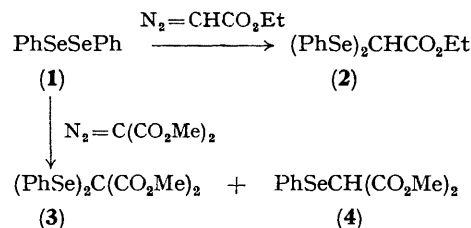


Catalysed Insertion Reactions of Diphenyl Diselenide with Ethyl Diazoacetate and Dimethyl Diazomalonate

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Summary Se-Se Insertion reactions were observed when ethyl diazoacetate and dimethyl diazomalonate were allowed to react with diphenyl diselenide (1) in the presence of catalysts such as copper-bronze or $\text{BF}_3 \cdot \text{Et}_2\text{O}$.

tetrahydrofuran (THF) solution of (1) and EDA in the presence of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ at 70 °C for 2 h (2) was obtained as the sole product in 43% yield.



In spite of extensive recent work on organoselenium chemistry,¹ the insertion reactions of organic diselenides with diazoesters appear not to have been reported.² We describe here the results of the catalysed decomposition of ethyl diazoacetate (EDA) and dimethyl diazomalonate (MDM) in the presence of diphenyl diselenide (1).

The decomposition of EDA with a catalytic amount of copper-bronze in the presence of (1) took place smoothly in xylene at 100 °C and was complete within 5 h. Ethyl bis(phenylseleno)acetate (2) [ν_{max} 1720 cm^{-1} ; ^1H n.m.r. δ 1.13 (t, 3H, CH_2CH_3), 4.06 (q, 2H, CH_2CH_3), 4.77 (1H, s, CH), and 7.17—7.75 (10H, m, ArH)]³ was obtained as the only product in 46% yield.^{3†} Similarly, upon heating a

The copper-bronze catalysed decomposition of MDM in xylene in the presence of (1) at 100 °C led to the slow formation of two products which, after 56 h, were identified as dimethyl bis(phenylseleno)malonate (3) (32% yield), m.p. 93—96 °C [ν_{max} 1720 cm^{-1} ; ^1H n.m.r. δ 3.05 (s, 6H, OCH_3) and 7.08—7.87 (m, 10H, ArH)]⁴ and dimethyl

† N.m.r. spectra were measured at 60 MHz in CHCl_3 vs. Me_4Si as internal reference. I.r. spectra were run in CCl_4 .

phenylselenomalonate (**4**) (12% yield) [ν_{\max} 1730 cm^{-1} ; ^1H n.m.r. δ 3.7 (s, 6H, OCH_3), 4.49 (s, 1H, CH), and 7.1—7.82 (m, 5H, ArH)]. Similar results were obtained when a mixture of MDM and (**1**) was heated at 70 °C in THF for 12 h in the presence of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ as catalyst⁴ to give (**3**) and (**4**) in 41 and 9% yields, respectively.

All the reactions were carried out by adding the diazo ester to the stirred solution of (**1**) at a constant rate, and then heating the mixture until N_2 evolution ceased.

¹ Cf. D. L. Clive, *Tetrahedron*, 1978, **34**, 1049.

² The reaction of diaryl diselenide with methylene formed by the photolysis of diazomethane has been studied by N. Petragnani and G. Schill, *Chem. Ber.*, 1970, **103**, 2271.

³ The formation of (**2**) and (**3**) as the products of the copper-bronze catalysed insertion reaction of EDA and MDM in the Se-Se bond can be explained by the initial formation of the metal carbenoid followed by the nucleophilic attack of diaryl diselenide on the carbenoid carbon atom resulting in the formation of an ylide intermediate which is then transformed into the respective insertion product by 1,2 migration or through homolytic cleavage. An analogous mechanism has been proposed for the insertion reactions of diazoesters with organic disulphides. For leading references see: (a) W. Ando, T. Yagihara, S. Tozune, I. Imai, J. Suzuki, T. Toyama, S. Nakaido, and T. Migita, *J. Org. Chem.*, 1972, **37**, 1721; (b) L. Fields and C. H. Banks, *ibid.*, 1975, **40**, 2774.

⁴ The use of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ as catalyst for insertion of the HCCO_2Et unit between the alkoxy groups and methynyl carbon of ortho-formates (A. Schonberg and K. Praefcke, *Chem. Ber.*, 1966, **99**, 196) and the S-S bond of organic disulphides (see ref. 3b) has been reported.

Varying amounts of (**1**) were recovered in each case, which were readily separated from the products by chromatography on an SiO_2 column using benzene as eluant. Yields obtained refer to isolated, purified material. All new compounds gave satisfactory combustion analytical data.

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