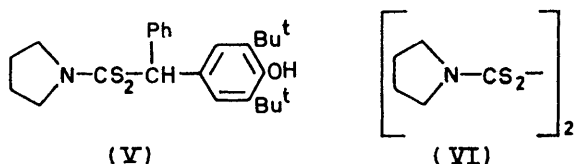
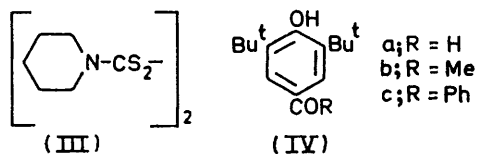
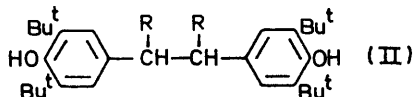
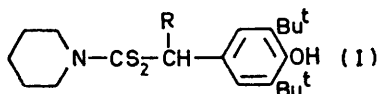


Studies in the Dithiocarbamate Series. Part IV.¹ Photolysis of Some 4-Hydroxybenzyl Dithiocarbamates

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Several 4-hydroxybenzyl dithiocarbamates have been photo-irradiated under various conditions. It is postulated that the initial photochemical step involves formation of dithiocarbamoyl and benzyl radicals. The former yields a thiuram disulphide by dimerisation and the benzyl radical either dimerises to a diphenylethane or dissociates to a *p*-quinone methide. When the irradiations were carried out in the presence of water, aromatic ketones were also produced and evidence is presented which indicates that these probably arise *via p*-quinone methide intermediates.

CERTAIN 4-hydroxybenzyl dithiocarbamates [*e.g.* (I)] have been shown to undergo thermal decomposition *via*



a Chugaev-type mechanism; in the presence of transition metals an additional pathway involving *p*-quinone

* 'Wet' methanol or benzene refers to undried commercial solvent.

¹ Part III, A. O. Fitton, M. Qutob, and W. Barber, *J. Chem. Soc. (C)*, 1971, 1245.

methides has been shown to be operative.² The present work describes light-induced decompositions of the 4-hydroxybenzyl dithiocarbamates (Ia—c) and (V). Recent papers have described the irradiation of some benzoyl dithiocarbamates.^{3,4}

With carefully dried and deoxygenated methanol as solvent, irradiation of 4-hydroxy-3,5-di-*t*-butylbenzyl piperidine-1-carbodithioate (Ia) under nitrogen led to two main products, 1,2-bis-(4-hydroxy-3,5-di-*t*-butylphenyl)ethane (IIa) and *NN,N'N'*-bistetramethylene-thiuram disulphide (III). The formation of these products (see Scheme) indicates that the initial photochemical step is homolytic fission of the benzylic carbon-sulphur bond with formation of the benzyl radical (VIII) and the dithiocarbamoyl radical (VII). Dimerisation of the radicals leads to the observed products; a similar process has been cited⁵ to explain the formation of 1,2-diphenylethanes during the oxidation of sterically hindered phenols.

When the irradiation was carried out in 'wet' * methanol, the foregoing products were accompanied by a significant amount of 4-hydroxy-3,5-di-*t*-butylbenzaldehyde (IVa). This compound was also produced when the irradiation was carried out under oxygen-free nitrogen; oxygen must therefore be introduced by interaction of a reaction intermediate with solvent moisture.

² A. O. Fitton, A. Rigby, and R. J. Hurlock, *J. Chem. Soc. (C)*, 1968, 996.

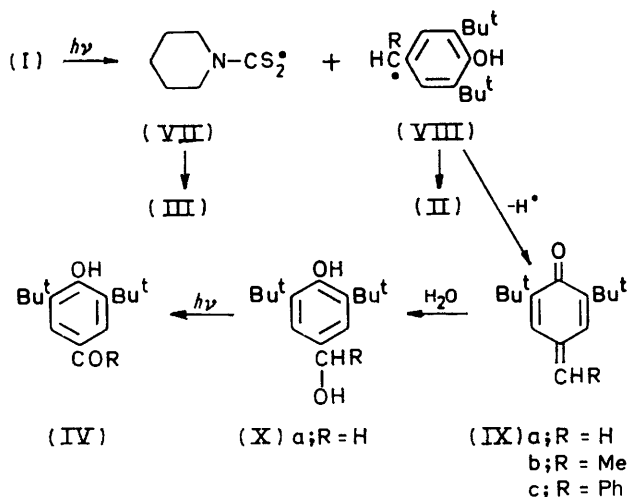
³ E. H. Hoffmeister and D. S. Tarbell, *Tetrahedron*, 1965, **21**, 35, 2857, 2865.

⁴ S. N. Singh and M. V. George, *J. Org. Chem.*, 1971, **36**, 615.

⁵ C. D. Cook, *J. Org. Chem.*, 1953, **18**, 261.

4-Hydroxybenzyl dithiocarbamates possessing a methyl or a phenyl substituent on the benzylic carbon atom were also irradiated in a 'wet' solvent (benzene); in each case an aryl ketone was formed. The results are described in the Table.

In order to explain the formation of an aldehyde or ketone, it is postulated (see Scheme) that the initially formed benzyl radical (VIII) dissociates to the *p*-quinone



SCHEME

methide (IX) which then is attacked by solvent moisture, yielding the benzyl alcohol (X). The carbonyl compound subsequently arises from the latter by photo-oxidation.

The formation of the quinone methide from the benzyl radical is a similar reaction to that postulated to explain the formation of 4-isopropylidene-2,6-di-*t*-butylcyclohexa-2,5-dienone during oxidation of 4-isopropyl-2,6-di-*t*-butylphenol,⁶ and in the present work, the relatively unreactive quinone methide, 4-benzylidene-2,6-di-*t*-butylcyclohexa-2,5-dienone (IXc), was isolated from the reaction mixture after irradiation of 4-hydroxy- α -phenyl-3,5-di-*t*-butylbenzyl piperidine-1-carbodithioate (Ic) or its pyrrolidine analogue (V). In these reactions, no 1,2-diphenylethane was isolated, presumably for steric reasons. When the irradiation of 4-hydroxy- α -methyl-3,5-di-*t*-butylbenzyl piperidine-1-carbodithioate (Ib) was stopped before completion, evidence for the presence of 4-ethylidene-2,6-di-*t*-butylcyclohexa-2,5-dienone (IXb) was obtained from its distinctive colour and R_F value on t.l.c. by comparison of the reaction mixture with a sample of the pure quinone methide. However, attempts to isolate it from the reaction mixture by column chromatography were unsuccessful, and it was subsequently shown that the quinone methide decomposed on the column. Presumably because of the highly unstable nature of quinone methides without

a substituent on the methylene group [*e.g.* (IXa)],^{6,7} that from irradiation of benzyl dithiocarbamate (Ia) was not detected.

The interaction of *p*-quinone methides with water to give benzyl alcohols is well known;^{8,9} it has been shown that such an alcohol can be oxidised under the reaction conditions by irradiating 4-hydroxy-3,5-di-*t*-butylbenzyl alcohol (Xa)⁹ to give the aldehyde (IVa). Similarly, 4-ethylidene-2,6-di-*t*-butylcyclohexa-2,5-dienone (IXb) was irradiated in 'wet' benzene.

The new dithiocarbamates (Ic) and (V) were obtained by insertion¹⁰ of carbon disulphide into the appropriate Mannich base. Compound (Ia) was obtained by the 'one-stage' process¹¹ and (Ib) by the insertion process.

EXPERIMENTAL

Irradiations were carried out with a medium-pressure mercury-vapour lamp (type Q 81, Quarzlampen GMBH Hanau) centrally situated in a water-cooled Pyrex cold-finger. 'Wet' methanol or benzene refers to undried commercial solvent. Silica gel for column chromatography was Hopkin and Williams M.F.C. grade, and that for t.l.c. was Merck Kieselgel G. N.m.r. spectra were determined at 60 MHz for solutions in carbon tetrachloride (unless otherwise stated) with tetramethylsilane as internal reference.

N-(4-Hydroxy- α -phenyl-3,5-di-*t*-butylbenzyl)piperidine.—A solution of 2,6-di-*t*-butylphenol (25.7 g), benzaldehyde (10.6 g), and piperidine (13.2 g) in ethanol (150 ml) was heated under reflux for 3 h, then cooled. The product was filtered off and gave *prisms* (27.2 g) (from ethanol), m.p. 148° (Found: C, 82.1; H, 9.7; N, 3.6. $C_{26}H_{37}NO$ requires C, 82.3; H, 9.7; N, 3.7%).

Similarly, 2,6-di-*t*-butylphenol (25.7 g), benzaldehyde (10.6 g), and pyrrolidine (7.1 g) in ethanol (150 ml) gave *N*-(4-hydroxy- α -phenyl-3,5-di-*t*-butylbenzyl)pyrrolidine (19 g) as *prisms* (from ethanol), m.p. 105° (Found: C, 81.9; H, 9.7; N, 3.6. $C_{25}H_{35}NO$ requires C, 82.2; H, 9.9; N, 3.8%).

4-Hydroxy- α -phenyl-3,5-di-*t*-butylbenzyl Piperidine-1-carbodithioate (Ic).—To a solution of *N*-(4-hydroxy- α -phenyl-3,5-di-*t*-butylbenzyl)piperidine (37.7 g) in ethanol (150 ml) was added carbon disulphide (7.6 g), and the mixture was stirred at 25° for 2 h, then filtered. The residue gave *needles* (31.1 g) (from ethanol), m.p. 103° (Found: C, 71.1; H, 8.0; N, 3.1. $C_{27}H_{37}NOS_2$ requires C, 71.2; H, 8.1; N, 3.1%); τ 2.7 (m) and 2.9 (m) (ArH), 3.55 (CH), 5.0 (OH), 5.95 (m, N-CH₂), 8.3 (m, 3 \times CH₂), and 8.6 (CMe₃).

Similarly, *N*-(4-hydroxy- α -phenyl-3,5-di-*t*-butylbenzyl)pyrrolidine (8.7 g) and carbon disulphide (1.9 g) in ethanol (50 ml) gave 4-hydroxy- α -phenyl-3,5-di-*t*-butylbenzyl pyrrolidine-1-carbodithioate (V) (6.1 g) as *needles* (from ethanol), m.p. 137° (Found: C, 82.1; H, 9.5; N, 3.7. $C_{26}H_{35}NOS_2$ requires C, 82.2; H, 9.5; N, 3.8%); τ 2.7 (m, ArH), 3.5 (m, CH), 4.95 (OH), 6.35 (m, NC-H₂), 8.1 (m, 3 \times CH₂), and 8.6 (CMe₃).

⁹ G. M. Coppinger and T. W. Campbell, *J. Amer. Chem. Soc.*, 1953, **75**, 734.

¹⁰ A. O. Fitton, A. Rigby, and R. J. Hurlock, *J. Chem. Soc. (C)*, 1969, 230.

¹¹ A. O. Fitton, A. Rigby, and R. J. Hurlock, *Chem. Comm.*, 1967, 163.

⁶ C. D. Cook and E. Norcross, *J. Amer. Chem. Soc.*, 1956, **78**, 3797.

⁷ L. J. Filar and S. Winstein, *Tetrahedron Letters*, 1960, 9.

⁸ C. D. Cook and N. D. Gilmour, *J. Org. Chem.*, 1960, **25**, 1429.

Irradiation of Hydroxybenzyl Dithiocarbamates: General Procedure.—A solution (ca. 1%) of the dithiocarbamate in the appropriate solvent was stirred and irradiated at room temperature for 7–12 h under oxygen-free nitrogen. When the reaction was complete (as indicated by t.l.c.) the solution was evaporated under reduced pressure and the

(b.p. 60–80°)–benzene (10 : 1) gave (successively) starting material (0.3 g) and 4-hydroxy-3,5-di-*t*-butylbenzaldehyde (0.14 g) as plates [from light petroleum (b.p. 40–60°)], m.p. 190° (lit.,⁹ 190°).

*Irradiation of 4-Ethylidene-2,6-di-*t*-butylcyclohexa-2,5-dienone.*—A solution of the dienone (0.5 g) in 'wet' benzene

Irradiation of dithiocarbamates

Dithio- carbamate	Solvent	Time (h)	Diphenylethane		Thiuram		Carbonyl compound		Quinone methide	
			Yield (%)	M.p. (°C) ^a	Yield (%)	M.p. (°C) ^a	Yield (%)	M.p. (°C) ^a	Yield (%)	M.p. (°C) ^a
(Ia)	Dry MeOH	7	60 (IIa)	173–174	32 (III)	130				
(Ia)	'Wet' MeOH	7	25 (IIa)	173–174	35 (III)	130	8 (IVa)	190		
(Ib)	'Wet' PhH	7	25 (IIb) ^b	213–215	32 (III)	130	9 (IVb)	^c		
(Ic)	'Wet' PhH	12			39 (III)	130	3 (IVc)	125	22 (IXc)	74
(V)	'Wet' PhH	12			25 (VI)	144	3 (IVc)	125	15 (IXc)	74

^a Lit. m.p.s (IIa) 174–175°,⁵ (III) 130°,⁴ (IVa) 190°,⁹ (IVc) 124–125°,⁸ (VI) 144–145°,⁴ and (IXc) 72–74°.¹² ^b Found: C, 82.8; H, 10.8. C₂₂H₃₀O₂ requires C, 82.6; H, 10.8%. ^c Isolated as its 2,4-dinitrophenylhydrazone, m.p. 217°, identical with the 2,4-dinitrophenylhydrazone of an authentic sample.⁸

residual mixture was separated chromatographically by preparative t.l.c. The results are shown in the Table.

*Irradiation of 4-Hydroxy-3,5-di-*t*-butylbenzyl Alcohol (Xa).*—After a solution of the alcohol (1 g) in benzene (75 ml) had been irradiated for 7 h, it was evaporated and the residue was column chromatographed. Elution with light petroleum (b.p. 60–80°) gave 1,2-bis-(4-hydroxy-3,5-di-*t*-butylphenyl)ethane (0.2 g). Elution with light petroleum

(75 ml) was irradiated for 7 h and then evaporated. The residue was subjected to preparative t.l.c. and gave 4-hydroxy-3,5-di-*t*-butylacetophenone (0.13 g), m.p. 148° (lit.,⁸ 147–148°).

[2/040 Received, 10th January, 1972]

¹² E. Muller, R. Mayer, U. Herlmann, and H. Scheffler, *Annalen*, 1961, **645**, 66.