

Photodecomposition of Alkyl Benzoates and S-Alkyl Thiobenzoates. Possibility of a Barton-type Transition State¹

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U.v. irradiation of alkyl (C₃—C₅) benzoates under nitrogen gives mainly benzoic acid (*ca.* 40%), *via* a Norrish type II process, along with benzaldehyde (<4%) and other products. In the case of pentyl benzoate, a small amount of propiophenone (1.6%) was obtained. In contrast, *S*-pentyl thiobenzoate gives mainly benzaldehyde (27%) (*via* a Norrish type I process), dipentyl disulphide (23%), and some other minor products, *viz.* biphenyl (1.4%), pentyl phenyl sulphide (3.2%), pentylbenzene (trace), and propiophenone (trace), but no thiobenzoic acid. Electron impact-induced fragmentation of these alkyl benzoates and of *S*-alkyl thiobenzoates correlates with their photochemical behaviour; 50—60% benzoic acid cation radical was obtained from alkyl benzoates, but only *ca.* 5% thiobenzoic acid cation radical from *S*-pentyl thiobenzoate.

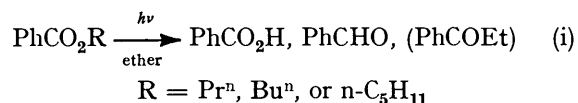
NORRISH type II photodecomposition of carbonyl compounds has been widely studied.¹ However, the secondary photoreaction of aromatic esters, *e.g.* alkyl benzoates, after fission α - or β - to the carbonyl group, seems not to have been elucidated, although some benzoates were recently reported to give the Norrish type II decomposition product (benzoic acid).²

We report here the secondary photoreactions of alkyl benzoates and *S*-pentyl thiobenzoate, and compare the results with the corresponding electron impact-induced fragmentation reactions.

RESULTS AND DISCUSSION

Photodecomposition of Alkyl Benzoates.—Ethereal solutions of alkyl (C₃—C₅) benzoates (0.06—0.07M)

were irradiated (Halos HIP lamp, 300 W) under nitrogen. The product was separated to afford the starting ester and benzoic acid. Other, minor products were detected by g.l.c.; the data are summarised in Table 1.



Photodecomposition of S-Pentyl Thiobenzoate.—A benzene solution of *S*-pentyl thiobenzoate (*ca.* 0.025M) was irradiated in a quartz tube until the starting ester had disappeared. The products were shown by g.l.c. to be benzaldehyde, dipentyl disulphide, biphenyl, pentyl

¹ For a comprehensive review, see for example, N. J. Turro, J. C. Dalton, K. Dewes, G. Farrington, R. Hautara, D. Morton, M. Niemczyk, and N. Schore, *Accounts Chem. Res.*, 1972, **5**, 92 and references therein.

² J. G. Pacifici and J. A. Hyatt, *Mol. Photochem.*, 1971, **3**, (a) p. 267; (b) p. 271; (c) J. A. Barltrop and J. D. Coyle, *J. Chem. Soc. (B)*, 1971, 251.

phenyl sulphide, propiophenone, and pentylbenzene (Table I).

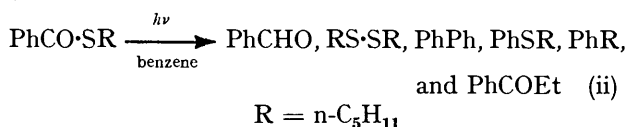


Table I shows the following features. (a) An increase of alkyl chain length from C₃ to C₅ has little effect on the efficiency of type II photoelimination to form benzoic acid and olefins. This photoreaction almost exclusively

aldehyde) *via* a radical-chain mechanism on u.v. irradiation, yielding some secondary products.³ The minor products except propiophenone can be explained as a result of a similar radical-chain reaction.

(b) The formation of propiophenone was observed only with pentyl benzoate and *S*-pentyl thiobenzoate; this fact is noteworthy in spite of the poor yield in view of the analogy with the well-known Barton reaction.⁴ In a Barton-type reaction, the primary product (III) may be easily photodecomposed; it would be expected to disappear 10³ times faster than the starting benzoate.^{2c,5}

TABLE I

Photoproducts from alkyl benzoates and thiobenzoates ^a

XR in PhCO·XR	Concn. (M)	Solvent	Irrad. time (h)	Conv. (%)	Products (%)							
					PhCO·XH	PhCHO	(XR) ₂	Ph ₂	PhCOEt	Ph·XR	PhR	
OPr ⁿ	0.07	Et ₂ O	100	22	45	2						
OBU ⁿ	0.08	Et ₂ O	100	26	43	2						
O-C ₅ H ₁₁ -n	0.07	Et ₂ O	100	25	42	2						
S-C ₅ H ₁₁ -n	0.06	PhH	50	83		32.4	28	1.7	2	3.8		Trace
S-C ₅ H ₁₁ -n	0.07	n-C ₈ H ₁₈	50	35		53	13	Trace	Trace	Trace		Trace
S-C ₅ H ₁₁ -n	0.06	MeCN	40	72		44	27	4.0	Trace	4.1		1.1
S-C ₅ H ₁₁ -n	0.04	Et ₂ O	5	74		30.3	27	5.0	0.5	3.5		1.4
S-C ₅ H ₁₁ -n	0.04	Et ₂ O	10	83		16.2	29.4	8.1	0.7	7.2		3.7
S-C ₅ H ₁₁ -n	0.04	Et ₂ O	20	88		13.1	31.1	10.2	1.1	8.7		5.7

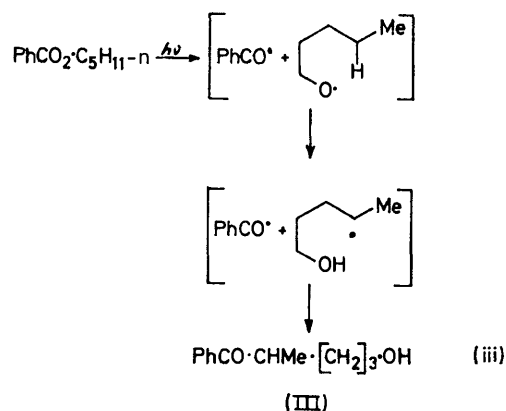
^a Yields determined by g.l.c.

involves cleavage β- to the carbonyl group; little α-cleavage to yield benzaldehyde and other products was observed, although the observed β-cleavage is less efficient than that of aromatic ketones.

On the other hand, *S*-pentyl thiobenzoate is photodecomposed easily, and the main process seems to be α-cleavage followed by the reaction giving benzaldehyde and disulphide. The formation of pentyl phenyl sulphide and pentylbenzene implies the occurrence of the process in which the benzoate eliminates CO or COS; this process was not observed with alkyl benzoates. These products are perhaps derived from the secondary stepwise reaction of benzoyl and sulphide radicals, as indicated by the facts that (i) biphenyl, a coupling product of phenyl radicals, was observed as a minor product, and (ii) the minor products increase gradually with time as shown in Table I.

In the photodecomposition of *S*-pentyl thiobenzoate, benzaldehyde accumulates rapidly at first and then decreases with a simultaneous but slower increase of the disulphide; *i.e.* benzaldehyde and disulphide are both unstable to irradiation. The other by-products, pentylbenzene, pentyl phenyl sulphide, and propiophenone increased throughout with time. Therefore, the primary photoproducts are mainly benzaldehyde and dipentyl disulphide. Thiol and sulphide radicals are known to facilitate decomposition of some aldehydes (*e.g.* benz-

Although this material (III) was not detected, the detection of propiophenone is convincing evidence for the occurrence of the Barton-type reaction.



Butoxyl and propoxyl radicals produced from butyl and propyl benzoates by α-cleavage would probably not undergo intramolecular hydrogen abstraction. The butoxyl radical has only a primary hydrogen atom available for transfer in a six-membered cyclic transition state, whereas the pentyloxyl radical has a secondary hydrogen available; the propoxyl radical cannot form a six-membered transition state.

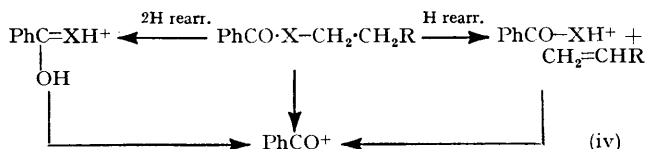
Mass Spectrometry of Alkyl Benzoates and S-Alkyl Thiobenzoates.—Hydrogen transfer reactions during electron impact are known to occur in alkyl benzoates

³ S. G. Cohen, J. D. Berman, and S. Orman, *Tetrahedron Letters*, 1962, 43.

⁴ (a) D. H. R. Barton, J. M. Barton, L. E. Geller, and M. M. Pechet, *J. Amer. Chem. Soc.*, 1961, **83**, 4076; (b) M. Akhtar and M. M. Pechet, *ibid.*, 1964, **86**, 265; (c) M. Akhtar, D. H. R. Barton, and P. G. Sammes, *ibid.*, 1965, **87**, 4601.

⁵ P. J. Wagner and A. E. Kemppainen, *J. Amer. Chem. Soc.*, 1968, **90**, 5896.

with alkyl chains longer than C₃.⁶ The β -cleavages of alkyl benzoates (C₃–C₅ chains) were reinvestigated, and formation of benzoic acid and olefinic fragments was confirmed, *i.e.* results similar to those reported previously were observed.⁶



Little information on the fragmentation of *S*-alkyl thiobenzoates has previously been available. Our results (Table 2) show that these compounds mainly undergo α -cleavage on electron bombardment.

With all the alkyl benzoates and *S*-alkyl thiobenzoates, the benzoyl fragment (*m/e* 105) is the base peak; other fragmentations show differences. Alkyl benzoates are generally cleaved to give benzoic acid and

However, a photoexcited electron-deficient oxygen atom becomes a more effective hydrogen abstractor when an electron-withdrawing group is introduced. Thus an aromatic ester bearing an electron-withdrawing group (*e.g.* *p*-CN or *p*-CO₂Me) in the ring can abstract a hydrogen atom from solvents, but an unsubstituted alkyl benzoate cannot react.⁷

The ready α -fission of CO–S in *S*-alkyl thiobenzoates should make the γ -hydrogen abstraction of the type II reaction difficult; in fact the dissociation energy of the C–S bond is lower by *ca.* 20 kcal mol⁻¹ than that of the C–O bond in an alkyl benzoate.⁸ This would also explain the difference in reactivities, *i.e.* the greater preference for α -fission of C–S than of C–O.

EXPERIMENTAL

I.r. spectra were recorded with a Perkin-Elmer grating spectrophotometer model 337. Gas chromatograms were recorded with a Yanaco GCG-550F gas chromatograph with

TABLE 2
Electron impact-induced fragmentation of alkyl benzoates^a

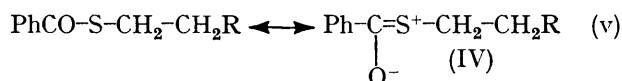
XR in PhCO·XR	Fragment ion (%)					
	PhCO·XH ⁺	PhCO·XH ₂ ⁺	PhCO ⁺	PhCOH ⁺	Ph ⁺	M ⁺
OPr ^a	54.7	60	100	40	68	2
OBu ^a	41	61	100	32	66.7	4.7
O-C ₅ H _{11-n}	38	68	100	37	59	4.7
SPr ^a	2.7	0	100	31	61	4.7
SBu ^a	3.3	0	100	42.6	62.7	4.7
S-C ₅ H _{11-n}	5.3	0	100	40	60	5.3

^a *m/e* < 76 not reported.

olefins in high yields by intramolecular hydrogen abstraction, whereas *S*-alkyl thiobenzoates yield benzoyl fragments *via* α -cleavage (although it is probable that some of the PhCO⁺ fragment is derived from PhCOSH⁺ rather than directly from PhCOSR⁺). These mass spectral observations correlate well with the photochemical behaviour.

The efficiency for formation of benzoic acid (or its cation radical) decreases with increasing length of the alkyl chain of alkyl benzoates; this may be attributed to steric hindrance to the formation of a six-membered cyclic transition state.

In the case of *S*-alkyl thiobenzoates, intramolecular γ -hydrogen abstraction by carbonyl oxygen followed by formation of benzoic acid and olefins is inefficient; this may be due to the interaction of the sulphur 3*d*-orbital with the carbonyl group. A resonance form such as (IV) probably contributes to reduce the hydrogen-abstraction ability, especially in its excited state, *i.e.* a more nucleophilic carbonyl oxygen atom would be less effective for hydrogen abstraction.



⁶ (a) F. W. McLafferty, *J. Amer. Chem. Soc.*, 1965, **87**, 5760; (b) T. Aczel and H. E. Lumpkin, *Analyt. Chem.*, 1962, **34**, 33.

a flame ionization detector (2 m × 2.5 mm column packed with Apiezon L and PEG 20M on Chamelite at 60–200°). Electron impact-induced fragmentation was studied by direct insertion into the source of a Hitachi RMS-4 mass spectrometer.

Materials.—Alkyl benzoates were obtained from treatment of benzoic acid with various alcohols in the presence of a small amount of sulphuric acid. *S*-Alkyl thiobenzoates were prepared by the reaction of equimolar amounts of benzoyl chloride and thiols in the presence of pyridine.^{9,10} The *S*-propyl compound (48%) had b.p. 121–122° at 7 mmHg (lit.,^{10b} 164–170° at 47 mmHg); the *S*-butyl compound (68%) had b.p. 125–126° at 6 mmHg; and the *S*-pentyl compound (78%) had b.p. 105–106° at 3 mmHg.

Authentic pentyl phenyl sulphide, synthesised by the procedure of Vogel,¹¹ had b.p. 80–82° at 30 mmHg (lit.,¹¹ 111.5° at 5 mmHg), and pentylbenzene¹² had b.p. 147–149° at 4 mmHg (lit.,¹² 198–202° at 760 mmHg).

Photodecomposition of Alkyl Benzoates.—Typical pro-

⁷ K. Fukui and Y. Odaira, *Tetrahedron Letters*, 1969, 5255.

⁸ C. K. Ingold, 'Structure and Mechanism in Organic Chemistry', 2nd edn., Cornell University Press, London, 1969, p. 253.

⁹ F. W. Wenzel, jun., and E. E. Reid, *J. Amer. Chem. Soc.*, 1937, **59**, 1089.

¹⁰ (a) R. L. Frank, S. S. Drake, P. V. Smith, jun., and C. Stevens, *J. Polymer Sci.*, 1948, **3**, 50; (b) W. R. Vaughan and J. B. Baumann, *J. Org. Chem.*, 1962, **27**, 739.

¹¹ A. I. Vogel, *J. Chem. Soc.*, 1948, 1822.

¹² H. Gilman and J. Robinson, *Org. Synth.*, 1943, Coll. Vol. II, p. 47.

cedure. A benzene solution (600 ml) of pentyl benzoate (2.51 g) was irradiated with a Halos HIP 300 W high pressure mercury lamp for 100 h under nitrogen. The reaction was monitored by t.l.c. The product mixture was evaporated and separated on a column of 80—100 mesh silica gel with benzene-acetone as eluant to yield benzoic acid (0.3 g, 12%), identical (m.p. and i.r. spectrum) with an authentic sample.

Other runs were carried out to identify and estimate other products by g.l.c.

Photodecomposition of S-Alkyl Thiobenzoates.—Typical procedure. A benzene solution (600 ml) of S-pentyl thio-benzoate (3.13 g) was similarly irradiated under nitrogen in a quartz vessel; t.l.c. confirmed that the benzoate was consumed during 50 h irradiation. Separation of the products

on a silica gel column with benzene-ethyl acetate as eluant yielded benzaldehyde (0.84 g, 32.4%), ν_{\max} (neat) 1700 cm^{-1} , δ (CCl_4) 7.6 (5H, m, Ph), and 9.8 (1H, s, CHO); propiophenone (trace); dipentyl disulphide (0.74 g, 28%), δ (CCl_4) 0.9 (6H, t, $2 \times \text{Me}$), 1.3 (12H, m, $6 \times \text{CH}_2$), and 2.5 (2H, t, $\text{S}\cdot\text{CH}_2$), n_D^{25} 1.495 (lit.,¹³ n_D^{20} 1.489); pentyl phenyl sulphide (0.1 g, 3.8%), ν_{\max} (neat) 720 cm^{-1} (C-S), δ (CCl_4) 0.9 (3H, t, Me), 1.3 (6H, m, $3 \times \text{CH}_2$), 2.5 (2H, t, $\text{S}\cdot\text{CH}_2$), and 7.6 (5H, m, Ph); pentylbenzene (trace); and biphenyl (0.04 g, 1.7%). Propiophenone, pentylbenzene, and biphenyl were identified by comparison with authentic samples (g.l.c. retention times on two different columns, with liquid phases PEG 20M and Apiezon L).

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¹³ A. I. Vogel and D. M. Cowan, *J. Chem. Soc.*, 1943, 16.