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The Reaction of 3*H*-1,2-Benzodithiole-3-thione with Diphenyldiazomethane[1]

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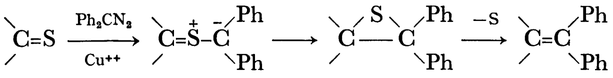
Synopsis. 3*H*-1,2-Benzodithiole-3-thione (^{35}S=C<) reacted with diphenyldiazomethane in the presence of copper(II) acetylacetonate to afford the corresponding 4,5-benzo-3-diphenylmethylene-1,2-dithiole with a predominant extrusion of the exocyclic sulfur atom, while with its selenium analog the exclusive loss of in-ring sulfur was observed, resulting in the formation of the selenium-migrated 4,5-benzo-3-diphenylmethylene-1,2-thiaselenole.

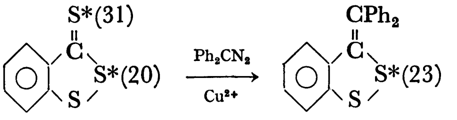
Recently, it has been extensively investigated by Schoenberg[2] and other workers[3–7] that thiocarbonyl compounds react with diphenyldiazomethane to afford, eventually olefinic compounds presumably *via* a transient ylide[8] which would cyclize,[9] and then eliminate sulfur, as is shown below:



Under similar conditions, however, 1,2-dithiole-3-thione' (trithione), bearing a relatively stable thiocarbonyl moiety, has been reported to fail to give the anticipated olefin.[2] In this report, we would like to present the results on one detailed mechanistic examination of the reaction between benzotrithione (I) and diphenyldiazomethane in the presence of a catalytic amount of copper salt. For the sake of comparison, ^{35}S-labeled 3*H*-1,2-benzodithiole-3-thione (^{35}S=C<) (II) and selenium-substituted 4,5-benzo-1,2-dithiole-3-selone (III) were synthesized and treated with diphenyldiazomethane.

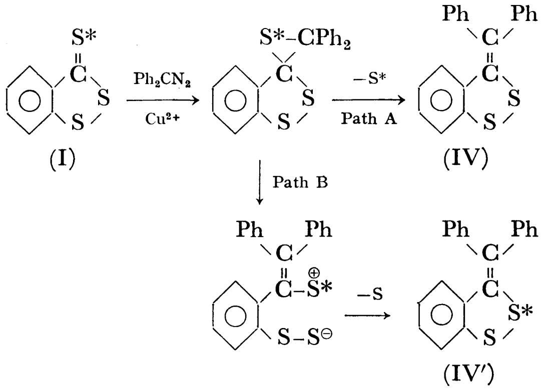
Results and Discussion

When 3*H*-1,2-benzodithiole-3-thione (I) was treated with three equivalents of diphenyldiazomethane in refluxing benzene in the presence of a catalytic amount of copper acetylacetonate, a product (IV) was obtained in a moderate yield. Similarly, the benzotrithione labeled with ^{35}S, both at the thione sulfur and the thiol sulfur by the ratio of 60: 40, was subjected to the same reaction. The ^{35}S-containing values are shown below:



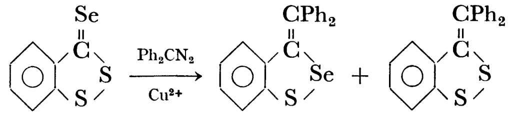
(I) or (II) (IV) (10⁴ cpm/mol)

An inspection of the ^{35}S-labeling experiment suggests that the major part (72.7%) of the reaction apparently proceeds through the incipient formation of the thiirane ring, which is subsequently converted to the corresponding olefin, with the extrusion of the sulfur atom of the three-membered ring itself, as observed in usual cases (as is shown below (Path A)), while the remaining minor portion (27.3%) of the reaction is considered to take an alternative migration, Path B:



Scheme 1.

Meanwhile, sulfur migration proceeding along Path B was observed to take place exclusively when the corresponding selenium-substituted trithione (III) was allowed to react, but at the somewhat lower temperature of 60 °C. The selenium-migrated olefin, *i.e.*, 4,5-benzo-3-diphenylmethylene-1,2-thiaselenole (V), was found to be formed as a sole product in a 43% yield, apparently resulting from the extrusion of thiol sulfur rather than from that of exocyclic selenium. In this case, no formation of the corresponding olefinic sulfur product (IV) is noticiably not even by a careful gas-chromatographic analysis of the reaction mixture.



(III) (V) (IV not detected)

The marked difference in reaction modes between the sulfur (II) and selenium (III) compounds can not be explained with our present knowledge. Several lines of experiments to clarify this point are now under way here.

Experimental

Reaction of I with Diphenyldiazomethane. Treating 0.3 g (1.6 mmol) of I with 1.0 g (5.1 mmol) of diphenyldiazomethane in 30 ml of refluxing benzene containing copper acetylacetonate as the catalyst for 6 hr afforded a viscous liquid, which was then subjected to column chromatography through silica gel, using *n*-hexane as the solvent. The major, orange-colored portion (IV) eluted second was collected and recrystallized from *n*-hexane. The yield was 0.2 g (40%); mp 162—163 °C; IR (KBr) 1610, 1585, 1500, 1450, 1170, 970, 750, 700 cm^{-1}; UV λ_{max} (CHCl$_3$) 385 nm (ε: 7300). Found: C, 75.11; H, 4.39%. Calcd for $C_{20}H_{14}S_2$: C, 75.48; H, 4.43%. Mass spectrum *m/e*: 318 (M^{+}), 286 ($M^{+}-S$), 257 (metastable).

Reaction of III with Diphenyldiazomethane. A mixture of 0.2 g (0.7 mmol) of III, 0.3 g (1.5 mmol) of diphenyldiazomethane, and a small amount of the catalyst was treated at 60 °C for 3 hr. A procedure similar to that employed above gave 0.1 g of V; mp 175—176 °C. IR (KBr) 1580, 1490, 1060, 750, 695 cm^{-1}; UV λ_{max} (CHCl$_3$) 391 nm (ε: 6400). Found: C, 65.29; H, 3.75%. Calcd for $C_{20}H_{14}SSe$: C, 65.74; H, 3.86%. Mass spectrum *m/e*: 366 (M^{+}), 286 ($M^{+}-Se$), 223.5 (metastable).

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