Synthesis and Structure of 3-Benzyl-2,6-diphenyl-2*H*-thiopyran-5-carboxaldehyde

By S. E. CREMER and A. V. SUBBARATNAM

(*Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois*)

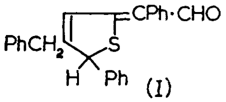
K. A. LATIF and co-workers[1] reported that treatment of benzaldehyde with sodium polysulphide in aqueous ethanol solution at reflux temperature gave a yellow, crystalline product, $C_{25}H_{20}OS$, m.p. 153°, of unknown constitution. These workers deduced the presence of three Ph–C groups, a sulphide linkage, and a *ketone* in this molecule. Repetition of this reaction[2] in our laboratories gave a similar product (15% yield), m.p. 153—154·5°, with a formula, $C_{25}H_{20}OS$, which was determined from combustion analysis and a precise molecular weight (*M*, 368; mass spectrum).

A number of carbonyl derivatives were readily prepared: phenylhydrazone (m.p. 158—161°), ethylene acetal (m.p. 150—152°, white), and a 2,4-dinitrophenylhydrazone (m.p. 192—194°, blood red); the compound was resistant to CrO_3/H_2SO_4, but gave benzoic acid on ozonolysis or oxidation with permanganate.

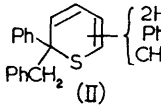
The n.m.r. spectrum ($CDCl_3$, 60 Mc./sec.) was in excellent agreement with the new formula: τ 0·37 (1 H singlet), 2·75 (15 H), 2·99 (1 H singlet), 5·50 (1 H singlet), 6·50 (2 H, AB pattern, $J_{AB} = 15$ c./sec.); moreover, an n.m.r. ($CDCl_3$) of the acetal confirmed the presence of an *aldehyde* in the parent compound: τ 0·37 was absent, a new peak appeared at 4·67 (1 H singlet, $\mathrm{HC}\!<^{\mathrm{O-}}_{\mathrm{O-}}$). The infrared spectrum (KBr) showed significant peaks at 1640 (strong, ν_{CO}) 2720, 2825 (weak, aldehyde C–H), and 700, 733 cm.$^{-1}$ (strong, monosubstituted benzene). An ultraviolet spectrum showed absorption at λ_{max} (MeOH) 265 (ϵ, 19,100), 365 (ϵ, 8400), and λ_{min} 236 (ϵ, 17,000). In addition the most predominant peak in the mass spectrum appeared at *m/e* 277, corresponding to the fragmentation of $PhCH_2^+$ (*m/e* 91).

Collectively these data are consistent with the structural features: 2 Ph–C, $PhCH_2$–, and C=CX·CHO (X≠H); furthermore, the $PhCH_2$– is adjacent or near to an asymmetric centre to account for the nonequivalent protons in the methylene group.[3] In addition, $PhCH_2$·CH is ruled out due to the absence of further coupling in the n.m.r. If one allows for two phenyl groups, one benzyl, and an $\alpha\beta$-unsaturated aldehyde, the residual C_3H_2S is consistent with an additional double bond and a ring system. A number of 5- and 6-membered-ring structures can plausibly accommodate the data; however, 5-membered-ring systems like (I) are unlikely (ready isomerization to a thiophen nucleus). Six-membered-ring systems such as (II) and (III) are more tenable structures.

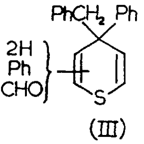
In the following Communication, Mazhar-Ul-Hague and Caughlan have determined the actual structure (IV) by *X*-ray analysis.[4]



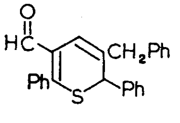
(I)



(II)

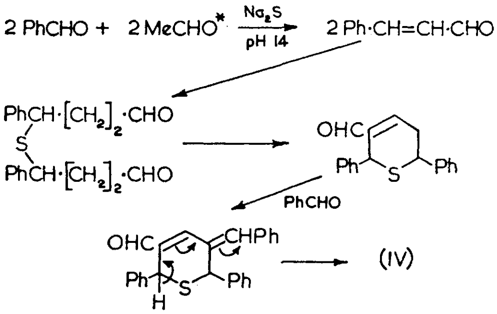


(III)



(IV)

This formulation is in keeping with the physical and chemical data and is mechanistically reasonable:



* Formed from oxidation of ethyl alcohol.

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[1] K. A. Latif, M. A. Razzaq, S. K. Adhikari, and M. M. Eunus, *J. Indian Chem. Soc.*, 1959, **36**, 209; K. A. Latif, S. K. Adhikari, and M. M. Eunus, *ibid.*, p. 212.

[2] Under the same conditions *p*-methylbenzaldehyde gave a product, m.p. 140—141°, whose n.m.r. spectrum was analogous to that derived from benzaldehyde—except for an additional peak due to CH_3Ph–(9H singlet).

[3] L. M. Jackman, "Application of NMR Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959, pp. 99—103.