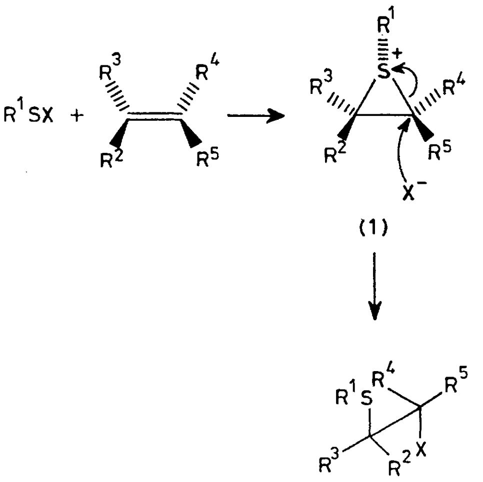
Preparation of Some *S*-Methyl Thiiranium Salts of Adamantylideneadamantane. Demethylation and Desulphurization with Nucleophiles

By John Bolster and Richard M. Kellogg*

(*Department of Organic Chemistry, University of Groningen, Nijenborgh, 9747 AG Groningen, The Netherlands*)

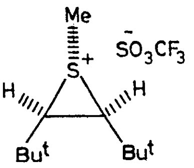
Summary *S*-Methylthiiranium salts derived from adamantylideneadamantane have been synthesized and their chemistry has been investigated; the first examples of dealkylation with preservation of the three-membered ring have been discovered.

Thiiranium salts (**1**) are commonly assumed to be intermediates in the additions of alkane- or arylarene-sulphenyl halides to alkenes; subsequent opening by halide ion in a *trans*-fashion gives the addition product [equation (1)].[1] In certain cases the salts (**1**) can be isolated if X^- can be made non-nucleophilic. Various synthetic methods to accomplish this end are known.[2,3] Some time ago we prepared (**2**),[3b] which on being treated with nucleophiles underwent ring-opening, despite the fact that the nucleophile must attack a neopentyl carbon. It was also surprising that no evidence was forthcoming for initial and reversible attack at sulphur to provide the sulphuran (**3**), in view of the fact that good precedent for this had been provided by Helmkamp,[4] who found ^1H n.m.r. evidence for the formation of (**4**) as a stable intermediate. In this regard arguments have been offered recently that a sulphuran structure may be a more correct representation of the intermediate formed in reaction (1).[4]

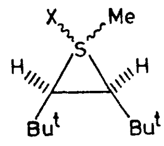


(1)

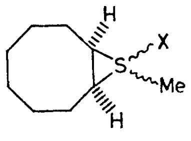
(1)



(2)

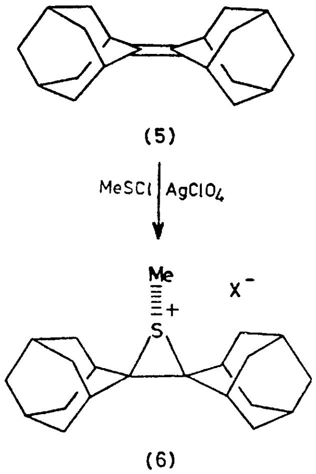


(3)



(4)

We now have prepared and examined the chemistry of thiiranium salts even more hindered at the ring carbon atoms than (**2**). Adamantylideneadamantane (**5**) in



(2)

(6)

a; $X^- = ClO_4^-$

b; $X^- = Br_3^-$

c; $X^- = Cl^- + Cl_3^-$

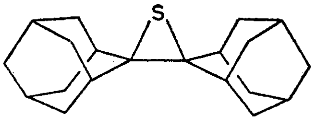
CH_2Cl_2–MeCN reacted with MeSCl (1 equiv.) and $AgClO_4$ (1 equiv.) to give (**6a**) as a soluble and stable salt†(reaction 2). In CCl_4 as solvent (**5**) reacts with an excess of MeSBr leading to the immediate precipitation of the orange (**6b**), stable as a solid; dimethyl disulphide presumably is also formed. In CCl_4 the reaction of methanesulphenyl chloride and (**5**) gives (**6c**) as a white precipitate the structure of which was established by the similarity of its i.r. and n.m.r. spectra to the spectra of (**6a**) and (**6b**); analytical results indicate that the counteranion is a mixture of Cl^- and Cl_3^-, the ratio of which depends on the amount of methanesulphenyl chloride used.†

TABLE. Reactions of (**6a**) with various nucleophiles in $CDCl_3$ at 35 °C.

Nucleophile	Product (% yield)
F^- [a]	(**5**) (100%) + decomposition product probably from MeSF
Cl^- [b]	(**5**) (37%) + (**7**) (63%) + MeCl (±60%)
Br^- [c]	(**5**) (18%) + (**7**) (82%) + MeBr (±80%)
I^- [d]	(**5**) (100%) + MeSSMe (±100%) + I_2 [e]
N_3^- [f]	(**5**) (100%) + MeSSMe (±100%) + N_2 [e]
MeLi	(**5**) (100%) — MeSMe [e]
MeS^- [g]	(**5**) (100%) + MeSSMe (±100%)

[a] Added as KF + catalytic amount of 18-crown-6. [b] Added as $Ph_3P^+CH_2PhCl^-$; yields determined by h.p.l.c. [c] Added as $Ph_3P^+MeBr^-$. Yields determined by h.p.l.c. [d] Added as KI; yields determined by ^1H n.m.r. spectroscopy. [e] Yield not determined. [f] Added as NaN_3 + catalytic amount of 18-crown-6. [g] Added as NaSMe + catalytic amount of 18-crown-6.

The results of the reactions of the salt (**6a**) with various nucleophiles are given in the Table. Desulphurization leading to adamantylideneadamantane (**5**) is the exclusive reaction except for reactions with chloride and bromide, which are capable of demethylating (**6a**) to give the thiiran (**7**). No evidence for a sulphurane‡ or for 1,2-addition products of the sulphenyl halides to (**5**) was obtained.



(7)

The course of the reaction, illustrated for the case of Br^-, is as shown in reaction (3). On following the reaction at 35 °C by ^1H n.m.r. spectroscopy in $CDCl_3$, it was seen that dimethyl disulphide (**8**) and (**5**) are formed within a few minutes. After 10 min the amount of (**8**) did not increase further and the absorptions for MeBr and (**7**) began to grow at the cost of (**8**). After about 4 h the reaction had ceased; very little (**8**) remained. In support of the posulated equilibrium between (**5**) and (**6**) it was found that addition of cyclohexene, which traps methanesulphenyl bromide,[4] leads to nearly quantitative production of (**5**) and formation of *trans*-1-bromo-2-methylthiocyclohexane. On dissolving the solids (**6c**) in $CDCl_3$ at 35 °C the same course of reaction is seen as starting from (**6a**) with added halide. The reactions of compound (**6b**) could not be investigated owing to its insolubility; it dissolves only in pure Br_2.

$$\begin{tikzcd}
(6a) + Br^- \arrow[r, shift left] \arrow[d, "Br^-"] & (5) + MeSBr \arrow[l, shift left] \arrow[d, shift left, "Br^-"] & (3) \\
(7) + MeBr & \underset{(8)}{0{\cdot}5\,MeSSMe} + Br_3^- \arrow[u, shift left] &
\end{tikzcd}$$

On the basis of these and other results[1–3] it is clear that thiiranium salts can undergo, depending on structure and conditions, three principal reactions: (a) ring-opening with a nucleophile either by S_N2 substitution or $E2$ elimination providing the latter reaction is structurally possible and that the nucleophile is sufficiently basic, (b) attack at sulphonium sulphur leading to ultimate desulphurization with retention of configuration of the alkene. For the case of chloride and bromide as nucleophile this reaction is reversible. A sulphuran seems to be a reasonable intermediate for this reaction although its concentration need not be sufficient to be detectable, and (c) dealkylation to afford thiiran and alkylated nucleophile. In non-hindered thiiranium salts reactions (a) and (b) normally compete. Steric factors affect markedly the rates of these processes. Excessive steric hindrance stops reaction (a) whereas reaction (b) appears to be suppressed in (**2**) owing to the necessity to attack *syn* to the t-butyl groups. To the best of our knowledge the present work provides the first example of reaction (c), which one would normally expect to be a much higher energy pathway. Note, however, that with chloride and bromide (*reversible*) desulphurization is in fact much faster than demethylation (reaction 3).

(*Received*, 20*th April* 1978; *Com.* 416.)

---

† Unless otherwise mentioned correct elemental analyses were obtained for all new compounds; spectral data were in accord with the postulated structures. Salt (**6a**), m.p. 199—203 °C (decomp.), has ^1H n.m.r. ($CDCl_3$) δ 2·51 (3H, s, Me) and δ 1·5—2·5 (28H, m, ring-H); ^{13}C n.m.r. (CH_2Cl_2, δ relative to Me_4Si) 11·1 (1C, q, J_{CH} 147 Hz), 26·1 (4C, d, J_{CH} 135 Hz), 29·3 (2C, d, J_{CH} 145 Hz), 33·1 (2C, d, J_{CH} 135 Hz), 35·7 (2C, t, J_{CH} 130 Hz), 36·2 (2C, t, J_{CH} 130 Hz), 37·5 (2C, t, J_{CH} 130 Hz), 37·8 (2C, t, J_{CH} 130 Hz), 38·2 (2C, t, J_{CH} 130 Hz), and 92·3 p.p.m. (2C, s). The symmetry is consistent with a pyramidal sulphur atom (the peak at δ 26·1 arises from coincidental overlap of two absorptions). Compound (**6b**), m.p. 173 °C (decomp.), has ^1H n.m.r. (pure Br_2) δ 2·40 (3H, s) and 1·50—2·40 (28H, m, ring H).

‡ Helmkamp[4] indicates that the methyl absorption in the ^1H n.m.r. spectrum for a sulphuran (**4**) should be about 128 Hz downfield from Me_4Si. The adamantyl skeleton has an absorption in this region; we estimate, however, that if >10% of a sulphuran had been formed we would have been able to see its absorption. Smaller amounts would go undetected.

[1] N. Kharasch in 'Organic Sulfur Compounds,' vol. I, ed. N. Kharasch, Pergamon Press, New York, 1961, p. 382; L. Rasteikiene, D. Greiciute, M. G. Linkova, and I. L. Knunyants, *Russ. Chem. Rev.*, 1977, **46**, 548; P. Sammes, *Chem. Rev.*, 1976, **76**, 117.

[2] G. Capozzi, O. De Lucchi, V. Luccini, and G. Modena, *Tetrahedron Letters*, 1975, 2603.

[3] (a) D. J. Pettitt and G. K. Helmkamp, *J. Org. Chem.*, 1963, **28**, 2932; 1964, **29**, 2702; (b) P. Raynolds, S. Zonnebelt, S. Bakker, and R. M. Kellogg, *J. Amer. Chem. Soc.*, 1974, **96**, 3146.

[4] (a) S. C. Owsley, G. K. Helmkamp, and S. N. Spurlock, *J. Amer. Chem. Soc.*, 1969, **91**, 3605; (b) D. C. Owsley, G. K. Helmkamp, and M. F. Rettig, *ibid.*, p. 5239.

[5] W. A. Smit, A. S. Gybin, V. S. Bogdanov, M. Z. Krimer, and E. A. Vorobieva, *Tetrahedron Letters*, 1978, 1085.

[6] J. Strating, J. H. Wieringa, and H. Wynberg, *Chem. Comm.*, 1969, 907.