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ALKYLTHIOLATION OF ALKENES

A NOVEL SYNTHESIS OF EPISULPHONIUM IONS (THIIRANIUM IONS)

G. Capozzi*, O. De Lucchi, V. Lucchini, and G. Modena*

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

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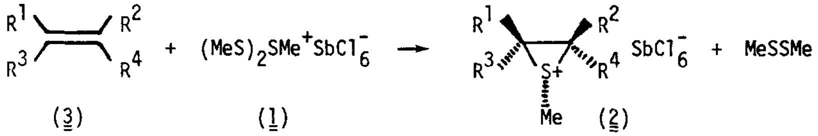
THE alkylthiolating properties of methyl(bismethylthio)sulphonium hexachloroantimonate **1** shown by its reaction with alkynes to give thiirenium ions,[1] prompted us to use this reagent for the synthesis of episulphonium ions **2** which has been so far realized in a few and somewhat particular cases.[2,3]

We report in this communication the synthesis of thiiranium hexachloroantimonate **2a-c**, obtained in high yields (85-90%) by addition of the appropriate alkene **3a-c** to a solution of **1** in methylene chloride at 0° or in sulphur dioxide at -60° (equation). Compounds **2** start to precipitate from the methylene chloride by cooling at -60°. Complete precipitation is achieved by addition of a small amount of pentane. After filtration the salts are washed with pentane and dried under vacuum [4] {m.p. (dec.): **2a**, 107-108°; **2b**, 108-109°; **2c**, 127-128°}. Alternatively **2a-c** are obtained from the sulphur dioxide solution after evaporating the solvent and washing with pentane to remove the dimethyl disulphide formed. Thiiranium ions **2a-c** are stable for weeks at -10°. However some decomposition occurred when they were left for hours at room temperature without exclusion of moisture. The ^{1}H nmr data of **2a-c** are reported in the table.



(**3**) (**1**) (**2**)

2a, **3a** : $R^1 = R^2 = R^3 = R^4 =$ Me
2b, **3b** : $R^1 = R^4 =$ Et; $R^2 = R^3 =$ H
2c, **3c** : $R^1R^2 = -(CH_2)_6-$; $R^3 = R^4 =$ H
2d, **3d** : $R^1 = R^3 =$ Me; $R^2 = R^4 =$ H
2e, **3e** : $R^1 = R^2 =$ Me; $R^3 = R^4 =$ H
2f, **3f** : $R^1 = R^4 =$ Me; $R^2 = R^3 =$ H
2g, **3g** : $R^1 = R^2 = R^3 =$ Me; $R^4 =$ H

TABLE

^{1}H nmr Chemical Shifts (δ) and Coupling Constants (Hz) for Ions **2a-g**[a]

2a, 1.93 (s, 6H), 1.97(s, 6H), 2.40 (s, SMe)

2b, 1.24 (t, J 7.2, 3H), 1.31 (t, J 7.2, 3H), 1.6-2.5 (broad m, 4H), 2.56 (s, SMe), 3.96 (m, 2H)

2c, 1.67 (m, 8H), 2.53 (m, 4H), 2.65 (s, SMe), 4.23 (m, 2H)

2d, 1.91 (s, 3H), 2.10 (s, 3H), 2.60 (s, SMe), 3.56 (d, J 6.0, 1H), 3.85 (d, 1H)

2e, 1.85 (d, 6H),[b] 2.64 (s, SMe), 4.32 (m, 2H)

2f, 1.84 (d, 3H),[b] 1.96 (d, 3H),[b] 2.55 (s, SMe), 4.0 (m, 2H)

2g, 1.87 (d, J 6.4, 3H), 1.90 (s, 3H), 2.07 (s, 3H), 2.58 (s, SMe), 4.09 (q, 1H)

[a] relative to internal TMS, in SO_2 at -60°; [b] apparent doublet, part of a more complex system.

The addition of **1** to *cis*- and *trans*-but-2-ene, isobutene, and 2-methylbut-2-ene also gave the expected thiiranium salts **2d-g** [5] characterized by their ^{1}H nmr spectra (see table).

The results suggest that only one compound is formed from *cis* alkenes although the pyramida arrangement of sulphonium sulphur allows the existence of two geometrical isomers.[6] Possibly because of steric hindrance, only the less crowded isomer, *i.e.* the one with the *Me-S* trans to the alkyl groups (or chain), is formed. A similar observation was reported by Kellogg *et al.* for the methylation of *cis*-di-*tert*-butylthiirane.[3]

The stability of thiiranium ions depends on the individual compound and in some instances decomposition was observed by rising the temperature. This problem, as well as the alkylthiolating properties of methyl(bismethylthio)sulphonium salts towards other substrates are being actively investigated in this laboratory.

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4. Satisfactory elemental analyses have been obtained.
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