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

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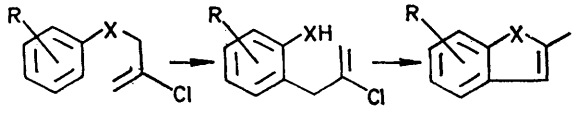
Summary 2-Methylbenzo[*b*]furans and 2-methybenzo[*b*]-thiophens were prepared in good yield from the corresponding chloroallyl phenyl ethers and chloroallyl phenyl sulphides, respectively.

ALTHOUGH there are several syntheses of benzofurans[1] and benzothiophens[2] 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–K_2CO_3 (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).

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%).



(1) X = O (3) X = O (5) X = O
(2) X = S (4) X = S (6) X = S

a; R = H **d**; R = *p*-Me
b; R = *p*-OMe **e**; R = *o*-Cl
c; R = *p*-Cl

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]

We thank the National Cancer Institute of the National Institutes of Health for partial financial support.

(*Received*, 26*th November* 1973; *Com.* 1618.)

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

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