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POLYCYCLIC CONDENSATION PRODUCTS FROM 3-METHYL-1,2-INDANDIONE

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THE preparation of 3-methyl-1,2-indandione (I) was first investigated by von Braun and Kirschbaum[3], who obtained it as a viscous red oil by treatment of 3-methyl-1,2-indandione 2-oxime (II) with aqueous formaldehyde and hydrochloric acid. Shortly thereafter, Steinkopf and Bessaritsch[4] reported the formation of two colorless crystalline products, m.p. 170-172° and 119-120°, from II on reaction with aqueous formaldehyde and a large excess of hydrochloric acid. Subsequently, Heller[5] obtained a single colorless product, m.p. 160-167° dec., by treatment of II with formaldehyde and hydrochloric acid in acetic acid. We have confirmed Heller's formulation of this compound as $C_{21}H_{18}O_5$ and have shown it to be identical with the product obtained under the conditions of Steinkopf and Bessaritsch[4,6]. We assign to it structure III (of undetermined stereochemistry) on the basis of the following data.

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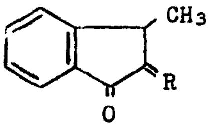
[3] J. von Braun and G. Kirschbaum, Ber. Dtsch. Chem. Ges. 46, 3041 (1913).

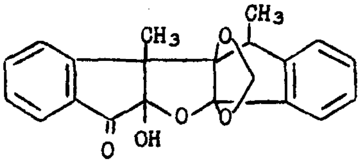
[4] W. Steinkopf and R. Bessaritsch, Ber. Dtsch. Chem. Ges. 47, 2925 (1914).

[5] G. Heller, Ber. Dtsch. Chem. Ges. 68, 1085 (1935).

[6] These authors assigned the formula $C_9H_8O_2$ to their higher-melting compound. No product corresponding to their lower-melting compound, to which they assigned the formula $C_9H_{10}O_3$, was obtained in the present investigation.

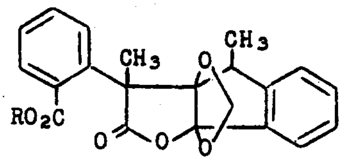


I, R = O
II, R = NOH



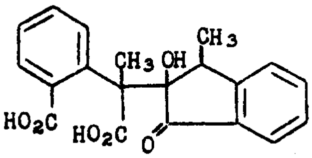
III

The product [Found: C, 72.26, 72.29; H, 4.93, 5.06; M.W. (isotherm. dist.), 334, 339], which turns yellow at 170° and melts to an orange oil at 180-185°, has $\lambda_{max}^{CHCl_3}$ 2.80, 5.78 μ and $\lambda_{max}^{Et_2O}$ 247 mμ (log ε 4.07). It dissolves slowly in aqueous-ethanolic base to give a deep indigo solution with the formation of formaldehyde. Treatment with benzoyl chloride and aqueous base gives the enol benzoate of I as yellow prisms, m.p. 109-110°, $\lambda_{max}^{CHCl_3}$ 5.73, 5.80, 6.06 (w) μ, λ_{max}^{EtOH} 242 mμ (log ε 4.74) [Found: C, 77.36; H, 4.47; M.W. (Rast), 298]. Oxidation with either lead tetraacetate in chloroform-tetrahydrofuran or sodium periodate in aqueous dimethylformamide gives a lactone-acid, $C_{21}H_{18}O_6$, m.p. 166-175° dec., λ_{max}^{KBr} 3.1-4.0, 5.62, 5.87 μ, λ_{max}^{EtOH} 223 mμ (shoulder, log ε 4.06) (Found: C, 68.87; H, 5.10; N.E., 362), which on treatment with diazomethane affords a monomethyl ester, m.p. 196-197°, $\lambda_{max}^{CH_2Cl_2}$ 5.61, 5.79 μ, λ_{max}^{EtOH} 230 mμ (shoulder, log ε 3.79) (Found: C, 69.58; H, 5.33). The N.M.R. spectrum ($CDCl_3$) of the ester shows, in addition to aromatic proton signals, signals with $\tau = 8.16$ (doublet, J = 7 c/s), 7.62, 6.07, 5.56 (quartet, J = 7 c/s), 4.68 and 4.27 p.p.m. with relative intensities _ca_. 3:3:3:1:1:1. Hydrolysis of the lactone acid with aqueous base gives a product (not obtained crystalline), whose ultraviolet spectrum has high intensity shoulders at 230 mμ and 250 mμ; its infrared spectrum in chloroform containing 20 per cent of N-methylmorpholine shows a band at 5.79 μ. The lactone-acid is assigned structure IV, its ester structure V,[7] and its hydrolysis product structure VI. Cleavage of V with methanolic sodium methoxide gives dimethyl α-methylhomophthalate, $\lambda_{max}^{CCl_4}$ 5.74, 5.79 μ (Found: C, 64.94; H, 6.31), and 3-methyl-1,2-indandione (I), characterized as its bis-semicarbazone.



IV, R = H

V, R = CH_3



VI

When conversion of II to I was attempted with hydrochloric acid and pyruvic acid in acetic acid,[8] two crystalline products were obtained which could be separated either by crystal-picking or by differential flotation. Each possesses the formula $C_{20}H_{16}O_4$, i.e. they are dimers of I: dimer A, m.p. 175-184° dec., $\lambda_{max}^{CHCl_3}$ 2.82, 5.59, 5.84, 11.23 μ, λ_{max}^{EtOH} 249 mμ (log ε 4.22), 294 mμ (log ε 3.16) [Found: C, 75.07; H, 4.77; M.W. (isotherm. dist.) 287] and isomer B, m.p. 179-182° dec., $\lambda_{max}^{CHCl_3}$ 2.81, 5.60, 5.83, 11.01 μ, λ_{max}^{EtOH} 250 mμ (log ε 4.20), 297 mμ (log ε 3.21) [Found: C, 74.66; H, 5.33; M.W. (isotherm. dist.), 268]. The very close similarity of the spectra of these products indicate that they are stereoisomers. They are assigned structures VII and VIII, respectively, on the basis of these data and the following evidence.

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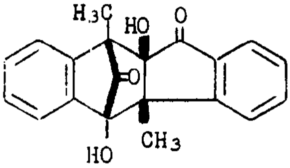
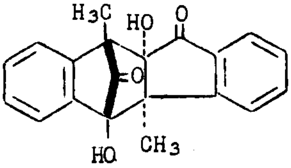
[7] The N.M.R. spectrum of the ester is readily interpretable in terms of structure V if J~0 for the protons of the methylenedioxy group, which are considered to give rise to the singlets with τ = 4.68 and 4.27 p.p.m. The lack of spin-spin coupling between these protons can be ascribed, at least in part, to their attachment to a carbon atom which bears two strongly electronegative atoms; cf. R.E. Glick and A.A. Bothner-By, J. Chem. Phys. 25, 362 (1956); T. Schaefer, Canad. J. Chem. 40, 1 (1962).

[8] Cf. C.F. Koelsch and C.D. LeClaire, J. Org. Chem. 6, 516 (1941).



VII



VIII

Both isomers give a deep indigo solution with ethanolic sodium hydroxide. Treatment of isomer B with benzoyl chloride and aqueous base gives the enol benzoate of I (60%). Oxidation of dimer A with lead tetra-acetate in chloroform-dioxane gives a neutral compound, $C_{20}H_{14}O_4$, m.p. 128-129°, $\lambda_{max}^{CHCl_3}$ 5.44, 5.80, 5.94 µ, λ_{max}^{EtOH} 252 mµ (log ε 4.34) (Found: C, 75.51; H, 4.68), assigned structure IX. This on hydrolysis in aqueous sodium carbonate gives a monobasic acid, $C_{20}H_{16}O_5$, (X), m.p. 181-183°, λ_{max} (CH_3CN -5% N-methylmorpholine) 5.82, 5.92, 6.16 µ (Found: C, 71.39; H, 4.82; N.E., 340); on treatment with pyridine and methyl chloroformate this regenerates the β-lactone function, as evidenced by the appearance of a band in the infrared spectrum of the product at 5.44 µ. Pyrolysis of IX at 180° leads to the loss of carbon dioxide and the formation of a yellow substance, $C_{19}H_{14}O_2$, (XI), m.p. 161-163°, $\lambda_{max}^{CHCl_3}$ 5.92, 6.15 (m) µ, λ_{max}^{EtOH} 227 mµ (log ε 4.32), 268 mµ (log ε 4.31), 318 mµ (log ε 4.07), 333 mµ (log ε 4.05) (Found: C, 82.85; H, 5.20). Reduction of the pyrolysis product with zinc and acetic acid gives a colorless substance, $C_{19}H_{16}O_2$, (XII), m.p. 123-124.5°, $\lambda_{max}^{CHCl_3}$ 5.86, 5.97 µ, λ_{max}^{EtOH} 246 mµ (log ε 4.34), 293 mµ (log ε 3.51) (Found: C, 82.70; H, 6.15). Reduction of XI with an excess of sodium borohydride in isopropyl alcohol followed by treatment of the crude product[9] with warm concentrated sulfuric acid gives a hydrocarbon,

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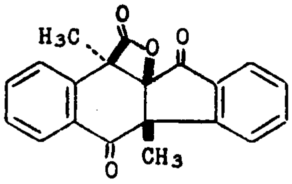
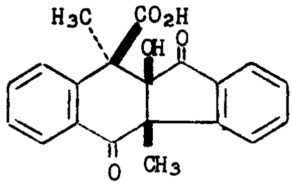
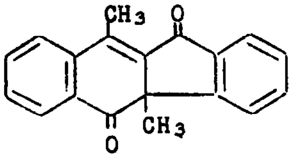
[9] The infrared spectrum of this product indicates that the carbonyl groups and the ethylenic double bond of XI have been reduced; cf. F. Sondheimer, M. Velasco, E. Batres and G. Rosenkranz, Chem. & Ind. 1482 (1954); C. Djerassi and W. Rittel, J. Amer. Chem. Soc. 79, 3529 (1957).



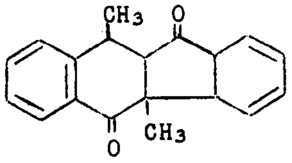
IX



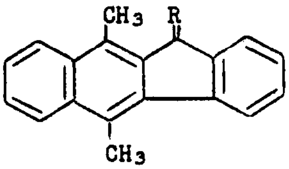
X

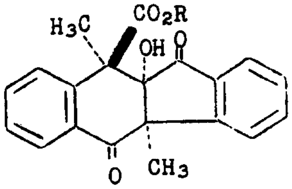


XI



XII





XIII, R = H_2

XIV, R = O

XV, R = H

XVI, R = CH_3

$C_{19}H_{16}$, (XIII), m.p. 117-119° (Found: C, 93.59; H, 6.73), which shows an intense blue fluorescence and has a complex ultraviolet spectrum very similar to that of 11H-benzo[*b*]fluoren[10]. Oxidation of the hydrocarbon with chromic acid converts it to a bright yellow substance, $C_{19}H_{14}O$, (XIV), m.p. 112-114°, $\lambda_{max}^{CHCl_3}$ 5.86 μ (Found: C, 88.26; H, 5.48), which shows a brilliant yellow fluorescence and has an ultraviolet spectrum closely resembling that of 11*H*-benzo[*b*]fluoren-11-one[10] ($\lambda_{max}^{CCl_4}$ 5.83 μ[11]).

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[10] R.A. Friedel and M. Orchin, *Ultraviolet Spectra of Aromatic Compounds*. John Wiley, New York (1951); G.R. Clemo and D.G.I. Felton, *J. Chem. Soc.* 1658 (1952).

[11] M.-L. Josien and N. Fuson, *C.R. Acad. Sci., Paris* **236**, 1879 (1953).

Treatment of isomer B with lead tetraacetate in chloroform-dioxane gives a monobasic acid, XV, m.p. 200-202°, stereoisomeric with X (Found: C, 71.27; H, 4.71; N.E., 334); its infrared spectrum in acetonitrile -5% N-methylmorpholine closely resembles that of X in the carbonyl region.[12] This acid is converted by diazomethane to a monomethyl ester, XVI, m.p. 187-192°, $\lambda_{max}^{CHCl_3}$ 2.78, 5.78, 5.93 μ (Found: C, 71.83; H, 5.34). On pyrolysis it gives, like X, the enedione XI.

Late in the course of this work, 3-methyl-1,2-indandione (I) was obtained in the crystalline state for the first time. When an ethereal solution of the red viscous oil obtained by the method of von Braun and Kirschbaum[3] was set aside for several weeks, a small amount of III crystallized. A tetrahydrofuran solution of the residue obtained by evaporation of the mother liquor was extracted with aqueous 5 per cent sodium hydroxide. Acidification of the aqueous phase, followed by extraction and molecular distillation, gave a semi-solid distillate. This on crystallization from ether gave I as pale orange needles, m.p. 123-125°, $\lambda_{max}^{CHCl_3}$ 2.83 (w), 5.68, 5.79, 5.81 (sh) μ, $\lambda_{max}^{Et_2O}$ 246 mμ (log ε 4.34), 293 mμ (log ε 3.51)[13] (Found: C, 74.56; H, 5.03).

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[12] Spectral evidence indicates that unionized X and XV can exist in solution as the corresponding δ-lactols.

[13] The infrared spectrum of I resembles that of 1,2-indandione in the 2.5-7 μ region. The latter compound, m.p. 114-115° (lit.[14] 95-115°, 95-102°) was prepared by Dr. M.R. Rice.

[14] W.H. Perkins, Jr., W.M. Roberts and R. Robinson, *J. Chem. Soc.* 232 (1912); R. Criegee and K. Klonk, *Liebigs Ann.* *564*, 1 (1949).