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CYCLOADDITION REACTION OF HEXAFLUOROTHIOACETONE DIMER IN THE PRESENCE OF FLUORIDE ION

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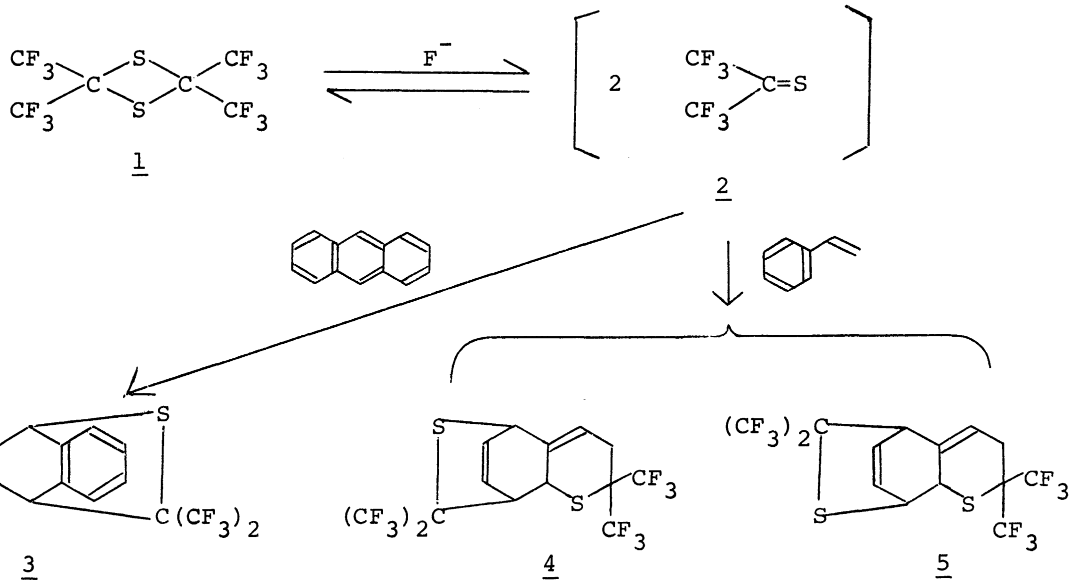
2,2,4,4-Tetrakis(trifluoromethyl)-1,3-dithietane [1] in KF/DMF system reacted with dienes such as anthracene and styrene, and with monoenes such as cyclohexene and dimethyl maleate, to give corresponding cycloadducts of these alkenes with hexafluorothioacetone [2].

Hexafluorothioacetone [2] is known as an unstable and reactive gas which gives cycloadducts with dienes by the Diels-Alder reaction1) and with certain electron-rich olefins.2)

On the other hand, the dimer of hexafluorothioacetone, 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietane [1], is known as a stable liquid, and we have found that the dimer reacts in KF/DMF system with alcohols, giving alkoxymercaptan compounds.3) In the course of this reaction the dimer seemed to release the reactive monomer 2 by the action of unsolvated powerful fluoride ion in the aprotic polar solvent.

For the purpose of obtaining an evidence for this hypothesis, we carried out the reaction of the dimer with dienes in KF/DMF system. As dienes, we chose anthracene and styrene, as these compounds were already used by Middleton1) to get cycloadducts with the monomer 2. In both cases we have obtained the corresponding cycloadducts which are similar to those obtained by above author.

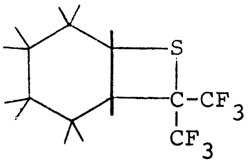


A mixture of 1 (7.3 g, 0.02 mol), anthracene (7.2 g, 0.04 mol), potassium fluoride (2.4 g) and dimethylformamide (30 ml) was stirred at room temperature for 24 hours, and the whole was poured into water. The precipitates (11.8 g, mp 118-119°C) were collected and recrystallized from n-hexane, giving 3, mp 121-122°C (lit.[1)]: mp 123-124°C). Found : F,31.5%. Calcd for $C_{17}H_{10}F_6S$: F,31.6%.

When styrene was used as diene, a mixture of two isomeric cycloadducts [4 + 5], bp 125-127°C/3 mmHg (lit.[1)]: bp 103-104°C/1.2 mmHg) was obtained as reported.[1)]

Furthermore, we examined the similar reactions with cyclohexene and dimethyl maleate as monoenes. The cycloadducts 6 (27%, bp 79-81°C/22 mmHg. F,43.4%. Calcd for $C_9H_{10}F_6S$: F,43.1%.) and 7 (53%, bp 145-148°C/22 mmHg. F,35.4%. Calcd for $C_9H_8F_6O_4S$: F,35.0%) were obtained respectively.

The structures of these products were determined by ir and nmr spectra. The ir spectra of these compounds contained neither SH nor C=C band. The ^{19}F nmr showed only one singlet for each compound, i.e., at -11.6 (δ ppm from ext. CF_3CO_2H in CCl_4) for 6 and -7.12 for 7. In the proton nmr for 6, five multiplets at τ 4.12, 4.42, 6.42, 8.00 and 8.16 (1:1:2:2:4), which should be due to ten hydrogens in cyclohexane ring. For 7, there were three singlets at 6.13, 6.18 and 6.28 (1:6:1), and these should be due to two ring-hydrogens and two methyl groups. It was interesting to have found that dimethyl maleate also gave the cycloadduct, because only electron-rich olefins are reported[2)] to undergo cycloaddition with 2.



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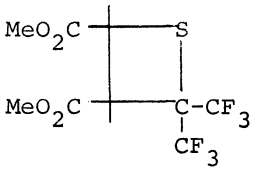

7

The results mentioned above and the fact that no reaction occurred in the absence of potassium fluoride in those reactions have revealed that the dimer 1 was depolymerized to monomer by the action of fluoride ion.

In the synthetic meaning, the dimer is more useful starting material than the monomer itself for the preparation of the cycloadducts and other compounds which are obtainable from hexafluorothioacetone.

References

1) W. J. Middleton, J. Org. Chem., 30, 1390(1965).
2) W. J. Middleton, Ibid., 30, 1395(1965).
3) N. Ishikawa and T. Kitazume, Chem. Lett., 1972, 947.

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