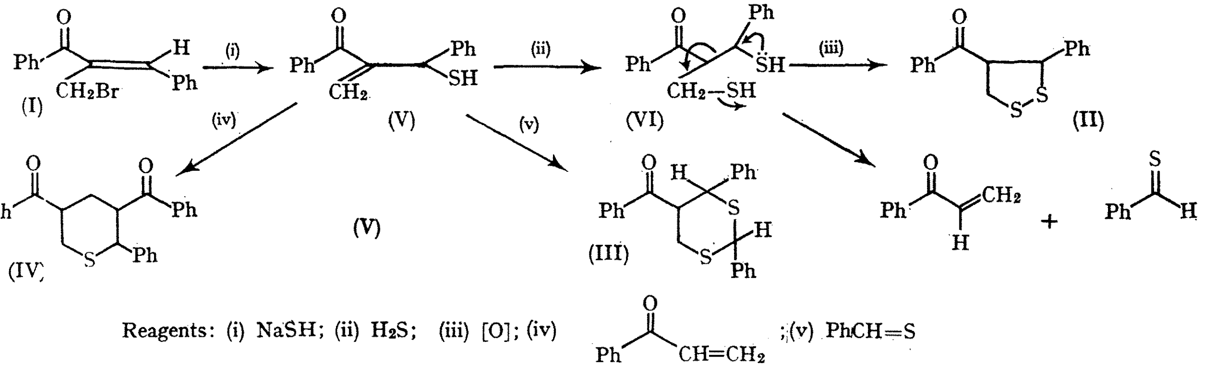
The Reaction of α-Bromomethylchalcone with Sodium Hydrogen Sulphide

By ALBERT PADWA* and ROBERT GRUBER

(*Department of Chemistry, State University of New York at Buffalo, Buffalo, New York* 14214)

RECENT communications have described the S_N2' reaction of amines with α-bromomethylchalcone (I).[1,2] We report on the complexity of the reaction of (I) with sodium hydrogen sulphide.

Treatment of *trans*-α-bromomethylchalcone with sodium hydrogen sulphide gives a mixture of three substances. One of these (18%, yellow crystals, $C_{16}H_{14}OS_2$, m.p. 81—82°) was shown to be 4-benzoyl-3-phenyl-1,2-dithiolan (II) by its spectroscopic properties and by chemical degradation; λ_{max} (KBr) 6·01, 6·95, 7·78, 9·95, and 13·05 μm.; n.m.r. ($CDCl_3$) shows a ABXY pattern, AB part centred at τ 6·50 and 6·25 (J_{AB} 11·5 c./sec., J_{AX}, J_{BX} 7·5 c./sec.) X proton 5·53 (q, J_{XY} 7·5 c./sec.), Y proton 4·80 (d, J_{XY} 7·5 c./sec.), aromatic protons 2·21 (m,10H). The remaining two products were subsequently identified as 5-benzoyl-2,4-diphenyl-1,3-dithian (III), (45%, m.p. 192–193°, $C_{23}H_{20}OS_2$; λ_{max} (KBr) 6·00, 7·78, 8·40, 12·95, and 14·51 μm.) and 3,5-dibenzoyl-2-phenylthian (IV), (30%, m.p. 180—181°, $C_{25}H_{22}O_2S$, λ_{max} (KBr) 5·95, 6·02, 6·95, 12·85, and 14·51 μm.) The dithian (III) showed the expected magnetic nonequivalence of the methylene protons adjacent to the sulphur atom, there being the predicted eight-line multiplet (AB part of an ABXY system) centred at τ 6·72 and 6·88 (J_{AB} 14 c./sec., J_{AX} 9 c./sec., and J_{BX} 4 c./sec.). The X proton of the ABXY system consisted of a triplet of doublets centred at 5·73 (J_{XY} 10 c./sec.). The remaining portion of the spectrum consisted of a doublet at 5·40 (J_{XY} 10 c./sec.), a singlet at 4·60 and a multiplet for the aromatic hydrogens centred at 2·52. The n.m.r. spectrum of the thian (IV) shows complex multiplets centred at 8·03 (2H) and 7·10 (2H), a triplet of triplets centred at 6·20 (1H, *J* 12 and 4·0 c./sec.,) a triplet of doublets at 5·85 (1H, *J* 10 and 4·0 c./sec.), a doublet at 5·65 (1H, *J* c./sec.) and a multiplet for the aromatic protons at 2·75 (15H). Desulphurization of the products (II) and (III) by nickel boride[3] gave a ketone, identified as 2-methyl-1,3-diphenylpropan-1-one.



Reagents: (i) NaSH; (ii) H_2S; (iii) [O]; (iv) $PhCOCH{=}CH_2$; (v) PhCH=S

The formation of the dithiolan (II) in the reaction mixture may be rationalized by a S_N2' displacement of bromide followed by Michael addition of hydrogen sulphide to yield a dithiol intermediate (VI). Under the basic conditions employed, the intermediate (VI) may be further oxidized[4] to the dithiolan (II). We envisage formation of (III) and (IV) as arising by fragmentation of (VI) to thiobenzaldehyde and phenyl vinyl ketone followed by recombination of these two species with the unsaturated sulphide (V), as pictured in the above scheme.

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[1] R. P. Rebman and N. H. Cromwell, *Tetrahedron Letters*, 1965, 4833.

[2] N. H. Cromwell and R. P. Rebman, *J. Org. Chem.*, 1967, **32**, 3830.

[3] W. E. Truce and F. M. Perry, *J. Org. Chem.*, 1965, **30**, 1316.

[4] J. A. Barltrop, P. M. Hayes, and M. Calvin, *J. Amer. Chem. Soc.*, 1954, **76**, 4348.