Tetrahedron Letters No. 46, pp 4491 - 4492.
©Pergamon Press Ltd. 1979. Printed in Great Britain.

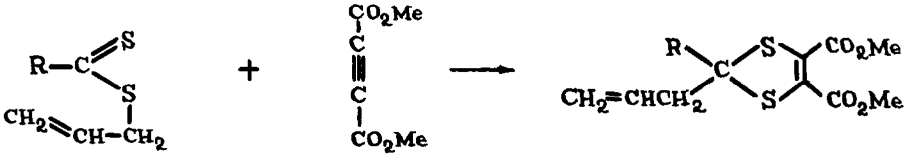
0040-4039/79/1108-4491$02.00/0

CYCLOADDITION ACCOMPANIED BY SIGMATROPIC SHIFT OF DITHIOCARBOXYLIC ESTERS WITH DIMETHYL ACETYLENEDICARBOXYLATE

V.N.Drozd* and O.A.Popova
Department of Organic Chemistry, Timiryazev Agricultural Academy, Moscow, 127550, USSR.

Allyl, propargyl and benzyl dithiocarboxylic esters react with dimethyl acetylenedicarboxylate to form 1,3-dithioles, with migration of the allyl, propargyl or benzyl group.

We have found a new reaction, cycloaddition accompanied by sigmatropic shift, on treatment of dithiocarboxylic esters with dimethyl acetylenedicarboxylate. Thus, the allylic esters of dithioacetic and dithiobenzoic acids react with dimethyl acetylenedicarboxylate to form 2-substituted 2-allyl-4,5-dicarbomethoxy-1,3-dithioles (1a,b)[1], isolated from the reaction mixtures as thick oils by column chromatography on silica gel (benzene eluent) in yields of 59 and 87%, respectively. The reaction goes in the absence of solvents at room temperature over several days.



1 a R=Me
b R=Ph

The migration of the allylic group seems to proceed according to schemes of both [1,2]- and [2,3]-sigmatropic shifts, since under the reaction conditions benzyl dithiobenzoate produces 2-benzyl-, while propargyl dithiobenzoate forms 2-allenyl-2-phenyl-4,5-dicarbomethoxy-1,3-dithioles (1c,d), the yield being 64% in both cases[2].

Probably, the possibility of a preliminary dithio-Cope rearrangement of the original compounds, involving a [3,3]-sigmatropic shift[3], should be taken into account in the reactions of the allyl and propargyl dithiocarboxylates.

The structures of 1,3-dithioles obtained were confirmed by their microanalysis, spectral data and by desulfuration with Raney nickel in methanol.

References and Notes

1. 1a, b.p. 169-170° (1 mm). PMR ($CDCl_3$): δ 1.82 (s, 3H), 3.75 (s, 6H), 2.78 (d, J = 7 Hz, 2H), 5.20 (d, J = 11 Hz, 1H), 5.20 (d, J = 14 Hz, 1H), 5.7-6.1 (m, 1H).

   1b, thick oil. PMR ($CDCl_3$): δ 3.72 (s, 6H), 3.18 (d, J = 7 Hz, 2H), 5.07 (d, J = 11 Hz, 1H), 5.11 (d, J = 14 Hz, 1H), 5.4-5.8 (m, 1H), 7.25-7.4 (m, 3H), 7.5-7.6 (m, 2H). Desulfuration with Raney nickel in methanol gives 1-phenylbutane and dimethylsuccinate.

2. 1c, thick oil. PMR ($CDCl_3$): δ 3.67 (s, 2H), 3.73 (s, 6H), 6.8-7.3 (m, 10H). Desulfuration with Raney nickel produces 1,2-diphenyletane and dimethylsuccinate.

   1d, thick oil. PMR ($CDCl_3$): δ 3.73 (s, 6H), 5.04 (d, J = 6.5 Hz, 2H), 5.80 (t, J = 6.5 Hz, 1H), 7.2-7.4 (m, 3H), 7.6-7.8 (m, 2H).

3. T.Hayashi, Tetrahedron Letters, **1974**, 339; T.Nakai, H.Shiono and M.Okawara, ibid., **1974**, 3625; T.Nakai and A.Ari-Izumi, ibid., **1976**, 2335; J.Meijer, P.Vermeer, H.J.Bos and L.Brandsma, Rec.trav.chim., **92**, 1067 (1973).

(Received in UK 10 September 1979)