tures of VII with V and VI are represented in Figs. 1 and 2. In the case of mixtures of V and VI, compositions of 14.6, 34.3, 51.0, 59.9 and 75.0% in the (+)-isomer VI corresponded to melting ranges of, respectively, 98.5–113, 98.5–105, 98–101, 98.5–100 and 98.5–113°.

NEW YORK 53, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE RICE INSTITUTE]

Synthetic Routes to 3,6-Dimethoxyphenanthrene

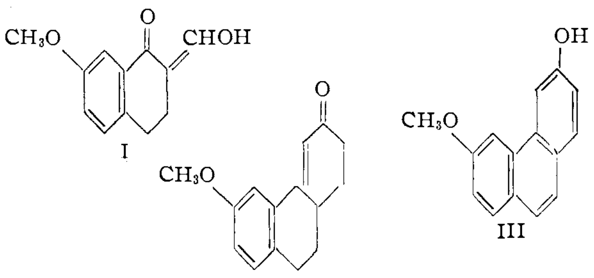
BY RICHARD B. TURNER, DONALD E. NETTLETON, JR., AND R. FEREBEE

RECEIVED JULY 9, 1956

A practical synthesis of 3,6-dimethoxyphenanthrene from readily available starting materials has been developed. The procedure involves condensation of 7-methoxytetralone-1 with ethyl formate, and reaction of the resulting hydroxymethylene derivative with methyl vinyl ketone. Cyclization of the Michael adduct, and dehydrogenation of the 3-keto-6-methoxy-1,2,3,9,10,10a-hexahydrophenanthrene thus obtained, gives 3,6-dihydroxyphenanthrene monomethyl ether, which is converted into the dimethyl ether by standard procedures. In the course of this investigation an anomalous reaction between 2-hydroxymethylene-7-methoxytetralone-1 and β-chlorovinyl methyl ketone was observed. The structure of the reaction product has been established, and the mechanism of its formation is discussed.

In connection with other work being carried out in this Laboratory, a satisfactory method for the preparation of 3,6-dimethoxyphenanthrene was desired. This substance was first obtained by Fieser[1] by stepwise sulfonation of phenanthrene, followed by alkali fusion of the resulting mixed disulfonic acids, and separation of the various dihydroxyphenanthrene isomers by fractional crystallization of the corresponding diacetates. The 3,6-diacetate obtained in this way, after saponification and methylation, afforded 3,6-dimethoxyphenanthrene, m.p. 104–105°. Although this process is reasonably direct, the over-all yield is low (about 12%), and the fractionation procedure is tedious, particularly when carried out on large scale. The only other preparation of 3,6-dimethoxyphenanthrene recorded in the literature is that of Tatevosyan, Zagorets and Vardanyan,[2] who obtained 3-keto-6-methoxy-1,2,3,9,10,10a-hexahydrophenanthrene (II) by a lengthy synthesis starting with *p*-methoxyphenylethyl bromide, and submitted this material to sulfur dehydrogenation and methylation. The Russian procedure, which appeared after our own experiments had been completed, is considerably longer than the original Fieser method and offers no significant improvement in over-all yield.

The synthesis described in the present paper also involves 3-keto-6-methoxy-1,2,3,9,10,10a-hexahydrophenanthrene as an intermediate, but employs as starting material 7-methoxytetralone-1, which is readily accessible from γ-4-anisylbutyric acid[3] by Friedel–Crafts cyclization in the presence of stannic chloride.[4] Attempts to effect condensation of this compound with 4-diethylaminobutanone-2, or with the corresponding methiodide, according to the general Robinson procedure,[5] showed little promise, and direct condensation of 7-methoxytetralone-1 with methyl vinyl ketone in the presence of various basic catalysts was without avail. The methoxytetralone was therefore converted into the corresponding 2-hydroxymethylene derivative I, which was added directly, without purification, to methyl vinyl ketone. Condensation proceeded smoothly in the presence of catalytic amounts of triethylamine, and the resulting Michael adduct, on treatment with base, furnished 3-keto-6-methoxy-1,2,3,9,10,10a-hexahydrophenanthrene (II), m.p. 112°, in an over-all yield of 89% from 7-methoxytetralone-1. An alternate, though less satisfactory, route to II involved the preparation of 2-piperidinomethyl-7-methoxytetralone-1, and condensation of this product with ethyl acetoacetate, followed by hydrolysis, decarboxylation and cyclization in a mixture of acetic acid and concentrated hydrochloric acid.



Dehydrogenation of II was accomplished readily in refluxing α-methylnaphthalene in the presence of a palladium–charcoal catalyst, and 3-hydroxy-6-methoxyphenanthrene m.p. 136°,[6] was obtained in a yield of 74%. The latter product, on methylation with dimethyl sulfate, gave the desired 3,6-dimethoxyphenanthrene, m.p. 105.5°, which proved to be identical in all respects with a comparison sample prepared by the method of Fieser.[1]

In 1953 Hills and McQuillin[7] observed that 2-methylcyclohexanone condenses with β-chlorovinyl ethyl ketone to yield, after β-elimination and cyclization, 1,10-dimethyl-2-keto-2,5,6,7,8,10-hexahydronaphthalene (IV), of interest in connection with syntheses in the santonin series. With regard to the synthesis of 3,6-dimethoxyphenanthrene, the possibility was thus presented that the reaction of

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[1] L. F. Fieser, THIS JOURNAL, **51**, 2471 (1929).

[2] G. T. Tatevosyan, P. A. Zagorets and A. G. Vardanyan, *Zhur. Obshcheĭ Khim.*, **23**, 941 (1953).

[3] R. D. Haworth and G. Sheldrick, *J. Chem. Soc.*, 1950 (1934).

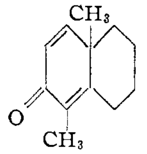
[4] W. E. Bachmann and W. J. Horton, THIS JOURNAL, **69**, 58 (1947).

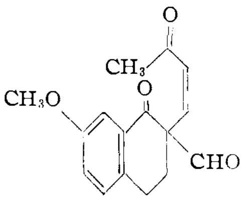
[5] E. C. du Feu, F. J. McQuillin and R. Robinson, *J. Chem. Soc.*, 53 (1937).

[6] Tatevosyan, Zagorets and Vardanyan (ref. 2) report a melting point of 125° for this substance.

[7] P. R. Hills and F. J. McQuillin, *J. Chem. Soc.*, 4060 (1953).

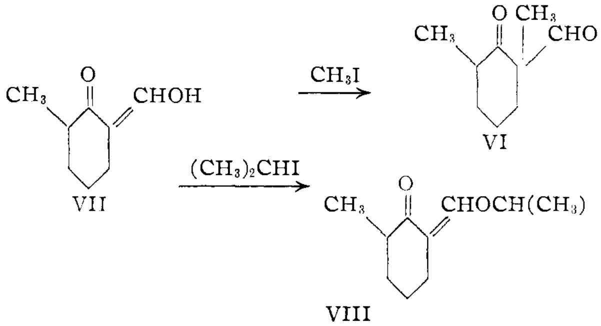
2-hydroxymethylene-7-methoxytetralone-1 (I) with β-chlorovinyl *methyl* ketone might yield an intermediate V, capable of direct conversion into the 9,10-dihydro derivative of III, assuming that prior cleavage of the vinylogous β-diketone system could be avoided. A methanol solution of 2-hydroxymethylene-7-methoxytetralone-1 (I) containing triethylamine was accordingly treated with β-chlorovinyl methyl ketone at 0°. Under these conditions an extremely insoluble crystalline product was obtained which melted at 212° dec. and showed two bands in the carbonyl region of the infrared at 1696 cm.$^{-1}$ and at 1677 cm.$^{-1}$.


IV


V

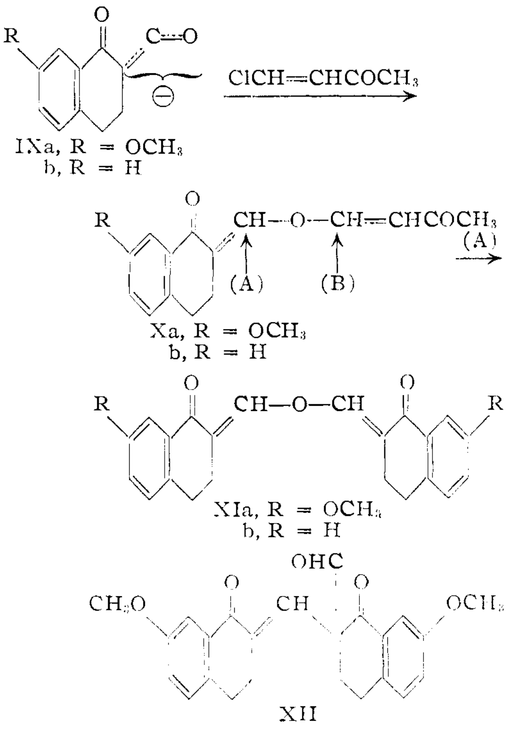
Carbon–hydrogen analyses were consistent with the formula $C_{24}H_{22}O_5$, and the chemical behavior of the substance was incompatible with structure V, or with any structure reasonably derivable from it. Thus, the material absorbed two molar equivalents of hydrogen on catalytic hydrogenation and furnished a tetrahydro derivative, m.p. 126–127°, the infrared spectrum of which possessed a single band in the carbonyl region (1678 cm.$^{-1}$) and no absorption attributable to a hydroxyl group. The tetrahydro derivative proved to be very unstable and on warming was converted into a red oil, from which no identifiable material could be isolated. A product, $C_{22}H_{18}O_3$, m.p. 223–224° dec., ν_{max} 1697, 1679 cm.$^{-1}$, possessing properties analogous to those of the methoxylated derivative, m.p. 212° dec., was also obtained by condensation of 2-hydroxymethylenetetralone-1 with β-chlorovinyl methyl ketone.

In attempting to account for the radically different nature of products obtained by condensation of I with methyl vinyl ketone on the one hand, and with β-chlorovinyl methyl ketone on the other, it appeared that steric factors, which play an important role in the Michael reaction,[8] might well be involved. Thus, increased hindrance of the α,β-unsaturated ketonic system resulting from β-substitution could reasonably be expected to suppress attack at carbon atom 2 of the hybrid anion IX, in favor of reaction at the relatively less hindered oxygen atom. In this connection it should be noted that an effect of this type has, indeed, been observed in a somewhat analogous case involving alkylations of 2-hydroxymethylene-6-methylcyclohexanone (VII) with methyl iodide and with isopropyl iodide, respectively.[9]



Whereas, alkylation with isopropyl iodide gives 2-isopropoxymethylene-6-methylcyclohexanone (VIII) in 80% yield, reaction of VII with methyl iodide gives material that appears to consist largely of the product of C-alkylation VI.

To the extent that this phenomenon is important in the reaction of 2-hydroxymethylene-7-methoxytetralone-1 with β-chlorovinyl methyl ketone, an intermediate Xa would result, which is capable of further reaction with the hydroxymethylenetetralone anion IXa in either of the senses, (A) or (B), indicated.



Both modes of attack are subject to hindrance by β-substitution of the particular conjugated carbonyl system involved and it may therefore be supposed that addition of the second anion will occur through oxygen as before. Since reaction at (B), followed by β-elimination, results in exchange of oxymethylenetetralone groupings, a net change can be brought about only by attack at (A). Such a reaction, followed by β-elimination of the formylacetone anion, would furnish a product of structure XIa, which satisfactorily accounts for all of the properties of the substance obtained experimentally. In this connection the following points are of special relevance.

1. The analytical results obtained for products derived from 2-hydroxymethylene-7-methoxytetralone-1 and from 2-hydroxymethylenetetralone-1 differ by the elements $C_2H_4O_2$, which clearly repre-

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[8] P. L. de Benneville, D. D. Clagett and R. Connor, *J. Org. Chem.*, **6**, 690 (1941); R. Connor and W. R. McClellan, *ibid.*, **3**, 570 (1938).

[9] W. S. Johnson and H. Posvik, THIS JOURNAL, **69**, 1361 (1947).

sent *two* methoxyl groups and hence the presence of two tetralone nuclei.

2. Hydrolysis of XIa yields a mixture of 7-methoxytetralone-1 and 2-hydroxymethylenetetralone-1, an observation that is consistent with the proposed structure. Furthermore, it has been shown that reaction of the condensation product with acetic anhydride and triethylamine affords 2-acetoxymethylene-7-methoxytetralone-1, identical in all respects with an authentic sample prepared by direct acetylation of I. The yield of acetate derived from XIa was 84% based upon the assumed structure.

3. The infrared spectra of XIa and XIb show no absorption in the carbonyl region corresponding to that of an aldehyde function (1740–1720 cm.$^{-1}$), and no absorption band characteristic of the C–H stretching vibration of the aldehyde group[10] is observed in the vicinity of 2720 cm.$^{-1}$ in either case. The appearance of two carbonyl bands (1696 and 1677 cm.$^{-1}$) in the spectrum of XIa (*cf.* also XIb) can be attributed to symmetry factors, and it should be noted that similar doublets occur in the spectra of anhydrides,[11] of which XIa and XIb are vinylogous examples.

4. The alternate structure XII is excluded by the infrared evidence, and by the observation, referred to previously, that catalytic hydrogenation affords a tetrahydro derivative, which does not possess a hydroxyl group. The latter result is clearly consistent with structure XIa, but finds no plausible explanation in terms of formulation XII.

A definitive argument in favor of XIa can finally be given on the basis of the ultraviolet absorption data shown in Fig. 1.

Compound XII contains two essentially isolated chromophores and should thus show ultraviolet absorption approximating that of the composite curve C, obtained from an equimolar mixture of 7-methoxytetralone-1 and 2-isopropoxymethylene-7-methoxytetralone-1. On the other hand, the absorbing system present in XIa consists of two identical chromophores of the 2-isopropoxymethylene-7-methoxytetralone-1 type. Hence, apart from certain disturbances resulting from crossed conjugation through the central oxygen atom, the spectrum of XIa (curve A), should resemble that of 2-isopropoxymethylene-7-methoxytetralone-1 with absorption intensity enhanced by a factor of two (curve B).

In connection with the mechanism proposed for the formation of XIa, it is of interest to note that the four carbon unit represented by β-chlorovinyl methyl ketone does not appear in the product, although involvement of this substance in the intermediate steps is assumed. Support for this hypothesis is found in the observation that no reaction occurs when 2-hydroxymethylene-7-methoxytetralone-1 is treated with triethylamine alone, the tetralone being recovered unchanged from the reaction mixture. Formation of XIa, is, however, observed when equimolar quantities of I and of the corresponding tosyl derivative are allowed to react in the presence of triethylamine, and small amounts of XIa are obtained when the hydroxymethylenetetralone is allowed to stand for prolonged periods in contact with half an equivalent of sodium methoxide. The mechanisms of the latter transformations are straightforward and require no special comment.

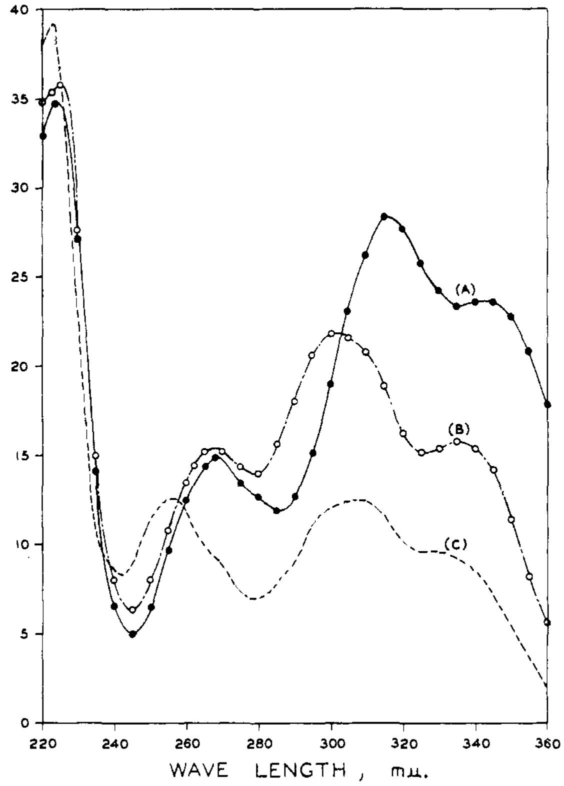

Fig. 1.—Ultraviolet absorption spectra: A, compound XIa; B, isopropoxymethylene-7-methoxytetralone-1 (plotted with double intensity); C, absorption spectrum for an equimolar mixture of 7-methoxytetralone-1 and 2-isopropoxymethylene-7-methoxytetralone-1.

Experimental[12]

Preparation of 2-Hydroxymethylene-7-methoxytetralone-1 (I).—Ethyl formate (12.0 ml.) was added with stirring to a suspension of alcohol-free sodium methoxide (prepared from 2.1 g. of sodium) in 50 ml. of anhydrous benzene. After 0.5 hour at room temperature, the mixture was cooled in an ice-bath, and the air in the reaction vessel was displaced by a slow stream of dry nitrogen. A solution of 5.0 g. of 7-methoxytetralone-1[4] in 75 ml. of dry benzene was then added dropwise over a period of 1 hour, and the reaction mixture was stirred at room temperature for an additional hour, during which time the sodium salt of I separated as a flocculent precipitate. The reaction mixture was finally cooled and acidified with cold, dilute sulfuric acid. The benzene layer was washed with water, and extracted repeatedly with 2 *N* potassium carbonate solution. Acidification of the alkaline extracts and ether extraction gave 5.8 g. (quantitative yield) of a crude oil that crystallized on standing at 0°. Recrystallization of this material from ether furnished a pure sample (3.3 g., 57%) of 2-hydroxymethylene-7-methoxytetralone-1 as pale yellow needles, m.p. 33–34°, λ_{max} 223, 259, 315, 367 mμ; ϵ 14,100, 5,700, 6,000, 10,400. The total crude product was sufficiently pure for further operations, and was normally employed directly for condensation with methyl vinyl ketone without recrystallization.

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[10] A. Pozefsky and N. D. Coggeshall, *Anal. Chem.*, **23**, 1611 (1951).

[11] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, New York, N. Y., 1954 p. 110.

[12] All melting points are corrected. Microanalyses were carried out by S. M. Nagy, M.I.T.

Anal. Calcd. for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found: C, 70.30; H, 6.06.

Preparation of 2-Piperidinomethyl-7-methoxytetralone-1.—A solution containing 3.0 g. of 7-methoxytetralone-1, 3.0 g. of piperidine hydrochloride and 0.9 g. of paraformaldehyde in 25 ml. of isoamyl alcohol was treated with two drops of concentrated hydrochloric acid and heated to reflux temperature in a nitrogen atmosphere for 30 minutes. The reaction mixture was then cooled, poured into dilute hydrochloric acid and washed with ether. The aqueous phase was finally made basic with sodium carbonate, and the product was extracted into ether. Removal of the solvent gave 3.0 g. (65%) of material, which, after recrystallization from methanol, furnished white needles, m.p. 79–80°.

Anal. Calcd. for $C_{17}H_{23}O_2N$: C, 74.69; H, 8.48; N, 5.12. Found: C, 74.67; H, 8.47; N, 5.06.

The **methiodide** was obtained by treatment of an ethereal solution of 1.0 g. of free base with 2.5 ml. of methyl iodide at room temperature. The quaternary salt precipitated in nearly quantitative yield and was recrystallized from isopropyl alcohol; m.p. 147–148°.

Anal. Calcd. for $C_{18}H_{26}O_2NI$: C, 52.05; H, 6.31; N, 3.37. Found: C, 51.85; H, 6.48; N, 3.41.

Preparation of 3-Keto-6-methoxy-1,2,3,9,10,10a-hexahydrophenanthrene (II). Procedure A (from 2-Hydroxymethylene-7-methoxytetralone-1).—A mixture of 4.9 g. of the crude hydroxymethylenetetralone (I) (prepared as described above) and 2.58 g. of methyl vinyl ketone (dried over anhydrous sodium sulfate and freshly distilled) was cooled to 0° and treated with 5 drops of triethylamine. The reaction mixture was cooled in ice for 1 hour and then allowed to stand at room temperature for 3 days. At the end of this time, the mixture was taken up in ether, washed repeatedly with sodium carbonate to remove unchanged starting material, and evaporated to dryness. A solution of the crude oily product (6.5 g.) in 200 ml. of methanol and 200 ml. of water containing 4.0 g. of potassium hydroxide was refluxed under nitrogen for 8 hours, and was finally cooled, diluted with water and extracted with ether. Removal of the solvent, followed by crystallization from di-*n*-butyl ether, or from methanol, gave 4.9 g. (89%) of 3-keto-6-methoxy-1,2,3,9,10,10a-hexahydrophenanthrene (II), m. p. 111–112°, λ_{max} 223, 294, 332(i)mμ; ϵ 13,600, 18,000, 7500.

Anal. Calcd. for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.68; H, 7.02.

The **semicarbazone** prepared as a derivative was crystallized from isoamyl alcohol; m.p. 226–228°.

Anal. Calcd. for $C_{16}H_{19}O_2N_3$: C, 67.34; H, 6.71. Found: C, 67.09; H, 6.59.

Procedure B (from 2-Piperidinomethyl-7-methoxytetralone-1 Methiodide).—A solution of the sodio derivative of ethyl acetoacetate, prepared from 0.28 g. of sodium and 1.50 g. of ethyl acetoacetate in 60 ml. of absolute ethanol, was cooled to 0°, and 3.35 g. of 2-piperidinomethyl-7-methoxytetralone-1 methiodide was added. The reaction mixture was heated on the steam-bath for 1 hour, at the end of which time an additional 0.23 g. of sodium was added. Refluxing was continued for an additional 2 hours, and the solution was then diluted with water and extracted with ether and benzene. Removal of the solvents gave an oil, which was taken up in a mixture of 7.5 ml. of acetic acid, 0.7 ml. of water and 3.5 ml. of concentrated hydrochloric acid, and refluxed overnight in a nitrogen atmosphere. Dilution with water and ether extraction furnished a dark oil that crystallized on trituration with ether. Recrystallization from ether–petroleum ether gave 0.6 g. (33%) of a compound identical in all respects with the product obtained in procedure A.

Preparation of 3-Hydroxy-6-methoxyphenanthrene (III).—A mixture of 5.0 g. of 3-keto-6-methoxy-1,2,3,9,10,10a-hexahydrophenanthrene (II) and 1.0 g. of 10% palladium-on-charcoal in 40 ml. of α-methylnaphthalene was heated to reflux temperature (240°) for 8 hours, during which time a slow stream of nitrogen was passed through the solution. The mixture was then diluted with ether, filtered and subjected to steam distillation until all of the α-methylnaphthalene had been removed. The methoxyphenanthrol was finally isolated by ether extraction and was crystallized from methylene chloride. In this way 3.7 g. (74%) of product was obtained, m.p. 135–136°, λ_{max} 238(i), 248, 255, 279(i), 286, 303, 331, 346 mμ; ϵ 28,500, 35,800, 38,400, 14,400, 15,000, 9,400, 800, 1200.

Anal. Calcd. for $C_{15}H_{12}O_2$: C, 80.33; H, 5.52. Found: C, 80.45; H, 5.29.

Preparation of 3,6-Dimethoxyphenanthrene.—3-Hydroxy-6-methoxyphenanthrene (3.0 g.) was dissolved in 40 ml. of methanol containing 0.8 g. of potassium hydroxide. Dimethyl sulfate (7.0 g.) was then added dropwise with stirring, the temperature of the reaction mixture being maintained between 25 and 35° by occasional cooling. Additional alkali was added from time to time during the addition of the dimethyl sulfate to keep the solution basic.

The reaction mixture was finally diluted with water and extracted with ether. The ether was then evaporated, and the residual material was taken up in benzene and decolorized by passage through a short alumina column. Removal of the solvent gave a quantitative yield of white, crystalline material, which on recrystallization from ether–petroleum ether afforded a first crop (81%), melting sharply at 105.5°, λ_{max} 235, 240, 248, 255, 287, 304, 347 mμ; ϵ 33,800, 35,400, 45,000, 47,000, 20,000, 12,300, 1,600. Additional material could be obtained from the mother liquors. The product did not depress the melting point of an authentic specimen of 3,6-dimethoxyphenanthrene, prepared by the method of Fieser,[1] and the infrared spectra of the two samples were indistinguishable.

Preparation of β-Chlorovinyl Methyl Ketone.—The procedure employed for the synthesis of β-chlorovinyl methyl ketone was based on that reported by Catch, Elliott, Hey and Jones,[13] but involved several modifications. Aluminum chloride (228 g.) was suspended in 500 ml. of petroleum ether (b.p. 20–40°) in a 3-neck flask equipped with a mechanical stirrer, dropping funnel and gas inlet tube extending below the surface of the solvent. The mixture was cooled in a salt–ice-bath, and 122 g. of acetyl chloride was added dropwise with stirring. Vinyl chloride was then passed into the suspension for 1.25 hours, and the reaction mixture was finally poured onto ice. Ether was added, and the organic layer was thoroughly washed with saturated potassium bicarbonate solution, dried, and distilled under reduced pressure. The product passed over as a colorless liquid, b.p. 55° (90 mm.), which solidified when the receiver was cooled to about −20°, yield 60%. β-Chlorovinyl methyl ketone can be stored for several months in the solid form and, although it turns black after about a week, most of the product can be recovered by distillation.

Reaction of 2-Hydroxymethylene-7-methoxytetralone-1 (I) with β-Chlorovinyl Methyl Ketone.—A solution of 11.0 g. of 2-hydroxymethylene-7-methoxytetralone-1 in 150 ml. of methanol was cooled to 0°, and 11.0 g. of β-chlorovinyl methyl ketone and 15.4 ml. of triethylamine (sufficient to neutralize the hydrogen chloride liberated) were added. Crystalline material began to separate after a few minutes, and after standing overnight the product XIa was collected and recrystallized from chloroform–ethanol; yield, 8.4 g. (79%) m.p. 211–212° dec., λ_{max} 224, 270, 316, 340 mμ; ϵ 33,800, 14,600, 27,600, 22,800. The substance showed bands at 1696 cm.$^{-1}$ and at 1677 cm.$^{-1}$ in the infrared.

Anal. Calcd. for $C_{24}H_{22}O_5$: C, 73.83; H, 5.68. Found: C, 73.72; H, 5.71.

Reaction of 2-Hydroxymethylenetetralone-1 with β-Chlorovinyl Methyl Ketone.—2-Hydroxymethylenetetralone-1 (6.5 g., prepared as previously described for the corresponding 7-methoxy derivative) in 20 ml. of methanol was treated with 9.0 g. of β-chlorovinyl methyl ketone and 9.2 g. of triethylamine according to the procedure of the preceding experiment. Recrystallization of the crude product from methylene chloride–methanol furnished 5.5 g. (89%) of XIb, m.p. 223–224° dec., λ_{max} 264, 326 mμ; ϵ 15,800, 22,200; ν_{max} 1697, 1679 cm.$^{-1}$.

Anal. Calcd. for $C_{22}H_{18}O_3$: C, 79.98; H, 5.49. Found: C, 79.67; H, 5.48.

Catalytic Hydrogenation of XIa.—The hydrogenation of 390 mg. of XIa in 20 ml. of dioxane in the presence of 25 mg. of 10% palladium-on-charcoal proceeded with the absorption of 2 molar equivalents of hydrogen and was complete after a period of 7 hours. The oily product, presumably con-

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[13] J. R. Catch, D. F. Elliott, D. N. Hey and E. R. H. Jones, *J. Chem. Soc.*, 278 (1948).

taining a mixture of stereoisomers, crystallized from ether and furnished 111 mg. of prisms melting at 126–127°, $\lambda_{\max}$ 222, 254, 320 mμ; ϵ 37,900, 17,000, 5,680; $\nu_{\max}$ 1678 cm.$^{-1}$.

Anal. Calcd. for $C_{24}H_{26}O_5$: C, 73.07; H, 6.64. Found: C, 72.87; H, 6.66.

Reaction of XIa with Acetic Anhydride.—A mixture of 1.0 g. of XIa and 10 ml. of acetic anhydride was treated with 1 ml. of triethylamine. The reaction mixture was heated on the steam-bath until all of the material had dissolved and was then allowed to stand at room temperature. At the end of 6 hours, a considerable amount of crystalline material had separated, and after standing overnight at 0°, 1.07 g. (84%) of product was obtained, which after crystallization from a small volume of methanol, melted at 117–118°. The same compound was obtained by treatment of XIa with acetic anhydride and *p*-toluenesulfonic acid, though in lower yield, and the substance was identified as 2-acetoxymethylene-7-methoxytetralone-1, by direct comparison with a sample obtained by acetylation of I in the presence of acetic anhydride and pyridine.

Anal. Calcd. for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 68.20; H, 5.93.

Preparation of XIa from 2-*p*-Toluenesulfonoxymethylene-7-methoxytetralone-1.—A mixture of 107 mg. of 2-*p*-toluenesulfonoxymethylene-7-methoxytetralone-1 (prepared by treatment of I with *p*-toluenesulfonyl chloride and triethylamine)[14] and 67 mg. of 2-hydroxymethylene-7-methoxytetralone-1 (I) was dissolved in 4 ml. of ethanol and treated with 0.1 ml. of triethylamine. After standing at room temperature for 8 hours, the reaction mixture, containing precipitated product, was cooled in ice and filtered. The crude material, m.p. 160–180°, on recrystallization from chloroform–ethanol, afforded 20% of XIa, m.p. 210–211°, identical in all respects with a sample obtained by the β-chlorovinyl methyl ketone synthesis.

Preparation of 2-Isopropoxymethylene-7-methoxytetralone-1.—To a solution of 1.03 g. of 2-hydroxymethylene-7-methoxytetralone-1 (I) and 1.0 ml. of isopropyl iodide in 25 ml. of dry acetone there was added 1.4 g. of freshly ignited potassium carbonate. The mixture was heated under reflux on the steam-bath for 24 hours, at the end of which time the acetone was removed *in vacuo*, and the residue was taken up in water and ether. The ether layer was then washed with potassium carbonate solution, dried and evaporated. The residual oil crystallized on standing, and after several recrystallizations from petroleum ether furnished a pure sample, m.p. 72°, $\lambda_{\max}$ 223, 268, 301, 335 mμ; ϵ 18,000, 7,600, 11,000, 8,000.

Anal. Calcd. for $C_{15}H_{18}O_3$: C, 73.14; H, 7.37. Found: C, 73.12; H, 7.42.

HOUSTON, TEXAS

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[14] The crude tosylate melted at about 76° and was too unstable to be submitted for analysis.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Quinone Imides. XL. Orientation in the Addition of Hydrogen Chloride to 2-Substituted-*p*-quinonedibenzimides

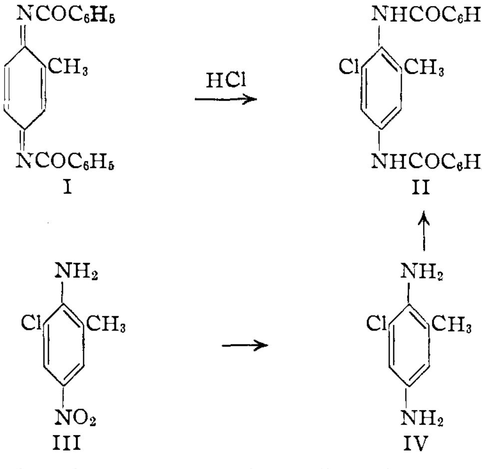
BY ROGER ADAMS AND M. D. NAIR[1]

RECEIVED JULY 30, 1956

2-Methyl-*p*-quinonedibenzimide adds hydrogen chloride to give exclusively 6-chloro-2-methyl-*p*-phenylenedibenzamide. The corresponding 2-phenylmercapto analog gives 3-chloro-2-phenylmercapto-*p*-phenylenedibenzamide. The 2-benzenesulfonyl derivative, on the other hand, gives a mixture composed of the 2-benzenesulfonyl-3-chloro- and 2-benzenesulfonyl-6-chloro-*p*-phenylenedibenzamides. The structures of the various derivatives were determined by unequivocal methods.

The addition of hydrogen chloride to 2-chloro-*p*-quinonedibenzenesulfonimide resulted in a mixture of at least two dichloro diamides, the 2,5-dichloro-*p*-phenylenedibenzenesulfonamide predominating with the 2,3-dichloro isomer in smaller amounts.[2] 2-Methyl-*p*-quinonedibenzenesulfonimide, however, gave only 5-chloro-2-methyl-*p*-phenylenedibenzenesulfonamide. The addition of hydrogen chloride to 2-chloro-*p*-quinonedibenzimide resulted in the exclusive formation of 2,6-dichloro-*p*-phenylenedibenzamide[3] and a similar orientation occurred when hydrogen chloride reacted with 2-chloro-*p*-quinonedipivalimide.[4]

In this communication, results are reported on the addition of hydrogen chloride to *p*-quinonedibenzimides with the 2-position occupied by methyl, phenylmercapto and benzenesulfonyl groups, respectively. From 2-methyl-*p*-quinonedibenzimide (I) only a single adduct was formed, 6-chloro-2-methyl-*p*-phenylenedibenzamide (II). Its constitution was established by synthesis from the known 2-chloro-4-nitro-6-methylaniline (III) by the reduction to the corresponding diamine IV followed by benzoylation.



2-Phenylmercapto-*p*-quinonedibenzimide (V), made by oxidation of the diamide obtained from thiophenol and *p*-quinonedibenzimide, however, added hydrogen chloride to give only one product which proved to be 3-chloro-2-phenylmercapto-*p*-phenylenedibenzamide (VI). Its structure was proved by oxidation to the corresponding benzenesulfonyl analog XI which was identical with a com-

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[1] An abstract of a portion of a thesis submitted by M. D. Nair to the Graduate College of the University of Illinois, 1956, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] R. Adams, E. F. Elslager and K. F. Heumann, THIS JOURNAL, **74**, 2608 (1952).

[3] R. Adams and D. S. Acker, *ibid.*, **74**, 3029 (1952).

[4] R. Adams and J. M. Stewart, *ibid.*, **74**, 3660 (1952).