Selective Photolysis of Thiobenzoic Acid *O*-Esters

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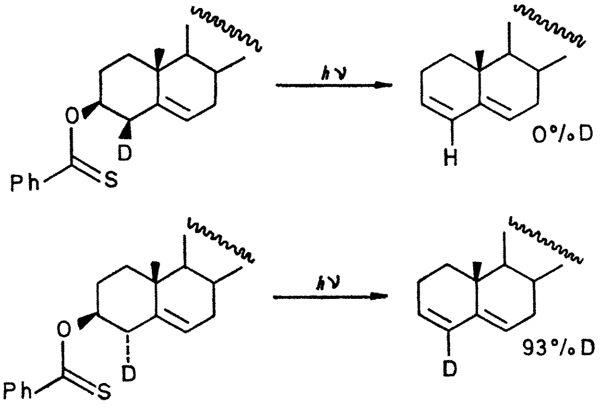
Summary Thiobenzoic acid *O*-esters of part structure $X{\cdot}\overset{|}{C}H{\cdot}\underset{|}{\overset{|}{C}}{\cdot}O{\cdot}C(S)Ph$ (X = olefinic linkage, aryl residue, or other conjugating function) are smoothly photolysed (in general in high yield) to the corresponding olefin and thiobenzoic acid; similar *O*-esters with the X function not in potential conjugation are photolysed only sluggishly.

IN an earlier paper[1] we showed that *S*-acyl-xanthates were smoothly converted into xanthate and acyl radicals on photolysis. This photochemical reaction is due, in principle, to the chromophoric thione grouping (n–π^* transition). Although it is known that thiobenzoic acid *O*-esters, unlike their *S*-ester and benzoate analogues, absorb in the visible region, no photolytic studies of these *O*-esters have been reported.

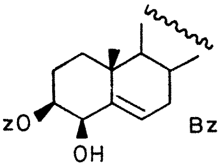


SCHEME

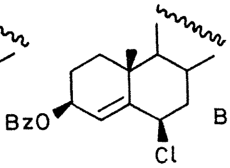
The cholesteryl thiobenzoate (*O*-ester; see Scheme),† m.p. 164—166°, $[\alpha]_D$ − 5° (c 1·0), $\lambda_{max.}$ 256, 288, and 420 nm (ϵ 7100, 8000, and 70 respectively), (prepared by procedures A or B) was photolysed in a Pyrex flask at room temperature in cyclohexane using a medium-pressure (125 W) mercury vapour lamp. Cholesta-3,5-diene,[2] m.p. 78—80°, was rapidly formed in very high yield. After aerial oxidation of the acid fraction dibenzoyl disulphide was also formed quantitatively. If the photolysis was prolonged the thio-acid added (radical addition) to the newly generated diene. To prevent this the photolysis was carried out in the presence of triethylamine. The photo-elimination was studied in 18 solvents (hydrocarbon, aromatic, ether, alcohol, and amide solvents) and the rate‡ of photolysis throughout this series was within experimental error as with cyclohexane. To ascertain whether the photo-elimination was stereospecific or not the 4α- and 4β-deuteriocholesteryl thiobenzoates were prepared by the following route. Cholesteryl benzoate was oxidised with selenium dioxide to the 4β-alcohol (I).[3,4] Treatment of the alcohol with thionyl chloride in ether gave (II).[5] Lithium aluminium deuteride reduction of (II) produced the 4β-deuteriocholesterol.[5] Oxidation of (I) with chromium trioxide in pyridine gave the 4-oxocholesteryl benzoate[6] which was reduced with sodium borodeuteride to give (III). Treatment of (III) with thionyl chloride in ether, followed by lithium aluminium hydride reduction gave 4α-deuteriocholesterol.§ Photolysis of the derived thiobenzoates (Scheme) gave from the 4β-deuteriocholesterol the 3,5-diene with complete loss of deuterium (n.m.r. and mass spectral analysis). Similarly, photolysis of the 4α-deuteriocholesteryl thiobenzoate gave the 3,5-diene with complete retention of the deuterium. The k_H/k_D ratio, determined by direct observation of the photolysis rates, was 1·4.

Cholestanyl thiobenzoate (*O*-ester) (procedure A), m.p. 141—142° $[\alpha]_D$ + 3° (c 1·0 in $CHCl_3$), was photolysed slowly (1/70th of rate of cholesteryl thiobenzoate; tungsten lamp) in ethanol to give two products in 21 and 17% yield respectively. These compounds were characterised as the 3α- and 3β-thiobenzoates (*S*-esters) by comparison with authentic samples.[7] Similarly, 4,4-dimethylcholesteryl thiobenzoate (*O*-ester) photolysed slowly and did not produce any characterisable elimination products. For this ready elimination of thiobenzoate to occur the transition state requires some conjugation of the newly forming double bond.

O-Phenethyl thiobenzoate (IV; R = H) (procedure A, B, or C), b.p. 116—118° at 0·1 mmHg, was photolysed in cyclohexane using a medium-pressure mercury vapour lamp to give styrene (90%) (isolated as the dibromide or adduct with *p*-nitrophenylcarbonitrile *N*-oxide). In this and other photolyses triethylamine may be added to prevent the readdition of the eliminated thioacid to the styrene (*p*-nitrobenzoyl peroxide was also used, *in situ*, to oxidise the thio-acid to dibenzoyl sulphide). *O*-(3-Phenylpropyl) thiobenzoate and *O*-(4-phenylbutyl) thiobenzoate were



(I)



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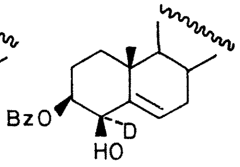

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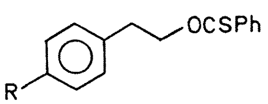

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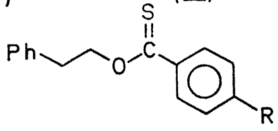

(V)

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† The thioesters described were prepared by one of three methods. These are referred to as procedure A, B, and C. A involves treatment of the alcohol in pyridine with thiobenzoyl chloride.[8] B involves treatment of the alcohol with sodium hydride in glyme followed by thiobenzoyl thioglycollic acid. C involves treatment of equivalent amounts of alcohol and benzonitrile in ether with dry hydrogen chloride. The resulting imino-ether hydrochloride is neutralised ($NaHCO_3$) and treated with hydrogen sulphide.

‡ Conc. of thiobenzoate 17·0 mg/50 ml of solvent. Times refer to 50% photolysis.

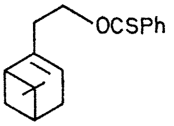
§ The 4α- and 4β-deuteriocholesterols contained 85% deuterium from the mass spectra of their trimethylsilyl ethers.

photolysed slowly, and gave complex mixtures. The *O*-(phenethyl) thiobenzoate derivatives (IV; R = OMe), (IV; R = NO_2), and (IV; R = NMe_2) were photolysed and gave the *p*-substituted styrenes in 68·5, 79·5, and 37% yields respectively. Through the above series (IV; R = H, OMe, NO_2, and NMe_2) the time for 50% photolysis (under identical conditions) was 7, 7, 47, and 13·5 min, respectively.

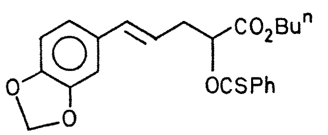
In the *p*-substituted thiobenzoate series (V; R = H, OMe, NO_2, or NMe_2) photolysis gave styrene in 90, 80, 76, and 10% respectively in times (as above) of 7, 8, 4, and 30 min, respectively.

To extend the general scope of this photo-elimination we irradiated the following thiobenzoates (*O*-esters). Nopol thiobenzoate (VI) (procedure B) was photolysed (12 min; half reaction) to give nopodiene[8] (85%) isolated as its adduct with *p*-benzoquinone. The thiobenzoate (VII) (procedure B) was photolysed (18 min, half reaction) to give the diene (78%) which was characterised as piperic acid. *O*-(2-Ethoxyethyl) thiobenzoate on photolysis gave ethyl vinyl ether (46%; 21 min, half reaction). *O*-(Pyrrolidin-2-yl)ethyl thiobenzoate, gave, on photolysis (18 min, half reaction) and acid work-up, acetaldehyde (28%; as its 2,4-dinitrophenylhydrazone). The thiobenzoates (VIII)—(X) were photolysed; (VIII) and (X) gave a complex mixture of products, but butadiene (18%: 14 min, half reaction) was isolated from (IX). The carbazole (XI; X = S) gave on photolysis the benzoate (XI; X = O) (70%). Photolysis of *meso*-dihydrobenzoin dithiobenzoate in the presence of triethylamine gave benzyl phenyl ketone (52%; 15 min; half reaction).

Synthetically this photo-elimination offers a neutral, high yield, and extremely mild (proceeds rapidly even at −76°) method for dehydrating homoallylic alcohols.



(VI)



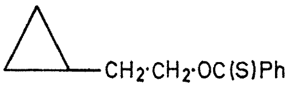
(VII)

$HC\equiv C\cdot CH_2\cdot CH_2\cdot OC(S)Ph$

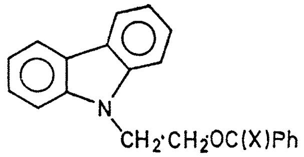
(VIII)

$H_2C=CH\cdot CH_2\cdot CH_2\cdot OC(S)Ph$

(IX)



(X)



(XI)

All new compounds were fully characterised by spectroscopic and microanalytical techniques.

(*Received, June 8th*, 1971; *Com.* 937.)

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[1] D. H. R. Barton, M. V. George, and M. Tomoeda, *J. Chem. Soc.*, 1962, 1967; see also R. H. Bell, D. Horton, and D. M. Williams, *Chem. Comm.*, 1968, 323.

[2] W. Bergmann and F. Hirschmann, *J. Org. Chem.*, 1939, **4**, 40.

[3] O. Rosenheim and W. W. Starling, *J. Chem. Soc.*, 1937, 377.

[4] V. A. Petrov, O. Rosenheim, and W. W. Starling, *J. Chem. Soc.*, 1943, 135.

[5] R. E. Ireland, T. I. Wrigley, and W. G. Young, *J. Amer. Chem. Soc.*, 1959, **81**, 2818.

[6] L. F. Fieser and R. Stevenson, *J. Amer. Chem. Soc.*, 1954, **76**, 1728.

[7] J. H. Turnbull, *Chem. and Ind.*, 1959, 515; R. Bourdon, *Bull. Soc. Chim.* (*France*), 1962, 844.

[8] L. J. Kitchen, *J. Amer. Chem. Soc.*, 1951, **73**, 2368.

[9] H. Staudinger and J. Siegwart, *Helv. Chim. Acta*, 1920, **3**, 824.