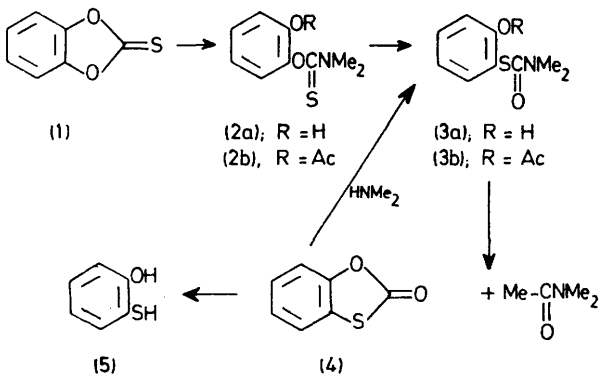
Thionocarbamate–Thiolcarbamate Rearrangement of Catechol Derivatives

By RAYMOND M. DODSON* and JOSEPH B. HANSON
(*Department of Chemistry, University of Minnesota, Minneapolis, Minnesota*, 55455)

Summary An efficient method for the synthesis of 2-mercaptophenol from catechol *via* the thionocarbamate–thiolcarbamate rearrangement is described.

FOR some time we have been studying the chemistry of small, highly reactive molecules[1] such as SO and S_2O formed from elements from the second and third periods of the Periodic Table. During attempts to prepare molecules that extrude CS on heating, we investigated the reactions of 1,3-benzodioxole-2-thione (**1**). Contrary to a previous report[2a] we found that the *O*-2-acetoxyphenyl thiocarbamate (**2b**) readily rearranged to the *S*-2-acetoxyphenyl thiocarbamate (**3b**).

Compound (**1**),[3] prepared in 90% yield from catechol and thiophosgene, was treated with Me_2NH in benzene to give the *O*-2-hydroxyphenyl thiocarbamate (**2a**) [2a], 79%, m.p. 65·5—68 °C, *m/e* 197·0528 (M^+). Acetylation of (**2a**) with acetic anhydride in pyridine–ether produced (**2b**),[2a] 87% m.p. 102—104 °C. Thermolysis (250 °C for 2·5 h) of (**2b**) produced an 8·5 : 8·3 : 1 molar ratio (n.m.r. spectrum) of 1,3-benzoxathiol-2-one (**4**), $MeCONMe_2$, and (**3b**). Pure (**4**)[4], b.p. 69—72 °C (at 0·25 mmHg, m.p. 25·8—27 °C ν_{CO} (neat) 1760vs, br cm^{-1}, *m/e* 151·9933, could be distilled from the reaction mixture in 75% yield. $MeCONMe_2$ was identified by direct comparison (i.r. and n.m.r. spectra) with an authentic sample.



(1) (2a); R = H (2b), R = Ac (3a); R = H (3b); R = Ac (5) (4)

The intermediacy of (**3b**) in the conversion of (**2b**) into (**4**) was established by following the reaction in the temperature range 180—250 °C by n.m.r. spectroscopy. Thus, on heating (**2b**) its n.m.r. spectrum in CS_2 [δ 3·33 and 3·23 (6H

2 × s, NMe_2) and 2·12 (3H, s, COMe)] gradually changed to that of (**3b**) [δ 2·92 (6H, s, NMe_2) and 2·13 3H, s, COMe)] and that, in turn, to the spectrum of $MeCONMe_2$ [δ 2·95 and 2·80 (6H, 2 × s, NMe_2) and 1·92 (3H, s, COMe)]. Compound (**3b**), b.p. 139—141 °C (0·15 mmHg), *m/e* 239·0611 (M^+), was independently synthesised by reaction of (**4**) with Me_2NH to give the *S*-2-hydroxyphenyl thiocarbamate (**3a**) [m.p. 98·5—100 °C, ν_{max} (KBr) 3240m, br (OH) and 1630s cm^{-1} (CO); δ (CS_2) 7·58 (1H, br s, D_2O exchangeable ArO*H*) and 3·08 (6H, br s, NMe_2)] followed by acetylation. The n.m.r. spectrum of (**3b**) was in agreement with that already described. When (**3b**) was heated at 250 °C for 100 min under nitrogen, it was converted into (**4**) and $MeCONMe_2$.

Compound (**4**) was hydrolysed with aqueous NaOH to 2-mercaptophenol (**5**), 88%, which was converted with thiophosgene into the crystalline 1,3-benzoxathiol-2-thione,[4] m.p. 96·5—98 °C. This modification of the thionocarbamate–thiolcarbamate rearrangement[2] may provide a method for converting many physiologically active catechol derivatives into their corresponding mono-mercapto analogues.

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