A New Method of Synthesis of Aromatic Dithioesters: Participation of Carbon Disulphide in Friedel–Crafts Reaction

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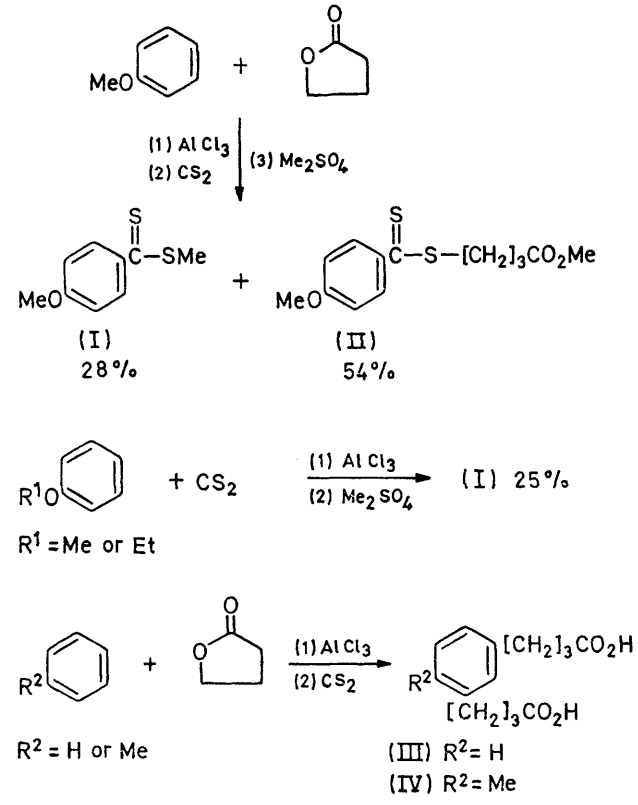
Summary Aralkyl ethers such as anisole reacted with γ-butyrolactone in carbon disulphide under Friedel–Crafts conditions affording the known methyl 4-methoxydithiobenzoate (I), in 28% yield and also the hitherto unknown ω-methoxycarbonylpropyl 4-methoxydithiobenzoate (II) in 54% yield after methylation and esterification of the initial reaction product, while benzene and toluene under similar conditions gave only the normal Friedel–Crafts products.

WITH a view to finding a single-step procedure for the synthesis of 5-methoxy-3-methylindan-1-one, the condensation of anisole with γ-butyrolactone in the presence of anhydrous $AlCl_3$ in CS_2 was carried out. Instead of the expected methoxyindanone, a red acidic product was isolated. This product, on methylation and esterification with dimethyl sulphate followed by chromatography over silica gel, afforded the known methyl 4-methoxydithiobenzoate (I) in 28% yield and ω-methoxycarbonylpropyl 4-methoxydithiobenzoate (II) in 54% yield as red oils. The structures assigned to (I) and (II) are based on chemical and spectroscopic evidence.

(I) and (II) on oxidation with alkaline $KMnO_4$ gave the expected *p*-anisic acid (*ca.* 35% yield) and on desulphurization with Raney nickel gave a cresyl methyl ether (15% yield). An authentic sample of methyl 4-methoxydithiobenzoate prepared according to the procedure of Mayer and his co-workers[1] was found to be identical with that of (I). (II): λ_{max} (ethanol) 246 (ε 7330), 330 (21,750), 496 nm (200) characteristic of an aromatic dithioester;[2] ν_{max} (CCl_4) 1175 ($CSSCH_2$–) 1310 cm^{-1} (S–CH_2–); δ ($CDCl_3$) 1·7—2·5 (m, 4H, αβ-CH_2), 3·3 (m, 2H, γ-CH_2), 3·6 (s, 3H, CO_2Me), 3·8 (s, 3H, OMe), 6·6—6·8 (d, 2H, *J* 9 Hz), and 7·8—8·0 (d, 2H, *J* 9 Hz). The mass spectrum of (II) indicated peaks at *m/e* 284 (M^+) (10%), 184 [*p*-MeO–C_6H_4(SH)S·]$^+$ (10%), and 151 (*p*-MeO–C_6H_4–C=S)$^+$ (100%).

Alkaline hydrolysis of (II) gave the expected ω-carboxypropyl 4-methoxydithiobenzoate in quantitative yield.

Both anisole and phenetole on treatment with anhydrous $AlCl_3$ in CS_2 (without γ-butyrolactone) yielded *p*-hydroxydithiobenzoic acid as the only isolable acidic product which



on treatment with dimethyl sulphate gave (I) in *ca.* 25% yield. These results indicate that dealkylation of aralkyl ethers constituted an important step in these reactions.

Jörg[3] had previously studied the participation of CS_2 in these reactions, but reported the formation of ethyl *p*-hydroxydithiobenzoate as one of the products in an unspecified yield from phenetole and methyl *p*-hydroxydithiobenzoate in 1% yield from anisole.

Condensation of nerolin with γ-butyrolactone under similar conditions furnished ω-methoxycarbonylpropyl 2-methoxy-1-dithionaphthoate in *ca.* 15% yield. The inclusion of γ-butyrolactone in these Friedel–Crafts reactions has resulted in considerable increase in the yield of these sulphur compounds. Substrates such as benzene and toluene under identical conditions gave no products corresponding to aromatic dithioesters but afforded only γ-phenylbutyric acid, (III) and (IV), respectively, in moderate yields.

Satisfactory elemental analyses were obtained for all new compounds.

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[1] R. Mayer, S. Scheithaur, and D. Kunz, *Chem. Ber.*, 1966, **99**, 1393.
[2] S. B. Knight, R. W. Bost, O. L. Shealy, and J. P. Williams, *J. Amer. Chem. Soc.*, **1951**, **73**, 29.
[3] H. Jörg, *Ber.*, **1927**, **60B**, 1466.