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INTERMEDIATES IN CYCLOPROPYLCARBINYL-CYCLOBUTYL-HOMOALLYL-REARRANGEMENT

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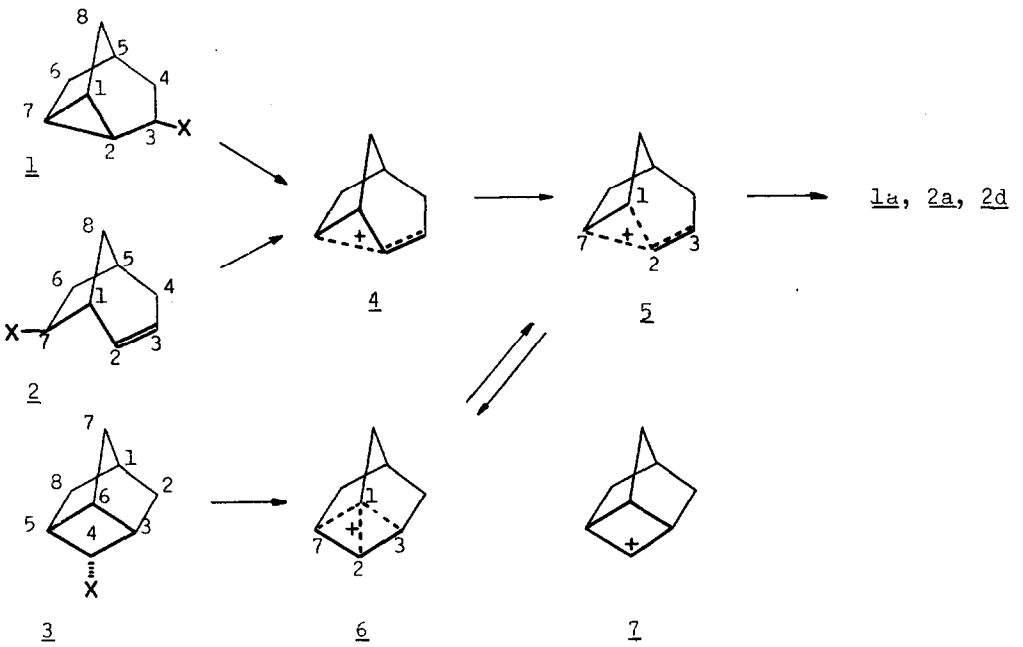
Two kinds of cationic intermediates are discernible in the solvolytic cyclopropylcarbinyl-cyclobutyl-homoallyl-rearrangement [1] of tricyclo[3.2.1.$0^{2,7}$]octan-3-ol (1a) [2], exo-bicyclo[3.2.1]oct-2-en-7-ol (2a) [2] and endo-tricyclo[3.2.1.$0^{3,6}$]-octan-4-ol (3a) [3] in 70 % aqueous dioxane and formic acid. This follows from rate and product studies employing optically active and deuterium-labeled esters of these isomeric secondary alcohols.



X = a) OH b) 2,4-$(NO_2)_2C_6H_3COO$ c) 4-$NO_2C_6H_4COO$ d) HCOO e) Cl

In formic acid the three 2,4-dinitrobenzoates 1b, 2b and 3b, respectively, reacted to give the formate of the most stable product, i.e. the homoallyl alcohol 2a. In 70 % dioxane buffered with triethylamine at 80° all three esters furnished the same mixture of 78 % cyclopropylcarbinol 1a and 22 % of homoallyl alcohol 2a (± 1 %). At 60° the 4-nitrobenzoate 1c also yielded ca. 13 % of rearranged 4-nitrobenzoate 2c by ion pair recombination.

Table. First order conductometric rate constants for 1b, 2b and 3b in 70 vol. % aqueous dioxane at 80° C with 1.5 mole equiv. Et_3N.

	$k(sec^{-1})$	k_{rel}	$E^{\neq}$(kcal)	$S^{\neq}$(cal/°)
1b	6.25×10^{-2}	5.5×10^{3}	19.77	-10.36
2b	1.13×10^{-5}	1	--	--
3b	6.65×10^{-5}	6	25.66	-7.29

As shown in the table the cyclopropylcarbinyl ester 1b and the cyclobutyl ester 3b react 5.5×10^3 and 6 times, respectively, as fast as the homoallyl ester 2b. Since the homoallyl chloride 2e reacts ca. 10^5 times as fast as the saturated analogue (7-exo-bicyclo[3.2.1]octyl chloride) all three esters 1b, 2b and 3b show the rate enhancements characteristic of their structures.

Reaction of optically active 1c [4] (α_D -71° in $CHCl_3$) and 2b [4] (α_D 31.4° in $CHCl_3$) in 70 % dioxane led to completely racemized alcohols 1a and 2a, and, in the case of 1c to racemized 4-nitrobenzoate 3c. Under the experimental conditions the alcohols 1a and 2a themselves are not racemized. The rate of loss of optical activity was 1.6 times the rate of solvolysis.

When the 3-deuterium labeled cyclopropylcarbinyl 4-nitrobenzoate 1c [5] was solvolyzed in 70 % dioxane the resulting alcohols 1a and 2a and rearranged 4-nitrobenzoate contained deuterium exclusively in position 3 [6]. Thus no isotope scrambling had occured. In formic acid, however, the deuterium label was nearly equally distributed among positions 1, 3 and 7 of the resulting homoallyl formate 2d. Finally, reaction of 4-deuterated cyclobutyl 2,4-dinitrobenzoate 3b

in 70 % dioxane led to 2-deutero-cyclopropylcarbinol 1a and to 2-deutero-homoallyl alcohol 2a, whereas in formic acid only the formate of the latter compound was obtained. With 2b, therefore, no isotope scrambling occurs.

The racemization of the cyclopropylcarbinyl and homoallyl esters 1c and 2b in 70 % dioxane implicate the formation of the symmetrical (bisected) cyclopropylcarbinyl ion 5 [1] by way of the unsymmetrical homoallyl ion 4 [1] which resembles 1c and 2b structurally. Since deuterium at C3 of the cyclopropylcarbinyl-ester 1c retains its position in the alcohols 1a and 2a the cation 5 must be trapped by solvent before further rearrangement occurs.

By contrast reaction in formic acid leads to the formate of the homoallyl alcohol 2a in which the label is nearly equally distributed among C1, C3 and C7. It can therefore be assumed that in the less nucleophilic solvent the cation 5 isomerizes reversibly to the symmetrical bisected bicyclobutonium ion 6 [7] in which C3 and C7 are equivalent. After reversion to the symmetrical cyclopropylcarbinyl ion 5 the deuterium label becomes distributed between the equivalent carbon atoms 1 and 7. The isotope scrambling can be explained less economically by two sets of three interconverting cations of the type 5 and 6, respectively.

Ionization of the symmetrical endo-cyclobutyl ester 3b in 70 % dioxane leads to the structurally related symmetrical bicyclobutonium ion 6 which is derived from the classical cyclobutyl cation 7 by partial delocalization of the 1,3 and 1,7 σ bonds. The highly strained cation 6 then rapidly rearranges to the symmetrical cyclopropylcarbinyl ion 5, the precursor of the alcohols 1a and 2a. The short life-time and the hindrance to endo attack by nucleophile in the case of the cation 6 account for the absence of cyclobutanol 2a in the products.

In the rearrangement of the 4-deuterated cyclobutyl ester 2b in 70 % dioxane and in formic acid no isotope scrambling occurs because position 4 (equal to position 2 in the ion 6) never becomes equivalent to other positions. This result also shows that the cation 6 or its classical counterpart 7 does not undergo hydride shifts and degenerate Wagner-Meerwein rearrangements [8].

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* To whom correspondence should be addressed.

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4) Obtained by resolution of the corresponding alcohols via their esters with 3β-acetoxy-Δ^5-etienic acid.

5) Obtained via the ketone of 1a (c.f. W.R. Moore, W.R. Moser and J.E. La Prade, J. Org. Chem. 28, 2200 (1963)) with $LiAlD_4$.

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