Synthesis and Decomposition of (Thiocarbamoyl)thiomethylphenols

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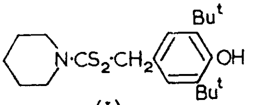
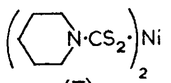
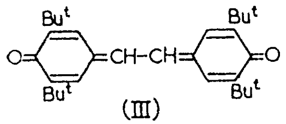
(THIOCARBAMOYL)THIOALKYLPHENOLS (*e.g.*, I) are readily synthesised by a single-stage process[1] related to the Mannich reaction, whereby secondary amines, phenols, paraformaldehyde, and carbon disulphide react in alcoholic solution. 4-Piperidino(thiocarbonyl)thiomethyl-2,6-di-t-butylphenol (I) resulted from interaction of piperidine, 2,6-di-t-butylphenol, paraformaldehyde, and carbon disulphide. Treatment of (I) with aqueous ethanolic nickel acetate lead to disruption of the molecule, and gave rise to nickel piperidinodithiocarbamate (II) in 80% yield, together with small amounts (1—5%) of 3,5,3′,5′-tetra-t-butylstilbene-4,4′-quinone (III), 1,2-bis-(4-hydroxy-3,5-di-t-butylphenyl)ethane (IVa) and 4-hydroxy-3,5-di-t-butylbenzyl alcohol (IVb).



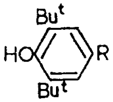
(I)



(II)

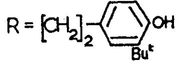


(III)

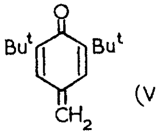


(IV)

(a)



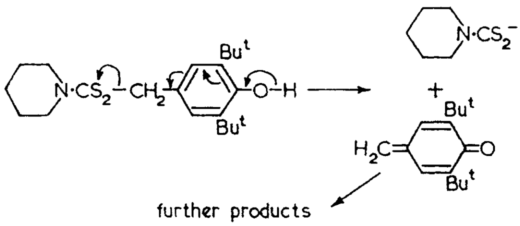
(b) R=CH$_2$·OH
(c) R=CH$_2$·OAc
(d) R=CHO
(e) R=CH$_2$·OMe



(V)

The formation of (III), (IVa), and (IVb) indicates that the reaction involves the unstable quinone methide (V), since disproportionation of the latter has been shown[2] to result in 3,5,3′,5′-tetra-t-butylstilbene-4,4′-quinone (III) and 1,2-bis-(4-hydroxy-3,5-di-t-butylphenyl)ethane (IVa), whilst interaction of the quinone methide with water could lead[3] to the benzyl alcohol (IVb).

The ultimate nature of the breakdown products depends on the reaction conditions. Nickel acetate in acetic acid, for example, afforded 4-hydroxy-3,5-di-t-butylbenzyl acetate (IVc) which presumably arose from attack[3] by acetic acid on the quinone methide. On the other hand, nickel nitrate in aqueous ethanol yielded 4-hydroxy-3,5-di-t-butylbenzaldehyde (IVd), through oxidation of the benzyl alcohol by small amounts of nitric acid present in the reaction mixture. The decomposition reaction is not confined to the action of nickel salts, since replacement of nickel acetate by cobalt acetate in the above reactions lead to essentially similar results. With methanolic sodium hydroxide, the thiocarbamoylthiomethylphenol again yielded the quinone methide which suffered attack by methanol to yield 4-hydroxy-3,5-di-t-butylbenzyl methyl ether[4] (IVe).



The quinone methide is considered to arise from elimination of the dithiocarbamate anion from the (thiocarbamoyl)thiomethylphenol. This elimination would be assisted either by initial complex formation between the (thiocarbamoyl)thiomethylphenol and a transition-metal cation, or by removal of the phenolic proton by base.

Work is in hand on the synthesis and decomposition of other (thiocarbamoyl)thioalkylphenols.

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[1] B.P. 966, 244.

[2] H. v. Euler, E. Adler, J. O. Cedwall, and O. Törngren, *Arkiv Kemi, Min., Geol.*, 1941, **15***A*, 7; H. v. Euler, E. Adler, and A. O. Caspersson, *ibid.*, 1942, **16***A*, 11; H. v. Euler, E. Adler, H. Hasselquist, and M. Lundin, *ibid.*, 1944, **18***A*, 7; L. J. Filar and S. Winstein, *Tetrahedron Letters*, 1960, No. 25, 9.

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

[4] M. S. Kharasch and B. S. Joshi, *J. Org. Chem.*, 1957, **22**, 1435.