Tetrahedron Letters, Vol.22, No.37, pp 3659 - 3662, 1981
Printed in Great Britain

0040-4039/81/373659-04$02.00/0

AN UNUSUAL REACTION OF TRIPHENYLMETHYLSULFENYL CHLORIDE WITH NORBORNENE AND NORBORNADIENE

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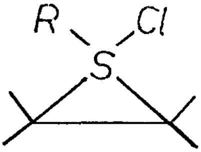
Summary: Triphenylmethylsulfenyl chloride reacts with norbornene and norbornadiene to yield chlorodisulfides instead of the expected products - chlorosulfides.

The reaction of sulfenyl halides with alkenes is generally considered to follow an Ad_E2 mechanism [1]. The formation of the bridged species such as: ∂-sulfuranse 1, ion pairs 2-3 or episulfonium ion 4, depending on the reaction condition is belived to be rate determining [2], these species subsequently undergo nucleophilic attack by the halide ion in a fast, product determining step.



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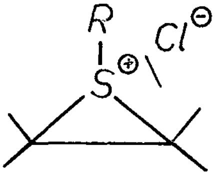

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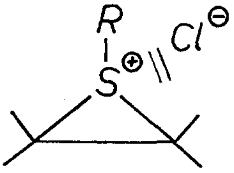

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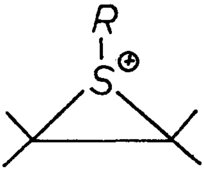

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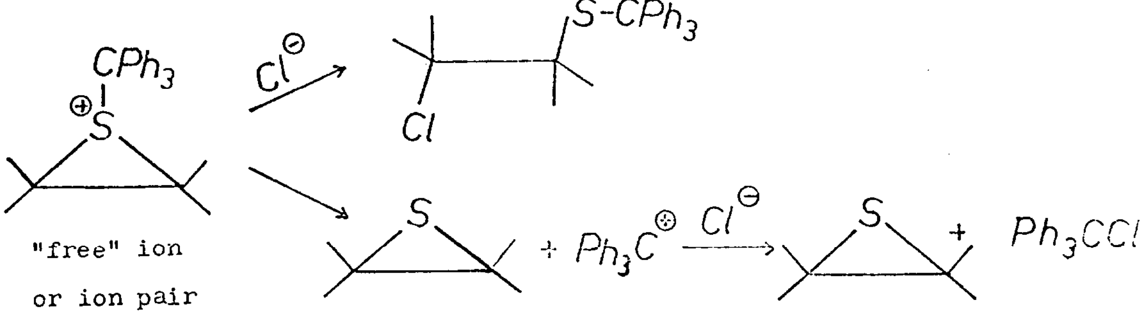
For the reaction of triphenylmethylsulfenyl chloride (Ph_3CSCl, 5) with alkenes the more complex mechanistic pathway might be expected. The fast abstraction of triphenylcarbenium ion from the ionic intermediates 2-4 seems to be possible [3], apart from the normal reaction (Scheme 1).

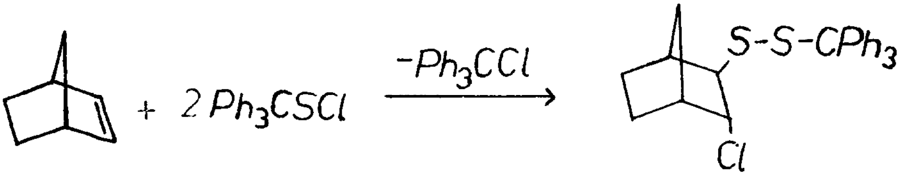
With the view of testing such scenario we have investigated the reaction of 5[4] with a series of cycloolefins (cyclohexene, cycloheptene, norbornene and norbornadiene). The reaction was carried out at ambient temperature and was monitored by the disappearance of yellow colouration of 5 and by ^{1}H-NMR.

Scheme 1



Both norbornene and norbornadiene reacts with 5 within 2-4 hrs, while the other olefins remain unaffected even in a few days.

We have found that norbornene reacts with 2 equivalents of Ph$_3$VSCl (even if equimolar amounts of reagents were used) to yield 6 (82%) apart from trityl chloride [5]. Neither "normal" addition product, not norbornene episulfide was detected in the reaction mixture.



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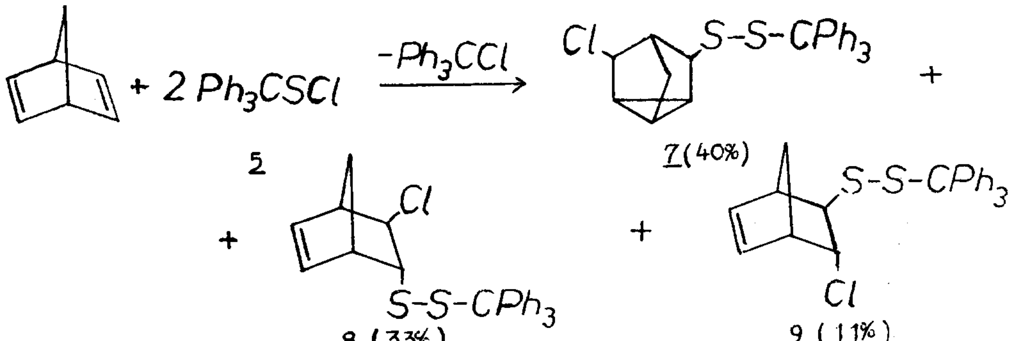
Similarly, norbornadiene after the reaction with 2 equivalents of 5 gives a mixture of isomeric chlorosulfides 7-9 apart from some amounts of unidentified products.



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7 (40%)

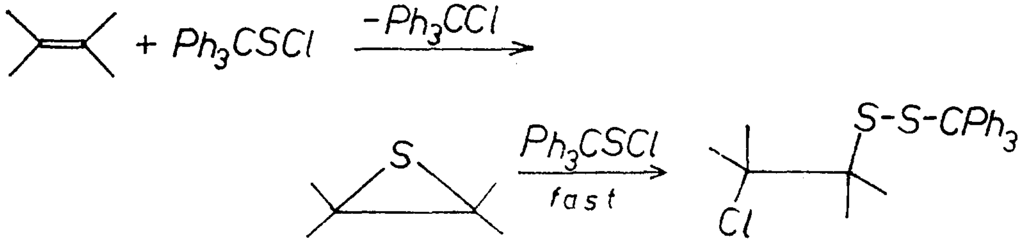
8 (33%)

9 (11%)

According to our knowledge, they are the first examples of the formation of chlorodisulfides as a result of the reaction of alkylsulfenyl chloride with alkene, while the formation of such compounds from acylsulfenyl chlorides has been observed in some cases [6].

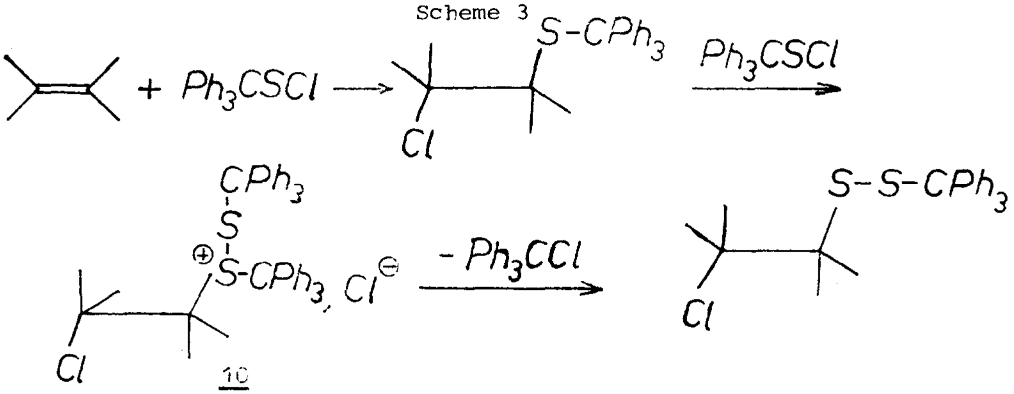
Assuming that thiirane is really formed in the first step of the reaction, one may rationalize the experimental data by subsequent fast addition of the second molecule of Ph_3CSCl Scheme 2.

Scheme 2



Another reasonable pathway explaining the formation of disulfides is presented in scheme 3. After the "normal" addition resulting β-chlorosulfide undergoes fast S-alkylthiolation [7], accompanied by the abstraction of triphenylcarbenium ion from the ionic intermediate 10.

Scheme 3



We have found that under the mentioned conditions thiiranes react rapidly with Ph_3CSCl to give chlorodisulfides, while alkyltriphenylmethylsulfides (e.g. Et S CPh_3) are almost completely unreactive [8]. In the light of these facts the latter mechanism seems highly unlikely.

Acknowledgement.

We thank Professor Z Kotkowska-Machnik for her interest in this work and helpful discussions.

References and Notes

1. a) G. H. Schmid and D. G. Garratt, "The Chemistry of Double-Bonded Functional Groups", edited by S. Patai, Wiley, N.Y. 1977, chapter 9.

   b) L. P. Rasteikene, D. I. Greitchute, M. G. Lin'kova and I. L. Knunyants, Uspekchi Khimii, 46, 1041 (1977).

2. a) W. A. Smit, N. S. Zefirov, I. V. Bodrikov and M. Z. Krimer, Acc. Chem. Res., 12, 282 (1979) and references cited therein.

   b) I. V. Bodrikov, A. V. Borisov, L. V. Chumakov, N. S. Zefirov and W. A. Smith, Tetrahedron Lett., 21, 115 (1980).

3. We prefer ionic intermediates to δ-sulfurane as the formation of the latter appears to be severely hindered by bulky triphenylmethyl group.

4. Prepared from Ph_3CSH (Aldrich) by chlorination with SO_2Cl_2. D. Vorlander and B. Mittag, Ber., 52, 413 (1919).

5. The reaction mixtures were analyzed by ^{1}H-NMR. Preparative TLC (Al_2O_3/hexane) was used for separation of the components, but with considerable lack of yield. Triphenylmethyl chloride hydrolyses rapidly under these conditions and has been isolated as triphenylcarbinol. All new compounds gave satisfactory IR, ^{1}H-NMR as well as elemental analyses data.

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8. J. M. Majewski and J. Zakrzewski, unpublished results.

(Received in UK 29 June 1981)