

Synthesis of 2-Methylbenzo[*b*]furans and 2-Methylbenzo[*b*]thiophens

By WAYNE K. ANDERSON* and EDMOND J. LAVOIE

(Department of Medicinal Chemistry, School of Pharmacy, State University of New York at Buffalo, Buffalo, New York 14214)

Summary 2-Methylbenzo[*b*]furans and 2-methylbenzo[*b*]thiophens were prepared in good yield from the corresponding chloroallyl phenyl ethers and chloroallyl phenyl sulphides, respectively.

ALTHOUGH there are several syntheses of benzofurans¹ and benzothiophens² they are often hampered by low yields or involve starting materials which are not easily accessible. 2,3-Dihydrobenzofurans have been synthesized by the acid-catalysed cyclization of *o*-allylphenols,¹ and a similar approach has yielded 2,3-dihydrobenzothiophens in low yield.³ We report a simple and versatile extension of this approach for the synthesis of benzofurans and benzothiophens, involving the cyclization of *o*-chloroallylphenols or sulphides.

The chloroallyl phenyl ethers (1) and sulphides (2) were readily synthesized in good yield (70–90%) by reaction of the corresponding phenol or benzenethiol with 2,3-dichloropropene in acetone–K₂CO₃ (reflux for *ca.* 15 h).†

The Claisen rearrangement of (1) to (3) proceeded in almost quantitative yield in *NN*-diethylaniline solution heated under reflux for *ca.* 48 h. Cyclization of (3a–c) in conc. HCl at 85° (5–6 h) proceeded in good yield (50–80%) to yield the corresponding 2-methylbenzo[*b*]furans (5a–c). No benzofuran product was obtained from (3e) using this procedure and only a 20% yield of (5e) was obtained upon cyclization of (3e) with trifluoroacetic acid (25° for 24 h).

† Satisfactory elemental analyses and spectroscopic data were obtained for all new compounds reported.

¹ R. C. Elderfield and V. B. Meyer, in 'Heterocyclic Compounds', Vol. 2, ed., R. C. Elderfield, Wiley, New York, 1951, pp. 1–67.

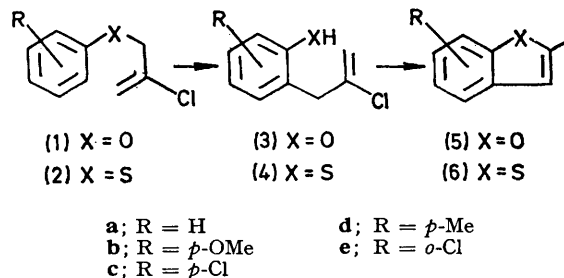
² B. Iddon and R. M. Scrowston, *Adv. Heterocyclic Chem.*, 1970, **11**, 177; H. D. Hartough and S. L. Meisel, 'The Chemistry of Heterocyclic Compounds. Compounds with Condensed Thiophene Rings,' Interscience, New York, 1954; P. M. Chakrabarti, N. B. Chapman, and K. Clarke, *Tetrahedron*, 1969, **25**, 2781; H. Hofmann and G. Salbeck, *Angew. Chem. Internat. Edn.*, 1969, **8**, 456.

³ H. Kwart and E. R. Evans, *J. Org. Chem.*, 1966, **31**, 413.

⁴ C. D. Hurd and C. N. Webb, *J. Amer. Chem. Soc.*, 1936, **58**, 2190.

⁵ H. Kwart and T. George, *Chem. Comm.*, 1970, 433.

The thermal rearrangement of (2) and the subsequent cyclization of (4) to (6) was accomplished in one reaction. Thus a solution of (2) in *NN*-diethylaniline heated at 225° for *ca.* 24 h under nitrogen yielded (6) directly (55–80%).



The formation of (5b) from (3b) was previously noted but only as a minor side product.⁴ Benzo[*b*]thiophens have also been prepared in poor yield by thermal cyclization of phenyl propynyl sulphides.⁵

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