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THE N,N-DIMETHYLCYCLOPROPANIMINIUM ION

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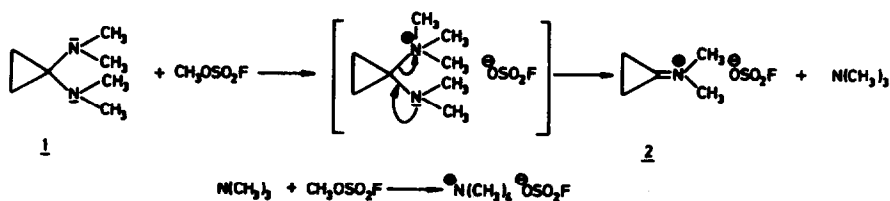
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It is well established that substitution reactions on cyclopropyl compounds generally proceed with ring opening^{4,5}. Exceptions are reported for certain bicyclo[4.1.0]-systems⁵ in which ring cleavage is thought to be prevented by excessive ring strain generated in the transition state. Substitution without ring opening can also occur in certain cyclopropanes with a hetero-atom attached to the same ring carbon atom as the leaving group⁶⁻⁹. In these cases the incipient cyclopropyl cation is apparently stabilised by the neighbouring hetero-atom, especially when this is nitrogen.

We report in this letter the spectroscopic observation of such a species, the relatively stable N,N-dimethylcyclopropaniminium ion 2.



When 1,1-bis(dimethylamino)cyclopropane⁷ 1 (NMR in CDCl_3 : singlets at $\delta = 2.34$ and at 0.75 ppm with intensity ratio 3:1) is added to a tenfold excess (v/v) of methyl fluorosulphonate¹⁰ at -78° , a white precipitate of tetramethylammonium fluorosulphonate is rapidly formed¹¹. After warming to ambient temperature, and filtration, a colourless solution remains. Its NMR-spectrum¹² shows, apart from absorptions due to some minor impurities and the solvent, two multiplets at $\delta = 3.71$ ppm (6H) and at 2.26 ppm (4H) relative to internal TMS, which we ascribe to the *N,N*-dimethylcyclopropaniminium ion 2. When recorded at 50 Hz sweep width (fig. 1 top) 5 lines can be discerned in the region of $\delta = 3.7$ ppm and 7 lines at $\delta = 2.3$ ppm, with distances of 1.20 ± 0.05 Hz within each multiplet. In a double resonance experiment (HA 100) irradiation of either multiplet makes the other collapse to a quasi singlet (width at half height 1.0 Hz) (fig. 1 bottom).

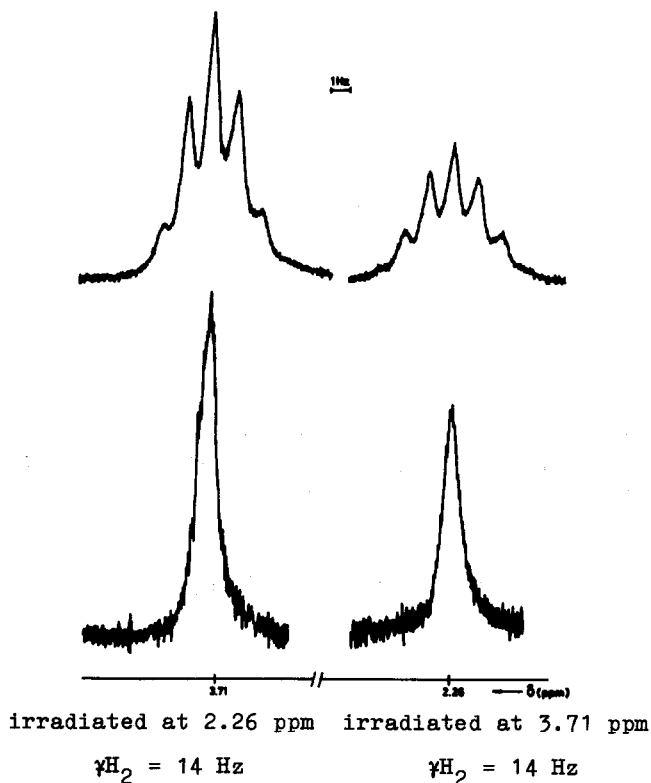
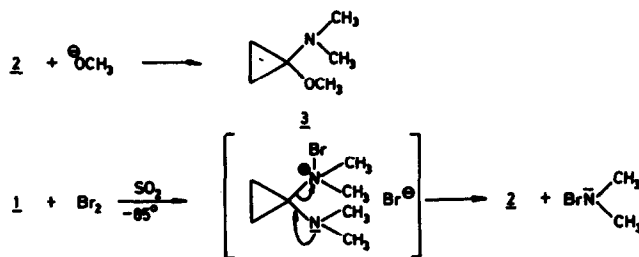


Figure 1. NMR-spectrum of *N,N*-dimethylcyclopropaniminium ion 2 in $\text{CH}_3\text{OSO}_2\text{F}$, before (top) and after decoupling (bottom).

This points to a planar ion 2, because a non-planar ion would have given a multiplet instead of a singlet for the four cyclopropyl protons after decoupling¹³. The high double bond character of the exocyclic C=N⁺ bond (despite the strain invoked) is supported by the chemical shift of the NCH₃ protons at 3.71 ppm, which is close to that reported for N,N-dimethylmethaniminium trifluoroacetate (3.82 ppm in CF₃COOH)¹⁴.

At the same time this means that there is little or no positive charge on C₁ and consequently the ion has no tendency to form an allyl cation by C₂-C₃ bond rupture^{4,5}. In agreement with the proposed structure, addition of a solution of 2 (counterion FSO₃⁻) to a cooled solution of sodium methoxide in methanol leads exclusively to 1-methoxy-1-dimethylaminocyclopropane 3¹⁵, NMR in CDCl₃: δ = 0.83 ppm (m, 4H); δ = 2.53 ppm (s, 6H); δ = 3.37 ppm (s, 3H).



When 1 is added to 1.2 eq. of Br₂ in liquid SO₂ at -65° according to the method of Dusseau, the spectrum of the ion 2 can also be observed^{15,16} (although less well resolved), together with an absorption at δ = 2.63 ppm (relative to external TMS) arising from N-bromodimethylamine¹⁷.

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11. It is interesting to note that no reaction takes place between -80° and -10° when 1 is added to 1 eq. of $\text{CH}_3\text{OSO}_2\text{F}$ in liquid SO_2 .
12. From -80° to $+30^\circ$ the spectrum does not change, but there are appreciable solvent effects.
The multiplets are observed at 3.52 ppm and 2.12 ppm in CH_2Cl_2 , and at 3.84 ppm and 2.37 ppm in $\text{CH}_3\text{OSO}_2\text{F}/\text{SO}_2$ relative to internal TMS.
13. It should be noted that the observed spectrum of 2 must be classified as an $\text{AA}'\text{A}''\text{B}_3\text{B}_3'$ system and not a deceptively simple A_4B_6 system with $J_{\text{AB}} = 1.20$ Hz, as might be concluded at first sight.
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