2-Trialkylphosphonio-1,3-dithiole-4-carboxylates. Reaction of Acetylene Carboxylic Acids with Trialkylphosphine–Carbon Disulphide Zwitterions

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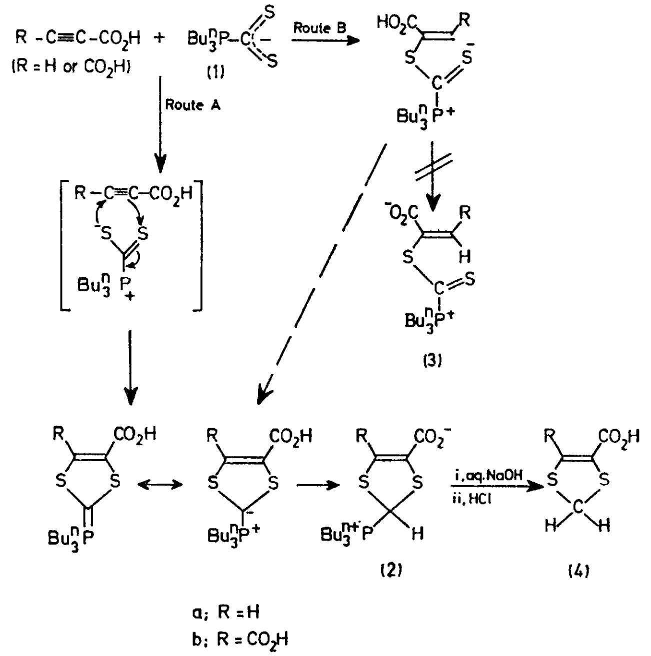
Summary Acetylene carboxylic acids were treated with trialkylphosphine–carbon disulphide zwitterions to produce fair to good yields of 2-trialkylphosphonio-1,3-dithiole-4-carboxylates; the zwitterionic structure of the products was established by i.r. and n.m.r. spectroscopy and from the structure of their hydrolysis products.

ELECTRON deficient or ring-strained acetylenes react with CS_2 to give a variety of complex structures including tetrathiafulvalenes.[1–4] These reactions were recently reviewed.[4]

We now report that propiolic acid and acetylenedicarboxylic acid rapidly react with the $Bu^n{}_3P–CS_2$ complex (**1**) to give the zwitterionic compounds (**2**). These reactions proceeded in tetrahydrofuran at temperatures as low as −20 to −30 °C to give the adducts (**2a**) (53%) and (**2b**) (87%) after recrystallisation from acetone. The formation of (**2**), instead of (**3**), suggests the reaction proceeded *via* route A (concerted one-step addition) rather than route B. A route similar to B had previously been favoured for the reaction of acetylenes with CS_2.[1] The formation of (**2**) also contrasts with the reaction of methyl propiolate with (**1**) which gave 2,6- and 2,7-bis(methoxycarbonyl)-tetrathiafulvalene (21%).[2]

Compounds (**2a**), m.p. 116—118 °C (decomp.), and (**2b**), m.p. 122 °C (decomp.), gave C, H, P, and S analyses within 0·3% of calculated values. Their i.r. spectra exhibited CO bands in the region 1600—1590 and 1350—1340 cm^{-1} ($-CO_2^-$) and no bands due to ester carbonyls. The zwitterionic structure of (**2**) was further confirmed by alkaline (NaOH) hydrolysis of (**2a**) and (**2b**) and acidification to give substituted 1,3-dithioles (**4a**) and (**4b**), respectively. The n.m.r. spectrum of (**2a**) in $(CD_3)_2SO$ consisted of peaks at δ 0·8—1·2 (9H, t, Me), 1·3—1·8 (12H, m, γ- and β-CH_2), 2·1—2·7 (6H, m, α-CH_2), 6·24 (1H, d, CH, exchangeable with CD_3OD, J_{P-CH} 2 Hz), and 6·37 (1H, s, vinyl H). The n.m.r. spectrum of (**2b**) in $(CD_3)_2SO$ also showed a singlet CH peak at δ 5·79, also exchangeable with CD_3OD, in addition to Bu^n peaks.



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