DESULFURISATION OF EPIDITHIA-2,5-PIPERAZINEDIONE DERIVATIVES

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The desulfurisation of 3,6-epidithia-3,6-diethoxycarbonyl-1,4-dimethyl-2,5-piperazinedione(I) with two equivalent of triphenyl phosphine(Ph_3P) in anhyd tetrahydrofuran(THF) removed both sulfur atoms to form a dimeric compound, 1,2,5,6-tetraethoxycarbonyl-3,8,10,12-tetramethyl-3,8,10,12-tetraaza-tricyclo[4.2.2.$2^{2,5}$] dodecane-4,7,9,11-tetraone(II), in 55% yield, and the epimonosulfide was not isolated. However desulfurisation of the corresponding epimonosulfide which was prepared by the other method, gave II in 72% yield under similar reaction conditions. When I was treated with Ph_3P in aqueous THF, II was not isolated but 3,6-diethoxycarbonyl-1,4-dimethyl-3-hydroxy-2,5-piperazinedione was obtained in 52% yield. The desulfurisation of I with Ph_3P in the presence of phenol gave the corresponding 3-phenoxy derivative. The desulfurisation of I with Ph_3P in ethyl vinyl ether gave II and a cycloaddition product, 1,4-diethoxycarbonyl-2,5-dimethyl-7-ethoxy-2,5-diazabicyclo[2.2.2] octane-3,6-dione. These results suggested that II may be derived by the dimerization of the 1,4-dipole formed as an intermediate during the desulfurisation of I. In the presence of benzofuran, indole, and skatole the desulfurisation of I gave two isomeric cycloaddition products, respectively.

As for the desulfurisation of open chain analogs, the reaction of dithiobis(acetamidomalonate) with Ph_3P in THF was carried out and no dimeric product was isolated, but acetamidomalonate(32%) and 5-ethoxy-4-ethoxycarbonyl-2-methyloxazole(28%) were obtained. Under similar conditions dithiobis(phthalimidomalonate) and N,N'-dithiobis(phthalimide) gave only reduced compound as the main product, respectively.