

and its contents were dissolved in chloroform. The solution was washed successively with 2 *N* hydrochloric acid, saturated aqueous sodium carbonate, and aqueous sodium chloride. The organic layer was dried over sodium sulfate and the solvent removed *in vacuo*. A dark solid (0.087 g.) was obtained, whose infrared spectrum showed it to be starting material containing traces of contaminants.

Other attempts to prepare a quinoxaline, using the methods of Fieser<sup>48</sup> and of Mathys, Prelog, and Woodward<sup>49</sup> or a modification of the latter procedure involving the use of mineral acid in addition to acetic acid, returned only starting material.

**Condensation of Deoxybenzoin with Oxalyl Chloride: Formation of IX and Tetraphenyl-4-pyrone (XLIII).**—Commercial sodamide (12.4 g., 0.318 mole) was added to a stirred solution of deoxybenzoin (62.0 g., 0.316 mole) in benzene (400 ml.) at 25° under nitrogen. The mixture was boiled at reflux for 13 hr.; evolution of ammonia commenced after 5 min. and the sodium derivative of deoxybenzoin began to crystallize from the hot solution after 15 min. At the end of the 13-hr. period, the mixture was cooled to 0°, and oxalyl chloride (20.1 g., 0.158 mole) in benzene (30 ml.) was added dropwise over a 30-min. period, while the mixture was maintained at 0°. The mixture was boiled under reflux with stirring for 6 hr., and aqueous 6 *N* hydrochloric acid was added to the wine-red solution. The organic layer was separated and the aqueous layer was extracted with benzene (400 ml.). The combined benzene solutions were dried over sodium sulfate and freed of solvent *in vacuo* to give a reddish paste. Addition of 95% ethanol (150 ml.), heating to boiling, and slow cooling gave a precipitate of yellow, powdery material (9.2 g., 13.6%). This product, m.p. 212–213° after repeated recrystallization from 95% ethanol, was shown to be identical with IX, obtained from methylenedeoxybenzoin dimer, by a mixture melting point determination and infrared spectral comparison.

On further standing at 25° followed by cooling with Dry Ice, the original filtrate deposited a yellowish solid (12.9 g.) which was shown to be mainly deoxybenzoin by its infrared spectrum.

(48) L. F. Fieser, "Experiments in Organic Chemistry," 3rd Ed. rev., D. C. Heath and Co., Boston, Mass., 1955, p. 174.

(49) F. Mathys, V. Prelog, and R. B. Woodward, *Helv. Chim. Acta*, **39**, 1095 (1956).

When a portion of the material was treated with a small amount of 95% ethanol and the mixture was heated above the melting point of deoxybenzoin, a solid remained in the otherwise clear solution. This was filtered and found to be very slightly soluble in common organic solvents other than dichloromethane and chloroform. Crystallization was effected by dissolving the product in dichloromethane, heating to boiling and maintaining a constant volume by dropwise addition of 95% ethanol. The product, XLIII, was obtained as faintly yellow needles, m.p. 270–280°, which crystallized directly from the boiling solution. After seven crystallizations in this manner an analytical sample was obtained as ivory-colored needles, m.p. 288–289°; infrared bands (CH<sub>2</sub>Cl<sub>2</sub>): 6.14, 6.20 μ; ultraviolet maximum (CH<sub>2</sub>Cl<sub>2</sub>): 270 mμ (log ε 4.29).

*Anal.* Calcd. for C<sub>23</sub>H<sub>20</sub>O<sub>2</sub>: C, 86.97; H, 5.03. Found: C, 86.72, 86.88; H, 5.22, 5.07.

**Condensation of Deoxybenzoin with Phosgene: Formation of Tetraphenyl-4-pyrone (XLIII).**—A suspension of the sodium salt of deoxybenzoin in benzene was prepared from deoxybenzoin (10.0 g., 0.051 mole) and commercial sodamide (2.0 g., 0.051 mole) in benzene (100 ml.) as described above. To the mixture at 25° there was added dropwise over a 10-min. period, an ice-cold saturated solution of phosgene in toluene (10 ml.). The solution was observed to warm slightly and a gelatinous deposit of sodium chloride separated. The mixture was then boiled under reflux with stirring for 75 min. and cooled while the system was thoroughly flushed with nitrogen. Hydrochloric acid (6 *N*, 25 ml.) was added and the organic layer was separated. The aqueous layer was extracted with benzene (50 ml.). The combined organic layers were washed with water and aqueous sodium chloride and dried over sodium sulfate. Removal of solvent *in vacuo* gave a product whose infrared spectrum indicated it to be a complex mixture. After long standing in 95% ethanol followed by heating to boiling, a white solid was deposited which did not dissolve in the hot alcohol. It was filtered, washed with hexane, and air-dried to give a white solid product (0.858 g., 8.5%), m.p. 275–278°. This was purified by two recrystallizations from dichloromethane–95% ethanol to give material of m.p. 284–286°, which was shown to be identical with the minor product obtained from the condensation of deoxybenzoin and oxalyl chloride by a mixture melting point determination and infrared spectral comparison.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY, CAMBRIDGE 38, MASS.]

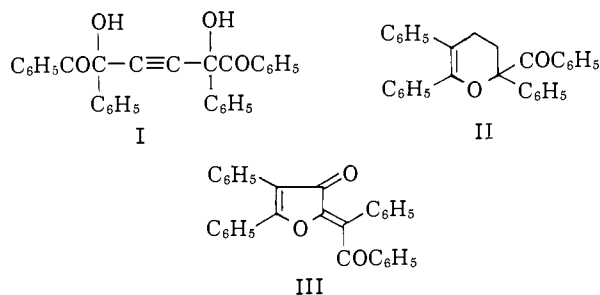
## 3-Furanones. II. The White Compound of Kleinfeller and Fiesselmann<sup>1</sup>

BY PETER YATES<sup>2a</sup> AND JERRY A. WEISBACH<sup>2b</sup>

RECEIVED FEBRUARY 23, 1963

The white compound obtained by Kleinfeller by acid-catalyzed isomerization of the yellow compound III formed by dehydration of 2,5-dihydroxy-1,2,5,6-tetraphenyl-3-hexyne-1,6-dione (I) and by Fiesselmann and co-workers by treatment of methylenedeoxybenzoin dimer (II) with bromine has been shown to be 3,3'-dioxo-2',4,5-triphenylspiro[furan-2(3*H*),1'-indan] (VI). Its infrared and ultraviolet spectra have been compared with those of model compounds. Its reactions have been investigated, including its conversion to 2-phenyl-3-phenylglyoxylylindone (XVII), whose reactions have also been studied.

The yellow compound obtained by Kleinfeller and Eckert<sup>3</sup> by the action of saturated alcoholic hydrogen chloride or bromine on 2,5-dihydroxy-1,2,5,6-tetraphenyl-3-hexyne-1,6-dione (I) and by Fiesselmann and co-workers<sup>4</sup> by the action of bromine on methylene-



deoxybenzoin dimer (II) has been shown<sup>1</sup> to be the 3-furanone derivative III. Kleinfeller<sup>5</sup> observed that treatment of III with concentrated sulfuric acid gave rise to a white, isomeric compound, which was also obtained by Fiesselmann<sup>4</sup> together with III from the reaction of II with bromine. We discuss here the structure and reactions of this isomer.

Its infrared spectrum (CH<sub>2</sub>Cl<sub>2</sub>) shows two bands in the carbonyl-stretching region at 5.80 and 5.90 μ, a complex quartet between 6.15 and 6.40 μ, and a strong band at 7.25 μ. Apart from the band at 5.80 μ, these features are strikingly similar to those found in the spectra of IV, the tetrahydro derivative of III, and of model 4,5-diphenyl-3-furanones of type V.<sup>6</sup> These data, therefore, are strongly indicative of the presence of the structural unit V in the isomer.

(4) H. Fiesselmann and J. Ribka, *ibid.*, **89**, 40 (1956); H. Fiesselmann and F. Miesel, *ibid.*, **89**, 657 (1956).

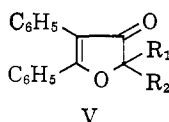
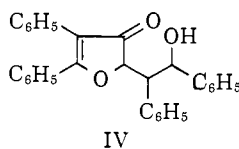
(5) H. Kleinfeller, *ibid.*, **72**, 249 (1939).

(6) Thus, for example, 2,4,5-triphenyl-3-furanone (V, R<sub>1</sub> = C<sub>6</sub>H<sub>5</sub>, R<sub>2</sub> = H) has λ<sub>max</sub><sup>CH<sub>2</sub>Cl<sub>2</sub></sup> 5.90, 7.26 μ, and a quartet at 6.15–6.40 μ, and λ<sub>max</sub><sup>CH<sub>2</sub>Cl<sub>2</sub></sup> 240 mμ (log ε 4.28) and 317 mμ (log ε 4.11). Spectral data for other model compounds are given in ref. 1.

(1) Paper I: P. Yates and J. A. Weisbach, *J. Am. Chem. Soc.*, **85**, 2943 (1963).

(2) (a) Department of Chemistry, University of Toronto, Toronto, Canada; Alfred P. Sloan Foundation Fellow, 1957–1960; (b) Eastman Kodak Co. Fellow, 1958–1959.

(3) H. Kleinfeller and F. Eckert, *Ber.*, **62**, 1598 (1929).

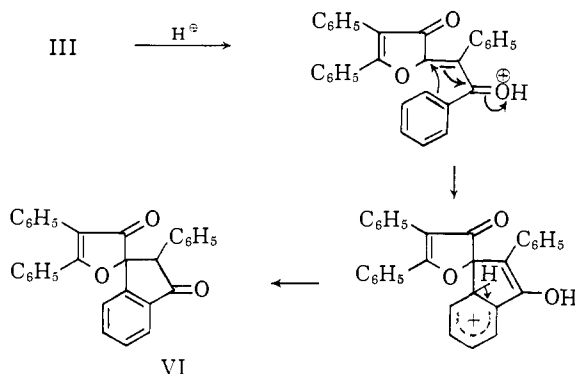


The presence of the additional band in the carbonyl-stretching region indicates that the third oxygen atom is present as a second ketonic function.

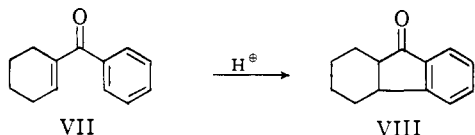
The ultraviolet spectrum (95% EtOH) of the isomer shows maxima at  $244 \text{ m}\mu$  ( $\log \epsilon 4.48$ ) and  $318 \text{ m}\mu$  ( $\log \epsilon 4.09$ ). The position of these bands is again typical of the system V.<sup>8</sup> The lower wave length maximum is, however, of abnormally high intensity, indicating that it results from superposition of a band due to another chromophore absorbing strongly in the 240–250  $\text{m}\mu$  region upon the absorption in this region characteristic of the system V.

In order to determine whether the isomerization of III had involved cyclization into an aromatic nucleus, the isomer was subjected to oxidation with hot alkaline potassium permanganate. Benzoic and phthalic acid were obtained as the products, establishing that such cyclization had occurred and that the isomer contains an *o*-disubstituted benzene ring.

This result, together with the spectral interpretations, led us to conclude that the best formulation for the isomer is VI, which could arise from III in the manner shown below.<sup>7</sup>



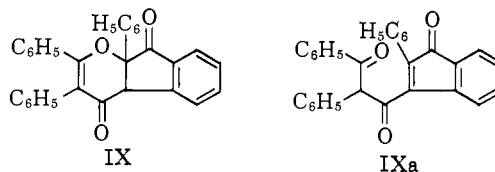
A route of this type has ample precedent<sup>9</sup> and is particularly closely related to the acid-catalyzed cyclization of 1-cyclohexenyl phenyl ketone (VII) to the hexahydrofluorenone VIII.<sup>8a</sup>



The infrared spectrum of the isomer is in accord with the structural assignment VI in that the band at  $5.80 \mu$  can be attributed to the 1-indanone carbonyl group (cf. 2-phenylindanone,  $\lambda_{\text{max}}^{\text{CH}_2\text{Cl}_2} 5.84 \mu$ ). The 1-indanone system would be expected to give rise to a high intensity ultraviolet band in the 240–250  $\text{m}\mu$  region [cf. 2-phenylindanone,  $\lambda_{\text{max}}^{\text{EtOH}} 245 \text{ m}\mu$  ( $\log \epsilon 4.18$ )], and thus structure VI is also compatible with the ultraviolet spectrum of the isomer.

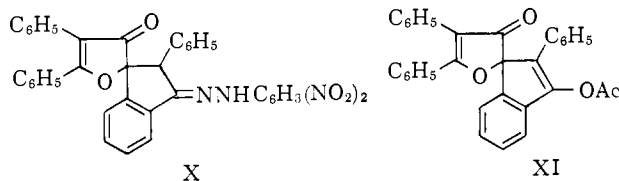
A related formulation, IX, for the isomer must be considered; such a product could arise from further

acid-catalyzed transformations of a compound of structure VI *via* IXa.



Although a compound of structure IX could give rise to the same ozonolysis product (*vide infra*) as that derived from VI, this structure is inadmissible for the isomer of III, since it would be expected to give rise to an infrared carbonyl-stretching band at an appreciably longer wave length than that observed (cf. 2,3-dihydro-2,6-dimethyl-4-pyrone,  $\lambda_{\text{max}}^{1\text{M}} 6.01 \mu$ <sup>9</sup>; 2-carboxymethyl-2,3-dihydro-4-pyrone,  $\lambda_{\text{max}}^{\text{CH}_2\text{Cl}_2} 5.98 \mu$ <sup>10</sup>).

Compound VI forms a mono-2,4-dinitrophenylhydrazone. The infrared spectrum of this derivative retains a carbonyl-stretching band at  $5.89 \mu$ , the quartet at  $6.15\text{--}6.40 \mu$  and the strong band at  $7.25 \mu$ . Thus, derivative formation occurs at the indanone carbonyl group, giving X, and the 4,5-diphenyl-3-furanone system is left intact. The resistance of the carbonyl group of this system to derivative formation can be attributed both to steric factors and to the fact that it forms part of a vinylogous ester group.<sup>11</sup> Acetylation of VI gave a monoacetyl derivative; this was formed without skeletal change since it was reconverted to VI on basic hydrolysis. It is assigned structure XI, in accordance with the retention of the chromophore V, as demonstrated by its infrared and ultraviolet spectra, and the presence of bands at  $5.64$  and  $8.40 \mu$  in its infrared spectrum, characteristic of the enol acetate group.



Compound VI was found to be resistant to hydrogenation at atmospheric pressure.<sup>12</sup> Treatment with lithium aluminum hydride followed by work-up under strongly acidic conditions gave a compound,  $\text{C}_{30}\text{H}_{20}\text{O}$ , whose infrared spectrum shows no bands attributable to hydroxyl or carbonyl groups. The ultraviolet spectrum of the reduction product is complex, with maxima at  $228 \text{ m}\mu$  ( $\log \epsilon 4.53$ ),  $277 \text{ m}\mu$  ( $\log \epsilon 4.61$ ),  $316 \text{ m}\mu$  ( $\log \epsilon 4.31$ ), and  $353 \text{ m}\mu$  ( $\log \epsilon 3.57$ ) and bespeaks the presence of a polynuclear aromatic system. Two compounds with such a system, XIII and XIV, could be formed in the acid work-up of XII, the simple reduction product of VI.

Compounds XVa<sup>13</sup> and XVb<sup>14</sup> were prepared as models for compounds XIII and XIV; the ultraviolet spectrum of XVa, but not that of XVb, was found to be very similar to the spectrum of the reduction product (Fig. 1).<sup>15</sup> Hence, the reduction product is assigned structure XIII.<sup>16</sup>

(9) E. S. Hand, Ph. D. Thesis, Radcliffe College, 1961.

(10) G. Singh, Ph. D. Thesis, Harvard University, 1949.

(11) Cf. the formation of a mono-2,4-dinitrophenylhydrazone from III.<sup>4</sup>

(12) Cf. the very slow uptake of hydrogen by IV and V ( $\text{R}_1 = \text{C}_6\text{H}_5$ ,  $\text{R}_2 = \text{OCH}_3$ ).<sup>1</sup>

(13) C. F. H. Allen and J. A. VanAllan, *J. Org. Chem.*, **16**, 716 (1951); C. F. H. Allen, *Can. J. Res.*, **4**, 264 (1931).

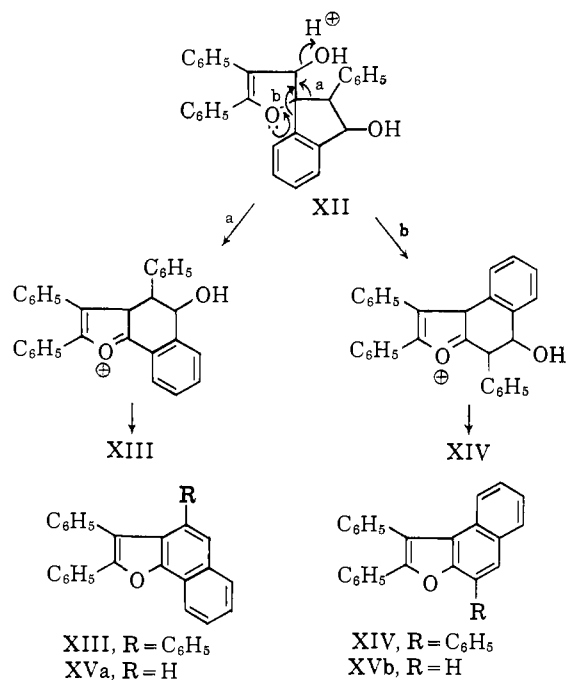
(14) O. Dischendorfer and E. Ofenheimer, *Monatsh.*, **74**, 135 (1943).

(15) The additional phenyl substituent in XIII would not be expected to influence the ultraviolet spectrum greatly, since steric factors must considerably inhibit its coplanarity with the fused ring system.

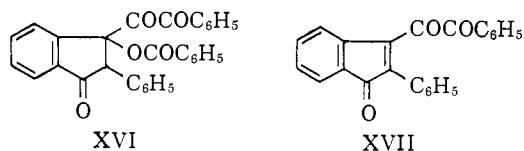
(16) The choice between the rearrangement routes a and b could well be dependent upon the stereochemistry of the intermediate, XII.

(7) In the case of the formation of VI by reaction of II with bromine, hydrogen bromide, formed in the conversion of II to III, could serve as the acid catalyst.

(8) (a) E. A. Braude and W. F. Forbes, *J. Chem. Soc.*, 2208 (1953); (b) E. A. Braude and J. A. Coles, *ibid.*, 1430 (1952); E. A. Braude, W. F. Forbes, and E. A. Evans, *ibid.*, 2202 (1953); P. Yates, N. Yoda, W. Brown, and B. Mann, *J. Am. Chem. Soc.*, **80**, 202 (1958).

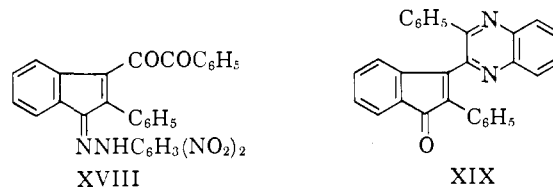


Ozonolysis of VI in dichloromethane proceeded slowly and gave a yellow product, which could not be crystallized, with complex absorption in the carbonyl-stretching region of its infrared spectrum, which included peaks at 5.78 and 5.95  $\mu$ . During the course of attempted purification of this product by chromatography on Florisil, it was observed that the column acquired a red tinge; the longer the residence time of the mixture on the column, the more intense was the coloration. When the ozonolysis product was left on the column for 3 days before desorption, elution yielded a red oil, a small amount of white solid, and benzoic acid. The white solid, which was not obtained in all runs, was identified as 2-phenyl-1,3-indandione by direct comparison with an authentic sample.<sup>17</sup> The red oil crystallized from methanol as orange-red cubes,  $\text{C}_{23}\text{H}_{14}\text{O}_3$ . We interpret these changes in the following way: ozonolysis of VI leads initially to the yellow  $\alpha$ -diketone XVI which, under the influence of the weakly basic Florisil, eliminates benzoic acid to give the red indone XVII. The 2-phenyl-1,3-indandione is thought to arise either by further oxidation of XVI during the ozonolysis or by air oxidation during the treatment with Florisil.

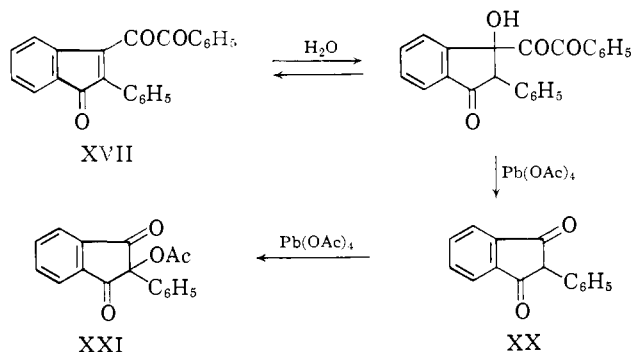


The assignment of structure XVII to the red product is corroborated by the following observations. It shows in its infrared spectrum ( $\text{CH}_2\text{Cl}_2$ ) a band at 5.80  $\mu$ , assigned to the indone carbonyl-stretching vibration (*cf.* the indone carbonyl bands at 5.80 and 5.84  $\mu$  in the spectra of 2-benzoyloxy-3-methylindone<sup>18</sup> and 2,3-diphenylindone, respectively), and a broad band at 5.97  $\mu$ , attributed to the superposition of bands due to the conjugated carbonyl groups of the  $\alpha$ -dione grouping (*cf.* benzil,  $\lambda_{\text{max}}^{\text{CH}_2\text{Cl}_2}$  5.96  $\mu$ ). Its ultraviolet spectrum ( $\text{CH}_2\text{Cl}_2$ ) has a maximum at 255  $m\mu$  ( $\log \epsilon$  4.49) and a long tail extending into the visible region and peaking slightly at *ca.* 450  $m\mu$  ( $\log \epsilon$  3.31).<sup>19</sup> It gave a mono-2,4-

dinitrophenylhydrazone whose infrared spectrum has two bands at 5.98 and 6.05  $\mu$ , in addition to the usual 2,4-dinitrophenylhydrazone bands. This spectrum supports the assignment to the red compound of XVII, a structure with three carbonyl groups. The loss of the 5.80  $\mu$  band indicates that derivative formation has occurred at the indone carbonyl group to give XVIII; the remaining two carbonyl bands, formerly overlapping, have now separated into distinct peaks. Treatment of XVII with *o*-phenylenediamine gave an orange quinoxaline XIX whose infrared spectrum has a single carbonyl-stretching band at 5.83  $\mu$ . The presence of three carbonyl groups in the red compound, with two of them present as an  $\alpha$ -diketone group, is therefore confirmed. The orange color of the quinoxaline also confirms the presence of a visible chromophore (*i.e.*, the indone system) in addition to the  $\alpha$ -diketone chromophore (*cf.* the fact that the quinoxaline derived from diphenyl triketone is colorless).



Oxidation of XVII with alkaline hydrogen peroxide gave benzoic and phthalic acids. Oxidation with lead tetraacetate in aqueous acetic acid gave benzoic acid and a colorless compound,  $\text{C}_{16}\text{H}_{12}\text{O}_4$ . This compound, which has infrared bands at 5.73 and 5.78  $\mu$  and ultraviolet maxima at 228.5 ( $\log \epsilon$  4.66) and 247  $m\mu$  ( $\log \epsilon$  4.11), was considered to be 2-acetoxy-2-phenyl-1,3-indandione (XXI), formed in the fashion shown below.<sup>20</sup>



Treatment of 2-phenyl-1,3-indandione (XX)<sup>17</sup> with lead tetraacetate under the conditions of the above reaction afforded a product in 42% yield, shown to be identical with the product  $\text{C}_{16}\text{H}_{12}\text{O}_4$  obtained from XVII.<sup>21</sup> Compound XVII was unaffected by periodic acid. However, hydrogenation followed by treatment with periodic acid led to cleavage with the formation of benzaldehyde, identified as its 2,4-dinitrophenylhydrazone, and a viscous oil, which could not be crystallized. The latter had infrared bands at 2.91 and 5.80  $\mu$  and is considered to be 3-hydroxy-2-phenyl-1-indancarboxaldehyde (XXII).

Compound XVII underwent interesting transformations in strongly acidic medium, whose nature has not yet been fully established. When it was treated with

(19) *Cf.* 2,3-diphenylindone,  $\lambda_{\text{max}}^{\text{EtOH}}$  260  $m\mu$  ( $\log \epsilon$  4.50) and 440  $m\mu$  ( $\log \epsilon$  3.24); E. D. Bergmann, E. Fischer, and J. H. Jaffe, *J. Am. Chem. Soc.*, **75**, 3230 (1953).

(20) Replacement of an activated hydrogen atom by an acetoxy group with lead tetraacetate is not uncommon: *cf.* R. Criegee in "Newer Methods of Preparative Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1948, p. 5.

(21) The preparation of this compound by another route has been reported recently: L. Horner, K. H. Weber, and W. Dürckheimer, *Chem. Ber.*, **94**, 2881 (1961).

(17) F. Nathanson, *Ber.*, **26**, 2576 (1893).

(18) R. S. Dewey, Ph.D. Thesis, Harvard University, 1959.

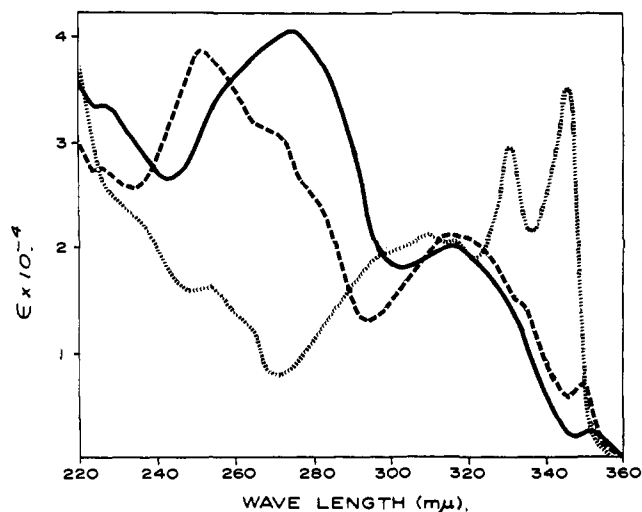
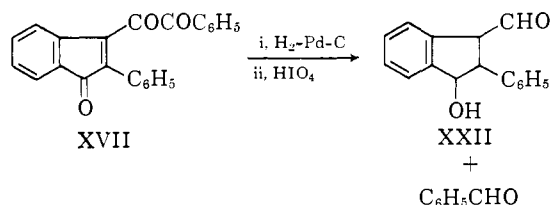


Fig. 1.—Ultraviolet spectra of: compound XIII, —; compound XVa, - - -; compound XVb, ·····; all compounds dissolved in 95% ethanol.

boiling 1:1 concentrated hydrochloric acid–acetic acid, there were formed an orange and a yellow compound. These substances, which are not interconvertible under the conditions of their formation, are also obtained when propionic acid is substituted for acetic acid. The orange compound is considered to have the compo-



sition  $C_{23}H_{14}O_2$  on the basis of the formation of an acetate,  $C_{25}H_{16}O_3$ , and a methyl ether,  $C_{24}H_{16}O_2$ , although consistent elemental analytical data could not be obtained for the parent compound itself. The ultraviolet spectra of this compound and its derivatives are notably complex and suggest the presence of a polynuclear aromatic system. A comparison of the spectrum of the acetate<sup>22</sup> and of 11-chrysofluorenone (XXIII)<sup>23</sup> shows them to be remarkably similar (Fig. 2). The orange compound is provisionally assigned structure XXIV on the basis of this similarity, bands in its infrared spectrum and the infrared spectra of its derivatives at  $5.84\text{--}5.90\ \mu$ <sup>24</sup> (cf. 5,10-dimethyl-11H-benzo[*b*]fluorene-11-one,  $\lambda_{\text{max}}^{\text{CHCl}_3}$   $5.86\ \mu$ <sup>15</sup>), the intense red-violet color of its solution in aqueous sodium hydroxide (cf. the intense red color of the sodium salt of 4-hydroxyfluorenone<sup>26</sup>), and its origin. This formulation requires reduction of XVII or a transformation product; the following scheme outlines a possible route for the formation of XXIV.

The reduction could be brought about either by reaction with unconsumed XVII with oxidative cleavage of the latter, or by hydrochloric acid.

(22) The acetate is chosen for this comparison, since attachment of an acetoxy group to an aromatic system normally affects its ultraviolet spectrum very little: cf. C. Daglish, *J. Am. Chem. Soc.*, **72**, 4859 (1950).

(23) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951, Fig. 423.

(24) In each case, the spectrum has a strong band at  $5.87\text{--}5.90\ \mu$  with a shoulder at  $5.83\text{--}5.84\ \mu$ ; this similarity among the spectra of the three compounds makes it most unlikely that the complexity of the carbonyl band is due to impurities. It may be due to Fermi resonance<sup>25</sup> with the first overtone of a relatively strong band appearing in the  $11.7\text{--}11.8\ \mu$  region.

(25) Cf. P. Yates and L. L. Williams, *J. Am. Chem. Soc.*, **80**, 5896 (1958).

(26) C. Graebe and P. Schestakow, *Ann.*, **284**, 306 (1895).

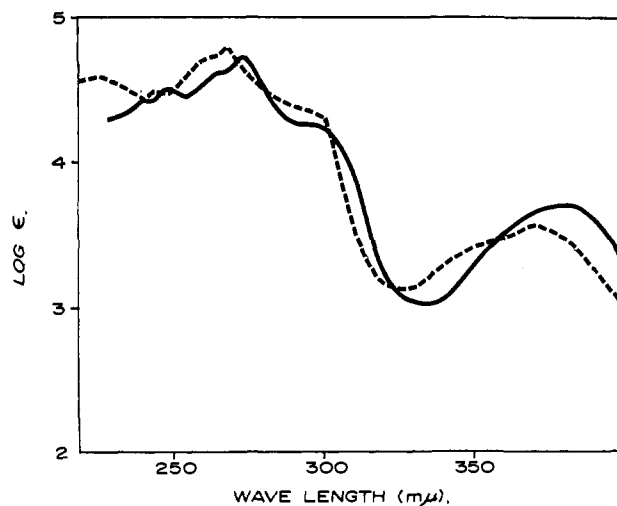
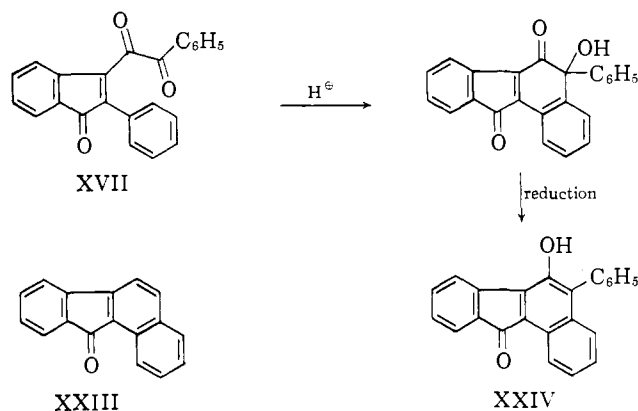
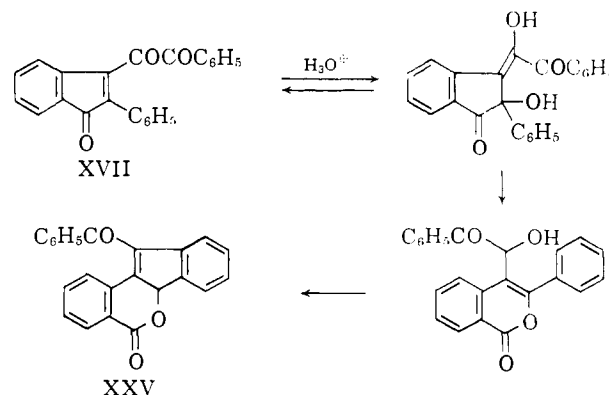


Fig. 2.—Ultraviolet spectra of: acetate of compound XXIV (in dichloromethane), —; 11-chrysofluorenone (XXIII) (in 95% ethanol),<sup>23</sup> - - -.

The yellow compound formed concomitantly with XXIV in the acid treatment of XVII is an isomer of XVII. Its infrared spectrum has bands at  $5.73$  and



$6.07\ \mu$  and, although it is not soluble in aqueous base, it dissolves in aqueous alcoholic base and is not reprecipitated on dilution of the solution with water. These properties suggest that it is a lactone with an additional, highly conjugated carbonyl group; the latter structural feature is also in accord with its ultraviolet spectrum. On treatment with hot aqueous alcoholic base, it slowly gave benzoic acid. On the basis of these data, it is provisionally assigned structure XXV, which could be formed from XVII as shown below.



### Experimental<sup>27</sup>

**The White Compound of Kleinfeller and Fiessmann (VI).**—The white product, m.p. 205–220°, obtained by the action of bromine on methylenedioxybenzoin dimer<sup>1</sup> was recrystallized repeatedly from acetic anhydride to give white, elongated prisms, m.p. 228–229°; infrared bands ( $\text{CH}_2\text{Cl}_2$ ): 5.80, 5.90, 7.25  $\mu$ ; ultraviolet maxima (95% EtOH): 244  $m\mu$  (log  $\epsilon$  4.48), 318  $m\mu$  (log  $\epsilon$  4.09).

*Anal.* Calcd. for  $\text{C}_{20}\text{H}_{20}\text{O}_3$ : C, 84.09; H, 4.71. Found: C, 84.30, 84.10; H, 4.85, 4.80.

**Reaction of VI with Potassium Permanganate.**—A solution of VI (0.229 g., 0.00054 mole) in dichloromethane (5 ml.) was added to a solution of potassium permanganate (2.445 g., 0.0155 mole) and potassium hydroxide (1.45 g., 0.026 mole) in water (25 ml.). The mixture was heated to remove the dichloromethane and then boiled under reflux for 23 hr. It was cooled to 25° and acidified with concentrated hydrochloric acid to pH 1. Aqueous sodium bisulfite was added dropwise with swirling until a clear solution was obtained. The solution was saturated with ammonium chloride and extracted with ethyl acetate. The organic layer was washed twice with water and dried over sodium sulfate. Removal of solvent *in vacuo* yielded a white solid (0.102 g.). Trituration of the product with dichloromethane or chloroform yielded an insoluble white solid, m.p. 195–205°. After two recrystallizations from ethyl acetate–carbon tetrachloride a white powdery sample was obtained, m.p. 201° dec., which gave no depression of melting point on admixture with phthalic acid and which had an infrared spectrum (KBr) identical with that of phthalic acid.

The portion of the oxidation product which dissolved during the above trituration process was identified as benzoic acid by comparison of its infrared spectrum with that of an authentic sample.

**2,4-Dinitrophenylhydrazone of VI (X).**—A mixture of VI (0.50 g., 0.0012 mole), 2,4-dinitrophenylhydrazine (0.46 g., 0.0023 mole), sulfuric acid (1 ml.), and dioxane (25 ml.) was boiled at reflux for 2 hr. The mixture was cooled to room temperature and poured into 2 *N* hydrochloric acid; a heavy brown solid precipitated and was separated by filtration. This material was passed over a Merck alkaline alumina column (15 g.) and all material which could be eluted with a 1:1 chloroform–methanol mixture was collected. This product was boiled at reflux with an ethyl acetate–95% ethanol mixture; flat, orange plates, m.p. 251–253°, gradually crystallized from the boiling solution. After three recrystallizations from ethyl acetate–95% ethanol, an analytical sample was obtained as light orange plates, m.p. 252.5–254°; infrared bands ( $\text{CH}_2\text{Cl}_2$ ): 3.07, 5.89  $\mu$ ; ultraviolet maxima (95% EtOH): 243  $m\mu$  (log  $\epsilon$  4.48), 372  $m\mu$  (log  $\epsilon$  4.53).

*Anal.* Calcd. for  $\text{C}_{26}\text{H}_{20}\text{O}_6\text{N}_4$ : C, 71.04; H, 3.98; N, 9.21. Found: C, 70.92, 70.85; H, 4.02, 4.18; N, 9.29.

**Acetylation of VI: Formation of XI.**—A solution of VI (0.258 g., 0.00060 mole) in acetic anhydride (15 ml.) and pyridine (2 ml.) was boiled under reflux for 1 hr. The solvent was removed *in vacuo* and the residual, pale yellow oil was crystallized with cooling and scratching from chloroform–hexane to give a white solid (0.243 g.), m.p. 193–204°. After nine recrystallizations from chloroform–hexane an analytical sample was obtained as white spars, m.p. 211.5–213°; infrared bands ( $\text{CH}_2\text{Cl}_2$ ): 5.64, 5.87, 8.40  $\mu$ ; ultraviolet maxima ( $\text{CH}_2\text{Cl}_2$ ): 240  $m\mu$  (log  $\epsilon$  4.49), 312.5  $m\mu$  (log  $\epsilon$  4.38).

*Anal.* Calcd. for  $\text{C}_{22}\text{H}_{22}\text{O}_4$ : C, 81.68; H, 4.71. Found: C, 81.85; H, 4.86.

Alkaline hydrolysis with aqueous alcoholic 5% potassium hydroxide at ca. 60° for 10 hr. reconverted this material to VI.

**Attempted Hydrogenation of VI.**—A solution of VI (0.103 g., 0.00024 mole) in 95% ethanol (40 ml.) was treated with hydrogen at atmospheric pressure and room temperature over 10% palladium–charcoal (0.03 g.) for 13 hr.; no significant uptake of hydrogen was observed to occur. The mixture was filtered and solvent removed *in vacuo* to give a white crystalline solid (0.100 g.) whose infrared spectrum showed it to be starting material.

Other attempts to effect hydrogenation using platinum oxide in acetic acid, both with and without catalytic amounts of perchloric acid, were likewise unsuccessful.

**Lithium Aluminum Hydride Reduction of VI: Formation of XIII.**—A mixture of VI (0.978 g., 0.00228 mole), lithium aluminum hydride (0.682 g., 0.034 mole), and ether (200 ml.) was boiled under reflux for 20 hr. The mixture was cooled in an ice-bath and moist ether was cautiously added until further addition caused no visible gas evolution. Concentrated hydrochloric acid (40 ml.) was added and the mixture was allowed to remain at room temperature for 8 hr. The organic layer was separated and the aqueous layer extracted with ether. The combined organic layers were washed with water and saturated aqueous

sodium chloride, and dried over sodium sulfate. Removal of solvent *in vacuo* yielded a viscous, yellow-orange oil, which was crystallized from methanol as white spars (0.250 g., 25%). After seven recrystallizations from dichloromethane–95% ethanol, an analytical sample was obtained as white needles, m.p. 180–180.5°; infrared bands ( $\text{CH}_2\text{Cl}_2$ ): no hydroxyl or carbonyl bands; ultraviolet maxima (95% EtOH): 228  $m\mu$  (log  $\epsilon$  4.53), 277  $m\mu$  (log  $\epsilon$  4.61), 316  $m\mu$  (log  $\epsilon$  4.31), 353  $m\mu$  (log  $\epsilon$  3.57).

*Anal.* Calcd. for  $\text{C}_{20}\text{H}_{20}\text{O}$ : C, 90.88; H, 5.08. Found: C, 91.08; H, 4.98.

**Ozonolysis of VI: Formation of XVII and XX.**—A solution of VI (1.854 g., 0.0043 mole) in dichloromethane (125 ml.) was cooled in a Dry Ice bath and treated with ozonized oxygen for 2.5 hr. The deep blue solution was immediately treated with a solution of sodium iodide (10.0 g., 0.067 mole) in acetic acid (30 ml.) and then allowed to warm to room temperature. Water was added to the mixture, followed by saturated aqueous sodium bisulfite added dropwise with swirling until the mixture was clear and colorless. The organic layer was separated and the aqueous layer extracted with additional dichloromethane. The combined organic layers were washed with water and saturated aqueous sodium chloride and dried over sodium sulfate. Removal of solvent *in vacuo* left a yellow foam (1.956 g.); infrared bands ( $\text{CH}_2\text{Cl}_2$ ): 5.78, 5.95  $\mu$ .

The crude product, in benzene, was added to a Florisil column (50 g.) prepared in benzene and allowed to remain on the column for periods varying from 3 days to 3 weeks (shorter times were found to give uncrystallizable products). Within a few hours a gradual change in the colored band from yellow to red could be observed; after a few days a large portion of the column had acquired the same red coloration. Elution of the column with benzene and removal of solvent *in vacuo* yielded a red oil (0.829 g.), which was crystallized from methanol as red cubes, m.p. 118.5–122.5°. After repeated recrystallization from methanol an analytical sample of XVII was obtained as red cubes, m.p. 123–123.5°; infrared bands ( $\text{CH}_2\text{Cl}_2$ ): 5.80, 5.97  $\mu$ ; ultraviolet maxima ( $\text{CH}_2\text{Cl}_2$ ): 255  $m\mu$  (log  $\epsilon$  4.49), 450  $m\mu$  (log  $\epsilon$  3.31).

*Anal.* Calcd. for  $\text{C}_{23}\text{H}_{14}\text{O}_3$ : C, 81.64; H, 4.17. Found: C, 81.71, 81.69; H, 4.42, 4.31.

Further elution with benzene yielded a light yellow solid (0.009 g.), which was crystallized from methanol as white plates, m.p. 143–147°. This material was identified as 2-phenyl-1,3-indandione (XX) (lit.<sup>17</sup> m.p. 147–148.5°) by an infrared spectral comparison with an authentic sample, prepared by the method of Nathanson.<sup>17</sup>

Continued elution, with ether, yielded a white solid (0.145 g.) shown to be benzoic acid by its infrared spectrum.

**2,4-Dinitrophenylhydrazone of XVII (XVIII).**—A solution of XVII (0.107 g., 0.00031 mole) in dichloromethane (2 ml.) was added to a hot solution of 2,4-dinitrophenylhydrazine (0.545 g., 0.00275 mole) in 95% ethanol (11 ml.) and hydrochloric acid (1 ml.). A precipitate was immediately formed in the hot solution. The mixture was heated to boiling and allowed to cool to room temperature. The solid product was separated by filtration and crystallized from a mixture of dimethylformamide, hydrochloric acid, and 95% ethanol as fine, orange needles, m.p. 285–287° dec. An analytical sample was obtained after five recrystallizations from dichloromethane–95% ethanol as orange needles, m.p. 289.5–290.5° dec.; infrared bands (KBr): 3.20, 5.98, 6.05  $\mu$ ; ultraviolet maxima ( $\text{CH}_2\text{Cl}_2$ ): 237  $m\mu$  (log  $\epsilon$  4.62), 255  $m\mu$  (log  $\epsilon$  4.58), 322  $m\mu$  (log  $\epsilon$  4.05), 393  $m\mu$  (log  $\epsilon$  4.38), 437  $m\mu$  (log  $\epsilon$  4.52).

*Anal.* Calcd. for  $\text{C}_{29}\text{H}_{18}\text{O}_6\text{N}_4$ : C, 67.16; H, 3.46; N, 10.90. Found: C, 67.35; H, 3.54; N, 10.81.

**Quinoxaline from XVII (XIX).**—A mixture of XVII (0.052 g., 0.00022 mole) of freshly sublimed *o*-phenylenediamine (0.050 g., 0.00047 mole) and acetic acid (5 ml.) was heated on a steam-bath for 1 hr. The mixture was cooled and taken up in chloroform (50 ml.); the solution was washed with hydrochloric acid (3 *N*) and saturated aqueous sodium chloride and dried over sodium sulfate. Removal of solvent *in vacuo* yielded a red-orange foam, which was directly chromatographed on a Florisil (2 g.) column. The benzene eluate yielded a product, which was crystallized from methanol as orange cubes, m.p. 159–160.5°. After five recrystallizations from methanol, an analytical sample was obtained as light orange prisms, m.p. 160.5–161.5°; infrared band ( $\text{CH}_2\text{Cl}_2$ ): 5.83  $\mu$ ; ultraviolet maxima (95% EtOH): 240  $m\mu$  (log  $\epsilon$  4.56), 262  $m\mu$  (log  $\epsilon$  4.59), 345  $m\mu$  (shoulder, log  $\epsilon$  3.87), 437  $m\mu$  (log  $\epsilon$  3.15).

*Anal.* Calcd. for  $\text{C}_{29}\text{H}_{18}\text{ON}_2$ : C, 84.86; H, 4.42; N, 6.83. Found: C, 84.84; H, 4.63; N, 6.80.

The above product was also prepared by the fusion method of Fieser.<sup>28</sup>

(27) Melting points are uncorrected. Infrared spectra were calibrated against the 5.88- $\mu$  band of atmospheric water vapor.

(28) L. F. Fieser, "Experiments in Organic Chemistry," 3rd Ed., rev., D. C. Heath and Co., Boston, Mass., 1957, p. 174.

**Oxidation of XVII with Alkaline Hydrogen Peroxide.**—Solutions of 30% hydrogen peroxide (1 ml., 0.0088 mole) in dioxane (10 ml.) and of potassium hydroxide (0.15 g., 0.0027 mole) in methanol (10 ml.) were simultaneously added to XVII (0.085 g., 0.0025 mole) and the resultant solution was stirred at 25° for 2 hr. The color of the solution initially deepened, but lightened within 5 min. and after 30 min. was pale yellow. The mixture was acidified with concentrated hydrochloric acid (2 ml.), treated with sodium bisulfite (2 g., 0.019 mole), stirred for 5 min., and evaporated to dryness. The residue was taken up in ethyl acetate and the solution was washed with saturated aqueous sodium chloride and dried over sodium sulfate. The solvent was removed *in vacuo* leaving a white crystalline residue (0.053 g.). Part of the residue was insoluble in dichloromethane and was separated by dissolving the bulk of the solid in this solvent and filtering the insoluble component, which had m.p. 188–192° dec. Its infrared spectrum (KBr) was found to be identical with that of an authentic sample of phthalic acid. The infrared spectrum of the component soluble in dichloromethane showed it to be benzoic acid.

**Reduction and Periodic Acid Cleavage of XVII.**—A solution of XVII (0.50 g., 0.0015 mole) in 95% ethanol (50 ml.) was hydrogenated at 25° and 760 mm. over 10% palladium-charcoal (0.227 g.) for 20 hr. The hydrogen uptake was 122 ml. (0.0050 mole). The solution was filtered to remove catalyst and the solvent removed *in vacuo* to yield a white foam, whose infrared spectrum showed residual traces of carbonyl bands and a pronounced hydroxyl band.

A mixture of the above product, water (20 ml.), 95% ethanol (20 ml.), and periodic acid (0.50 g., 0.0022 mole) was stirred at 25° for 30 hr. This was poured into water, and the mixture was extracted with chloroform. The organic layer was washed with water and saturated aqueous sodium chloride and dried over sodium sulfate. Removal of solvent *in vacuo* gave a colorless oil (0.326 g.), which had a very pronounced odor of benzaldehyde. The oil was chromatographed on a Florisil column (15 g.). The benzene eluate contained a colorless oil (0.061 g.), which was identified as benzaldehyde by its infrared spectrum. In addition, its 2,4-dinitrophenylhydrazone, m.p. 236–237°, prepared by the method of Shriner, Fuson, and Curtin<sup>29</sup> gave no depression of melting point on admixture with authentic benzaldehyde 2,4-dinitrophenylhydrazone.

Further elution of the column with ether yielded a viscous oil (0.079 g.), which could not be crystallized; infrared bands ( $\text{CH}_2\text{Cl}_2$ ): 2.91, 5.80  $\mu$ .

**Reaction of Lead Tetraacetate with XVII: Formation of XXI.**—A mixture of XVII (0.224 g., 0.00066 mole), acetic acid (12 ml.), water (6 ml.), and lead tetraacetate (0.5 g., 0.0011 mole) was stirred at 25° for 42 hr.; additional lead tetraacetate (0.5 g. per addition) was added after 6, 18, and 24 hr. Hydrochloric acid (6 N, 50 ml.) was added with stirring to the mixture and it was extracted with chloroform. The organic extract was washed with water and saturated aqueous sodium chloride and dried over sodium sulfate. Removal of solvent *in vacuo* gave a reddish solid (0.194 g.).

A chromatogram of this product on Florisil (6 g.) yielded in the 5% ether–benzene eluate, a pale yellow oil (0.096 g.), which was crystallized from hexane as pale yellow needles, m.p. 163–166°. After five recrystallizations from hexane an analytical sample was obtained as white needles, m.p. 166–167°; infrared bands ( $\text{CH}_2\text{Cl}_2$ ): 5.73, 5.78  $\mu$ ; ultraviolet maxima (95% EtOH): 228.5  $\mu$  ( $\log \epsilon$  4.66), 247  $\mu$  ( $\log \epsilon$  4.11).

*Anal.* Calcd. for  $\text{C}_{17}\text{H}_{12}\text{O}_4$ : C, 72.85; H, 4.32. Found: C, 72.81; H, 4.42.

This material was shown to be identical with a synthetic sample of 2-acetoxy-2-phenyl-1,3-indandione (*vide infra*) by a mixture melting point determination and infrared spectral comparison.

Further elution of the chromatographic column with ether gave an eluate containing a white solid (0.027 g.), which was identified as benzoic acid by an infrared spectral comparison.

**2-Acetoxy-2-phenyl-1,3-indandione (XXI).**—A mixture of 2-phenyl-1,3-indandione (XX)<sup>17</sup> (0.50 g., 0.0019 mole), acetic acid (25 ml.), water (12.5 ml.), and lead tetraacetate (1.0 g., 0.0013 mole) was stirred at room temperature for 45 hr. Additional lead tetraacetate (1.0 g., per addition) was added after 17 and 25 hr. Hydrochloric acid (6 N, 50 ml.) was added with swirling, followed by water (100 ml.) and chloroform (115 ml.). The organic layer was separated, washed with water and saturated aqueous sodium chloride, and dried over sodium sulfate. Removal of solvent *in vacuo* yielded a yellow, foamy oil, which was immediately chromatographed on Florisil (30 g.). The colorless oil (0.225 g., 42.5%) obtained from the benzene eluate was crystallized from hexane to give white micro-needles, m.p. 125–155°. Three recrystallizations from hexane produced material of

m.p. 135–153°. This material was sublimed at 140–150° (1 mm.) for 4 hr. The sublimate was crystallized from hexane as small white needles, m.p. 165–166° (lit.<sup>21</sup> m.p. 165–166°); infrared bands ( $\text{CH}_2\text{Cl}_2$ ): 5.73, 5.78  $\mu$ .

**Acid Treatment of XVII: Formation of XXIV and XXV.**—A mixture of XVII (0.757 g., 0.0024 mole), concentrated hydrochloric acid (40 ml.), and acetic acid (40 ml.) was boiled under reflux for 19 hr.; pale yellow needles were observed in the yellow-orange liquid after *ca.* 1 hr. The mixture was cooled to room temperature and filtered to give a yellow-orange crystalline solid, m.p. 190–204° (0.526 g.). A chromatogram on Woelm nonalkaline alumina (activity grade 1) yielded a yellow compound, m.p. 207–210° (XXV), in the benzene eluate and an orange compound, m.p. 244–254° (XXIV), in the chloroform–methanol eluate; these products were obtained in a ratio of *ca.* 2.5:1. After five recrystallizations from dichloromethane–95% ethanol an analytical sample of XXV was obtained as pale yellow needles, m.p. 211–212°; infrared bands ( $\text{CH}_2\text{Cl}_2$ ): 5.73, 6.07  $\mu$ ; ultraviolet maxima (95% EtOH): 221  $\mu$  ( $\log \epsilon$  4.50), 243  $\mu$  ( $\log \epsilon$  4.42), 273  $\mu$  ( $\log \epsilon$  4.55), 330  $\mu$  (shoulder,  $\log \epsilon$  4.09).

*Anal.* Calcd. for  $\text{C}_{23}\text{H}_{14}\text{O}_3$ : C, 81.64; H, 4.17; mol. wt., 338. Found: C, 81.75, 81.57; H, 4.26, 4.12; mol. wt. (Rast), 377.

After four recrystallizations from dichloromethane–95% ethanol, a second chromatogram in the above manner, three additional recrystallizations from dichloromethane–95% ethanol, and two from dichloromethane–hexane, an analytical sample of XXIV was obtained as orange needles, m.p. 253–254°; infrared bands (KBr): 2.86, 5.84 (shoulder), 5.90  $\mu$ ; ultraviolet maxima (95% EtOH): 257  $\mu$  ( $\log \epsilon$  4.39), 265  $\mu$  ( $\log \epsilon$  4.33), 306  $\mu$  (shoulder,  $\log \epsilon$  3.49), 419  $\mu$  ( $\log \epsilon$  3.58).

*Anal.* Calcd. for  $\text{C}_{23}\text{H}_{14}\text{O}_2$ : C, 85.70; H, 4.38; mol. wt., 322. Found: C, 84.97; H, 4.29; mol. wt. (Rast), 293.

**Acetylation of XXIV.**—A mixture of XXIV (0.038 g., 0.00012 mole), acetic anhydride (6 ml.), and pyridine (1 ml.) was boiled at reflux for 1 hr. and allowed to remain at room temperature for 2 additional hours. Removal of solvent *in vacuo* yielded a yellow solid, which was crystallized from dichloromethane–hexane as yellow needles, m.p. 236–238°. After four recrystallizations from hexane, an analytical sample was obtained as yellow needles, m.p. 241.5–242°; infrared bands ( $\text{CH}_2\text{Cl}_2$ ): 5.65, 5.83 (shoulder), 5.87, 8.45  $\mu$ ; ultraviolet maxima ( $\text{CH}_2\text{Cl}_2$ ): 241  $\mu$  ( $\log \epsilon$  4.43), 248  $\mu$  ( $\log \epsilon$  4.50), 264  $\mu$  (shoulder,  $\log \epsilon$  4.60), 273  $\mu$  ( $\log \epsilon$  4.73), 296  $\mu$  (shoulder,  $\log \epsilon$  4.26), 383  $\mu$  ( $\log \epsilon$  3.71).

*Anal.* Calcd. for  $\text{C}_{25}\text{H}_{16}\text{O}_3$ : C, 82.40; H, 4.43. Found: C, 82.11; H, 4.38.

Alkaline hydrolysis with 3% aqueous alcoholic potassium hydroxide at 25° for 24 hr. reconverted this material to XXIV.

**Methylation of XXIV.**—To a stirred solution of XXIV (0.081 g., 0.00028 mole) in methanol (25 ml.) cooled in an ice-bath, there was added, alternately in small portions, dimethyl sulfate (10 ml.) and aqueous 50% potassium hydroxide (30 ml.), the addition being performed over a 20-min. period. The alkaline mixture was stirred for 15 min. at 25° and acidified with concentrated hydrochloric acid to pH 1. The mixture was extracted with chloroform; the organic extract was washed with water and saturated aqueous sodium chloride and dried over sodium sulfate. Removal of solvent *in vacuo* yielded a yellow-orange solid (0.082 g., 90%). After five recrystallizations from dichloromethane–95% ethanol, an analytical sample was obtained as orange needles, m.p. 176.5–177.5°; infrared bands ( $\text{CH}_2\text{Cl}_2$ ): 5.84 (shoulder), 5.90  $\mu$ ; ultraviolet maxima (95% EtOH): 252  $\mu$  ( $\log \epsilon$  4.60), 263  $\mu$  (shoulder,  $\log \epsilon$  4.65), 272  $\mu$  ( $\log \epsilon$  4.69), 296  $\mu$  ( $\log \epsilon$  4.23), 389  $\mu$  ( $\log \epsilon$  3.86).

*Anal.* Calcd. for  $\text{C}_{27}\text{H}_{18}\text{O}_2$ : C, 85.69; H, 4.79. Found: C, 85.65, 85.35, 85.41; H, 4.88, 4.78, 4.84.

**Treatment of XXV with Sodium Hydroxide.**—A mixture of XXV (0.144 g., 0.00043 mole), potassium hydroxide (0.60 g., 0.011 mole), water (6 ml.), and 95% ethanol (6 ml.) was boiled at reflux for 68 hr. The alkaline solution was extracted with ether; the extract was washed with saturated aqueous sodium chloride and dried over sodium sulfate. Removal of solvent *in vacuo* left no appreciable residue (<1 mg.). The alkaline solution was acidified with hydrochloric acid to pH 1 and extracted with chloroform; the organic extract was washed with saturated aqueous sodium chloride and dried over sodium sulfate. Removal of solvent *in vacuo* yielded a yellowish oil (0.140 g.). A chromatogram on Florisil yielded small amounts of a white solid in the later benzene fractions, which was purified by sublimation at 50–70° (1 mm.) for 3 hr. and shown to be benzoic acid by an infrared spectral comparison. The bulk of the material was eluted with dichloromethane–methanol. It was separated into acidic and neutral fractions with saturated aqueous sodium bicarbonate. The neutral product was crystallized from a small volume of methanol as white prisms, m.p. 135–138° with prior softening; infrared bands ( $\text{CH}_2\text{Cl}_2$ ): 2.73, 5.79  $\mu$ ; ultraviolet maxima (95% EtOH): 235  $\mu$  ( $E_{1\text{cm}}^{1\%}$  370), 291  $\mu$  ( $E_{1\text{cm}}^{1\%}$  41).

(29) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 219.