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REARRANGEMENT STUDIES WITH CARBON-14. XXV.

THE SOLVOLYSES OF 2-(Δ^3-CYCLOPENTENYL)-2-^{14}C-ETHYL p-NITROBENZENESULFONATE[*1]

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To obtain a comparison between the isotope position rearrangements accompanying the σ- and π-routes to the norbornyl cation, the acetolysis and formolysis of 2-(Δ^3-cyclopentenyl)-2-^{14}C-ethyl p-nitrobenzenesulfonate (I) were studied and the resulting extents of rearrangement compared with those reported by Roberts and coworkers (1, 2) for the solvolyses of exo-2,3-$^{14}C_2$-2-norbornyl brosylate (II-OBs-2,3-$^{14}C_2$). I was prepared from 4-bromocyclopentene (3) and diethyl 2-^{14}C-malonate[*3] by procedures previousl described (4). Solvolyses were carried out at 60° for 30 hr. in reagent grade, glacial acetic acid or 98-100% formic acid. The product, II-OAc-^{14}C or II-OCHO-^{14}C, was converted to II-OH-^{14}C which was degraded (2) to cis-cyclopentane-1,3-dicarboxylic acid (III) to cis-cyclopentane-1,3-diamine (IV) to succinic acid (V) to ethylene diamine (VI). Measurement of the ^{14}C-activities of III, IV, V and VI, with IV and VI assayed as their respective dibenzamides, gave data from which the ^{14}C-contents at C-2,3

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C-1,4, C-7 and C-5,6 can be evaluated (2). The results are summarised in Table I.

TABLE I

^{14}C-Distribution in the Norbornyl Products

from Solvolyses of I

	% ^{14}C[a]			
Reaction	C-2,3	C-1,4	C-7	C-5,6
Acetolysis				
Observed	38.5; 37.1	0.4; 1.4	23.8; 25.9	37.3; 35.6
Calculated[b]	37.9	0.9	24.4	36.9
Formolysis				
Observed	31.5; 31.4	2.8; 4.0	26.0; 26.9	39.7; 37.7
Calculated[b]	31.4	3.4	26.7	38.4

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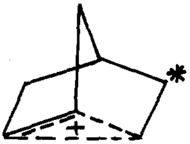
[a] Activities measured by a liquid scintillation counter. For the various runs, 100% corresponded to specific activities ranging from about 33,300 to 61, 400 c.p.m./mmole. [b] Based on estimated contributions from various processes discussed in the text of this communication.

If solvolyses of I were to give rise to the norbornonium ion VIIa, or its equivalent of a pair of rapidly equilibrating classical ions VIIIa and VIIIb, without further rearrangement, the ^{14}C-label would be located only at the C-5 position of the product. The results in Table I, however, definitely indicate extensive ^{14}C-scrambling.

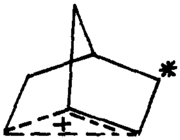
While it is not possible to differentiate between the nonclassical ion and rapidly equilibrating classical ions solely from the observed ^{14}C-distributions, nonclassical ions will be utilised in the following discussion since Bartlett and coworkers (5, 6) have recently provided strong evidence for the symmetrical norbornonium ion (VII) as an intermediate in solvolyses of I. The initially formed ion VIIa may give rise to a product with the label at C-5 or it may undergo 6,2- and 6,1-hydride shifts to VIIb and VIIc. The products from VIIb ⇌ VIIa ⇌ VIIc would have the label equally located at C-3, C-5 and C-7. 3,2-Hydride shift together with VIIb ⇌ VIIa ⇌ VIIc would render all seven carbon positions equivalent. Apparently all these processes could occur when the norbornyl cation is generated by the σ-route (2, 7, 8). The optimum combination of the three processes of (1) complete equivalence of all carbon positions, (2) reaction with VIIa, and (3) reaction with VIIb ⇌ VIIa ⇌ VIIc will, however, still leave an excess of observed ^{14}C-activity at C-2,3. To account for this, process (4), consisting of a concerted rearrangement involving action of the solvent with the incipient ion, possibly depicted by IXa or IXb, is tentatively proposed. If contributions from these processes (1), (2), (3) and (4), respectively, were 3%, 12%, 72% and 13% for acetolysis and 12%, 10%, 75% and 3% for formolysis, the calculated ^{14}C-distributions are in good agreement with the observed results (Table I).

An alternative interpretation of the observed ^{14}C-distributions is, however, possible. Ion VIIa may rearrange to VIIb via edge-protonated ion X. Products from X and VII, respectively, would have the ^{14}C-label located at C-3 and C-5 and at C-3 and C-7. If the contributions from the set of alternative processes of (1) complete equivalence of all carbon positions, (2) reaction with VIIa, (3') reaction with X, and (4') reaction with VIIb, respectively, were 3%, 23%, 26% and 48% for acetolysis and 12%, 32%, 6% and 50% for formolysis, the same calculated ^{14}C-distributions given in Table I are also obtained.

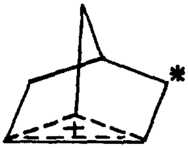
A possible differentiation between processes (1), (2), (3), (4) and (1), (2), (3'), (4') may be considered on the following grounds. The results



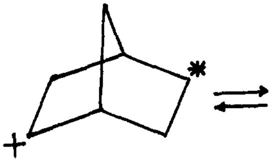
VIIa



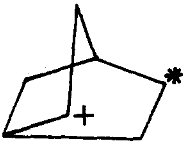
VIIb



VIIc



VIIIa



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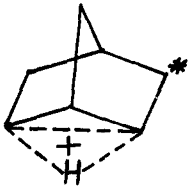
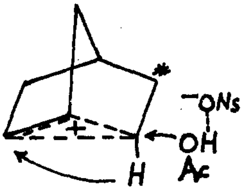
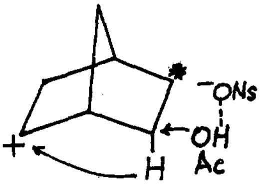


X

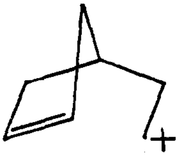
I



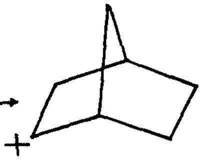
IXa



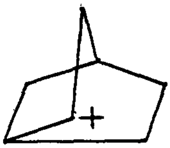
IXb



XIa



XIb



XIc

from the acetolysis of II-OBs-2,3-$^{14}C_2$ (1, 2) could be explained by reactions with ions analogous to VIIa and VIIb ⇄ VIIa ⇄ VIIc (processes 2 and 3), but not by reactions with ions analogous to VIIa, X and VIIb (processes 2, 3' and 4'). Moreover, if processes (1), (2), (3') and (4') were obtained in the solvolyses of I, there is no obviously reason for the rise and fall, respectivel in the extents of product formation from VIIa and X as the solvent is changed from acetic to formic acid. If processes (1), (2), (3) and (4) were operative, the observed higher contribution of concerted rearrangement (process 4) in acetolysis than in formolysis would be consistent with the more nucleophilic nature of acetic acid. On these grounds, processes (1), (2), (3) and (4) may be preferable to (1), (2), (3') and (4').

The present results indicate that a difference in isotopic scrambling does exist in the σ- and π-routes to the norbornyl cation. If the concerted rearrangement IIa or IIb proves to be valid on further experimentation, its involvement in solvolyses of I and not II-OBs-2,3-$^{14}C_2$ could be the result of a greater contribution of IIa to the hybrid ion produced by the π-route (cf. ref. 9). Other factors that may cause some of the differences between the present results and those of Roberts and coworkers (1, 2) are that the leaving groups in the two systems studied are different and that unlike the earlier work (1, 2), no acetate or formate ions were added to the reaction mixture during the solvolyses of I.

The results reported in this communication together with the observation of only minor secondary α-deuterium kinetic isotope effects (4) suggest that hydride shifts (and the concerted rearrangement) take place sequentially following VIIa rather than competitively with VIIa (2). A similar conclusion was also arrived at recently by Humski, Borčić and Sunko (10) from their studies on the solvolysis of 2-(Δ^3-cyclopentenyl)ethyl-1,1-d_2 tosylate in 80% aqueous acetic acid.

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