hydrate in 25 ml. of 70% acetic acid[14] resulted in the precipitation of a small amount of cuprous oxide when the mixture was heated at the reflux for 15 minutes. The acid was diluted with water, potassium carbonate was added cautiously to saturation, and the aqueous mixture was extracted with ether. The ethereal extracts were dried and the ether was removed at reduced pressure. A small quantity of deep yellow oil remained. Treatment of the oil with excess hydroxylamine hydrochloride and pyridine in refluxing ethanol for two hours gave 0.13 g. of VIf (see above).

1-Methyl-1-azacyclopentadecan-8,9-dione dioxime (VIh) was obtained by oxidation of IIIh with cupric acetate in acetic acid[14] obtained by oxidation of IIIh with cupric acetate in acetic acid[14] followed by oximation,[13a] slightly pink needles from aqueous ethanol, m.p. 206–207°.

*Anal.* Calcd. for $C_{15}H_{29}N_3O_2$: C, 63.57; H, 10.31; N, 14.83. Found: C, 63.62; H, 10.24; N, 14.77.

1-Methyl-1-azacycloheptadecan-9,10-dione dioxime (VIj) was obtained in the same way, slightly pink needles from aqueous ethanol, m.p. 188–189°.

*Anal.* Calcd. for $C_{17}H_{33}N_3O_2$: C, 65.55; H, 10.68; N, 13.49. Found: C, 65.73; H, 10.94; N, 13.62.

1-Methyl-1-azacyclononadecan-10,11-dione dioxime (VIk), prepared by the same sequence, slightly pink needles from aqueous ethanol, m.p. 189°.

*Anal.* Calcd. for $C_{19}H_{37}N_3O_2$: C, 67.21; H, 10.99; N, 12.38. Found: C, 67.39; H, 11.37; N, 12.65.

URBANA, ILLINOIS

---

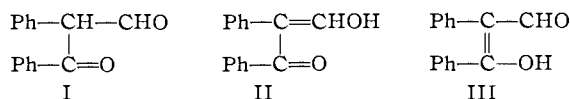# The Structures of the Isomeric Enols and Methyl Ethers of Formyldesoxybenzoin

BY PETER B. RUSSELL[a] AND ERNEST CSENDES[b,1]

RECEIVED APRIL 29, 1954

Two enolic forms of formyldesoxybenzoin (α-formyl-α-benzoyltoluene) were described by Wislicenus and Ruthing.[2] The α-form (m.p. 76–80°) is now shown to be a chelate of α,β-diphenyl-β-hydroxyacrolein (III) while the β-form (m.p. 112–113°) is the open hydroxy methylene compound, α-phenyl-β-hydroxyacrylophenone (II). The evidence upon which these conclusions are based was obtained by infrared and ultraviolet spectroscopy and from a study of the reactions of the two forms with diazomethane. The study illustrates the influence of steric factors in determining the structure of the enol under any set condition.

Wislicenus and Ruthing[2] obtained two crystalline modifications of formyldesoxybenzoin (I). One, the α-form, crystallized from petroleum ether and melted at 76–80°; the second, the β-form, melted at 112–113° after recrystallization from aqueous ethanol. Both forms gave a reaction with ferric chloride solution and both gave one and the same copper complex. The α-form was converted to the β-form by treatment with alcohol or by heating near its melting point. The conversion takes place slowly at room temperature. The β-form was converted to the α-form by crystallization from a nonpolar solvent (*e.g.*, benzene, petroleum ether), by heating above its melting point and cooling rapidly or by distillation.

Wislicenus[2] considered the α-form to be the hydroxymethylene compound II[3] and the β-form to be the enol-aldehyde III. These conclusions were based on the observation that only the β-form gave an immediate fuchsin reaction.

Ph—CH—CHO    Ph—C=CHOH    Ph—C—CHO
 |              |               ||
Ph—C=O       Ph—C=O      Ph—C—OH
   I                  II             III

Scheiber and Hopfer[4] reported that both the α- and β-forms of formyldesoxybenzoin gave benzil on ozonolysis in carbon tetrachloride at −20°, together with formic acid and a little benzoic acid. These authors concluded that the two forms were geometrical isomers of the hydroxymethylene form II.

Apart from the undesirability of basing conclusions regarding the structure of compounds containing mobile systems on the results of ozonolysis, the views of Scheiber and Hopfer are open to objection on other, more specific, grounds. As reported by Wislicenus[2] both forms of formyldesoxybenzoin give *immediate* reactions with ferric chloride and both react *at once* with copper to give the same complex. It is well recognized that one member of a pair of geometrically isomeric enols, the *trans* member, does not give either of these reactions although the ferric chloride color often develops after standing some time.[5,6] The best known examples of such geometrically isomeric pairs of enols are the *cis*- and *trans*-methyl and ethyl formylphenylacetates (hydroxymethylenephenylacetates).[7,8] In these compounds the *trans* form is not converted to the *cis* or *vice versa* by simple treatment with solvents, but heating is required. Both α- and β-forms of formyldesoxybenzoin would appear to be *cis*-isomers. It is probable then that one is an F-enol while the other is a B-enol.

**The Infrared and Ultraviolet Spectra of α- and β-Formyldesoxybenzoins.**—While the infrared spectra of the solid α- and β-forms (in Nujol mull) are very different, both show evidence of hydrogen bonding. The spectrum of the α-form (Table III, Experimental) shows a strong band between 6.1 and 6.2 μ similar to that shown by dibenzoylmethane[9] or benzoylacetone.[10] The β-form shows a sharp band at 6.3 μ and a strong broad band between 6.3 and 6.62 μ. Both forms show a weak band at

(1) Organic Chemicals Department, E. I. du Pont de Nemours and Co., Jackson Laboratory, Wilmington 99, Del.

(2) W. Wislicenus and A. Ruthing, *Ann.*, **379**, 229 (1912).

(3) Enols and their derivatives related to II (*i.e.*, having the formyl group enolized) will be called "F-enols" or derivatives while enols of the type III (benzoyl group enolized) will be called "B-enols."

(4) F. Scheiber and G. Hopfer, *Ber.*, **47**, 2704 (1914).

(5) H. Henecka, *Chem. Ber.*, **81**, 189 (1948).

(6) B. Eistert, F. Arndt, L. Loewe and E. Ayça, *ibid.*, **84**, 156 (1951).

(7) W. Wislicenus, *Ann.*, **413**, 272 (1917).

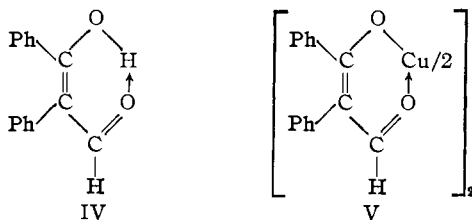(8) W. Dieckmann, *Ber.*, **50**, 1375 (1917).

(9) B. Eistert, F. Weygand and E. Csendes, *ibid.*, **84**, 756 (1951).

(10) B. Eistert and E. Merkel, *ibid.*, **86**, 904 (1953).

about 3.8 $\mu$ which is considered to be a hydrogen bonded hydroxyl frequency.[11] The broad bands at 6.1–6.63 $\mu$ and 6.32–6.6 $\mu$ are considered to be due to a hydrogen bonded carbonyl group,[11] while the sharp band at 6.3 $\mu$ in the spectrum of the β-form is probably a phenyl frequency. Solutions of the β-form in chloroform show a spectrum identical with that of the α-form in the solid state. The conversion β → α must take place readily in non-polar solvents.

The ultraviolet spectrum of formyldesoxybenzoin in hexane, that is, the spectrum of the α-form, has maxima at 238 and 323 m$\mu$ (Table II). The spectrum in other non-polar solvents is similar. In form this spectrum is not unlike that of stilbene,[12,13] but the bands fall at somewhat longer wave lengths and have lower intensities than the bands in the spectrum of either cis or trans forms of the hydrocarbon. A similar displacement to the longer wave length is observed when the spectrum of cis-dibenzoylmethane is compared with that of the corresponding methyl ether ($\lambda_{max}$ 339 m$\mu$ in heptane–methyl ether $\lambda_{max}$ 285 m$\mu$).[9] This shift of the bands of a chromophore to longer wave lengths appears to occur when the compound exists in a chelated form. Lewis and Calvin[14] have pointed out that the wave length of absorbed light is longer (i.e., the frequency is lower) when the electronic displacements are such as to diminish the double bond characteristics in bonds of high strain. Such conditions are very probably fulfilled in chelate enols.

A comparison of the spectrum of formyldesoxybenzoin in hexane with that of the copper complex in ether or alcohol solution reveals no important difference; the bands in the spectrum of the copper complex are shifted some 10 m$\mu$ to the longer wave lengths (Table II). The absorption maxima in the spectrum of cis-dibenzoylmethane[9] are shifted somewhat to the longer wave lengths on conversion to the copper complex ($\lambda_{max}$ 260 m$\mu$, $\lambda_{max}$ 346 m$\mu$). Similar differences exist between the spectrum of acetylacetone ($\lambda_{max}$ 270 m$\mu$)[15] and that of its copper derivative ($\lambda_{max}$ 242, 295 m$\mu$). Since the copper derivatives must have the cis-chelate structure V, the observations recorded above confirm the cis-chelate B-enol structure IV for α-formyldesoxybenzoin.



IV                         V

In alcoholic solution formyldesoxybenzoin is enolized completely.[16] Since the evaporation of the solvent in vacuo yields the β-form[2] it is probable

that this form, as a solvated modification, exists in the alcoholic solution. The ultraviolet spectrum of formyldesoxybenzoin in alcoholic solution differs from the spectrum in hexane. In the polar solvent only one band, $\lambda_{max}$ 245 m$\mu$ (Table II), is present. This spectrum is similar to that of desoxybenzoin[17] or α-phenylacrylophenone; it shows no evidence of conjugation between the benzene rings. The spectrum suggests that the β-form is an enol of the F-series II. Since this form gives a color with ferric chloride it must be a cis-F-enol.

The van't Hoff–Dimroth hypothesis[18] states that the ratio of the concentrations of the forms of a tautomeric compound in any solvent is proportional to the ratio of the solubilities of the forms in that solvent. For the α- and β-forms of formyldesoxybenzoin this may be written

$$\frac{[\alpha\text{-form}]}{[\beta\text{-form}]} = G\frac{S_\alpha}{S_\beta}$$

Since in non-polar solvents formyldesoxybenzoin exists almost exclusively in the α-form it follows that in these solvents $S_\alpha \gg S_\beta$. In polar solvents, however, the β-form predominates; here therefore, $S_\beta \gg S_\alpha$. The high solubility of the α-form in non-polar solvents is in complete accord with the chelate structure IV.[19] It has been shown that the β-form is a cis-F-enol; it is inconceivable that the solubility differences between the α- and β-forms which follow from the above argument should exist if the β-form were the chelate F-enol VI. The solubilities of the β-form are in fact reminiscent of a non-chelate enol.[17,20] In polar solvents the non-chelate β-form is probably solvated. In the solid state the hydrogen bonding apparent in the infrared spectrum must be intermolecular.

The cause of the conversion of the α- to the β-form and vice versa under appropriate conditions is revealed by a study of models or scale drawings of the various possible enols. It is remarked: (a) that in the cis-chelate-F-enol VI there is interference between the o-hydrogens of the phenyl groups amounting to an overlap of about 0.8 Å.; (b) that in the cis-chelate-B-enol IV this overlap is much less (ca. 0.2 Å.). These figures make no allowance for the shortening of the O—H...O distance by the hydrogen bond. As a result of this interference with the planarity of the benzoyl and styrene



VI                         VII
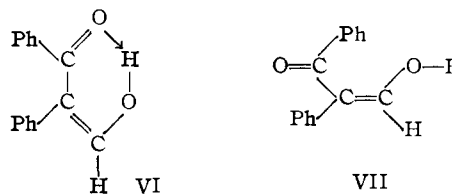
groups, a loss in resonance energy of some 20 kcal./mole is to be expected in VI. A gain in resonance energy from the hydrogen bond (7 kcal./mole) and the planar C=C—C=O system (3 kcal./mole) also would be expected. The cis-chelate B-enol IV, on the other hand, can have a planar or almost planar configuration; here the gain in resonance

(11) R. S. Rasmussen, D. D. Tunnicliff and R. R. Brattain, THIS JOURNAL, 71, 1068 (1949).

(12) A. Smakula and A. Wasserman, Z. physik. Chem., 155, 353 (1931).

(13) B. Arends, Ber., 64, 1936 (1931).

(14) G. N. Lewis and M. Calvin, Chem. Revs., 25, 273 (1939).

(15) P. Grossmann, Z. physik. Chem., 109, 305 (1924).

(16) M. M. Bokadia and S. S. Deshapande, J. Indian Chem. Soc., 26, 456 (1949); 27, 549 (1950).

(17) P. B. Russell, THIS JOURNAL, 74, 2654 (1952).

(18) G. Dimroth, Ann., 399, 110 (1913).

(19) N. V. Sidgwick, J. Chem. Soc., 127, 907 (1925).

(20) B. Eistert and W. Reiss, Chem. Ber., 87, 92 (1954).

energy from the stilbene system and the hydrogen bond is considerable (ca. 20–25 kcal./mole). Thus under conditions favoring chelation (e.g., in vapor or in non-polar solvents) the form IV should exist to the exclusion of VI. When the hydrogen bond is broken, either by thermal motion or by solvation with polar solvents, it is to be expected that the cis-B-enol would still be more stable than the cis-F-enol since there is less interference with the planarity of the molecule. However, by a simple rotation around the =C—CO— single bond the cis-F-enol may assume a conformation VII where no interference with the planarity of the various groups exists. The structure VII accounts satisfactorily for the properties, both chemical and physical, of the β-form of formyldesoxybenzoin.[21] In the solid a linear association of structures of the type VII held together by the hydrogen bonds is postulated. It should be pointed out that a linear association of cis- and trans-F-enols would account equally well for the properties of the β-form. Indeed, such a formulation accounts for the observation of Wislicenus and Ruthing[2] that the ferric chloride color given by the β-form in alcohol increases in intensity and equals that of the α-form only after some time.

Substances which, like VI and VII, differ in the rotational conformation of a carbonyl group around a single bond have been called "hemitropic" isomers by Eistert and co-workers.[9,10] These authors have used this concept to account for differences between enols and enol ethers of dibenzoylmethane and benzoylacetone which have the same structure and geometrical configuration.

While an α-formyl ketone is theoretically capable of enolizing in two directions it is generally assumed that only the formyl group enolizes. Such compounds are referred to as hydroxymethylene compounds. Formyldesoxybenzoin has been shown to enolize in either direction according to the conditions. It seems not unlikely that other so-called "hydroxymethyleneketones" will, on closer examination, be shown to have the alternative enolaldehyde structure.

The conclusions regarding the structures of the α- and β-forms of formyldesoxybenzoin reached above are the reverse of those of Wislicenus and Ruthing.[2] Nevertheless, the new structures are confirmed by the results of the reactions of these forms with diazomethane as will be described below.

**The Reactions of α- and β-Formyldesoxybenzoins with Diazomethane.**—Before the present work only one methyl ether of formyldesoxybenzoin had been described.[22] This was obtained by the action of diazomethane in ether on a chloroform solution of IV.[23] Blatt considered this ether (m.p. 130–131°) to have the structure VIII. It gave no
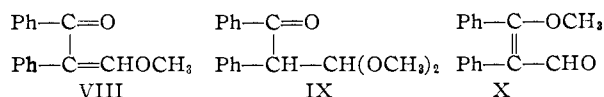
(21) It cannot be stated definitely whether or not the benzoyl and styrene groups in VII be in the same plane. Leonard, Blout and co-workers (THIS JOURNAL, 71, 2997 (1949); 72, 484 (1950)) have given an elegant spectroscopic demonstration that in the related compound benzil both benzoyl groups are planar and inclined to one another by twisting around the central bond. In the present case it might be expected that repulsion between the two oxygens will force the molecule into a planar form.

(22) Jörissen (Dissertation, Basel, 1893, quoted by Wislicenus ref. 2, page 253) claimed to have prepared a methyl ether, m.p. 56°, by the action of dry hydrogen chloride on I in methanol. However, using this method Blatt[23] obtained no ether but only desoxybenzoin, m.p. 56°.

(23) A. H. Blatt, THIS JOURNAL, 60, 1164 (1938).

immediate color with ferric chloride, but a color developed on standing. With concentrated hydrochloric acid in methanol it gave, like formyldesoxybenzoin itself, the acetal IX.[23]

Methylation of α-formyldesoxybenzoin with diazomethane in benzene was found to give two enol ethers. One was obtained in crystalline form (m.p. 134°) and was obviously identical with Blatt's ether. The second was an oil (b.p. 110° (bath temperature) (0.15 mm.)).

Ph—C=O        Ph—C=O        Ph—C—OCH₃
|             |                  ‖
Ph—C=CHOCH₃  Ph—CH—CH(OCH₃)₂  Ph—C—CHO
VIII          IX                X

The spectrum of the crystalline ether in alcohol or hexane (Table II) shows only one maximum at 285 mμ. This suggests strongly the presence of a stilbene system.[12,13] Such a spectrum is not compatible with Blatt's suggested structure VIII but is in complete harmony with the structure X. Treatment of this ether with hydroxylamine gave an oxime XI, which on refluxing with acetic anhydride gave the methyl enol ether of cyanodesoxybenzoin (α,β - diphenyl - β - methoxyacrylonitrile (XII)), m.p. 108°, in almost quantitative yield. The enol ether XII was identical with a sample prepared by Russell and Whittaker[24] by the action of diazomethane and other methylating agents on cyanodesoxybenzoin (XIII). This series of reactions establishes that the ether m.p. 134° is an ether of the B-series (X).[25]
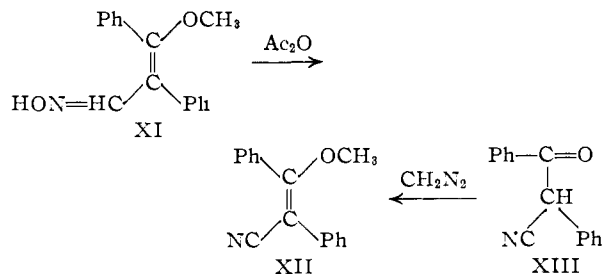


The oily ether, obtained in about 50% yield from α-formyldesoxybenzoin in benzene with diazomethane, becomes the main product (90–95%) when the solid β-form is added to a solution of diazomethane in ether, a solvent in which the β-form is not very soluble. The remaining 5–10% of the product was the "ether-B" X. The ultraviolet spectrum of the oily ether (Table II) shows only a single maximum at about 250 mμ. Such a band suggests a benzoyl and/or a styrene chromophore.[26] The spectrum resembles that of desoxybenzoin[17] but

(24) P. B. Russell and N. Whittaker, ibid., 74, 1310 (1952).

(25) The above series of reactions does not establish the configuration of the ether X or the enol from which it was obtained. However, it can be said that since the oxime XI gives no isoxazole with alcoholic alkali (L. Claisen, Ber., 59, 144 (1926)), it is probably a trans compound. Further J. Matti and P. Reynaud (Bull. soc. chim. France, 21, 410 (1954)) have described recently two isomeric methyl enol ethers of cyanodesoxybenzoin, m.p. 106° and 84.5°. The ether m.p. 106° probably corresponds with the above ether, m.p. 108°; data given by the French authors indicates that this is a trans-ether. It seems most unlikely then that the ether X is a trans-ether; since cis ethers usually are unstable with respect to the trans (see Eistert, Arndt, et al., ref. 5) this cannot be taken as an indication of the configuration of the original enol from which it was obtained.

(26) E. A. Braude in Rodd's "Chemistry of the Carbon Compounds," Vol. Ia, Elsevier Publishing Co., London, 1951, p. 88.

has a higher intensity of absorption. It is virtually identical with the spectrum of α-phenylacrylophenone. This suggests that the oily ether is an ether of the F series (ether-F, VIII).

The ether-F like the ether-B gave no immediate color with ferric chloride, but on standing the color developed. A qualitative comparison indicates that the color develops more rapidly with ether-F than with ether-B. On treatment with concentrated hydrochloric in methanol ether-F, like ether-B, gave the acetal IX.

Both ethers-B and -F reacted with aniline. The ether-B gave a mixture of two anilino derivatives, m.p. 200° (B₁) and 154° (B₂). Ether-F, on the other hand, gave an oil which on standing under ligroin crystallized to a yellow compound, m.p. 95–96°, identical in every respect with the anilino compound prepared from formyldesoxybenzoin itself.[2] The structure of this compound has been discussed previously.[27] The structures of the anilino compounds B₁ and B₂ have not been determined but they are probably geometrical isomers of XIV.

$$\text{Ph(PhNH)C}=\text{CPh(CHO)}$$
$$\text{XIV}$$
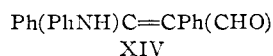
The fact that the treatment of the solid β-form of formyldesoxybenzoin with diazomethane gives the ether-F almost exclusively indicates clearly that this form of the compound is in fact an F-enol.[28] This confirms the conclusions reached from an examination of the physical properties of this form. The observation that the ether-B is formed to a much greater extent from formyldesoxybenzoin in non-polar solvents is quite consistent with the conclusions reached earlier regarding the nature of the α-form. Since some ether-F is formed also it is apparent that at least a small amount of the F-enol must be present in solutions of the α-form. This explains the formation of benzil in the ozonolysis of the α-form in carbon tetrachloride; any F-enol would be expected to react in preference to the B-enol since the double bond in the latter is heavily hindered.

### Experimental

Formyldesoxybenzoin was prepared by the method of Wislicenus and Ruthing.[2] The α-form was obtained by melting the crude product followed by rapid cooling and crystallization from benzene. The β-form was obtained by crystallization of the crude product from alcohol. Both forms had the properties recorded by Wislicenus.

The Reaction of Formyldesoxybenzoin with Diazomethane. (a) The α-Form.—The enol (4 g.) was dissolved in benzene (60 ml.) and treated with a solution of diazomethane[29] (from nitrosomethylurea (5 g.)) in benzene (100 ml.). Nitrogen was evolved slowly. After 24 hours the benzene and excess diazomethane were removed at room temperature in vacuo. The residual oil became partly solid on standing and the crystals after washing with methanol (0.8 g.) melted at 135°. The methanol solution was evaporated at room temperature in vacuo and the procedure repeated. In all, 1.7 g. of the pure crystalline ether-B was obtained. The mother liquors yielded an oily residue on evaporation of the solvent; this was dissolved in petroleum ether (Skelly A) and washed well with water to remove methanol. The dried petroleum solution was run down a column of active alumina (8 ×

³/₄ in.) and the chromatogram developed with petroleum containing a little ether. Fractions of 50 ml. were collected. The first fraction contained an oil (ca. 1.5 g.), the second, third and fourth fractions crystallized and on recrystallization gave a further quantity of ether-B (0.4 g.). The oily fraction was distilled at 0.15 mm., a small fraction boiling at 95° was collected and then the main fraction (ca. 1.2 g.) boiling at 110° (bath temp.) distilled. This was almost pure ether-F. It was distilled twice more before analysis.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.7; H, 5.9; OMe (1), 13.0. Found: Ether-B: OMe, 12.9. Ether-F: C, 80.7; H, 6.1; OMe, 12.5.

(b) The β-Form.—The solid enol (10 g.) was added in small portions over about 2 hours to a solution of diazomethane (from nitrosomethylurea (10 g.)) in ether (200 ml.). The reaction appeared to take place at the surface of the solid which gradually dissolved. At the end of 24 hours the solution was homogeneous. The solvent and excess of diazomethane were removed in vacuo and the products separated and purified as in the previous example to give ether-B (0.3–0.4 g.) and ether-F (ca. 6 g.).

Ferric Chloride Reaction of Ethers-B and -F.—The ethers (10 mg.) were each dissolved in methanol (5 ml.) and a solution of ferric chloride in methanol (3 drops of 1%) was added to both solutions. Both solutions were then kept at 50° in a water-bath. The enol-ether-F gave a definite color in two minutes, but at this time there was no color with ether-B. In five minutes the color given by ether-F was equal to that given at once by formyldesoxybenzoin under the same conditions, while the color given by ether-B at this time was much less intense and was not equal to that of formyldesoxybenzoin until 15 minutes after the

### TABLE I
ULTRAVIOLET ABSORPTION SPECTRA OF MODEL COMPOUNDS

| Compound | $\lambda_{max}$, mμ | $E \times 10^{-3}$ | $\lambda_{min}$, mμ | $E \times 10^{-3}$ |
|---|---|---|---|---|
| Desoxybenzoin[a,b] | 245 | 12.6 | | |
| α-Phenylacrylonitrile[b,c] | 247 | 18.7 | | |
| cis-Stilbene[d] | <230 | >5 | 246 | 4.4 |
| | 278 | 9.5 | | |
| trans-Stilbene[d] | <230 | >18 | 246 | 2.3 |
| | 295 | 24.0 | | |
| α,β-Diphenyl-β-methoxyacrylonitrile[a,b] | <230 | >9 | 245 | 6.5 |
| | 283 | 16 | | |

[a] P. B. Russell, ref. 17. [b] In alcohol. [c] In hexane. [d] B. Arends, ref. 13.

### TABLE II
ULTRAVIOLET ABSORPTION SPECTRA OF FORMYLDESOXYBENZOIN DERIVATIVES

| Compound | $\lambda_{max}$, mμ | $E \times 10^{-3}$ | $\lambda_{min}$, mμ | $E \times 10^{-3}$ |
|---|---|---|---|---|
| Formyldesoxybenzoin[a] | 245 | 13.5 | | |
| Formyldesoxybenzoin[b] | 238 | 14.0 | 275 | 3.0 |
| | 323 | 9.5 | | |
| Formyldesoxybenzoin Cu deriv.[a,c,d] | 245 | 16.0 | 294 | 6.0 |
| | 335 | 11.0 | | |
| Ether-B[a,b] | <230 | >16 | 257 | 9.0 |
| | 282 | 12.5 | | |
| Ether-F[a,b] | 246 | 19.5 | | |
| Formyldesoxybenzoin dimethylacetal[a,b] | 248 | 14.0 | | |
| Anilino compound B₁[a] | 238 | 10.6 | 305 | |
| | 365 | 8.0 | | |
| Anilino compound B₂[a] | <230 | >15.0 | 238 | 9.9 |
| | 244 | 15.0 | | |
| | 378 | 18.0 | 292 | 5.2 |
| Anilino compound F[a] | 242 | 15.0 | 255–265[e] | 12.0 |
| | 385 | 11.5 | 308 | 5.0 |

[a] In alcohol. [b] In hexane. [c] In ether. [d] Value given as ¹/₂ E. [e] $\lambda_{inf}$, mμ.

(27) P. B. Russell, THIS JOURNAL, 75, 5315 (1953).

(28) F. Arndt, in "Organic Analysis," Interscience Publishers, Inc., New York, N. Y., 1953, Vol. I, p. 217.

(29) F. Arndt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 165.

TABLE III

INFRARED SPECTRA OF SOME FORMYLDESOXYBENZOIN DERIVATIVES

| Compound | Spectra, $\mu$ |
| --- | --- |
| α-Formyldesoxybenzoin in Nujol mull | ~3.8 (broad), 6.22 (s, broad band 6.1–6.62), 7.63 (m), 8.5 (m), 9.3 (m), 9.8 (m), 9.96 (w), 10.1 (w), 10.3 (w), 10.8 (m), 12.6 (w), 13.02 (m), 13.93 (m), 14.2 (s), 14.59 (m). No absorpt. at 8.0 |
| β-Formyldesoxybenzoin in Nujol mull | ~3.8 (w), 6.12 (w), 6.3 (m), 6.4 (s, broad band 6.32–6.62), 6.68 (w), 6.9 (s), 7.18 (m), 7.6 (w), 7.7 (m), 8.05 (s, broad band 7.9–8.38), 8.45 (m), 9.15, 9.2, 9.28 (w), 9.76 (w), 10.0 (w), 10.57 (w), 10.9 (w), 11.58 (m), ~11.75 (w), 12.1 (w), 12.59 (m), 13.0 (m), 13.73 (s, broad 13.3–14.1), 14.33 (s) |
| Ether-B in $CHCl_3$ | 3.69 (w) (ald., C–H), 6.02 (s) (>C=O), 7.66 (s) (unsatd. –O–CH₃) |
| Ether-F in $CHCl_3$ | 3.54 (w) (C–H tert.), 6.02 (s) (>C=O) |
| Formyldesoxybenzoin dimethylacetal in $CHCl_3$ | 3.58 (w), (C–H tert.), 5.95 (s) (>C=O), 8.92 (s) (satd. ether) |
| Oxime in $CHCl_3$ | 2.82 (OH), 2.9–3.25 (H bonded OH), 6.15 (>C=N—) |
| α-Phenylacrylophenone in $CHCl_3$ | 5.97 (s) (>C=O) |
| α,β-Diphenyl-β-methoxyacrylonitrile in $CHCl_3$ | 4.61 (m) (—C=N), 7.65 (s) (unsatd. –O–CH₃), no >C=O absorption |

start of the experiment. If the ethers were dissolved in a mixture of methanol and pyridine (1:1) in place of methanol, no color developed although formyldesoxybenzoin itself gave a definite color.

**Formation of Formyldesoxybenzoin Dimethylacetal (IX) from Ether-F.**—The ether (1.0 g.) was dissolved in methanol (10 ml.) and concentrated hydrochloric acid (5 drops) added. After standing in a stoppered flask overnight the solution was cooled and scratched. Colorless needles separated, which after recrystallization from methanol melted at 99°. This melting point was not depressed on admixture with an authentic sample of the acetal prepared as described by Blatt.[23]

**Oxime of Ether-B.**—The ether (0.5 g.) was dissolved in methanol (10 ml.) and a solution prepared from hydroxylamine hydrochloride (0.5 g.), and anhydrous sodium acetate (0.5 g.) in water (10 ml.) was added. The oxime crystallized at once. After recrystallization from methanol it formed colorless prisms, m.p. 207°.

*Anal.* Calcd. for $C_{16}H_{15}NO_2$: C, 75.9; H, 5.9. Found: C, 76.2; H, 5.7.

**Conversion of the Oxime to α,β-Diphenyl-β-methoxyacrylonitrile.**—The above oxime (0.2 g.) was refluxed with acetic anhydride (3 ml.) for two hours. The mixture was poured onto ice (25 g.) and when all the acetic anhydride had been destroyed the crystals were filtered off. After recrystallization from aqueous methanol the material melted at 108° and was identical in all respects (melting point, mixed melting point and ultraviolet spectrum) with the original sample of Russell and Whittaker.[24]

**The Reaction of Ether-B with Aniline.**—The ether (0.5 g.) in methanol (5 ml.) was heated with aniline (0.2 g.) on a steam-bath for 1 hour. On cooling, yellow prisms separated which after several recrystallizations from methanol formed canary-yellow prisms, m.p. 199–200° (ca. 0.1 g.). This was anilino compound B₁.

*Anal.* Calcd. for $C_{21}H_{17}ON$: C, 84.3; H, 5.7. Found: C, 84.2; H, 6.0; OCH₃, 0.0.

The mother liquors from the above recrystallizations deposited clusters of fine needles which after recrystallization from methanol melted at 154° (0.4 g.).

*Anal.* Calcd. for $C_{21}H_{17}ON$: C, 84.3; H, 5.7. Found: C, 84.6; H, 6.0; OCH₃, 0.0.

**Reaction of Ether-F with Aniline.**—The ether (0.5 g.) was treated with aniline in the same way as above. The resulting oil was allowed to stand under petroleum ether in the ice-box. After several days the oil began to crystallize and recrystallization from ethanol gave yellow needles (0.6 g.), m.p. 95–96°. This compound was identical with the anilino compound prepared from formyldesoxybenzoin itself by the method of Wislicenus and Ruthing.[2]

**α-Phenylacrylophenone.**—This compound was prepared by the dehydration of methylbenzoin with sulfuric acid in acetic acid after the (unpublished) procedure of Becker and Mehr,[30] b.p. 190–193° (11 mm.).

*Anal.* Calcd. for $C_{15}H_{12}O$: C, 86.5; H, 5.8. Found: C, 86.3; H, 6.0.

**Ultraviolet Absorption Spectra.**—Solutions of the tautomeric substances at a concentration of 10 mg./l. were prepared. The solution was allowed to stand until equilibrium was established (about 1–2 hours). Solutions of other substances at a concentration of 10 mg./l. were examined at once.

The spectra were measured on a Beckman model DU quartz spectrophotometer (cell length 1 cm.). All recorded spectra are the result of at least two independent measurements. The results are given in Tables I and II.

**Infrared Spectra.**—The infrared spectra were measured with a Baird recording infrared spectrophotometer equipped with sodium chloride cells. The spectra in Nujol mull were carried out with 30 mg./6 drops of Nujol. The chloroform solutions were made at a concentration of 15% and the solutions were examined immediately after preparation.

TUCKAHOE, N. Y.
CAMBRIDGE, MASS.

(30) The authors are indebted to Dr. E. I. Becker and Mr. Louis Mehr of the Polytechnic Institute of Brooklyn for details of this procedure.