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NEW REACTIONS OF SULPHUR DICHLORIDE WITH OLEFINES

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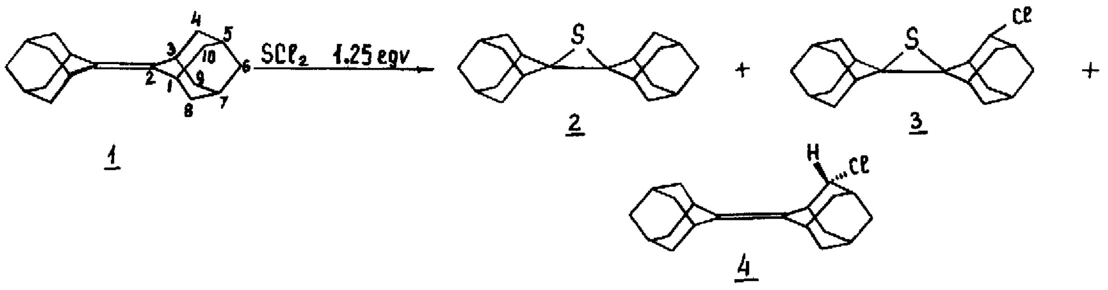
Summary. The interaction between SCl_2 and adamantylideneadamantane produces epithiocompounds 2 and 3 or polychloroadamantylideneadamantanes 4-7 depending upon conditions. The structure of 3 was determined by X-ray analysis.

We wish to report here a new reaction between sulphur dichloride and sterically hindered olefines, leading to epithiocompounds. Thus, the reaction of SCl_2 with adamantylideneadamantane (1) in chloroformal solution (100-fold excess of the solvent) with molar ratio of 1 to SCl_2 1:1.25 by addition of SCl_2 within 5 min at room temperature led to thiiran 2 in yield of 80%, m.p. 131-132° (EtOH); m/e 300 (M^+); δ ($CDCl_3$) 1.92 (28H, CH,CH_2). In CH_2Cl_2 as a solvent the reaction between SCl_2 and 1, the time of adding of SCl_2 being 80 min at 0°, gave quantitatively 4e-chloro-2,2'-epithio-2-(2'-adamantyl)adamantane 3, m.p. 149-151° (EtOH); m/e 334 (M^+); δ ($CDCl_3$) 1.92 (26H, CH,CH_2), 4.57 (1H, CHCl). The latter was obtained also as the main product (76% yield) together with 2 in $CHCl_3$, containing traces of acid after drying upon P_2O_5.



The position of epithiocycle between two adamantyl nuclei, the endo-position of chlorine atom regarding to the atom of sulphur and its e-configuration with respect to the 2,4-substituted cyclohexane ring follow from the X-ray analysis data.

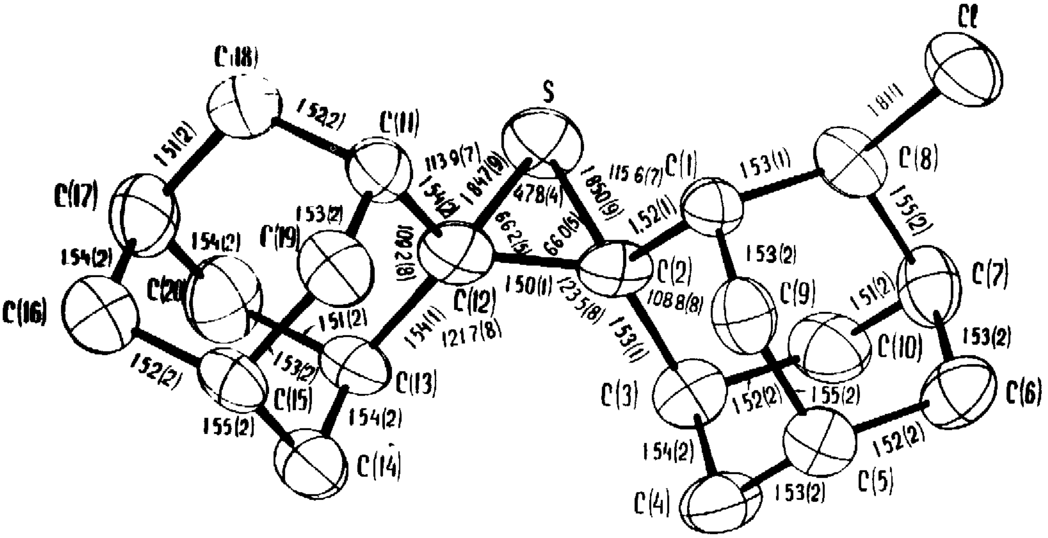


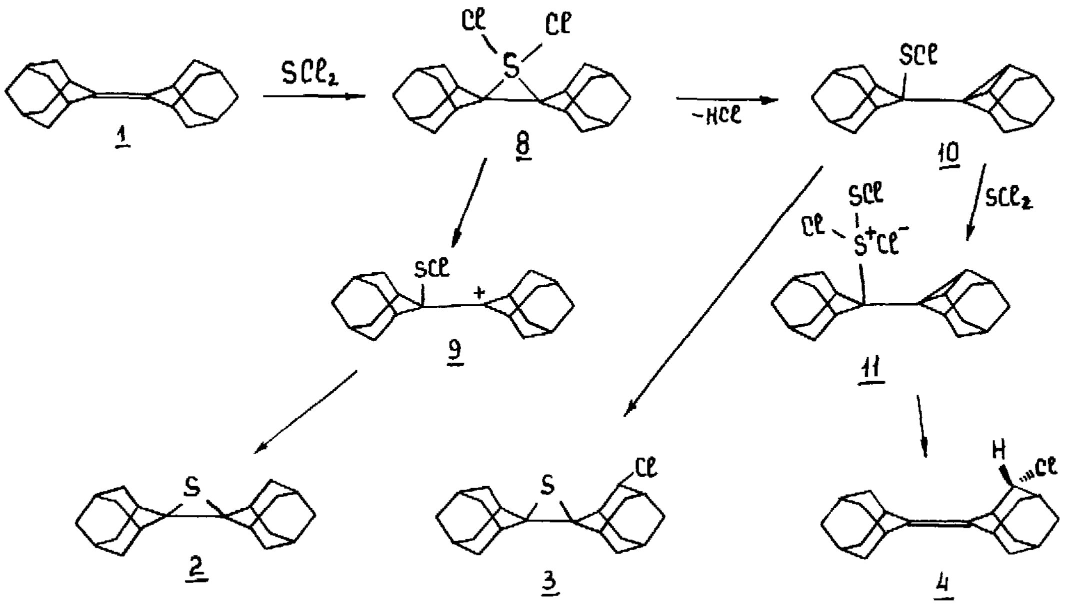
Figure. Bond lengths and some bond angles for 3.

Crystals are monoclinic: at 20° a=18.524(3), b=7.1455(7), c=12.875(2)Å, β=100.49(1)°, V=1675.7(7)Å^3, z=4, d_{calc}=1.33 g/cm^3, space group P 2_1/c. The structure was solved by the direct method and refined by anisotropic (isotropic for H-atom) least squares procedure, R=0.0804.

The molecular structure of 3 with bond lengths and selected bond angles is shown in the Figure. Bond lengths and angles are unexceptional. The length of the thiiran C-C bond of 1.50(1)Å is in a good agreement with the values found earlier in thiiran derivatives (these values fall in the interval 1.468-1.550 Å)[1], and also with the C-C bond length of 1.492 Å obtained in the ab initio calculation of the thiiran molecule[2].

We suggest that the formation of compounds 2 and 3 occurs via mechanism, involving intermediacy of sulphurane 8, followed by loss of Cl$^-$ or HCl depending upon conditions. The cation 9 obtained transformes into thiolate, intramolecular cyclization of which leads to compound 2. The intermediate 10 undergoes itself intramolecular addition to yield 3, but with excess of SCl_2 it gives rise to sulphonic salt 11, which decomposes to give chloride 4.

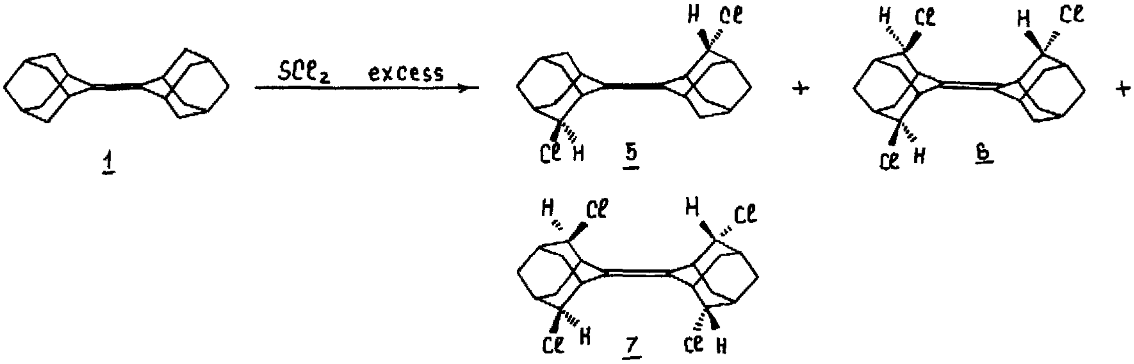
The 10 ⟶ 4 transformation is analogous to the one described for 4, which was obtained by reaction of 1 with 2 eqv. of $PhSCl$[3]. We include sulphurane 8 as an intermediate instead of thiiranium salt on the ground of recent works by Zefirov, Smit, Bodrikov and Krimer[4].



The opening of thiiran ring in compounds 2 and 3 with nucleophilic or electrophilic reagents resulted only in products of desulphurization. Thus, the treatment of thiiranechloride 3 by $LiAlH_4$ in ether gave chloride 4. The latter was obtained also by reaction of 3 with excess of hydrogen chloride in ether at -20°. The desulphurization of both thiiran 2 and thiiranechloride 3 was achieved by action of excess of CH_3J (16 hr, 20°) resulting in the formation of compounds 1 or 4, respectively.

The treatment of compound 1 with excess of SCl_2 led to its chlorination. Even under equimolar conditions about 50% of chloride 4 was formed together with compound 3 as a consequence of temporary excess of SCl_2 in reaction medium when SCl_2 was added to 1 within a few minutes. The increase of percentage of SCl_2 resulted in accumulation of chlorides 5-7 in a ratio, dependent on the excess of SCl_2. The maximum content of dichloride 5 in the mixture (56% yield) being up to 80% was reached by using 5-fold excess of SCl_2 added for 1.3 hr at 0°; the same percentage of trichloride 6 was obtained when molar ratio of 1 to SCl_2 was 1:7. Chromatographic fractionation of the mixture of 5 and 6 (SiO_2, hexane) gave 4e,4'e-dichloroadamantylideneadamantane 5, m.p. 123-125°; m/e 336 (M^+); δ ($CDCl_3$) 4.16 (2H, CHCl), 2.86 (2H, $CH_2C\underline{H}C{=}C$), 2.96 (2H, $CHClC\underline{H}C{=}C$) and 4e,4'e,8a-trichloroadamantylideneadamantane 6, m.p. 132-134°; m/e 371 (M^+); δ ($CDCl_3$) 4.15 (2H, CHCl), 4.02 (1H, CHCl), 2.86 (1H, $CH_2C\underline{H}C{=}C$), 2.96 (3H, CHClC$\underline{H}$C=C). The mixtures of chlorides 5 and 6 were obtained also in reactions of compounds 2-4 with excess of SCl_2.

When compound 1 was treated with 15 moles of SCl_2 for 48 hr at 20°, 4e,4'e,8a,8'a-tetrachloroadamantylideneadamantane 7 was obtained in quantitative yield,[5] m.p. 198-202° (EtOH); m/e 404 (M^+); δ ($CDCl_3$) 4.06 (2H, CHCl), 3.96 (2H, CHCl), 2.96 (4H, CHClC$\underline{H}$C=C).



The polychlorination of 1 by means of excess of SCl_2 proceeds presumably via stages of subsequent addition of SCl_2 to double bonds of mono-, di- and trichlorides obtained with further transformations such as were shown above for 4.

REFERENCES AND NOTES

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5. The satisfactory data from elemental analysis have been obtained for all the compounds involved.

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