Syntheses and Structures of Acetylformoin and Related Compounds. V. *p-t*-Butylbenzoylformoin and *t*-Toluylformoin

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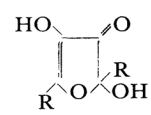
In our earlier investigations[1] it has been reported that α-ketoaldehydes undergo a self-condensation similar to benzoin condensation to give formoins, for which several structures are possible. The results may be summarized as follow: structure I is preferred in solutions in alcohols and ethers; structure II is preferred in solutions in chloroform and carbon tetrachloride; the structure in the solid state is dependent on the substituent R. The two struc tures have been found to have quite different spectral characteristics. Compound

$$2\ \mathrm{RCOCHO} \xrightarrow{\mathrm{CN^-}} \mathrm{RCOCH(OH)COCOR}$$

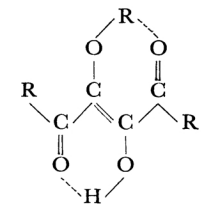
I shows $\nu_{C=C}$ at ca. 1605, $\nu_{C=O}$ a ca. 1685, and two bands of ν_{OH} between 3000and 4000 cm^{-1} in the solid state, and $\nu_{C=C}$ at ca. 1615, $\nu_{C=O}$ at ca. 1705 and one band of ν_{OH} between 3500 and 3800 cm^{-1} in a solution. Compound II shows $\nu_{C=C}$ at ca. 1620 cm^{-1} and no discernible bands of ν_{OH} and $\nu_{C=C}$ in either state. λ_{max} is located ca. 360 and 240 mμ in compound I and ca. 400 and 300 mμ in compound II when R is the phenyl group.

In this paper the authors will report on the condensation products of *p-t*-butylphenylglyoxal and *t*-tolylglyoxal, namely, *p-t*-butylbenzoylformoin (BBF) and *t*-toluylformoin (TF).[2] The glyoxals prepared by the selenium oxide oxidation of the *p*-substituted acetophenones were subjected to condensation in an aqueous alcoholic solution containing sodium cyanide.

It has been established by elementary analysis and molecular weight determination that the product is composed of two molecules of the glyoxal.



I



II

The infrared spectrum of BBF has the spectral characteristics of structure I in the solid state: $\nu_{C=C}$ 1593, $\nu_{C=O}$ 1680 and ν_{OH} 3100 and 3300 cm^{-1}. In THF or ethanol it also shows the spectral properties of structure I: $\nu_{C=C}$ 1625, $\nu_{C=O}$ 1700 and ν_{OH} 3260 cm^{-1}; λ_{max}^{EtOH} 358 (ε, 13700) and 245 (ε, 12500) mμ.

When BBF is dissolved in chloroform in air, it is rapidly oxidized to give a red solution as benzoylformoin.[1d] For this reason, the ultraviolet spectrum in this solvent was measured in a cell sealed in vacuc. The situation is rather complicated, as in the case cf benzoylformoin. In ethanol-free chloroform, λ_{max}'s are located at 400 and 300 mμ, indicating structure II. The solution in ethanol-containing (ca. 1%) chloroform shows λ_{max} 371 and 245 mμ. However, it can not be thereby concluded that this spectrum indicates structure II, for benzoylformoin may react with ethanol in chloroform to give *O*-ethyl

1) a) R. Goto, Y. Miyagi and H. Inokawa, This Bulletin, **36**, 147 (1963); b) Y. Miyagi and R. Goto, ibid., **36**, 650; c) Ibid., **36**, 921; d) Y. Miyagi, ibid., **37**, 12 (1964).

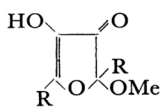
2) TF was first synthesized by Abenius and Söderbaum (*Ber.*, **25**, 3473 (1892)), but its structure needs to be investigated further.

benzoylformoin II (R=OH, R'=Et).[3]

When the ultraviolet spectrum is quickly recorded in the 340—420 mμ range, it is found that the absorption arises around 370 mμ immediately after dissolving in ethanol-free chloroform and that it shifts to 405 mμ in about five minutes. This fact indicates that the structure of BBF, which is I soon after dissolving, turns to II by a quick shift of the equilibrium between I and II.

TF also has the spectral properties of structure I in the solid state and in solution in THF and ethanol: $\nu_{C=C}$ 1598, $\nu_{C=O}$ 1693, and ν_{OH} 3240 and 3520 cm^{-1} in the solid state; $\nu_{C=C}$ 1630, $\nu_{C=O}$ 1705 and ν_{OH} 3280 and 3540 cm^{-1} in THF; λ_{max}^{EtOH} 355 (ε, 11100) and 245 (ε, 11100) mμ.

The ultraviolet spectrum of TF in chloroform is also complicated. In ethanol-free chloroform, λ_{max} is located at 400 mμ. In ethanol-containing chloroform it shifts to 380 mμ, a position a little longer in wavelength than the band of BBF in this solvent, 371 mμ. Moreover, a shoulder is observed on the longer wavelength side of the 380 mμ band. This spectrum indicates the presence of a mixture of two components. One of these may be established as II with certainty. However, the other component can not be concluded unequivocally to be I for the same reason as has held in the case of BBF.



III

As does benzoylformoin,[1b-c,4] BBF and TF undergo methanolysis by methanolic hydrogen chloride to give *O*-methyl dericatives with spectral properties similar to those of structure I. Since etherification by alcoholic hydrogen chloride is characteristic of glycosidic linkage, the structure of these *O*-methyl derivatives may be established as III.

The situation is now being investigated in more detail.

3) B. Eistert, private communcation; see also Ref. 1d.
4) A. H. Blatt, *J. Am. Chem. Soc.*, **58**, 1894 (1936).

Experimental

Glyoxals.—*p-t*-Butylacetophenone[5] and *p*-methylacetophenone[6] were oxidized with selenium oxide by the general procedure[7] to *p-t*-butylphenylglyoxal and *p*-tolylglyoxal respectively. The latter was isolated as a hydrate, m. p. 105.5—106.5°C. The former, however, failed to give a hydrate.

***p-t*-Butylbenzoylformoin (BBF).**—Crude *p-t*-butylphenylglyoxal was redistilled to give a yellow liquid boiling at 99—104°C/4 mmHg. After 10 g. of this had been dissolved in 80% aqueous ethanol (65 ml.), to this solution an aqueous solution (5 ml.) containing 0.2 g. of sodium cyanide was added. The color of the solution turned a reddish yellow, and yellow crystals were deposited. After 2 hr., the crystals were filtered off, which were dissolved in warm ethanol and recrystallized by adding water: yield, 7 g.; m. p. 168.5—169.0°C.

Found: C, 75.43; H, 7.44; mol. wt. (Rast), 400. Calcd. for $C_{24}H_{28}O_4$: C, 75.76; H, 7.42%; mol. wt., 380.

***p*-Toluylformoin (TF).**—The procedure was the same as above except that glyoxal hydrate was used instead of the glyoxal monomer. Yellow needles: recrystallized from 50% aqueous ethanol; m. p. 154—159°C (lit. 161°C[2]). Found: C, 72.98; H, 5.15; mol. wt. (Rast), 298. Calcd. for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44%; mol. wt., 296.

***O*-Methyl *p-t*-Butylbenzoylformoin.**—BBF (3 g.) was dissolved in 10% methanolic hydrogen chloride (50 ml). Immediately pale yellow crystals were deposited. The whole mixture was allowed to stand overnight in a refrigerator. Crystals were collected and recrystallized from methanol; yield, 2.5 g.; m. p. 206—207°C; ν_{max}^{Nujol} 1615, 1690 and 3360 cm^{-1}; λ_{max}^{EtOH} 358 (ε, 12900) and 245 (ε, 12000) mμ.

Found: C, 75.95; H, 7.81; CH_3O, 7.73. Calcd. for $C_{25}H_{30}O_4$: C, 76.11; H, 7.67; CH_3O, 7.68%.

***O*-Methyl *p*-Toluylformoin.**—The procedure was the same as above. Pale yellow needles, recrystallized from methanol; m. p. 195—196°.2C; ν_{max}^{Nujol} 1615, 1690 and 3400 cm^{-1}; ν_{max}^{EtOH} 358 (ε, 12400) and 245 (ε, 11300) mμ.

Found: C, 73.38; H, 5.81; CH_3O, 10.18. Calcd. for $C_{19}H_{18}O_4$: C, 73.53; H, 5.85; CH_3O, 10.00%.

5) H. C. Brown, J. P. Brady, M. Grayson and W. H. Bonner, *J. Am. Chem. Soc.*, **79**, 1897 (1957).
6) R. Adams and C. R. Noller, "Organic Syntheses," Coll. Vol. I, 111.
7) H. A. Riley and A. R. Gray, ibid., Coll. Vol. II, 513.