Tetrahedron Letters No. 11, pp 911 - 912, 1977. Pergamon Press. Printed in Great Britain.

SYNTHESIS AND ISOLATION OF STABLE THIIRENIUM SALTS

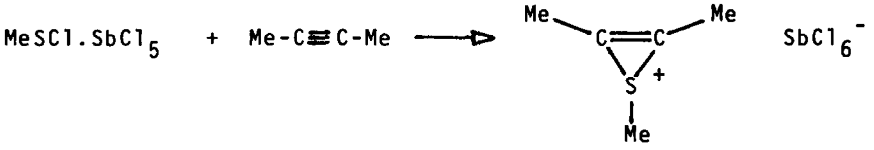
G. Capozzi, V. Lucchini, G. Modena, and P. Scrimin

Centro Meccanismi di Reazioni Organiche del C.N.R.,
Istituto di Chimica Organica, Università di Padova, 35100 Padova, Italy

(Received in UK 24 January 1977; accepted for publication 4 February 1977)

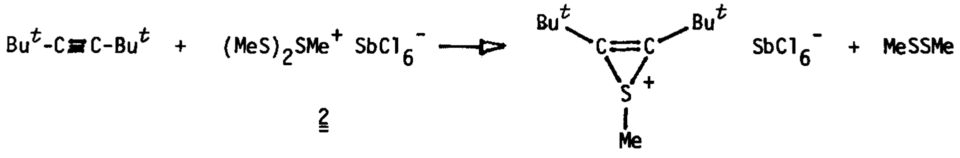
THE recently reported observation[1] that trimethylthiirenium 1a and 1-methyl-2,3-diethylthiirenium 1b hexachloroantimonates are stable for long times at low temperature in liquid sulphur dioxide, let us hope that salts of this new heterocycle might be isolated in the solid state and that an appropriate choice of the alkyl residues may improve their stability. Both expectations have been fulfilled.

Addition of dimethylacetylene to a solution of methanesulphenyl chloride and antimony pentachloride[2] in dichloromethane frozen at -120°, followed by slow warming up to -80°, causes the precipitation of trimethylthiirenium hexachloroantimonate 1a as a white solid (equation 1). The salt was washed with cold (-80°) dichloromethane and dried under vacuum. The ^1H nmr spectrum of 1a in sulphur dioxide at -60° shows singlet signals at δ 2.51 and 2.77 with intensity ratio 1:2. Chemical shifts and intensity ratio are identical with those previously reported for 1a when prepared *in situ* by reaction of dimethylacetylene with methyl(bismethylthio)sulphonium hexachloroantimonate 2 in sulphur dioxide solution at -60°. Trimethylthiirenium hexachloroantimonate 1a decomposes in the solid state above -40° and is very sensitive to moisture.



1a (1)

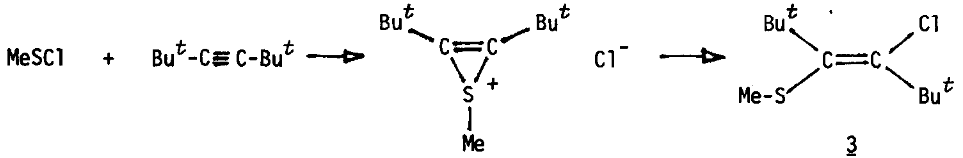
1-Methyl-2,3-di-*t*-butylthiirenium salts 1c proved to be much more stable. The hexachloroantimonate salt of 1c was obtained in form of white crystals stable at room temperature from di-*t*-butylacetylene and 2 in dichloromethane at 0° (equation 2). Addition of pentane to the solution causes the precipitation of the salt which was recrystallized from dichloromethane-pentane (yield 85 %; m.p. 151-152° dec.).[3] The ^1H nmr spectrum of 1c (SO_2 solution at -60° or CH_2Cl_2



1c (2)

solution at room temperature) shows a singlet (3H) at 2.62 δ for the methyl group bonded to the sulphur atom and a singlet (18H) at 1.54 δ for the two equivalent *t*-butyl residues. The ^{13}C nmr spectrum in liquid SO_2 at -50° or in CD_2Cl_2 at room temperature (values in parentheses) shows signals at δ 113.42 (115.11) for the ring carbons, 33.12 (34.00) for the quaternary carbons, 28.63 (30.60) for the methyl carbon bonded to sulphur, and 26.67 (28.65) for the methyl carbons in the *t*-butyl moieties, in good agreement with the data for trimethylthiirenium salts **1a**.[1]

The great stability of **1c** is also shown by the fact that the reaction of methanesulphenyl chloride with di-*t*-butylacetylene at -60° in sulphur dioxide gives 1-methyl-2,3-di-*t*-butylthiirenium chloride **1c** as the only product (equation 3). Addition of silver tetrafluoroborate gives, after evaporation of sulphur dioxide and extraction with dichloromethane followed by addition of pentane, the thiirenium tetrafluoroborate in 60 % yield (m.p. 137-138° dec.).[4] The ^1H nmr spectra of the chloride and tetrafluoroborate salts are identical with that of hexachloroantimonate.



(3)

1c **3**

The easy preparation of the fluoroborate salt of **1c** implies that its stability towards chloride ion in liquid sulphur dioxide is much greater than that of trimethylthiirenium ion **1a**.[5] Indeed solutions of **1c** chloride in this solvent are stable for days at room temperature. However when the reaction (3) is carried out in dichloromethane at low temperature, the firstly observed ^1H nmr spectrum of **1c** is slowly substituted with the spectrum of the final adduct, *E*-1,2-di-*t*-butyl(2-methylthio)vinyl chloride **3**.[6] [^1H nmr in CH_2Cl_2: δ 2.21 (s, 3H), 1.46 (s, 9H), 1.38 (s, 9H)].

Compounds **1a** and **1c** are the first examples of stable thiirenium ions, a new heterocyclic unsaturated three-membered ring system. As already observed in the cyclopropyl cation series as well as in other small ring compounds,[7] alkyl substitution and particularly bulky alkyl substitution stabilizes very efficiently the system.

REFERENCES

1. G. Capozzi, O. DeLucchi, V. Lucchini, and G. Modena, *J.C.S. Chem. Comm.*, 248 (1975).
2. G. Capozzi, V. Lucchini, G. Modena, and F. Rivetti, *J.C.S. Perkin II*, 361 (1975).
3. Elemental analysis, found % (calcd for $C_{11}H_{21}Cl_6SSb$): C 25.2(25.42); H 4.0(4.06); Cl 41.0(40.92)
4. Elemental analysis, found % (calcd for $C_{11}H_{21}BF_4S$): C 48.8(48.54); H 7.65(7.78); F 27.9(27.92); S 12.0(11.78).
5. Trimethylthiirenium ion **1a** reacts in sulphur dioxide at -60° with chloride ion to give *E*-1,2-dimethyl(2-methylthio)vinyl chloride.[1]
6. Oxidation of **3** with MCPBA gives *E*-1,2-di-*t*-butyl(2-methylsulphonyl)vinyl chloride (m.p. 131-133°). ^1H nmr in $CDCl_3$: δ 3.14 (s, 3H), 1.48 (s, 9H), 1.42 (s, 9H). Elemental analysis, found % (calcd for $C_{11}H_{21}ClO_2S$): C 52.1(52.26); H 8.35(8.37).
7. J. Ciabattoni and E. C. Nathan, *Tetrahedron Letters*, 4997 (1969); P. Raynolds, S. Zonnebelt, S. Bakker, and R. M. Kellogg, *J. Amer. Chem. Soc.*, **96**, 3146 (1974); and references cited therein.