tered and evaporated at 35° and 30–40 mm. pressure yielding 5.52 g. of residual oil. This was combined with 0.83 g. of a corresponding crude product obtained in a preliminary experiment using 1.00 g. of IX. Distillation through a short Vigreux column furnished 4.19 g. (64%) of 4,7-dihydroxy-7-phenylheptanoic acid γ-lactone (XI) as a slightly yellowish oil, b.p. 170–174° at 0.13 mm., n^{20}D 1.5390; infrared bands (liq. film): 2.86, 5.64, 6.26, 6.33, 8.46 μ.

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 71.08; H, 7.16.

Conversion of 6-Benzoyl-4-hydroxyhexanoic Acid Lactone (VII) to 2-Benzoylcyclopropanepropionic Acid (IV).—A solution of potassium *t*-butoxide was prepared in the usual manner by dissolving freshly cut potassium (0.30 g., 0.0077 g.-atom) in 30 ml. of dried *t*-butyl alcohol at the reflux temperature. This required 1.5 hr. The solution was cooled slightly, and 6-benzoyl-4-hydroxyhexanoic acid lactone (VII, 1.50 g., 0.00689 mole, dried over phosphorus pentoxide at reduced pressure) was added. The mixture was refluxed under dry nitrogen for 45 min., cooled to 15–20°, and treated with 3.3 ml. of 6 N hydrochloric acid.

The pale yellow mixture was evaporated, finally at 30° and 30–40 mm. pressure. Water (10 ml.) was added to the residue, and the insoluble yellow oil was collected by extraction with three 15-ml. portions of ethyl acetate. The combined extracts were washed with three 20-ml. portions of aqueous 1 N sodium bicarbonate. Evaporation of the washed ethyl acetate solution and recrystallization of the waxy residue (206 mg.) from benzene–hexane yielded 83 mg. of recovered VII, m.p. 72–74°. A further recrystallization from water afforded 69 mg., m.p. 75–76°; mixture m.p. with starting material, 74.5–75.5°.

The combined sodium bicarbonate washes were acidified with concentrated hydrochloric acid and extracted with three 20-ml. portions of chloroform. Evaporation of the combined, dried extracts yielded 1.25 g. of crude 2-benzoylcyclopropanepropionic acid (IV), m.p. 63–68°. Recrystallization from 33% aqueous acetic acid afforded two crops: (a) 0.76 g., m.p. 67.5–68.5°, mixture m.p. with IV prepared from II 67.5–68.5°; and (b) 0.20 g., m.p. 66–67.5°. These together represent a 64% yield. The infrared spectrum of the first crop was identical with that of IV prepared from II.


3-Furanones. I. The Yellow Compound of Kleinfeller and Fiesselmann[1]

BY PETER YATES[2a] AND JERRY A. WEISBACH[2b]

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The yellow compound obtained by Kleinfeller and Eckert by the action of 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 by the action of bromine on methylenedeoxybenzoin dimer (III) has been shown to be 2-desylidene-4,5-diphenyl-3(2H)-furanone (IX). Its reactions have been investigated and its infrared and ultraviolet spectra and those of its tetrahydro derivative, 2-(2-hydroxy-1,2-diphenylethyl)-4,5-diphenyl-3(2H)-furanone (XII), compared with the spectra of a series of model compounds containing the 4,5-diphenyl-3-furanone system. A new, rational synthesis of the yellow compound has been effected *via* the action of oxalyl chloride on the sodium derivative of deoxybenzoin.

Kleinfeller and Eckert[3] observed that when 2,5-dihydroxy-1,2,5,6-tetraphenyl-3-hexyne-1,6-dione (I) is treated with saturated alcoholic hydrogen chloride, it is converted to a yellow compound, $C_{30}H_{20}O_3$. This product, which was reported to form a trioxime, was suggested to have structure II.

I   II
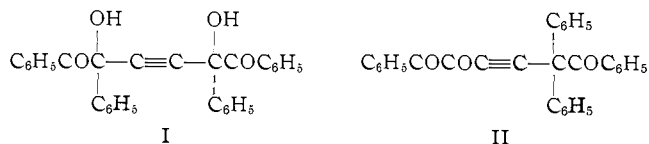
In the course of further work, Kleinfeller[4] found that the yellow compound is also formed, together with benzil, by the action of bromine in chloroform or acetic acid on I, that it forms a monosemicarbazone, fails to give a quinoxaline derivative, and is converted by concentrated sulfuric acid to a white, isomeric compound.

Fiesselmann and Ribka,[5] in the course of an investigation of the structure and reactions of methylenedeoxybenzoin dimer (III), discovered that treatment of this dimer with bromine in acetic acid gives a yellow compound, $C_{30}H_{20}O_3$, and two white compounds, one of which is isomeric with the yellow compound. They showed that this yellow compound, which forms a mono-2,4-dinitrophenylhydrazone, is identical with the yellow compound obtained by Kleinfeller and Eckert[3] from I, and that the isomeric white compound formed from III is identical with the compound obtained by the action of sulfuric acid on the yellow compound.

Fiesselmann and Meisel[6] investigated the oxidative degradation of the yellow compound with ozone and with chromic acid; the major products were found to be benzoic acid and benzil, which were the only products identified. They also carried out an investigation of the course of the bromination by isolation of reaction intermediates and were able to establish that the formation of the yellow compound very probably proceeds *via* the consecutive formation of the 1,3-dienes IV and V. They suggested that its formation from the acetylenic

III

IV, X = H
V, X = Br
VI, X = OAc

VII   VIII
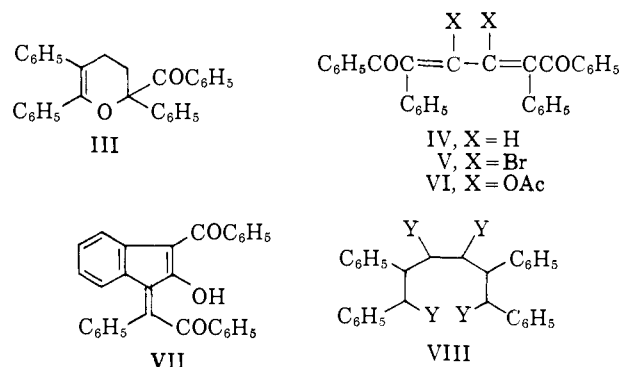
diol I also proceeds *via* V or an equivalent intermediate,[7] and Fiesselmann and Lindner[8] subsequently showed that it can be formed in high yield by the action of warm 47% hydrobromic acid on the diene VI. The conversion of V to the yellow compound was considered[6] to involve substitution into a phenyl ring[9] and structure VII was assigned to it.

We have reinvestigated these compounds and in this and the following paper[10] discuss new experimental

(1) A preliminary report on part of this work has appeared previously: P. Yates and J. A. Weisbach, *Chem. Ind.* (London), 1482 (1957).

(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).

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

(5) H. Fiesselmann and J. Ribka, *ibid.*, **89**, 40 (1956).

(6) H. Fiesselmann and F. Meisel, *ibid.*, **89**, 657 (1956).

(7) *Cf.* J. Salkind and A. Kruglow, *ibid.*, **59**, 1936 (1926).

(8) H. Fiesselmann and H. J. Lindner, *ibid.*, **89**, 1799 (1956).

(9) *Cf.* H. Wieland and H. Kloss, *Ann.*, **470**, 201 (1929).

(10) P. Yates and J. A. Weisbach, *J. Am. Chem. Soc.*, **85**, 2950 (1963).

evidence which leads us to propose a revised structure for the yellow compound and a structure for its isomerization product.

Although oxidation of the yellow compound with chromic acid, potassium permanganate, and ozone was investigated in the earlier studies, in no case was the formation of phthalic acid or other disubstituted benzene derivative demonstrated. We also were unable to detect the formation of such products in oxidation experiments. This circumstance led us to the view that the formation of the yellow compound most probably does not involve further substitution on any of the four monosubstituted phenyl rings of I or III.

A strong band at 5.95 μ in the infrared spectrum of the yellow compound showed that it possesses one or more conjugated carbonyl groups. That at least two of its three oxygen atoms are present as carbonyl groups was demonstrated by the fact that its mono-2,4-dinitrophenylhydrazone[5] retains in its infrared spectrum a band at 5.95 μ. The yellow compound gave on reductive acetylation a compound, $C_{34}H_{26}O_5$, with no hydroxyl-stretching band and a single carbonyl-stretching band at 5.67 μ in its infrared spectrum. These data were most simply interpreted in terms of the formation of the diacetate of a dihydro derivative and implied that all of the carbonyl functions of the yellow compound had been converted to two acetoxy groups and thus that the latter possesses only two such functions.[11] Since the infrared spectrum of the yellow compound shows no hydroxyl-stretching band, it followed that the third oxygen atom is present as an ether linkage.

Fiesselmann's convincing argument that the formation of the yellow compound proceeds *via* the diene V suggested VIII as the simplest part-formulation for the yellow compound, where Y represents a singly or doubly bound oxygen atom. This part structure, when considered in conjunction with the tentative conclusions regarding the functionality of the oxygen atoms discussed above, led to the alternative formulations IX and X for the yellow compound. We next describe experiments which established IX as the correct structure.[12,13]

IX

X
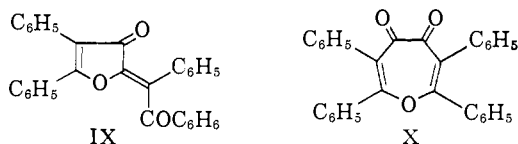
Catalytic hydrogenation of IX led to the slow uptake of two molar equivalents of hydrogen and the formation of a tetrahydro compound. This shows in its infrared spectrum (CH_2Cl_2) bands at 2.81 and 5.90 μ, a quartet of bands between 6.15 and 6.40 μ, and a band at 7.25 μ, whose intensity approximates that of the carbonyl-stretching band; its ultraviolet spectrum (CH_2Cl_2) has maxima at 235 mμ (log ϵ 4.24) and 316 mμ (log ϵ 4.07). These spectral data provide strong evidence for the presence of the chromophoric system XI, and the tetrahydro compound is formulated as XII.[14] To provide models for this chromophoric system the 4,5-diphenyl-3-furanones XIII–XVIII were
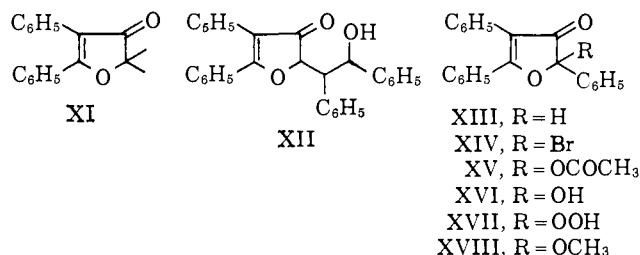
prepared by the methods of Kohler, Westheimer, and Tishler[15]; spectral data for these compounds are given in Table I. The infrared spectra of all of the model 3-furanones show a carbonyl band in the 5.81–5.90 μ region and the variation of band position within this

XI

XII

XIII, R = H
XIV, R = Br
XV, R = OCOCH₃
XVI, R = OH
XVII, R = OOH
XVIII, R = OCH₃

range may readily be interpreted in terms of the nature of the R group in XIII–XVIII.[16] In addition, they all show a quartet of bands between 6.15 and 6.40 μ and a strong band in the 7.2–7.3 μ region. The bands at 6.15–6.40 μ must be associated with the stretching vibrations of the ethylenic and aromatic bonds. The band at 7.2–7.3 μ may be assigned to the stretching vibration of the 1,5-carbon–oxygen bond in the 3-furanones, which is expected to have unusually high double bond character because of a considerable contribution of structure XIX to the resonance hybrid. It may be compared with the band at 7.85–8.15 μ, which is considered to result from the corresponding vibration in simple vinyl and aryl ethers.[17]

XI   XIX
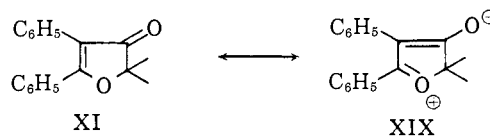
The ultraviolet spectra of XII and XIII are very similar. The spectra of the other model compounds also show a maximum in the 320–340 mμ region, but in most cases show maxima in both the 225–235 and 245–260 mμ regions. It appears probable that the single short wave length maximum in the 235–246 mμ region in the spectra of XII, XIII, and XV is composed of two overlapping maxima.[18] Related ultraviolet spectra have been reported previously for 5-phenyl-3-furanone derivatives.[19,20]

Although absorption of hydrogen was still proceeding when, in the formation of XII from IX, hydrogenation was stopped after the uptake of slightly more than two molar equivalents, the rate of this further absorption was very slow. The resistance of the benzyl alcohol function of XII to hydrogenolysis can be attributed to steric factors, while the preservation of the diphenylfuranone system may be interpreted in terms of both steric factors and the high delocalization energy of this system, which can be regarded as a vinylogous ester. A similar resistance to hydrogenation was found in the case of 2-methoxy-2,4,5-triphenyl-

(11) Although the formation of a trioxime has been reported,[3] this product was later suggested to be a dioxime.[6] In the present work, the reaction of the yellow compound with hydroxylamine gave a product which was found not to be a simple polyoxime (*vide infra*).

(12) Although structure IX as written represents one of two possible geometrical isomers, no conclusion has been reached regarding the stereochemistry of the yellow compound and its derivatives and this representation is not meant to imply such a conclusion.

(13) In order to simplify the exposition, this structure will be used immediately in the discussion of the degradative results.

(14) The yield of tetrahydro compound was relatively low and it is possible that more than one diastereomer was formed, although only one reduction product was isolated.

(15) E. P. Kohler, F. H. Westheimer, and M. Tishler, *J. Am. Chem. Soc.*, **58**, 264 (1936); F. H. Westheimer, Ph.D. Thesis, Harvard University, 1935.

(16) *Cf.* (a) P. Yates, S. Lipinsky, and D. Vossius, *Can. J. Chem.*, **39**, 1977 (1961), and references therein quoted; (b) R. N. Jones and C. Sandorfy in "Chemical Applications of Spectroscopy," ed. by W. West, Interscience Publishers, Inc., New York, N. Y., 1956, pp. 477–481.

(17) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen and Co., Ltd., London, 2nd Ed., 1958, p. 115.

(18) The absorption of dichloromethane increases steeply in the ultraviolet region below 240 mμ; however, the correspondence between the spectra observed for solutions in 95% ethanol and those for solutions in dichloromethane (see Table I) indicate that the data in the latter case are valid.

(19) R. E. Lutz, T. Amaker, S. M. King, and N. H. Shearer, *J. Org. Chem.*, **15**, 181 (1950).

(20) The similarity between the ultraviolet and infrared spectra of compounds XII and XIII, and those of compounds XIV–XVIII, shows that there is little tendency for the carbonyl group in XII and XIII to enolize.
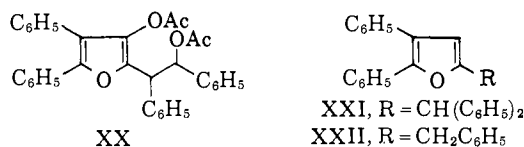
Compound	$\lambda^{CH_2Cl_2}_{max}$, μ			λ_{max}, $m\mu$	$\log \epsilon$	Solvent[a]
XIII		5.90	7.26	240	4.28	D
				317	4.11	
XIV		5.81	7.29	232	4.28	D
				256	4.20	
				338	4.00	
XV	5.63	5.82	7.27	246	4.18	D
				321	4.12	
XVI	2.81	5.85	7.23	227	4.26	E
				245	4.23	
				326	4.09	
XVII[b]	2.86	5.84	7.26	231	4.22	D
				247	4.17	
				327	4.00	
XVIII		5.84	7.24	227	4.27	E
				247	4.21	
				326	4.11	

[a] Solvent for ultraviolet spectrum: D = dichloromethane, E = 95% ethanol. [b] The infrared and ultraviolet spectra of XVII verify the conclusion of Rigaudy[21] that this compound exists as the furanone hydroperoxide.

3-furanone (XVIII), which, after treatment for 24 hr. under somewhat more stringent hydrogenation conditions than those used in the case of IX, gave a crude product which retained to an appreciable degree the 3-furanone chromophore (λ_{max} 326 mμ).

Acetylation of the tetrahydro compound yielded a diacetate, $C_{34}H_{28}O_5$, assigned structure XX. Its infrared spectrum, with carbonyl-stretching bands at 5.67 and 5.76 μ, is in accord with the presence of acetoxyl groups, both attached to an aromatic ring and to a saturated carbon atom. Its ultraviolet spectrum [λ^{EtOH}_{max} 229 mμ (shoulder, log ϵ 4.31) and 293 mμ (log ϵ 4.25)] shows excellent correspondence with the spectra of the 2,3-diphenylfuran derivatives XXI[22] and XXII[23] [λ^{EtOH}_{max} 238 mμ (shoulder, log ϵ 4.41), 297 mμ (log ϵ 4.24), and 225 mμ (log ϵ 4.37), 297 mμ (log ϵ 4.14), respectively].[24]

XX

XXI, R = CH$(C_6H_5)_2$
XXII, R = CH$_2C_6H_5$

Treatment of the tetrahydro compound with p-toluenesulfonic acid in benzene with azeotropic removal of water gave a yellow dehydration product, $C_{30}H_{22}O_2$. The infrared and ultraviolet spectra of this compound resemble those of IX and it is considered to have structure XXIII.[12] It was shown not to be the furan derivative XXIV by direct comparison with an authentic sample.[23] The formation of such a product would have been anticipated from the dehydration of XXV or XXVI, other formally possible formulations for the tetrahydro derivative of IX, which are also inadmissible on the basis of the spectral and degradative evidence.

Ozonolysis of the tetrahydro compound gave a product, $C_{30}H_{24}O_5$, with bands in its infrared spectrum at 2.84, 2.94(br), 5.79, and 5.92 μ and a maximum in its ultraviolet spectrum at 235 mμ (log ϵ 4.30) with a

(21) M. J. Rigaudy, Compt. rend., 226, 1993 (1948).
(22) L. L. Williams, private communication.
(23) D. R. Moore, Ph.D. Thesis, Harvard University, 1958.
(24) The acetoxyl group on the furan ring in XX is not expected to affect its ultraviolet spectrum significantly: cf. the similarity of the spectra of 3-acetoxy-2,5-diphenylfuran and 2,5-diphenylfuran.[25]
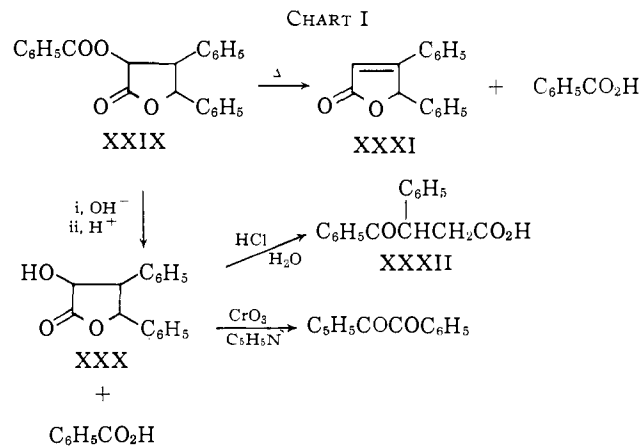(25) S. M. King, C. R. Bauer, and R. E. Lutz, J. Am. Chem. Soc., 73, 2253 (1951).

XXIII

XXIV

XXV
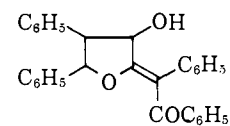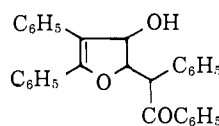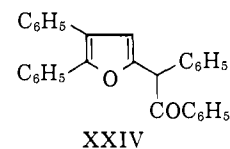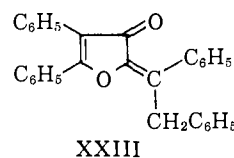
XXVI

shoulder at 252 mμ (log ϵ 4.14). This product cannot be formulated as the simple oxidative cleavage product XXVII or its enol, since it is colorless[26] and fails to give a positive test with ferric chloride in either ethanol or chloroform–pyridine.[27] However, these observations and the spectral data are in accord with its formulation as XXVIII, the cyclic tautomer of XXVII.

XXVII

XXVIII
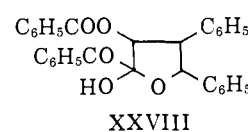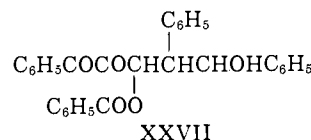
The presence of an α-ketol function in the structure of the ozonolysis product was corroborated by the oxidation of the latter with lead tetraacetate to give benzoic acid and a compound, $C_{16}H_{14}O_3$, to which structure XXIX is assigned. This assignment is in accord with the single high intensity maximum in the ultraviolet spectrum of the product at 233 mμ (log ϵ 4.19) (benzoate ester) and bands in its infrared spectrum at 5.55 and 5.79 μ (γ-lactone and benzoate ester, respectively). The fact that both carbonyl-stretching bands fall at shorter wave lengths than normal can be ascribed to the structural feature of substitution on the carbon atom α to the lactone carbonyl group by the benzoyloxy group; the origin of this shift is very probably similar to that of the well-known effect in the case of the spectra of α-acyloxy ketones.[16b] Hydrolysis of XXIX with aqueous alcoholic potassium hydroxide gave benzoic acid and a hydroxy lactone XXX, with bands in its infrared spectrum at 2.82 and 5.59 μ and no high intensity ultraviolet absorption above 210 mμ.

The structures assigned to this product and its precursor were confirmed by their degradation to the known compounds XXXI and XXXII by the routes depicted in Chart I.[28] These results, together with the

CHART I

XXIX

XXXI

+ $C_6H_5CO_2H$

i, OH$^-$
ii, H$^+$

XXX

HCl / H$_2$O

$C_6H_5COCHCH_2CO_2H$
XXXII

$\xrightarrow[C_5H_5N]{CrO_3}$ $C_5H_5COCOC_6H_5$

+

$C_6H_5CO_2H$

(26) Cf., for example, the yellow 1,4-diphenyl-1,2-butanedione: P. Ruggli, P. Weis, and H. Rupe, Helv. Chim. Acta, 29, 1788 (1946).
(27) S. Soloway and S. H. Wilen, Anal. Chem., 24, 979 (1952).
(28) The formation of desylacetic acid (XXXII) from XXX may be envisioned as occurring via dehydration to XXXI, followed by equilibration of this with the β,γ-unsaturated isomer and hydrolysis of the latter.

spectral evidence, firmly establish all features of XXX but the position of the hydroxyl group. Of the two other possible locations for this group, that on the γ-carbon atom of the lactone ring corresponds to structure XXXIII for the hydroxy lactone, which is the lactol tautomer of desylacetic acid (XXXII); the lack of any correspondence between the infrared spectrum of XXXII and that of the hydroxy lactone in solution eliminates this formulation. The location of the hydroxyl group on the β-carbon atom of the lactone ring is contraindicated by the failure of the hydroxy lactone to undergo dehydration on treatment with thionyl chloride and pyridine, for a compound of structure XXXIV would be expected to undergo facile dehydration under these conditions.[29] The infrared spectrum of the benzoate corroborates the α-placement of the benzoyloxyl group in XXIX (vide supra) and thus of the hydroxyl group in XXX.

XXXIII   XXXIV

XXXV   XXXVI
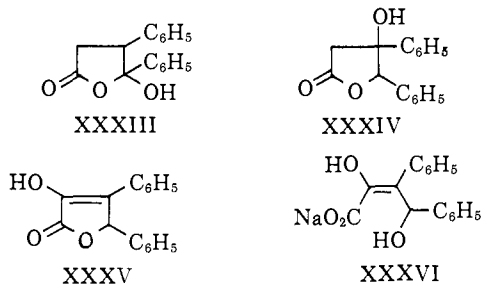
The preparation of all of the four possible racemates with structure XXX has already been claimed.[30,31] They are reported to have the following melting points: 127, 127, 170, and 171° (cf. the melting point of the product obtained in the present work: 183.5–184.5°). They were prepared in two pairs, each consisting of one low- and one high-melting isomer, by the sodium amalgam reduction of the lactone XXXV[30] and of the corresponding sodium salt XXXVI.[31] Differentiation between the isomers of similar melting point was made on the basis of their crystalline form and solubility properties; no mixture melting points are noted. We suggest that this apparent superfluidity of stereoisomers can best be interpreted in terms of the configurational identity of the materials of similar melting point obtained earlier.

The establishment of XII as the structure of the tetrahydro product provides strong evidence for the assignment of structure IX to the yellow compound itself. We turn now to the discussion of its spectra and reactions in terms of this structure. The strong band at 5.95 μ in its infrared spectrum can be considered as arising by the overlap of bands due to the carbonyl-stretching vibrations of each of the carbonyl groups. It would be anticipated, as observed, that the band due to the ring carbonyl group would lie at a somewhat longer wave length than the carbonyl bands of XII and XIII because of increased conjugation; the appearance of the carbonyl-stretching band of XXIII at 5.97 μ is in accord with this view and with the assignment of this structure to the yellow dehydration product of XII. The side-chain benzoyl group of IX could also give rise to a band at ca. 5.95 μ, for, whatever the stereochemistry of IX, steric interactions would be expected to prevent coplanarity of the benzoyl group with the five-membered ring and thus make its carbonyl-stretching band resemble that of an isolated benzoyl group. The infrared spectra of both IX and XXIII show the strong band at 7.2–7.3 μ, characteristic
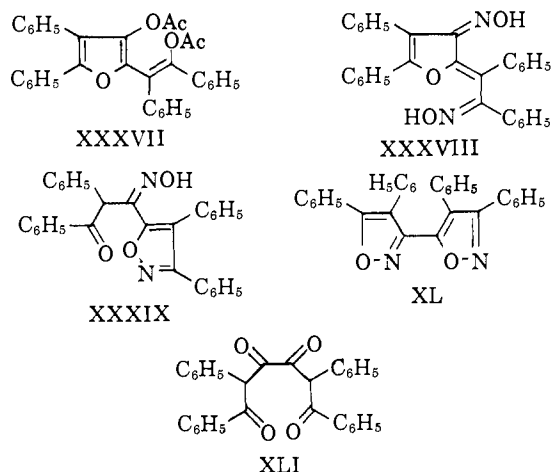
of XII and the model compounds XIII–XVIII. The relationship between the ultraviolet spectra of IX and XXIII and those of XII and XIII (Table II) is also in accord with the greater degree of conjugation of the ring carbonyl group in IX and XXIII compared with that in XII and XIII. The difference in position of the long wave length bands of IX and XXIII is not unexpected since, although the benzoyl group in IX is not coplanar with the five-membered ring (vide supra), electronic interaction may still occur[32] and give rise to a bathochromic shift of the long wave length band relative to that of XXIII.

TABLE II

Compound	Solvent[a]	λ_{max}, mμ (log ε)		
IX	E	240 (4.34)	262[b] (4.24)	342.5 (4.34)
XXIII	E	232 (4.31)	253 (4.21)	327 (4.28)
XII	E	242 (4.18)		315 (4.06)
	D	235 (4.24)		316 (4.07)
XIII	D	240 (4.28)		317 (4.11)

[a] E = 95% ethanol, D = dichloromethane. [b] Shoulder.

The reductive acetylation product obtained from the yellow compound can now be formulated as XXXVII.[12] The single carbonyl-stretching band at 5.67 μ in its infrared spectrum is attributed to the overlap of bands due to both the enolic and the aromatic acetate groups. Its ultraviolet spectrum, λ_{max}^{EtOH} 234 mμ (log ε 4.35), 278 mμ (log ε 4.23), and 338 mμ (log ε 4.37), is in accord with the extended conjugated system of structure XXXVII.[33]

XXXVII   XXXVIII

XXXIX   XL

XLI

Kleinfeller[3] obtained a product by treatment of the yellow compound with hydroxylamine, which he considered to be a trioxime. Fiesselmann and Meisel[6] later concluded that this compound is a dioxime. The elemental composition of the product obtained in the present work is in best agreement with the formula $C_{30}H_{20}O_2N_2$, corresponding formally to a dioxime less a molecule of water. This compound has no bands in either the 2.7–3.2 or 5.5–6.2 μ regions of its infrared spectrum; it has a single ultraviolet maximum at 287 mμ (log ε 4.22). These data clearly indicate that the compound is not a simple polyoxime and suggest that it is a tetraphenylbiisoxazole.[34] A rational reaction

(29) J. W. Cook and C. A. Lawrence, J. Chem. Soc., 1637 (1935); R. P. Linstead and E. M. Meade, ibid., 935 (1934).

(30) E. Erlenmeyer and M. Lux, Ber., 31, 2224 (1898).

(31) E. Erlenmeyer, ibid., 38, 3119 (1905).

(32) Cf. E. A. Braude and F. Sondheimer, J. Chem. Soc., 3754 (1955); L. L. Ingraham in "Steric Effects in Organic Chemistry," ed. by M. S. Newman, John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 11.

(33) Thus, the long wave length maximum shows an appreciable bathochromic shift relative to the corresponding bands of XX–XXII and XXIV, as expected.

(34) We have found that the infrared spectrum (CH₂Cl₂) of 3,5-diphenyl-isoxazole, m.p. 141–142°, has no bands in the 5.5–6.1 μ region, in contrast to an earlier report[35] of the presence of a band at 5.85 μ (dioxane solution).

(35) R. P. Barnes, G. E. Pinkney, and G. M. Phillips, J. Am. Chem. Soc., 76, 276 (1954).

sequence could lead from the simple dioxime XXXVIII *via* the monoisoxazole XXXIX to the biisoxazole XL; alternative paths are possible, however, leading to other tetraphenylbiisoxazoles related to 1,2,5,6-tetraphenyl-1,3,4,6-hexanetetrone (XLI).

Ozonolysis of the yellow compound in dichloromethane followed by treatment of the reaction mixture with sodium iodide in acetic acid gave a mixture of benzil, benzoic acid, and benzoic anhydride.[36] The formation of the last requires comment. It represents a so-called "abnormal" ozonolysis product and its formation can be rationalized in terms of the following type of reaction route, analogous to the routes proposed by Criegee in cognate cases[37]
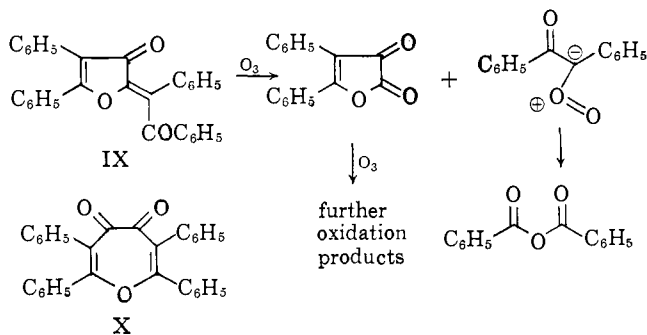
The relationship of benzoic anhydride to the alternative structure X for the yellow compound makes it appropriate at this point to discuss the bases for the rejection of this formulation. They are: (i) The yellow compound is unattacked by periodic acid in aqueous dioxane or by lead tetraacetate and pyridine in acetic acid.[38] (ii) It fails to form a quinoxaline,[4] even under forcing conditions. (iii) The structure of the hydrogenation product has been established as XII; although it is possible that a tetrahydro derivative of X could rearrange to XII, it seems highly unlikely that such a rearrangement would occur under the conditions of hydrogenation. (iv) The isomerization of the yellow compound by sulfuric acid is readily explicable[10] in terms of structure IX, but not of X. (v) Ring closure in the formation of the yellow compound is most unlikely to favor a seven- rather than a five-membered ring when comparable pathways are open for either type of closure (*vide infra*).

The diene V, suggested by Fiesselmann and Meisel[6] as a common intermediate in the formation of the yellow compound from either methylenedeoxybenzoin dimer (III) or from 2,5-dihydroxy-1,2,5,6-tetraphenyl-3-hexyne-1,6-dione (I), can also serve as an intermediate in a reasonable reaction sequence accounting for the formation of a product with structure IX.[40]

The revision of the structure of the yellow compound permitted us to evolve an alternative and more direct synthesis of this compound. Treatment of the sodium derivative of deoxybenzoin (XLII), formed by reaction

(36) Oxidation of the yellow compound with potassium permanganate in acetone gave benzil in high yield (86%, based on the formation of two molar equivalents); none of the isomeric white compound reported by Kleinfeller[4] was obtained.

(37) *Cf.* R. Criegee, P. deBruyn, and G. Lohaus, *Ann.*, **583**, 19 (1953); P. S. Bailey, *Chem. Rev.*, **58**, 925 (1958); we thank Professor R. B. Woodward for drawing our attention to this point.

(38) Although the cleavage of α-diketones by these reagents is an unusually slow reaction in general,[39] benzil was oxidized by periodic acid under the conditions used in the attempted oxidation of the yellow compound with periodic acid.

(39) P. W. Clutterbuck and F. Reuter, *J. Chem. Soc.*, 1467 (1935).

(40) In the case where III is the starting material, hydrogen bromide, formed in the oxidation of III to V by bromine, can serve as the acid catalyst for the ring-closure step. In the case where I is the starting material and bromine the other reactant, it may be surmised that hydrogen bromide is again the acid catalyst, being formed in the accompanying reaction leading to the degradation of I to benzil.
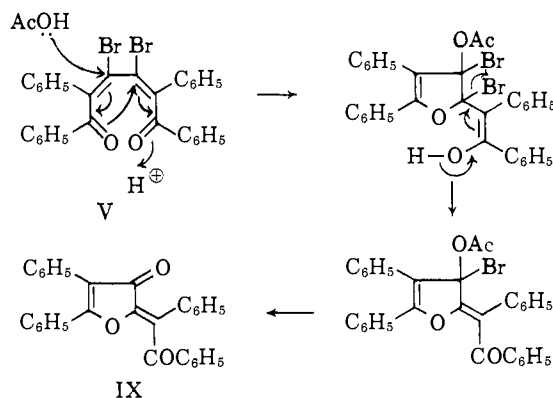
of deoxybenzoin with sodamide, with oxalyl chloride gave the yellow compound (14%), substantial amounts of deoxybenzoin, and a small amount of a white, crystalline solid, $C_{29}H_{20}O_2$. The spectra of this compound [$\lambda_{max}^{CH_2Cl_2}$ 6.14, 6.20 μ; 270 mμ (log ϵ 4.29)] suggested that it is a γ-pyrone[41] and it was identified by its synthesis by the action of phosgene on XLII as tetraphenyl-4-pyrone (XLIII).[42] The conception of the synthesis of IX in this fashion originated with our
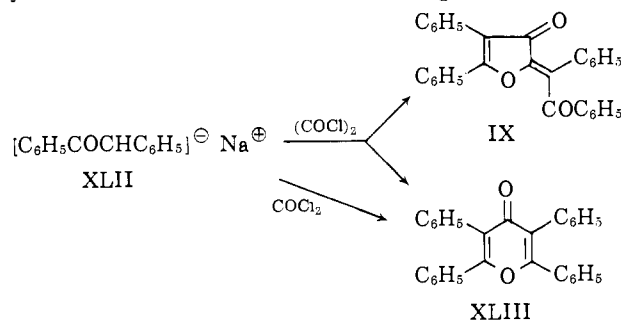
early deductions regarding the skeleton and oxygen sites of the yellow compound (*cf.* VIII). The reaction is thought to proceed *via* the tetrone XLI. The closure to a cyclic compound is again expected to favor formation of a five- rather than a seven-membered ring and this synthesis thus provides further support for the assignment of structure IX to the yellow compound. The relatively low yield of IX can be attributed to competing O-acylation of XLII by the oxalyl chloride. The minor product XLIII might have been formed from small amounts of phosgene arising from the decomposition of the oxalyl chloride. A more interesting, but unestablished, possibility is that it is formed by decarbonylation of small amounts of compound X formed along with IX in the ring closure of the intermediate XLI.

Experimental[43]

Methylenedeoxybenzoin Dimer (III, 2-Benzoyl-3,4-dihydro-2,5,6-triphenyl-2H-pyran).—The following modification of Fiesselmann's procedure[5,44] was used. Deoxybenzoin (50 g., 0.25 mole) was added to a mixture of methanol (200 ml.) and 37% formaldehyde (75 ml., 0.79 mole). The solution was boiled under reflux and piperidine (2.3 ml., 0.027 mole) was added dropwise over a period of 5 min. The heating was continued for 3 hr. Water (250 ml.) was added to the hot solution and the mixture cooled to room temperature. It was extracted with chloroform (250 ml.) and the organic layer was washed successively with dilute sulfuric acid, saturated aqueous sodium carbonate, water, and aqueous sodium chloride and dried over calcium

(41) *Cf.* 2,6-diphenyl-4-pyrone: $\lambda_{max}^{CHCl_3}$ 6.07, 6.22 μ; P. Franzosini, G. Traverso, and M. Senesi, *Ann. chim.* (Rome), **45**, 128 (1955).

(42) J. D. v. Mikusch, *Angew. Chem.*, **71**, 311 (1959), has prepared this compound recently by heating benzoic anhydride with dibenzyl ketone in the presence of boric acid. *Cf.*, also, J. J. Basselier, *Ann. chim.* (Paris), [13] **6**, 1131 (1961).

(43) Melting points are uncorrected. Infrared spectra were calibrated against the 5.88 μ band of atmospheric water vapor.

(44) H. Fiesselmann and J. Ribka, *Chem. Ber.*, **89**, 27 (1956).

chloride. After filtration, the solution of methylenedeoxy-benzoin was divided into three equal parts and the solvent removed *in vacuo*.

Each of these portions was dimerized separately and the products subsequently combined. The crude monomer was heated in an oil-bath at 130 ± 2° for 5 hr. (the use of lower temperatures was found to give less complete dimerization, while at higher temperatures other products were formed). Methanol (15–20 ml.) was added to the hot, viscous, yellowish brown oil and the mixture was swirled to effect homogeneity and allowed to cool to room temperature. Crystallization was observed in different runs after periods varying from 2 to 5 hr. and could be induced almost immediately by the addition of seed crystals. The combined product from the three runs (35 g., 70%) was recrystallized from methanol to give large, white prisms, m.p. 108–109° (lit.[5] 108.5–109°); infrared bands (CHCl₃): 5.95, 6.10 μ.

Repetition of this process with the residue from the mother liquor from the crystallization of the crude dimerization product gave additional dimer (7 g.), bringing the total yield to 84%.

Reaction of Methylenedeoxybenzoin Dimer with Bromine.—The following procedure was a modification of that of Fiesselmann.[5] Methylenedeoxybenzoin dimer (33.2 g., 0.080 mole) was dissolved in hot acetic acid (250 ml.), and a solution of bromine (25 g., 0.16 mole) in acetic acid (50 ml.) was added dropwise over a period of 30 min. The flask was placed deep in a steam-bath, its exposed surface wrapped with a towel and the bath set for a high steam output (a boiling water-bath could be used instead, but the use of a normal flow of steam on an unwrapped flask gave very much poorer results). Heating was continued for periods varying from 8 to 24 hr.; 12 to 14 hr. heating was found to give optimum yields. After heating was terminated the maroon-colored solution was permitted to cool to room temperature and was filtered after 2 hr. and again after 18 hr. The combined solids from these filtrations were washed with acetic acid and recrystallized from 95% ethanol to give a white product (11 g., 33%), m.p. 205–220°.[10]

The original filtrate was allowed to stand and refiltered periodically. The solid obtained in this manner was triturated with acetone to give a white solid (usually *ca.* 0.3 g.) and a yellow solution. After repeated recrystallization of the white solid from acetic anhydride an analytical sample was obtained as white needles, m.p. 252–253°; infrared band (KBr): 5.95 μ.

Anal. Found: C, 86.16, 85.74, 86.32; H, 6.44, 6.28, 6.50.

Yields of this product were not consistent, although they were always in this general range. It sometimes was found precipitated with the other white compound. In that case separation was also effected by trituration of the mixture with acetone.

The yellow solution was evaporated to dryness to give compound **IX** as a yellow solid (7 g., 21%), which was washed with acetic acid and crystallized from 95% ethanol as yellow needles, m.p. 212–213°; infrared bands (CH₂Cl₂): 5.95, 7.30 μ; ultraviolet maxima (95% EtOH): 240 mμ (log ε 4.34), 262 mμ (shoulder, log ε 4.24), 342.5 mμ (log ε 4.34).

Anal. Calcd. for C₃₀H₂₀O₃: C, 84.09; H, 4.71. Found: C, 83.73; H, 4.73.

Oxidation of IX with Potassium Permanganate.—A solution of potassium permanganate (0.5 g., 0.0031 mole) in acetone (98 ml.) was added over a period of 10 min., with swirling and warming (*ca.* 40°), to a solution of IX (0.314 g., 0.00073 mole) in acetone (75 ml.). The addition was stopped when the solution retained a persistent violet coloration for 2 to 3 min. Formic acid (85%) was added dropwise with warming and swirling until the violet color of the solution was destroyed; the mixture was then filtered with suction through a Celite pad. Removal of solvent *in vacuo* yielded a pale yellow solid, which was dissolved in warm benzene and refiltered to give a small amount of white solid (*ca.* 3–4 mg.) and a yellow solution. The white material was slightly soluble in water, insoluble in dichloromethane, and darkened on heating to 295°, but did not melt. Evaporation of the filtrate to dryness *in vacuo* yielded a yellow oil which rapidly crystallized as light yellow needles, m.p. 93–96° (0.264 g., 86% for two moles). This material was identified as benzil by an infrared spectral comparison.

Ozonolysis of IX.—A solution of IX (0.461 g., 0.0011 mole) in dichloromethane (*ca.* 150 ml.) was cooled in a Dry Ice bath and treated with ozonized oxygen for 90 min. A solution of sodium iodide (25 g., 0.17 mole) in acetic acid (35 ml.) was added immediately and the mixture was allowed to warm to room temperature; saturated aqueous sodium thiosulfate was then added dropwise with swirling until the red color of the mixture had been discharged. The organic layer was separated and the aqueous layer was 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* yielded a pale yellow solid, whose infrared spectrum indicated that it was a mixture of benzoic anhydride, benzoic acid, and benzil. A chromatogram on Florisil gave benzil in the first benzene eluate (50 ml.). Frac-

tions immediately following this were identified by their infrared spectra as mixtures of benzoic anhydride and benzoic acid. Later fractions (1:1 benzene–ether) yielded pure benzoic acid. Attempted fractional crystallization of the benzoic anhydride-benzoic acid mixtures produced either pure benzoic acid or benzoic anhydride containing significant amounts of benzoic acid. These binary mixtures were identified by means of their infrared spectra.

Hydrogenation of IX: Formation of XII.—A solution of IX (2.19 g., 0.0055 mole) in 95% ethanol (75 ml.) was hydrogenated at 760 mm. and 25° over 10% palladium–charcoal (0.5 g.). Hydrogen uptake essentially ceased after 45 hr., when 332 ml. (2.08 molar equivalents) had been absorbed. The catalyst was filtered and *ca.* 60 ml. of the ethanol was distilled. Upon slow cooling of the concentrate the reduced product was obtained as white needles (0.610 g., 27%), m.p. 190–195°. Seven crystallizations from 95% ethanol gave an analytical sample as white rhombs, m.p. 194–195°; infrared bands (CH₂Cl₂): 2.81, 5.90, 7.25 μ; ultraviolet maxima (95% EtOH): 242 mμ (log ε 4.18), 315 mμ (log ε 4.06).

Anal. Calcd. for C₃₀H₂₄O₃: C, 83.31; H, 5.59. Found: C, 83.56, 83.55; H, 5.69, 5.78.

Reductive Acetylation of IX: Formation of XXXVII.—A mixture of IX (0.200 g., 0.00047 mole), zinc dust (0.21 g., 0.0032 mole), sodium acetate (0.021 g., 0.00026 mole), and acetic anhydride (4.6 ml.) was boiled at reflux for 1 hr. The mixture was cooled to room temperature, filtered, and the solvent removed *in vacuo*. The residue was taken up in chloroform and the solution was washed successively with aqueous sodium bicarbonate, water, and aqueous sodium chloride and dried over sodium sulfate. Removal of solvent *in vacuo* gave a glassy solid (0.2 g.) which crystallized from benzene–hexane as white prisms, 189–193°. After three recrystallizations from benzene–hexane an analytical sample was obtained as white, elongated prisms, m.p. 201–202.5°; infrared bands (CH₂Cl₂): 5.67, 8.40 μ; ultraviolet maxima (95% EtOH): 234 mμ (log ε 4.35), 278 mμ (log ε 4.25), 338 mμ (log ε 4.37).

Anal. Calcd. for C₃₁H₂₆O₅: C, 79.36; H, 5.09. Found: C, 79.30; H, 4.89.

Acetylation of XII: Formation of XX.—A solution of XII (0.162 g., 0.00038 mole) in acetic anhydride (7 ml.) and pyridine (1 ml.) was boiled at reflux for 50 min. The mixture was cooled to 25° and the solvent removed *in vacuo* to yield a yellow oil, which crystallized from methanol as small, white needles, m.p. 126–129°. After four recrystallizations from methanol, an analytical sample was obtained as white needles, m.p. 131–132°; infrared bands (CH₂Cl₂): 5.67, 5.76, 8.16 μ; ultraviolet maxima (95% EtOH): 229 mμ (shoulder, log ε 4.31), 293 mμ (log ε 4.23).

Anal. Calcd. for C₃₄H₂₈O₅: C, 79.05; H, 5.46. Found: C, 78.71; H, 5.52.

Acid Treatment of XII: Formation of XXIII.—A solution of XII (0.067 g., 0.00016 mole) and *p*-toluenesulfonic acid (0.063 g., 0.00040 mole) in benzene (50 ml.) was boiled under reflux for 1 hr. During this period, benzene (30 ml.) was slowly distilled from the reaction mixture. The yellow solution was cooled and poured into water; the organic layer was separated and the aqueous layer extracted with benzene (30 ml.). 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 yellow, semisolid material, which was crystallized from 95% ethanol as yellow needles, m.p. 47–153°. After three recrystallizations from hexane, an analytical sample was obtained as yellow needles, m.p. 152–153°; infrared bands (CH₂Cl₂): 5.97, 7.29 μ; ultraviolet maxima (95% EtOH): 232 mμ (log ε 4.31), 253 mμ (log ε 4.21), 327 mμ (log ε 4.28).

Anal. Calcd. for C₃₀H₂₂O₂: C, 86.93; H, 5.35. Found: C, 86.46; H, 5.95.

Attempted Oxidation of XII with Periodic Acid.—A mixture of compound XII (0.030 g., 0.000069 mole), periodic acid (0.025 g., 0.00011 mole), water (7 ml.), dioxane (15 ml.), and methanol (15 ml.) was stirred at room temperature for 22 hr. The mixture was extracted with dichloromethane, and the extract was washed with water and saturated aqueous sodium chloride and dried over sodium sulfate. Removal of solvent *in vacuo* gave a colorless oil, which was shown to be essentially unchanged starting material by its infrared spectrum.

Ozonolysis of XII: Formation of XXVIII.—Compound XII (0.103 g., 0.00024 mole) was dissolved in dichloromethane (25 ml.) and the solution was cooled with Dry Ice. Ozonized oxygen was passed in until a deep blue coloration persisted for a period of 5 min. Sodium iodide (5 g., 0.033 mole) in acetic acid (10 ml.) was immediately added to the blue solution. The mixture was allowed to remain in the Dry Ice bath for 15 min. and then heated to boiling on a steam-bath. Saturated aqueous sodium bisulfite was added slowly until the reddish color of the mixture was discharged. The organic layer was separated and the aque-

ous solution extracted with dichloromethane (75 ml.). The combined organic layers were washed with water and saturated aqueous sodium chloride and dried over sodium sulfate. After removal of the solvent *in vacuo* a white solid (0.111 g.) remained which was crystallized from 95% ethanol to give white needles, m.p. 185–190°, which gave negative ferric chloride tests in alcohol and pyridine–chloroform.[27] After four recrystallizations from 95% ethanol, an analytical sample was obtained as white needles, m.p. 191.5–193°; infrared bands (CH$_2$Cl$_2$): 2.84, 2.94, 5.79, 5.92 μ; ultraviolet maxima (95% EtOH): 235 mμ (log ϵ 4.30), 252 mμ (shoulder, log ϵ 4.14).

Anal. Calcd. for C$_{30}$H$_{24}$O$_5$: C, 77.57; H, 5.21. Found: C, 77.40; H, 5.31.

Oxidation of XXVIII with Lead Tetraacetate: Formation of XXIX.—Compound XXVIII (0.250 g., 0.00054 mole) and lead tetraacetate (2.0 g., 0.0045 mole) were added to a mixture of acetic acid (110 ml.), water (25 ml.), and methanol (85 ml.). After the solution had been stirred for 9 hr. at room temperature, additional lead tetraacetate (1.0 g., 0.0023 mole) was added. After a total reaction time of 24 hr., 2 N hydrochloric acid was added and the mixture was extracted with chloroform; the organic extract was washed with aqueous sodium chloride and dried over sodium sulfate. On removal of solvent *in vacuo*, a product (0.220 g.) was obtained as a yellowish, semisolid residue, which had a strong odor resembling that of methyl benzoate.

The product was chromatographed on a Florisil column, which was packed in a 1:1 petroleum ether–benzene mixture; the reaction product was added in this same solvent combination. A product (0.160 g.), a colorless oil still faintly retaining the sweet aroma of methyl benzoate, was eluted with a 1:3 petroleum ether–benzene solvent pair. White needles were obtained when this material was allowed to remain under reduced pressure overnight. After four recrystallizations from hexane, an analytical sample was obtained as white needles, m.p. 127.5–128°; infrared bands (CH$_2$Cl$_2$): 5.55, 5.79 μ; ultraviolet maximum (95% EtOH): 233 mμ (log ϵ 4.19).

Anal. Calcd. for C$_{23}$H$_{18}$O$_4$: C, 77.08; H, 5.06. Found: C, 77.12, 77.40; H, 5.20, 5.11.

A repetition of this reaction in the absence of methanol, but otherwise under the same conditions, gave a crude product lacking the benzoate ester odor, which on chromatography gave both the above product and an additional solid product. The latter was shown to be benzoic acid by its infrared spectrum, which was identical in all respects to that of an authentic sample.

Alkaline Hydrolysis of XXIX: Formation of XXX.—A solution of XXIX (0.190 g., 0.00053 mole) in dichloromethane was added to a solution of sodium hydroxide (0.055 g., 0.00138 mole) in 95% ethanol (25 ml.) and water (25 ml.). The mixture was heated to remove the dichloromethane and then boiled at reflux for 12 hr. It was then acidified with concentrated hydrochloric acid (5 ml.), allowed to cool to room temperature, and extracted with chloroform. The organic layer was washed with water, dried over sodium sulfate, and the solvent was removed *in vacuo*. The crude product was sublimed at 40–50° (1 mm.) for 33 hr. The sublimate (0.040 g., 61.5% for 1 mole) was shown to be benzoic acid by its infrared spectrum and a mixture melting point with an authentic sample. The residue (0.110 g., 81.5%) was crystallized from chloroform–hexane to give white plates, m.p. 175–182°. After four recrystallizations from chloroform, an analytical sample was obtained as white plates, m.p. 183.5–184.5°; infrared bands (CH$_2$Cl$_2$): 2.82, 5.59 μ; ultraviolet spectrum (95% EtOH): no high intensity ultraviolet absorption above 210 mμ.

Anal. Calcd. for C$_{16}$H$_{14}$O$_3$: C, 75.57; H, 5.55. Found: C, 75.47; H, 5.49.

Oxidation of XXX with Chromium Trioxide–Pyridine.—The complex of chromic anhydride (0.50 g., 0.0050 mole) and pyridine (2 ml.) was prepared by the method of Sarett.[45] Compound XXX (0.096 g., 0.00038 mole) in pyridine (3 ml.) was added to the complex at 0° and the mixture allowed to warm to 25° and remain at that temperature for 63 hr. The mixture was poured into cold 6 N hydrochloric acid and saturated aqueous sodium bisulfite was added dropwise with swirling until all of the solid material had dissolved and a clear, green solution was obtained. The aqueous solution was extracted with chloroform and the organic layer was washed with saturated aqueous sodium chloride and dried over sodium sulfate. Removal of the solvent *in vacuo* gave a yellow, solid product (0.062 g.), whose infrared spectrum indicated it to be a mixture of benzil and benzoic acid. A chromatogram on Merck alumina (2 g.) gave in the benzene eluate a pale yellow, crystalline solid (0.040 g., 50.5%), m.p. 94–95°, shown to be benzil by a mixture melting point determination and infrared spectral comparison.

Acid Treatment of XXX: Formation of Desylacetic Acid (XXXII).—Compound XXX (0.069 g., 0.00027 mole) was added

to a mixture of methanol (15 ml.) and concentrated hydrochloric acid (15 ml.). The solution was boiled under reflux for 48 hr., and the methanol was then allowed to boil off. Water (9 ml.) and concentrated hydrochloric acid (1 ml.) were added and the mixture boiled in the open flask until the temperature reached 110° and remained constant at that point (constant boiling hydrochloric acid). The mixture was then boiled under reflux for 130 hr. After it had cooled to room temperature, it was extracted with chloroform; the organic layer was washed with aqueous sodium chloride and dried over sodium sulfate. Removal of the solvent *in vacuo* left a colorless oil (0.040 g., 58%), which was crystallized from hexane to give white needles. One recrystallization from hexane gave white needles, m.p. 160–162°, which did not depress the melting point of an authentic sample of desylacetic acid,[46] m.p. 160–161°, and whose infrared spectrum was identical with that of desylacetic acid.

Pyrolysis of XXIX: Formation of 4-Hydroxy-3,4-diphenyl-2-butenoic Acid Lactone (XXXI).—Three evacuated sealed tubes, each containing compound XXIX (0.17 g. per tube, 0.00048 mole), were heated at 320–340° in a Wood's metal bath for 50 min. The tubes were allowed to cool to room temperature; their contents were taken up in ether and the ethereal solutions combined. The resulting solution was extracted with 2% aqueous sodium carbonate. The organic layer was separated, washed with saturated aqueous sodium chloride, and dried over sodium sulfate. Removal of solvent *in vacuo* yielded a pale yellow oil which was chromatographed on Florisil (1.5 g.). A small amount of unconsumed starting material was found in the initial benzene eluates; from the later benzene eluates a colorless oil was obtained which crystallized from 95% ethanol as short, white needles, m.p. 147.5–150°. This material was identified as 4-hydroxy-3,4-diphenyl-2-butenoic acid lactone (XXXI) by a mixture melting point determination with an authentic sample[47] and infrared spectral comparison.

The aqueous sodium carbonate layer was acidified with concentrated hydrochloric acid and extracted with chloroform. The organic layer was separated, washed with saturated aqueous sodium chloride, and dried over sodium sulfate. Removal of solvent *in vacuo* yielded a white solid, which was identified as benzoic acid by its infrared spectrum.

Attempted Dehydration of XXX.—Thionyl chloride (1 ml.) was added dropwise to a solution of compound XXX (0.030 g., 0.00012 mole) in pyridine (1 ml.) at 0°. The mixture was allowed to remain at 25° for 30 min., heated at reflux for 10 min., cooled to 25°, and then poured onto ice. Concentrated hydrochloric acid (4 ml.) was added 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, which was identified by its infrared spectrum as starting material.

Reaction of IX with Hydroxylamine: Formation of XL.—A mixture of IX (0.92 g., 0.0022 mole), hydroxylamine hydrochloride (2.0 g., 0.029 mole), pyridine (10 ml.), and absolute ethanol (10 ml.) was boiled under reflux for 2.5 hr. The mixture was cooled to room temperature, poured into excess 2 N hydrochloric acid, and stirred to coagulate the pasty, yellowish material which separated. The material was filtered and the spongy, semisolid product was crystallized from chloroform–95% ethanol as white needles, m.p. 232–237°. An analytical sample was obtained after nine recrystallizations from chloroform–95% ethanol as white needles, m.p. 246.5–247.5°; infrared bands (Nujol): no hydroxyl or carbonyl absorption; ultraviolet maximum (CH$_2$Cl$_2$): 287 mμ (log ϵ 4.22).

Anal. Calcd. for C$_{30}$H$_{20}$O$_2$N$_2$: C, 81.80; H, 4.58; N, 6.36. Found: C, 81.24; H, 4.47; N, 6.30.

Attempted Oxidation of IX with Periodic Acid.—A solution of IX (0.50 g., 0.0012 mole) in dioxane (40 ml.) was added to a solution of periodic acid (0.30 g., 0.0013 mole) in water (20 ml.). The slightly cloudy mixture was shielded from light with aluminum foil and stirred at 25° for 24 hr. The mixture was extracted with chloroform and the organic extract washed with water and saturated aqueous sodium chloride and dried over sodium sulfate. On removal of solvent *in vacuo* a product was obtained whose infrared spectrum closely resembled that of the starting material. Further treatment with fresh periodic acid (0.90 g., 0.0039 mole) for another 7 days under the same conditions gave material (0.41 g.) identical in infrared spectrum with that obtained with the shorter reaction time.

Other attempts to effect cleavage of IX with lead tetraacetate in acetic acid and added pyridine or methanol were likewise unsuccessful.

Attempted Conversion of IX to a Quinoxaline Derivative.—Compound IX (0.100 g., 0.00023 mole), freshly sublimed *o*-phenylenediamine (0.050 g., 0.00046 mole), and glacial acetic acid (0.35 ml.) were heated in a sealed tube immersed in a sandbath at *ca.* 250° for 70 hr. After cooling, the tube was opened

(45) G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *J. Am. Chem. Soc.*, **75**, 422 (1953).

(46) E. Knoevenagel, *Ber.*, **21**, 1344 (1888).

(47) J. Thiele, *Ann.*, **306**, 194 (1899).

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[48] and of Mathys, Prelog, and Woodward[49] 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_2Cl_2): 6.14, 6.20 μ; ultraviolet maximum (CH_2Cl_2): 270 mμ (log ϵ 4.29).

Anal. Calcd. for $C_{29}H_{20}O_2$: 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.
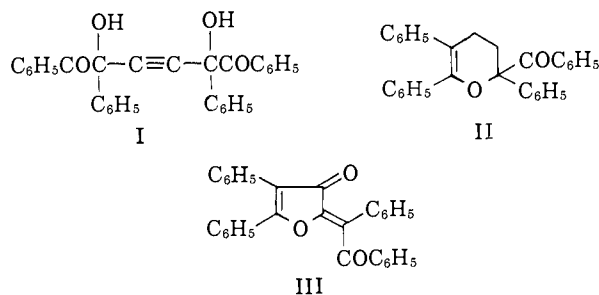

3-Furanones. II. The White Compound of Kleinfeller and Fiesselmann[1]

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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(3H),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[3] 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[4] by the action of bromine on methylene-

I

II

III

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

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

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

Its infrared spectrum (CH_2Cl_2) 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.[6] 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. Meisel, *ibid.*, **89**, 657 (1956).

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

(6) Thus, for example, 2,4,5-triphenyl-3-furanone (V, $R_1 = C_6H_5$, $R_2 = H$) has $\lambda_{max}^{CH_2Cl_2}$ 5.90, 7.26 μ, and a quartet at 6.15–6.40 μ, and $\lambda_{max}^{CH_2Cl_2}$ 240 mμ (log ϵ 4.28) and 317 mμ (log ϵ 4.11). Spectral data for other model compounds are given in ref. 1.