

concentration. The infrared spectrum of this oil showed absorption at 695 cm^{-1} , characteristic of a monosubstituted phenyl group.⁴⁶ However, there was no evidence for benzoic acid in this acid fraction, as was seen by the infrared spectrum (1460 cm^{-1}).

The neutral fraction was boiled with *n*-hexane and the suspension was filtered on cooling to give 0.09 g. of an unidentified tan solid, m.p. $141\text{--}146^\circ$. The remainder of the neutral fraction (3.03 g.) was chromatographed on 144 g. of ethyl acetate-treated alumina activated by heating at 300° (0.2 mm.) overnight. Elution with *n*-hexane gave 0.34 g. (11% recovery) of XXI, m.p. $88\text{--}89^\circ$. A mixed m.p. with an authentic sample of this chloride showed no depression. Elution with *n*-hexane and with benzene-hexane (5:95) gave 1-phenyl-2,3,6,7-dibenz-2,6,8-cyclo-octatriene (0.88 g., 23% yield, m.p. $83\text{--}84^\circ$). A mixed m.p. with chloromethylenedibenzcycloheptadiene XXI showed m.p. $64\text{--}80^\circ$.

Anal. Calcd. for $\text{C}_{22}\text{H}_{18}$: C, 93.6; H, 6.4. Found: C, 93.0; H, 6.4.

An unidentified compound (0.33 g., 8.8% yield), m.p. $271\text{--}272^\circ$ dec., was obtained by elution with benzene-hexane (10:90). Its molecular weight was 508 to 567 as determined by the Rast method.⁴⁷

Anal. Calcd. for $\text{C}_{44}\text{H}_{36}$: C, 93.6; H, 6.4. Found: C, 92.5; H, 6.1.

A further unidentified product was obtained from a latter fraction eluted with benzene-hexane (10:90). A bright yellow solid, it was found to weigh 0.17 g., m.p. $150\text{--}155^\circ$ dec. The visible spectrum was completely unlike those of the trienes VII and XIX.

Anal. Calcd. for $\text{C}_{18}\text{H}_{14}$: C, 93.2; H, 6.8. Found: C, 92.9; H, 6.1.

Reaction of 9-Chloro-9-chloromethyl-9,10-dihydro-10,10-di-*n*-propylanthracene (XXVIII) with Alcoholic Potassium Hydroxide.—A mixture of 8.15 g. (2.24×10^{-2} mole) of XXVIII and 50 g. of a 10% alcoholic potassium hydroxide solution was shaken for 1.5 hr. at room temperature. The mixture was filtered to give 6.2 g., m.p. $118.5\text{--}120^\circ$, of a white solid. Recrystallization of this solid from absolute ethanol was found to give 5.9 g. (71% yield), m.p. $123\text{--}124^\circ$, of what is probably 9-chloromethyl-9-ethoxy-9,10-dihydro-10,10-di-*n*-propylanthracene. A product, m.p. $123\text{--}124^\circ$, which showed no m.p. depression on admixture with the sample prepared with ethanolic potassium hydroxide was also obtained when the recrystallization of the dichloride XXVIII from ethanol was attempted. The infrared spectrum showed strong absorption at 1082 and 1118 cm^{-1} and no absorption in the hydroxyl or carbonyl stretching regions. The ultraviolet spectrum showed only a modest absorption maximum at approximately $255\text{ m}\mu$, indicative of the presence of unconjugated phenyl rings.

Anal. Calcd. for $\text{C}_{25}\text{H}_{20}\text{OCl}$: C, 77.4; H, 8.2. Found: C, 77.6; H, 8.6.

Alkylation of the Lithium Salt of Anthrone with Methyl Iodide.—A mixture of 3.88 g. (2.00×10^{-2} mole) of anthrone, 0.14 g. (2.00×10^{-2} g.-atom) of lithium and 40 ml. of dry toluene (distilled from sodium) was allowed to reflux overnight under nitrogen. The toluene was distilled under nitrogen, after which a vacuum was applied for 5 min. The deep red colored salt was transferred to a Carius tube and 25 ml. of methyl iodide was added. The tube was swept with nitrogen, sealed and placed in an oven at 130° for 24 hr. The methyl iodide was removed and the above procedure was repeated.

To the resulting solid was added 25 ml. of ether and 20 ml. of Claisen alkali. The insoluble material was filtered and later was added to the Claisen alkali fraction. The ether phase was separated, extracted with additional Claisen alkali and then washed with water. After drying over magnesium sulfate, the ether extract was concentrated to give 1.56 g. of a deep red oil. From the infrared spectrum of this oil it was ascertained that a maximum of 23% yield of 10,10-dimethylanthrone was obtained. The estimate may be high, since the calculation was based on the carbonyl absorption (1662 cm^{-1}) and higher melting compounds with carbonyl absorption of this frequency had been observed in previous attempted methylations of anthrone. Crystallization of the red oil from absolute ethanol was carried out, yielding 0.29 g. (6.5% yield from anthrone) of an orange solid, m.p. $104.5\text{--}105.5^\circ$ (lit.⁴⁸ $99.5\text{--}100.5^\circ$, $102.5\text{--}103^\circ$).³ A mixed m.p. with an authentic sample of 10,10-dimethylanthrone kindly supplied by Dr. N. J. Leonard showed no depression. No other product was isolated.

(46) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., p. 55.

(47) N. D. Cheronis, *Technique of Org. Chem.*, **6**, 211 (1944).

(48) A. J. Kresge, Ph.D. Thesis, University of Illinois, 1954.

URBANA, ILL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF SMITH COLLEGE]

Ring Size in the Dienone-Phenol Rearrangement

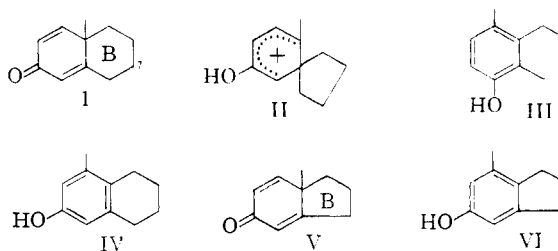
By STANLEY M. BLOOM*

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The synthesis and acid-catalyzed rearrangement under anhydrous conditions of 8-methyl- $\Delta^{4,9,6,7}$ -dihydroindane (V) is reported. The *m*-phenol 7-methyl-5-indanol (VI) is obtained and the significance of this result discussed.

In the acid-catalyzed rearrangement of a number of polycyclic cyclohexadienones,¹ the formation of a *p*-phenol has been shown to proceed *via* a five-membered spiran.^{2a,b} Thus 10-methyl-2-keto- $\Delta^{1,9}$; $3,4$ hexahydronaphthalene (I) rearranges in acidic media to 8-methyl-5-hydroxy-1,2,3,4-tetrahydronaphthalene^{1a} (III) *via* the spiran II. Compound I, on change of solvent³ or by introduction

of a $\Delta^{7,8}$ -double bond into ring B followed by hydrogenation,⁴ has been shown to rearrange *via* a simple 1,2-methyl shift to the *m*-phenol 8-methyl-6-hydroxy-1,2,3,4-tetrahydronaphthalene (IV).



* Children's Cancer Research Foundation, 35 Binney Street, Boston, 15, Mass.

(1) (a) R. B. Woodward and T. Singh, *THIS JOURNAL*, **72**, 494 (1950); (b) H. H. Inhoffen, *Angew. Chem.*, **63**, 297 (1951); (c) C. Herran, O. Mancera, G. Rosenkranz and C. Djerassi, *J. Org. Chem.*, **16**, 899 (1951).

(2) (a) R. B. Woodward, "Perspectives in Organic Chemistry," Interscience Publishers, Inc., New York N. Y., 1956, p. 178; (b) S. M. Bloom, *THIS JOURNAL*, **80**, 6280 (1958).

(3) A. S. Dreiding, W. J. Pummer and A. J. Tomasewski, *ibid.*, **75**, 3159 (1953).

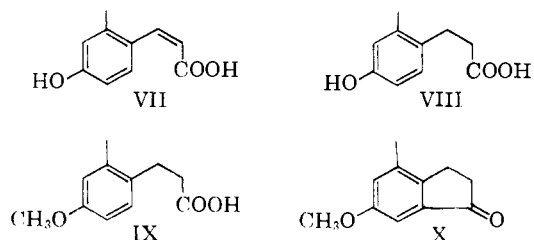
(4) A. Sandoval, L. Miramontes, G. Rosenkranz and C. Djerassi, *ibid.*, **73**, 990 (1951).

Variation of the size of ring B would seem to provide another means of altering the course of the reaction in favor of the *meta* product. If the size of ring B permits the formation of a relatively strainless spiran, the *p*-phenol should result. Conversely, if the size of ring B necessitates the formation of a highly strained spiran, the reaction should take a different course and the *m*-phenol should result.

To test this hypothesis we have synthesized and rearranged 8-methyl-5-keto- $\Delta^{4,9};6,7$ -dihydroindane (V) in which the intermediate spiran, if formed, would be four-membered and highly strained.⁵ The ready isolation of 7-methyl-5-indanol (VI) provides evidence in favor of the above hypothesis.

The 8-methyl-5-keto- $\Delta^{4,9};6,7$ -dihydroindane (V) necessary for this study was synthesized from 8-methyl-5-keto- $\Delta^{4,9}$ -tetrahydroindane⁶ in 23% yield employing selenium dioxide in *t*-butyl alcohol.⁷ Rearrangement of V in acetic anhydride, to which a trace of sulfuric acid had been added, gave an oily acetate. Upon saponification of the oil with ethanolic hydrochloric acid, a phenol, m.p. 83–84°, was isolated in a 25% over-all yield. The compound was identified as 7-methyl-5-indanol by independent synthesis.

2-Methyl-4-hydroxybenzaldehyde⁸ on Doebner condensation with malonic acid gave the expected substituted acrylic acid VII in good yield. Hydrogenation led to β -(2-methyl-4-hydroxyphenyl)propionic acid (VIII), which on methylation gave the acid IX. Cyclization of IX with polyphosphoric acid gave 7-methyl-3-keto-5-methoxyindane (X), which on Clemmensen reduction and cleavage of the resulting phenolic ether provided the desired 7-methyl-5-indanol (VI), m.p. 83–84°. The compound so synthesized was found to be identical with the phenol obtained from the rearrangement of V by comparison of infrared spectra and by mixed melting point determination.



Experimental Part⁹

8-Methyl-5-keto- $\Delta^{4,9};6,7$ -dihydroindane (V).—The method of Yanagita, *et al.*,⁷ was adopted. A mixture of 8-methyl-5-keto- $\Delta^{4,9}$ -tetrahydroindane,⁶ 14.5 g., in 950 ml. of dry *t*-butyl

(5) The Dissertation of D. M. Marquis, Harvard University, 1955, records several attempts to synthesize V before the development of the method used successfully in this work. While the synthesis and rearrangement of 8-acetoxy-1-5-keto- $\Delta^{4,9};6,7$ -dihydroindane is recorded in the dissertation, the presence of the acetoxy group appreciably complicates the conclusions that may be drawn from the data.

(6) E. C. du Feu, F. J. McQuillin and R. Robinson, *J. Chem. Soc.*, 53 (1937), and F. J. McQuillin and R. Robinson, *ibid.*, 1097 (1938).

(7) The procedure of M. Yanagita, S. Inayama, M. Hirakura and F. Seki, *J. Org. Chem.*, **23**, 690 (1958), was utilized.

(8) F. Tiemann and C. Shotten, *Ber.*, **11**, 767 (1878).

(9) All melting points are corrected and boiling points uncorrected. Analyses are by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Ultraviolet absorption spectra were determined in 95% ethanol and infrared spectra in the solvent indicated.

alcohol, 9 ml. of glacial acetic acid and 10.8 g. of selenium dioxide was refluxed under nitrogen for 47 hours. The *t*-butyl alcohol was removed at the water-pump and ether was added. After filtration of the precipitated selenium, the ether filtrate was extracted repeatedly with 5% aqueous sodium hydroxide until only a slight yellow color appeared in the aqueous layer. The ether layer was washed until the water extract was clear, dried over anhydrous sodium sulfate, concentrated and distilled to give V as a pale yellow oil, b.p. 69–70° at 0.65 mm., weight 3.4 g. (23%) which darkened on standing.

Anal. Calcd. for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 80.84; H, 8.58.

The compound possessed an ultraviolet maximum at 244 $m\mu$, $\log \epsilon$ 3.5, and maxima in the infrared at 6.03 and 6.12 μ (unresolved) taken in carbon tetrachloride. The 2,4-dinitrophenylhydrazone on crystallization from absolute ethanol-chloroform and twice from absolute ethanol melted at 127–128.5°.

Anal. Calcd. for $C_{15}H_{18}N_4O_4$: C, 58.53; H, 4.91; N, 17.07. Found: C, 58.80; H, 4.81; N, 17.29.

Rearrangement of 8-methyl-5-keto- $\Delta^{4,9};6,7$ -dihydroindane.—The dienone V, 3.4 g., was dissolved in 40 ml. of acetic anhydride. Concentrated sulfuric acid, 10 drops, and 5 ml. of acetic anhydride, previously mixed, were added with swirling, and the flask was stoppered and allowed to stand at room temperature 5 hours. The reaction mixture was added to 200 ml. of ice-water, allowed to stand in a refrigerator overnight, and extracted twice with ether. The combined ether extract was washed twice with saturated sodium bicarbonate solution, then with brine, dried and concentrated to yield a dark oil weighing 3.4 g. which was refluxed for 6.25 hours in 100 ml. of absolute ethanol and 10 ml. of concd. hydrochloric acid. Three-quarters of the ethanol was removed at the water-pump at 35–40°. Water and dichloromethane were added and the dichloromethane layer was washed with water, dried over anhydrous magnesium sulfate, and concentrated to a heavy oil, weight 2.2 g., at the water-pump at room temperature. The oil was taken into ethyl ether and extracted with 5% aqueous potassium hydroxide.¹⁰ The potassium hydroxide extract was washed with ether, acidified with concd. hydrochloric acid, and the acidified solution extracted with dichloromethane. The dichloromethane extract was washed with water, dried over anhydrous magnesium sulfate, and concentrated at the water-pump at room temperature to give an oil which crystallized completely. The phenol, melting from 72–74°, weighed 850 mg. (25% over-all) which was sublimed at the water-pump at 100°. The sublimate on recrystallization from petroleum ether (b.p. 30–60°)-dichloromethane and resublimation melted from 83–84°.

Anal. Calcd. for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 81.30; H, 8.15.

Synthesis of 7-Methyl-5-indanol.—2-Methyl-4-hydroxybenzaldehyde,⁸ 2.43 g., 3.1 g. of malonic acid, 6 ml. of dry pyridine and 7 drops of piperidine were heated on the steam-bath 2 hours. The reaction was poured into cold dilute hydrochloric acid. On rubbing, a pale yellow crystalline solid was obtained which was collected, washed with water and air-dried. The product VII, weight 1.93 g. (60%), melted from 184–186°. On recrystallization from ethyl acetate-ethanol and then from ethyl acetate, fine pale yellow needles were obtained, m.p. 195–196° dec.

Anal. Calcd. for $C_{10}H_{10}O_3$: C, 67.40; H, 5.66. Found: C, 67.18; H, 5.77.

The acrylic acid VII, 1.93 g., was dissolved in a mixture of 30 ml. of ethyl acetate and 20 ml. of ethanol and hydrogenated at 1.4 atm. for 2 hours over 100 mg. of 10% Pd-C (Baker). After removal of the catalyst and solvent, addition of petroleum ether (b.p. 30–60°) and scratching induced crystallization. The product VIII was separated from a small amount of oil by filtration and washed with petroleum ether (b.p. 30–60°). The β -(2-methyl-4-hydroxyphenyl)propionic acid obtained weighed 1.21 g. (62%) and melted from 92–94°. On recrystallization twice from-cyclohexane-ethyl acetate the compound melted from 99.0–99.5°.

Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.47; H, 6.56.

(10) Extraction with aqueous base would be expected to remove all monomeric phenols obtained from the rearrangement. Both 4-indanol and 5-indanol are soluble in 5% aqueous base.

Methylation of the phenolic acid VIII, 1.21 g., in the usual manner with several portions of sodium hydroxide and dimethyl sulfate gave 1.05 g. (81%) of the methoxy acid IX, m.p. 95.5–98°, which was recrystallized three times for analysis; fine white needles, m.p. 98–99°.

Anal. Calcd. for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27. Found: C, 68.16; H, 7.39.

The methoxy acid IX, 1.00 g., was added to 50 g. of polyphosphoric acid (Victor) and stirred while being heated on the steam-bath. After 2 hours the red polyphosphoric acid solution was allowed to cool and ice-water was added. The reaction was extracted with ethyl ether and the yellow ether layer was washed successively with water, saturated potassium bicarbonate solution and water. The ether layer was dried over anhydrous sodium sulfate and concentrated at the steam-bath to an oil which readily crystallized; 410 mg. (46%), m.p. 88–92° (cloudy melt). For analysis the indanone X was distilled at high vacuum, m.p. 88–93°, then recrystallized from cyclohexane in prisms, m.p. 100–100.5°.

Anal. Calcd. for $C_{11}H_{12}O_2$: C, 74.97; H, 6.86. Found: C, 74.88; H, 6.89.

The purified indanone X, 210 mg., 1 g. of activated mossy zinc, 0.4 ml. of water, 0.8 ml. of concd. hydrochloric acid, one drop of glacial acetic acid and 0.4 ml. of toluene were

refluxed 51 hours. Approximately every 8 hours, 0.8 ml. of concd. hydrochloric acid was added to the reaction. Ethyl ether and water were then added and the ether layer was separated, washed with water, dried over anhydrous sodium sulfate, concentrated and the oily residue was taken up in 2 ml. of glacial acetic acid. Hydrobromic acid (48%), 0.6 ml., was added and the reaction was refluxed 6 hours. Water and ethyl ether were added and the ether layer was washed successively with saturated sodium bicarbonate solution and water. After drying over sodium sulfate the ether was removed on the steam-bath. The remaining oil, weight 142 mg., crystallized on scratching. Purification of the 7-methyl-5-indanol (VI) was effected by sublimation at the water-pump at 100° followed by recrystallization from petroleum ether (b.p. 30–60°)–dichloromethane and resublimation. The compound, m.p. 83–84°, gave on admixture with the phenol obtained from the acid-catalyzed rearrangement of V, m.p. 82.5–84°. The infrared spectra of the synthetic material and the phenol from V taken in carbon disulfide were identical.

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NORTHAMPTON, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

A Study of the Hydroxylation of Olefins and the Reaction of Osmium Tetroxide with 1,2-Glycols

BY NICHOLAS A. MILAS, JOSEPH H. TREPAGNIER,¹ JOHN T. NOLAN, JR.,² AND MILTIADIS I. ILIOPULOS³

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The hydroxylation of trimethylethylene and cyclohexene in *t*-butyl alcohol with hydrogen peroxide in the presence of osmium tetroxide as catalyst has been studied spectroscopically. It has been found that the maximum absorption band due to osmium tetroxide–hydrogen peroxide in *t*-butyl alcohol shifted during hydroxylation from 244 to 286 $m\mu$ with trimethylethylene and 288 $m\mu$ with cyclohexene. These maxima were also observed to occur when osmium tetroxide was allowed to react in *t*-butyl alcohol with vicinal glycols in the absence of hydrogen peroxide. In the presence of excess hydrogen peroxide these maxima shifted back to the maximum of osmium tetroxide–hydrogen peroxide mixture. It has been concluded that the maxima at 286–288 $m\mu$ are due to complexes between osmium tetroxide and the glycols. These complexes were also studied by means of paper chromatography and in the case of ethylene glycol and pinacol they were actually detected and separated.

Introduction

The stereospecificity of hydroxylation of carbon-carbon double bonds with osmium tetroxide alone or in the presence of oxidizing agents such as chlorates or hydrogen peroxide is well known.⁴ This fact led Criegee⁵ to support the original Wagner-Böeseken^{6,7} hypothesis in which osmium tetroxide is used either as a hydroxylation agent or as a catalyst of hydroxylation. Some evidence, however, seems to be at variance with this view. Hofmann⁸ reported that the solubility of potassium chlorate in water was increased in the presence of osmium tetroxide, and the oxidation potential of the solution was greater than that of each of the components alone. This seems to indicate that a complex is formed between the chlorate and osmium

tetroxide. In a study of the kinetics of hydroxylation of maleic and fumaric acids using osmium tetroxide and chlorates, Zelikoff and Taylor⁹ found that the reactive species was a complex between osmium tetroxide and the unsaturated compound, the subsequent step of the formation of the glycol being very rapid. The complex postulated was not entirely in agreement with the Wagner-Böeseken hypothesis.

The hydroxylation of olefins with hydrogen peroxide using osmium tetroxide as a catalyst was originally studied by Milas and co-workers¹ who made the suggestion that the reactive species might be peroxyosmic acid which breaks down to give hydroxyl groups which in turn add to the double bonds to form 1,2-glycols. This view, however, is not entirely consistent with the experimental results of the present investigation. It is well known that osmium tetroxide forms a weak acid, H_2OsO_5 , with water, and it is quite possible that in the presence of hydrogen peroxide, which is a stronger acid than water, it may form a highly unstable peroxyosmic acid, H_2OsO_6 . This peroxyosmic acid is highly unstable in water and breaks spontaneously and exothermically into

(1) From Ph.D. Thesis, M.I.T., July, 1939.

(2) From Ph.D. Thesis, M.I.T., May, 1955.

(3) U. S. Public Health Service Research Associate, 1957 to date.

(4) N. A. Milas, Chapter 37 in "The Chemistry of Petroleum Hydrocarbons," edited by B. T. Brooks, *et al.*, Reinhold Publishing Corp., New York, N. Y., 1955.

(5) R. Criegee, *Ann.*, **522**, 75 (1936).

(6) G. Wagner, *Ber.*, **21**, 1230, 3343, 3347 (1888); **23**, 2307 (1890); **27**, 1636 (1894).

(7) I. Böeseken, *Rec. trav. chim.*, **41**, 199 (1922).

(8) K. A. Hofmann, O. Ehrhart and O. Schneider, *Ber.*, **46**, 1657 (1913).

(9) M. Zelikoff and H. A. Taylor, *THIS JOURNAL*, **72**, 5039 (1950).