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TABLE

Sulphide	Solvent	Reaction time (hr.)	Yield (%) ^a		
			Benzo[b]thiophen	Disulphide (V)	Bidesyl (III)
(Ia)	MeOH	13	6 (IVa)	b	1
(Ia)	n-Hexane	29		22	11
(Ia)	PhH	19	1 (IVa)	20	18
(Ia)	Pr ⁱ OH	25	10 (IVa)	19	
(IIb)	MeOH-PhH	25	18 (IVa)		
(Ib)	MeOH-PhH	16	5 (IVb)	20	
(Ic)	MeOH	17	4 (IVc)	13	
(VII)	Pr ⁱ OH-PhH	19	39(19.5) ^c (IVa)		3.5(1.75) ^c

^a A high-pressure mercury vapour lamp with Pyrex filter was used for all irradiations. Starting material was present on termination of each experiment, and, in some cases, the low yield or absence of bidesyl was due to difficulty in separation during work-up.

^b Polymer (PhCH₂S)_n formed. ^c The yield, based on the assumption that 1 mole of (VII) gives 2 moles of product, is given in parentheses.

To determine which of the benzene rings of (Ia) becomes the 2-phenyl substituent of benzo[b]thiophen (IVa), the methyl homologues (Ib) and (Ic) were irradiated. The formation of benzo[b]thiophens (IVb) and (IVc), respectively, shows that direct cyclisation of a homolysis product (B) to a benzo[b]thiophen precursor does not occur (see Scheme). The results may be rationalised as shown in the accompanying Scheme. Differentiation between paths (a) and (b) leading to the episulphide (C) cannot be made from the evidence at hand, which also does not exclude ionic character for path (b).

Fission of the other C-S bond of the sulphide (Ia) [path (c)] yields the photoproducts bidesyl¹ (III) and dibenzyl disulphide² (V). If the benzyl group of (I) is replaced by a group which forms a more stable radical (or ion), then path (b) [or (a)] should be more favoured relative to path (c) resulting in a higher yield of the benzo[b]thiophen. This was found to be the case when desyl triphenylmethyl

sulphide (IIb) was irradiated, a higher yield of benzo[b]thiophen (IVa) being obtained. Photolysis of the disulphide (VII)³ resulted principally in fission of the S-S bond and benzo[b]thiophen (IVa) was the major product. The photolysis of (Ia) was influenced by the solvent, reaction path (c), leading to bidesyl (III) and disulphide (V), predominating in hexane or benzene.

The presence of both benzene rings in the sulphide may be necessary for benzo[b]thiophen formation, as irradiation of the sulphide (VI) did not give 2-methylbenzo[b]thiophen.

Benzo[b]thiophens (IVa),⁴ (IVb), and (IVc)⁴ were identical with the products of high-temperature cyclisation in polyphosphoric acid of the keto-sulphides (VIIIa),⁴ (VIIIb), and (VIIIc),⁴ respectively. Sulphides (Ia-c), (IIb), (VI), and (VIIIb) were prepared from the appropriate α -chloro-ketone and thiol. Satisfactory analyses were obtained for all new compounds.

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