Label Scrambling in the Hydrolysis and Borohydride Trapping Products of [1,1-$^2H_2$]Cyclopropylmethyl, [1-$^2H_1$]Cyclobutyl, and [2,2,4,4-$^2H_4$]Cyclobutyl Methanesulphonates

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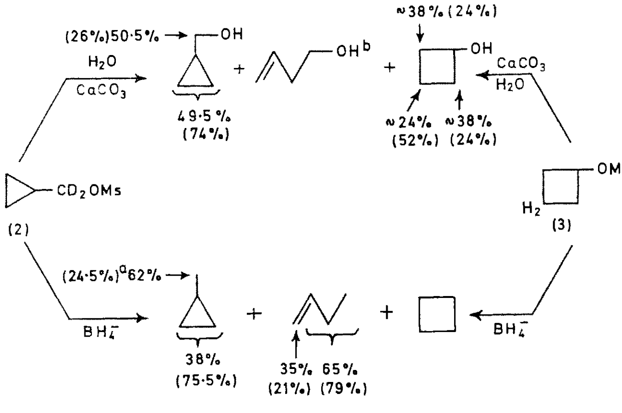
Summary Cyclopropylmethyl and cyclobutyl methanesulphonates appear to solvolyse by forming in the rate-determining step two and one intimate ion pairs, respectively, which then further ionize to the corresponding equilibrating solvent-separated ion pairs.

CYCLOPROPYLMETHYL and cyclobutyl derivatives solvolyse with remarkably enhanced rates, yielding rearranged and position-scrambled products.[1] These rearrangements appear to be highly stereospecific.[2] It seems well established that the intermediate cation(s) is nonclassical and bisected.[1] A number of structures has been suggested over the last twenty years.[1]

Our recent results[3] indicate that cyclopropylmethyl and cyclobutyl methanesulphonates solvolyse through different, although similar, intermediates. This conclusion was based on different spreads of the hydrolysis and borohydride trapping products. However, since the solvated bulky borohydride attacks preferentially at a primary carbon, forming primary products,[4] it was desirable to determine the preferred position(s) of nucleophile attack in each of the products separately.

We have studied deuterium scrambling in the hydrolysis and borohydride trapping products of [1-$^2H_1$]cyclobutyl (**1**, 98·7% D), [1,1-$^2H_2$]cyclopropylmethyl (**2**, 98·7% D), and [2,2,4,4-$^2H_4$]cyclobutyl (**3**, 92·2% D by n.m.r.) methanesulphonates. The methanesulphonates (**1**), (**2**), and (**3**) were obtained[5] from the corresponding alcohols[6] and solvolysed[3] for about 7 half-lives in 60% aqueous diglyme at 40° in the presence of an excess of base ($CaCO_3$ or $NaBH_4$, 2·25 M). The products (see Scheme 1) were isolated[3] and analysed by n.m.r. (Varian HA-100 and/or Varian A-60A spectrometer).



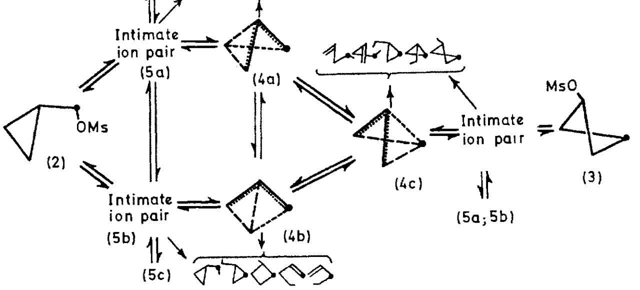
SCHEME 1. *Distribution of the label* (CD_2 *group in* **2**, CH_2 *group in* **3**) *in the hydrolysis and borohydride trapping products of* [1,1-$^2H_2$]*cyclopropylmethyl* (**2**) *and* [2,2,4,4-$^2H_4$]*cyclobutyl* (**3**) *methanesulphonates* (60% *aq. diglyme*, 2·25 M $NaBH_4$, 40°). *The values in parenthesis correspond to the products from* (**3**).

[a] *Determined in* [$^2H_5$]*methylcyclopropane obtained from* [1,2,2,4,4-$^2H_5$]*cyclobutylmethanesulphonate*; [b] *the yield was too low for analysis.*

No deuterium scrambling was observed in any analysed products of (**1**); deuterium at the originally methine position was found exclusively at the methine positions in cyclopropylmethanol, cyclobutanol, methylcyclopropane, and but-1-ene.† These results are in a good agreement with the ^{14}C distribution in cyclobutanol obtained by deamination of [1-^{14}C]cyclopropylmethylamine.[7] The nonappearance of deuterium scrambling indicates that: (i) there is no hydrogen shift between the methine position and the methylene positions and, consequently, (ii) potentially olefinic bonds in the intermediates have to involve the methine carbon.

The label distributions in the products of (**2**) and (**3**) are shown in Scheme 1. The indicated label distributions (CD_2 group in **2** and CH_2 group in **3**) were calculated from the amount of hydrogen at each of the three methylene positions in (**2**) or (**3**) and in the product, taking into account the equivalence of the 3- and 4-positions in cyclopropylmethyl and the 2- and 4-positions in cyclobutyl compounds. The *cis–trans* γ-hydrogen ratio in all cyclopropylmethyl products was 1 : 1, indicating that there is no hydrogen shift among the three methylene positions. Recent results on the solvolysis of *cis*-[3-$^1H_1$]perdeuteriocyclopropylmethyl methanesulphonate[2a] confirmed this observation.

The results presented in Scheme 1 demonstrate that the three methylene groups are not equivalent. This is in accord with the results on deamination of [1-^{14}C]cyclopropylmethylamine reported by Roberts[7] who suggested three equilibrating asymmetrical bicyclobutonium ions as intermediates. The nonequivalence is more pronounced in the products having the same structure as the starting



SCHEME 2. *The intermediates* (**4a**—**c**) *are solvent-separated ion pairs. These structures* (**4a**—**c**) *are drawn as essentially symmetrical bicyclobutonium ions* (*Baldwin*[8]) *but with indicated memory effect* (– –) *and positions of the potentially olefinic bond* (· · · ·). *In principle Roberts' assymetrical bicyclobutonium ion*[7] *could be used as well.*

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† The methine proton signals are completely missing from the n.m.r. spectra of all analysed products and the characteristic methyl and carbinyl doublets of the cyclopropylmethyl derivatives appear as singlets.

methanesulphonate, the label being preferentially attached at the original position. As direct displacement reactions are unimportant under the conditions used,[3] the results indicate a memory effect and can be explained as follows (see Scheme 2). In the rate-determining step, cyclopropylmethyl methanesulphonate (**2**) forms two (**5a**,**6b**) and cyclobutyl methanesulphonate (**3**) one (**5c**) intimate ion pairs which can either: (a) react with a strong nucleophile yielding preferentially product(s) of the original structure; (b) isomerize to another intimate ion pair; or (c) ionize further to give two (**2** $\rightarrow$ **4a** + **4b**) and one (**3** $\rightarrow$ **4c**) solvent-separated ion pairs, respectively. The structure of the intimate ion pair(s) is somewhere between the structure of the original methanesulphonates and that of the solvent-separated ion pair(s). The solvent-separated ion pairs react readily with water. Borohydride as the strongest nucleophile used in these experiments preferentially attacks at the intimate ion pair stage[3] yielding hydrocarbons with less scrambled methylene positions than is the case in the corresponding alcohols. If the equilibrium (**4a** $\rightleftharpoons$ **4b** $\rightleftharpoons$ (**4c**) is fast but not instantaneous the label distribution in the products (see Scheme 1) is understandable because (**2**) solvolyses *via* two and (**3**) *via* one intermediate (intimate and solvent-separated ion pairs). Alternatively, the equilibrating structures (**4a** $\rightleftharpoons$ **4b**) $\rightleftharpoons$ (**4c**) could be considered as one common intermediate, "tetrahedronium" ion (pair) with unsymmetrical electron charge distribution due to the different position of the leaving group. This position is determined by the structure of the starting methanesulphonate.

(*Received, October 5th*, 1970; *Com.* 1713.)

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