of 2 were collected (12.4 g, 50%, mp 283–285°). The analyzed sample (from 2-methoxyethanol) melted at 286° (with sublimation): ir 1720 (cyclic ketone), 1732 (lactone), 1610 cm^{-1} (conjugated double bond); uv max 470 (ϵ 3100), 348 (2400), 280 (35,000), 263 (24,200, sh), 210 mμ (50,000); mass spectrum *m/e* 248.0471 (theoretical parent peak for $C_{16}H_8O_3$ 248.0473) and 163.0552 (theoretical for $C_{13}H_7$ 163.0548).

Anal. Calcd for $C_{16}H_8O_3$: C, 77.41; H, 3.25. Found: C, 77.59; H, 3.28.

The oxime, red crystals (from 2-methoxyethanol), had mp 276–277°.

Anal. Calcd for $C_{16}H_9NO_3$: C, 73.00; H, 3.45; N, 5.32. Found: C, 72.86; H, 3.75; N, 5.59.

Nitration of 2 (0.50 g, 0.0020 mol) at 0–10° in sulfuric acid (10 ml) was carried out by adding a solution of 0.6 g of potassium nitrate in 5 ml of sulfuric acid during 15 min. The mixture was poured over 25 g of ice and the red-orange precipitate collected. Crystallization from *o*-dichlorobenzene yielded 0.50 g, mp 289–291°.

Anal. Calcd for $C_{16}H_6N_2O_7$: C, 56.81; H, 1.79; N, 8.28. Found: C, 57.07; H, 2.10; N, 8.29.

Compound 2 from 4-(2-Chlorobenzylidene)homophthalic Anhydride and 3-(2-Carboxyphenyl)coumarin (5).—In a typical experiment piperidine (1 drop) and 0.10 g of 1 were heated at 170–180° for 6 hr, yielding 0.06 g (87%) of 2, mp 285° (from 2-methoxyethanol). Mixture melting point with authentic 2 was not depressed.

Methylation of 2 Using Dimethyl Sulfate.—A mixture of 4.96 g (0.200 mol) of 2, 6.48 g (0.120 mol) of potassium hydroxide, and 50 ml of methanol was heated under reflux for 10 min to effect complete opening of the lactone ring, followed by removal of methanol *in vacuo*. The red-orange residue was dissolved in 50 ml of water and cooled to 0–10°; 14 ml of dimethyl sulfate was added over 2 hr in 2-ml portions. After stirring overnight at room temperature, 11.2 g (0.200 mol) of potassium hydroxide was added; the mixture was heated under reflux until the orange oil which separated on standing overnight had disappeared (15 min). Fifty grams of ice and 50 ml of hydrochloric acid were added to the solution and the precipitate containing 6 was collected. Unreacted 2 was separated from 6 by stirring the precipitate with 100 ml of 20% sodium carbonate and acidifying. Crystallization from methanol furnished magenta crystals of 6 (2.1 g, 38%): mp 204–205°; ir 1722 (cyclic ketone), 2500–3300 (carboxylic acid), 1605 cm^{-1} (conjugated carbonyl); uv max 450 (ϵ 1800), 320 (2000, sh), 275 (16,000), 252 mμ (22,000).

Anal. Calcd for $C_{17}H_{12}O_4$: C, 72.85; H, 4.32; O, 22.84. Found: C, 72.90; H, 4.35; O, 22.63.

2-(2-Hydroxy-4-chlorophenyl)indenone-3-carboxylic Acid Lactone (4).—This compound was prepared as described for 2: 25.9 g (91.8%); mp 252–253° (2-methoxyethanol); ir 1730, 1715, 1600 cm^{-1}; uv 460 (ϵ 4400), 287 (41,000), 212 mμ (53,000).

Anal. Calcd for $C_{16}H_7ClO_3$: C, 67.98; H, 2.50; Cl, 12.54. Found: C, 67.96; H, 2.46; Cl, 12.58.

The oxime, red crystals (from *o*-dichlorobenzene), had mp 263–265°.

Anal. Calcd for $C_{16}H_8ClNO_3$: C, 64.55; H, 2.71; Cl, 11.91, N, 4.71. Found: C, 64.58; H, 2.78: Cl, 12.23, N, 4.77.

2-(2-Hydroxy-6-chlorophenyl)indenone-3-carboxylic Acid Lactone (3).—This compound was prepared as described for 2: 14.4 g (51.1%); mp 226–228° (2-methoxyethanol); ir 1725 (broad), 1595 cm^{-1}; uv 428 (ϵ 1150), 334 (2100), 277 (6400), 245 (29,400), 208 mμ (30,000).

Anal. Calcd for $C_{16}H_7ClO_3$: C, 67.98; H, 2.50; Cl, 12.54. Found: C, 68.21; H, 2.65; Cl, 12.50.

Registry No.—Homophthalic acid, 89-51-0; 2, 7703-04-0; 2 oxime, 25109-93-7; 2 nitrate, 25109-94-8;

(2) R. L. Horton and K. C. Murdock, *J. Org. Chem.*, **25**, 938 (1960).

(3) J. H. Beynon, "Mass Spectrometry and its applications to Organic Chemistry," Elsevier, Amsterdam, 1968.

(4) M. Buu Hoi, *C. R. Acad. Sci.*, **218**, 942 (1944).

(5) All melting points are corrected and were determined with a Hershberg melting point apparatus. Ultraviolet spectra were measured in methanol using a Model 202 Perkin-Elmer spectrophotometer, ir spectra were measured as potassium bromide pellets on a Model 21 Perkin-Elmer spectrophotometer, and mass spectra were obtained with a AEI, MS-9 mass spectrometer utilizing a direct probe with source temperature 200°.

3, 25109-95-9; 4, 25109-96-0; 4 oxime, 25158-23-0; 6, 25109-97-1.

Acknowledgment.—The author is indebted to Dr. Ralph Dougherty for assistance in obtaining the mass spectrum and to Miss Florence Kraft and Mr. Marvin Pflaumer for technical assistance.

Synthesis of *cis,cis*-2,6-Dimethyl-*cis*-9-oxabicyclo[5.3.0]decane. A Novel Stereospecific Synthetic Route to Bicyclic Systems Containing *cis*-1,4-Dimethylcycloheptane Rings

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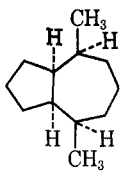
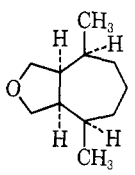
Received January 8, 1970

In a projected synthetic sequence leading to bicyclo[5.3.0]decane systems possessing methyl substituents as formulated in **1**, we wish to report a stereospecific synthesis of **2**, a model heterocyclic analog of **1**.[2]



1



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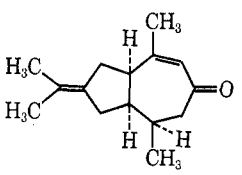
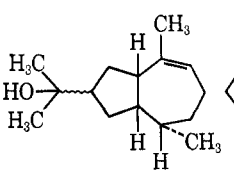


3

At the inception of this research synthetic routes to methyl-substituted bicyclo[5.3.0]decane systems of the type **1** were sought in order to develop a total synthesis of β-vetivone and hinesol. The sesquiterpene β-vetivone had been formulated as **3** in 1941.[3] Hinesol had been converted into the enantiomer of β-vetivone and it was therefore assigned structure **4**.[4]



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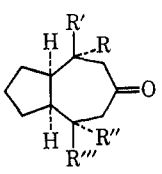

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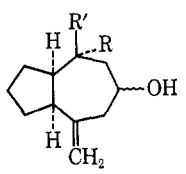


6

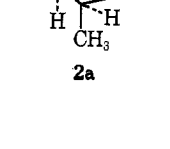
a, R = R″ = CH_3; R′ = R‴ = H **a**, R = CH_3; R′ = H

b, R = R‴ = CH_3; R′ = R″ = H **b**, R = H; R′ = CH_3

c, R′ = R‴ = CH_3; R = R″ = H

(1) (a) Abstracted in part from a thesis presented to the Graduate College of the University of Vermont, Aug 1969, in partial fulfillment of the requirements for the Ph.D. degree; (b) National Aeronautics and Space Administration Predoctoral Traineeship, 1965–1968.

(2) A keto analog **2a** has been prepared by A. P. Krapcho and B. P. Mundy, *J. Org. Chem.*, **32**, 2041 (1967).

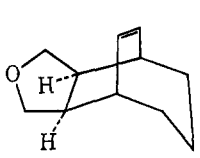


2a

The recent investigations of Marshall and coworkers have necessitated a structural revision of **3** and **4** to spiro[4.5]decane skeletons.[5] The total synthesis of β-vetivone[6] and hinesol[7] has unambiguously supported this structural revision.

Marshall and coworkers have reported a *stereoselective* route to bicyclo[5.3.0]decanes of type **5**.[5] This synthetic sequence leads to methyl isomers. Catalytic hydrogenation of **6a** followed by chromic acid oxidation led to the ketones **5a** and **5b** and a similar reaction sequence on **6b** led to **5b** and **5c**.

The accessibility of compounds such as **7** led us to investigate the stereospecific conversion of the carbon atoms of the double bond into methyl groups to lead to **2**. A route of this type had obvious potential for systems with carbocyclic skeletons.



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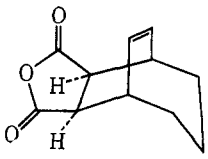
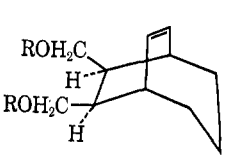


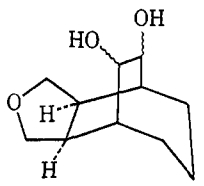
8



9

Results and Discussion

The reaction of cycloheptadiene with maleic anhydride led to the adduct **8** in an excellent yield.[8] This adduct **8** was reduced to the diol **9** (R = H) using lithium aluminum hydride in refluxing 1,2-dimethoxyethane. If the reduction was performed in ether, the formation of the lactone occurred along with the diol **9** (R = H).[9] The diol **9** (R = H) was converted into the cyclic ether **7** by addition of *p*-toluenesulfonyl chloride to a refluxing pyridine solution of the diol.[10] The ether **7** was treated with osmium tetroxide in pyridine to form the osmate ester which was cleaved by (1) a basic mannitol solution or (2) reaction with lithium aluminum hydride to yield a *cis*-diol **10** of undetermined stereochemistry.[11] This *cis*-diol **10** was cleaved to the dialdehyde **11** by reaction with sodium metaperiodate in an aqueous solution.[2,12] Compound **11** was not obtained analytically pure, but the alde-



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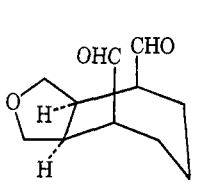
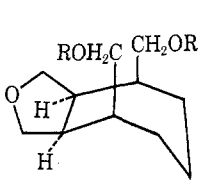


11



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(3) (a) Y. R. Naves and E. Perrottet, *Helv. Chim. Acta*, **24**, 3 (1941); (b) for a summary of the experimental data, see J. L. Simonsen and D. H. R. Barton, "The Terpenes," Vol III, Cambridge University Press, London, 1952, pp 224–232.

(4) I. Yosioka and T. Kimura, *Chem. Pharm. Bull.*, **13**, 1430 (1965).

(5) (a) J. A. Marshall, N. H. Andersen, and P. C. Johnson, *J. Amer. Chem. Soc.*, **89**, 2748 (1967); *J. Org. Chem.*, **35**, 186 (1970); (b) J. A. Marshall and P. C. Johnson, *J. Amer. Chem. Soc.*, **89**, 2750 (1967); *J. Org. Chem.*, **35**, 192 (1970).

(6) J. A. Marshall and P. C. Johnson, *Chem. Commun.*, 391 (1968).

(7) J. A. Marshall and S. F. Brady, *Tetrahedron Lett.*, 1387 (1969).

(8) K. Alder and H. H. Molls, *Chem. Ber.*, **89**, 1960 (1956).

(9) B. E. Cross and J. C. Stewart, *Tetrahedron Lett.*, 3589 (1968).

(10) A. P. Krapcho and B. P. Mundy, *J. Heterocycl. Chem.*, **2**, 355 (1965).

(11) F. D. Gunstone, *Advan. Org. Chem.*, **1**, 103 (1960).

(12) C. A. Bunton, "Oxidations in Organic Chemistry, Part A," K. Wiberg, Ed., Academic Press, New York, N. Y., 1965, Chapter 6.