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THE CHEMISTRY OF SMALL RING COMPOUNDS. PART 34[1]
THE N,N-DIMETHYL-2,2-DIMETHYLCYCLOPROPANIMINIUM ION

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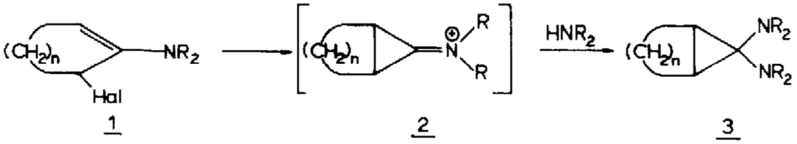
The Favorskii-type reaction of 2-dialkylamino-3-halocycloalkenes 1, which takes place via the iminium ions 2, provides an elegant entry into cyclopropane chemistry[3-8]. Thus far the reaction has only been applied to cyclic enamines 1 and consequently only bicyclic cyclopropane derivatives have been prepared by this method.

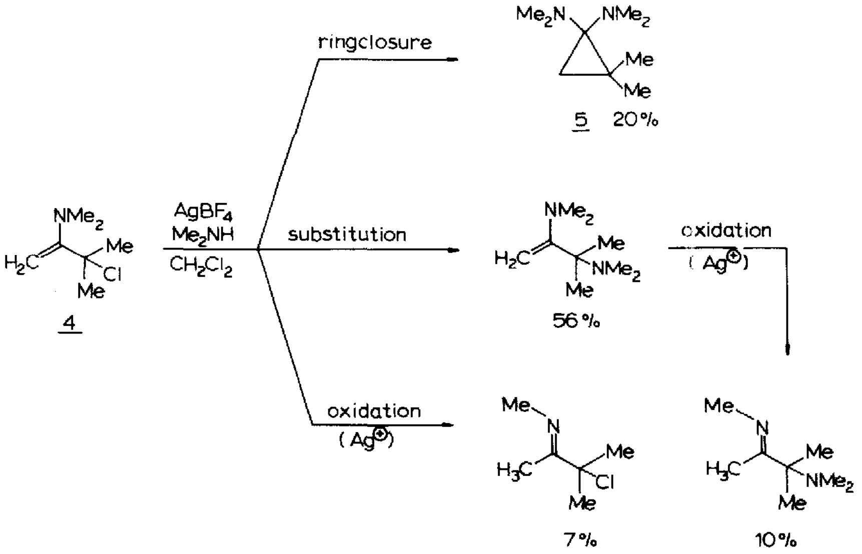


1 2 3

n = 3,4

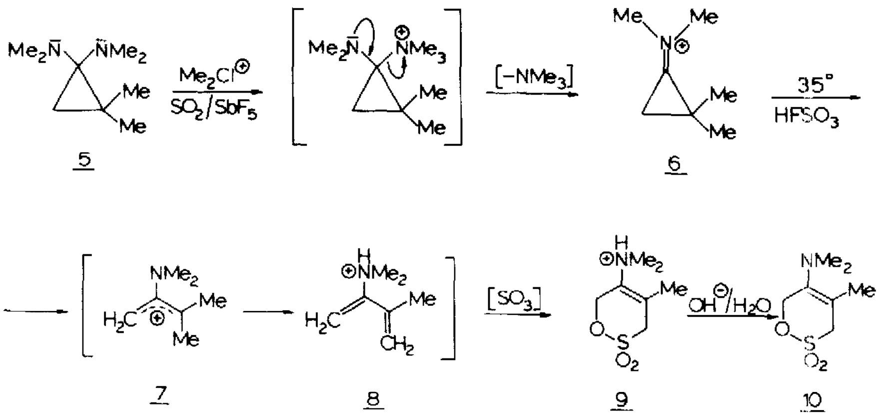
Because of our interest in cyclopropaniminium ions in general[9] we investigated the possibility of extension to acyclic enamines in order to prepare simpler cyclopropane derivatives. Thus we reacted the acyclic chloro enamine 4 (prepared from 2-chloro-2-methylbutan-3-one and $(CH_3)_2NH/TiCl_4$) with $AgBF_4$ and an excess of dimethylamine in CH_2Cl_2[10]. Although these reaction conditions give excellent results with the cyclic enamines 1 [7], an intricate mixture of substitution-, oxidation- and ring-closed compounds is produced from the acyclic enamine 4 in yields as indicated[11].

The reaction takes a far more selective course, when the enamine 4, $AgBF_4$ and dimethylamine are reacted in a 1:1:2 molar ratio in ether. Contrary to CH_2Cl_2, this solvent gives a heterogeneous reaction mixture, from which the bisamine 5 is formed almost quantitatively[12].



Methylation of 5 with CH_3OSO_2F gives only polymer. In contrast, reaction with dimethylchloronium ion in SO_2[13] at -78° results in formation of the N,N-dimethyl-2,2-dimethylcyclopropaniminium ion 6 and tetramethylammonium ion.

The NMR-spectrum (HA 100, -18°) shows a six proton singlet at δ = 1.51 ($C(CH_3)_2$), a two proton quasi septet (J = 1.3) at δ = 2.18 and a six proton multiplet at δ = 3.74 ($\overset{\oplus}{N}(CH_3)_2$). In a double resonance experiment irradiation at δ = 2.18 causes the multiplet at δ = 3.74 to collapse to two singlets[14] separated by 0.01 ppm. Conversely, irradiation at δ = 3.74 causes the septet at δ = 2.18 to collapse to a singlet[14]. These data are in close agreement with those of the N,N-dimethylcyclopropaniminium ion, obtained earlier via an entirely different route starting with cyclopropanone[9].
When a solution of the ion 6 in fluorosulfonic acid is warmed to ca 35°, ring opening occurs whereby the sultone 9 is produced[15]. This probably originates from cycloaddition[16] of SO_3 (present in $HFSO_3$) to the diene 8. After quenching with saturated Na_2CO_3 and rapid extraction with CH_2Cl_2 the neutral sultone 10 is obtained, which can be purified by crystallisation from ether/pentane[17] (mp 62-63°).



Thus 6 is thermally much less stable than the cyclopropaniminium ion without ring substituents which does not undergo ring opening until 150° [11]. The two C-methyl groups in the allylic cation 7 clearly facilitate its formation as compared with the allylic cation carrying no such stabilising methyl groups.

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2. Part of the forthcoming thesis of E. Jongejan.
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8. J.C. Blazejewski, D. Cantacuzene and C. Wakselman, Tetrahedron 29, 4233 (1973).
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10. This provides a homogeneous reaction mixture.
11. Full details will be published elsewhere.
12. NMR (CCl_4): singlets in a 1:3:6 ratio at δ = 0.37, δ = 1.19 and δ = 2.52.
    IR (liq.) : 3060 cm^{-1}
    MS : $M^{+\cdot}$ at m/e 156, 0.6% of the base peak at m/e 44.

13. From SbF_5 and an excess of CH_3Cl, see G.A. Olah and J.R. DeMember, J. Amer. Chem. Soc. 92, 2562 (1970).
14. The singlet is somewhat broadened (width at half height 1.5 Hz) possibly due to coupling with ^{14}N.
15. NMR ($HFSO_3$): $\delta = 2.05$ (m, 3H), $\delta = 3.22$ (d, J = 5.2, 6H), $\delta = 4.12$ (m, 2H), $\delta = 5.25$ (m, 2H), $\delta = 7.6$ (broad, 1H).
16. F.G. Bordwell, R.D. Chapman and C.E. Osborne, J. Amer. Chem. Soc. 81, 2002 (1959).
17. NMR ($CDCl_3$): $\delta = 1.76$ (triplet of triplets, J = 0.92 and J = 1.85, CH_3-C), $\delta = 2.54$ (s, CH_3-N), $\delta = 3.67$ (triplet of quartets, J = 2.20 and J = 0.92, CH_2-SO_2) and $\delta = 4.88$ (triplet of quartets, J = 2.20 and J = 1.85, CH_2-O). IR ($CHCl_3$): 3020, 2980, 2940, 2910, 2870, 2835 and 2790 cm^{-1} (all m, CH stretch); 1675 cm^{-1} (w, C=C stretch); 1370, 1362, 1175 (all s, sultone bands[18]).

    MS: $M^{+\cdot}$ at m/e 191, 18% of the base peak at m/e 82.
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