Another portion of each sample of *exo*-I-OH-*t* was degraded by the procedures of Roberts and co-workers.[2] This involved oxidation first to *cis*-cyclopentane-1,3-dicarboxylic acid (III), mp 119–120° (lit.[2] 120–121°). *Anal.* Calcd for $C_7H_{10}O_4$: C, 53.10; H, 6.37. Found: C, 52.95; H, 6.30. III was converted to *cis*-cyclopentane-1,3-diamine which, in turn, was oxidized to succinic acid (IV), mp 185° (lit.[16b] mp 185°). *Anal.* Calcd for $C_4H_6O_4$: C, 40.67; H, 5.08. Found: C, 40.63; H, 5.01.

Samples of *exo*-I-OH-*t*, the semicarbazone of II, and acids III and IV were repeatedly recrystallized until their specific activities were constant. All calculations of isotopic rearrangements were based on the activities of these purified samples.

Rearrangement Studies with Carbon-14. XXVII. The Acetolysis and Formolysis of 2-(Δ^3-Cyclopentenyl)-2-^{14}C-ethyl *p*-Nitrobenzenesulfonate[1a]

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Abstract: The acetolysis and formolysis of 2-(Δ^3-cyclopentenyl)-2-^{14}C-ethyl *p*-nitrobenzenesulfonate were studied to provide data on isotope position rearrangements in the norbornyl cation generated by the π route. A comparison with earlier results on such rearrangements in the norbornyl cation generated by the σ route showed that differences do exist. A novel process which leads to a nonequivalent distribution of the tracer at C-3 and C-7 of the norbornyl product is noted for the π route. This process may be depicted as a concerted rearrangement involving hydride shift and reaction with solvent, and it occurs to a greater extent in acetolysis than in formolysis. An alternative explanation invoking product formation from edge-protonated nortricyclene is also discussed, but it appears to be the less preferable of the two possibilities.

In conjunction with the studies on the acetolysis of *exo*- and *endo*-2-*t*-2-norbornyl brosylates (*exo*- and *endo*-I-OBs-2-*t*),[2] an investigation was undertaken on the acetolysis and formolysis of 2-(Δ^3-cyclopentenyl)-2-^{14}C-ethyl *p*-nitrobenzenesulfonate (II-2-^{14}C) which gave norbornyl products by the π route.[3] It is expected that this work will provide data for a comparison between the processes that give rise to isotope position rearrangements in the norbornyl cation generated by the σ and π routes.

Results and Discussion

II-2-^{14}C was prepared from 4-bromocyclopentene[4] and diethyl 2-^{14}C-malonate[5] by procedures previously described.[6] Solvolyses of II-2-^{14}C were carried out at 60° for 30 hr in reagent grade glacial acetic acid or 98–100% formic acid. The product, *exo*-I-OAc-^{14}C or *exo*-I-OCHO-^{14}C, was treated with $LiAlH_4$ to give *exo*-I-OH-^{14}C which was degraded[7] by conversions to *cis*-cyclopentane-1,3-dicarboxylic acid (III) to *cis*-cyclopentane-1,3-diamine (IV) to succinic acid (V) to ethylenediamine (VI). Measurement of the ^{14}C activities of III, IV, V, and VI, with the diamines IV and VI assayed as their respective dibenzamides, gave the necessary data from which the ^{14}C-contents at C-2,3, C-1,4, C-7, and C-5,6 can be evaluated.[7] The results are summarized in Table I.

Table I. ^{14}C Distributions in *exo*-Norbornyl Products from Solvolyses of II-2-^{14}C

	^{14}C distribution, %[a]							
	C-2,3		C-1,4		C-7		C-5,6	
Reaction	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2
Acetolysis	38.5	37.1	0.4	1.4	23.8	25.9	37.3	35.6
Formolysis	31.5	31.4	2.8	4.0	26.0	26.9	39.7	37.7

[a] Assayed by a liquid scintillation counter. For the various runs, 100% corresponded to specific activities ranging from about 33,300 to 61,400 counts/min/mmole.

If solvolyses of II-2-^{14}C were to give rise to the norbornonium ion VIIa (or its equivalent of a pair of rapidly equilibrating classical ions) without further rearrangements, the ^{14}C label would be located only at the C-5 position of the product. In view of the propensity for 6,2 (and the analogous 6,1) hydride shift, as well as the possibility of some 3,2 hydride shift, observed in the norbornyl cation generated by the σ route from solvolyses of *exo*-I-OBs-2-*t*[2] and *exo*-I-OBs-2,3-$^{14}C_2$,[7] it is not surprising to note the extensive isotopic rearrangements as recorded in Table I. Indeed, the solvolysis of II-1,1-d_2 in 80% aqueous acetic acid has been reported to give about 15% rearrangement of the deuterium label to C-1 and C-2 of the norbornyl product,[8] indicating the occurrence of some 6,2 hydride

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[1] (a) Supported by a grant from the National Research Council of Canada; (b) holder of a Canadian Industries Limited Fellowship, 1964–1966.

[2] C. C. Lee and L. K. M. Lam, *J. Am. Chem. Soc.*, 2831 (1966).

[3] (a) R. G. Lawton, *ibid.*, **83**, 2399 (1961); (b) P. D. Bartlett and S. Bank, *ibid.*, **83**, 2591 (1961); (c) P. D. Bartlett, *Ann.*, **653**, 45 (1962); (d) P. D. Bartlett, S. Bank, R. J. Crawford, and G. H. Schmid, *J. Am. Chem. Soc.*, **87**, 1288 (1965); (e) P. D. Bartlett and G. D. Sargent, *ibid.*, **87**, 1297 (1965).

[4] P. D. Bartlett and M. R. Rice, *J. Org. Chem.*, **28**, 3351 (1963).

[5] Supplied by New England Nuclear Corp.

[6] C. C. Lee and E. W. C. Wong, *Tetrahedron*, **21**, 539 (1965).

[7] J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, **76**, 4501 (1954).

[8] K. Humski, S. Borčić, and D. E. Sunko, *Croat. Chem. Acta*, **37**, 3 (1965).

Table II. Calculated ^{14}C Distributions for Solvolyses of II-2-^{14}C

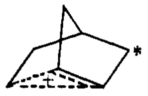
	% Contribution		Calculated % ^{14}C							
			Acetolysis				Formolysis			
	In HOAc	In HCOOH	C-2,3	C-1,4	C-7	C-5,6	C-2,3	C-1,4	C-7	C-5,6
All carbons equivalent	3	12	0.9	0.9	0.4	0.9	3.4	3.4	1.7	3.4
Reaction with VIIa	12	10				12.0				10.0
VIIb $\leftrightarrows$ VIIa $\leftrightarrows$ VIIc	72	75	24.0		24.0	24.0	25.0		25.0	25.0
Concerted rearrangement	13	3	13.0				3.0			
Calcd ^{14}C distribution			37.9	0.9	24.4	36.9	31.4	3.4	26.7	38.4

shift. Evidence for the 6,2 hydride shift has also been obtained in the acetolysis of 1-(Δ^3-cyclopentenyl)-2-propyl *p*-nitrobenzenesulfonate.[3e]

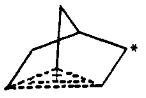
Recently, Bartlett and co-workers[3d,e] have provided strong evidence for the symmetrical norbornonium ion (VII) as an intermediate in the solvolysis of II. The present results will be discussed in terms of nonclassical structures although, as pointed out in the preceding paper, the isotopic distribution derived from a nonclassical ion may be equally well explained by a pair of rapidly equilibrating classical ions.

The major pathways in the acetolysis of II-2-^{14}C can be attributed to the nonclassical ion processes described for the acetolysis of *exo*-I-OBs-2-*t*.[2] Solvent capture by the initially formed ion VIIa will give *exo*-I-OAc-5-^{14}C. Subsequent equilibration of VIIa, VIIb, and VIIc, through 6,2 and 6,1 hydride shifts, will result in the formation of equal amounts of *exo*-I-OAc-3-^{14}C, *exo*-I-OAc-5-^{14}C, and *exo*-I-OAc-7-^{14}C. 3,2 hydride shift together with equilibration of VIIa–c will give rise to a complete equivalence of all carbon positions, which is responsible for the observed presence of some of the label at C-1,4. The optimum combination of these processes, however, will still leave an excess of ^{14}C activity at C-2,3. This observation suggests that there is a novel process which leads to products with a nonequivalent distribution of the tracer at C-3 and at C-7, equivalence of C-3 and C-7 being required by Wagner–Meerwein types of intermediates. To account for this finding, a concerted rearrangement involving hydride shift and reaction with solvent is tentatively proposed. This may be depicted for acetolysis by VIIIa or VIIIb, which will result in the formation of *exo*-I-OAc-3-^{14}C. The estimated contributions of the four processes of (1) complete equivalence of all carbons, (2) reaction with VIIa, (3) reaction with VIIb $\leftrightarrows$ VIIa $\leftrightarrows$ VIIc, and (4) concerted rearrangement and the calculated ^{14}C distributions are shown in Table II. The calculated values are in good agreement with the experimental results given in Table I.

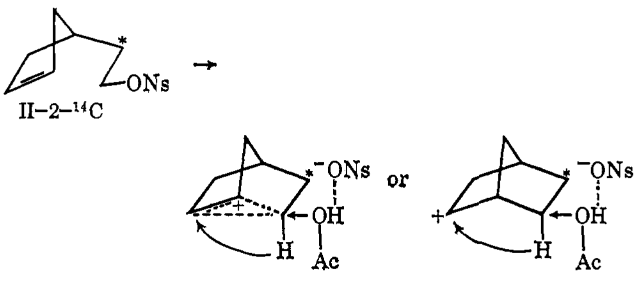
VIIa



VIIb



VIIc



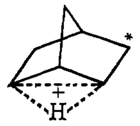
II-2-^{14}C

or

VIIIa

VIIIb

An alternative interpretation of the observed ^{14}C distributions is, however, possible. The nonequivalent distribution of the label at C-3 and C-7 could be accommodated if products were to arise from edge-protonated nortricyclene IX. Ion VIIa may rearrange to VIIb *via* IX.[8,9] Products from VIIa, IX, and VIIb, respectively, would have the label at C-5, at C-3, C-5, and at C-3, C-7. If contributions from the set of alternative processes of (1) complete equivalence of all carbons, (2) reaction with VIIa, (3′) reaction with IX, 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 II would also be obtained.



IX

A possible differentiation between processes 1, 2, 3, and 4 and 1, 2, 3′, and 4′ may be considered. The isotopic rearrangements in the norbornyl cation generated by the σ route[2,7] could be explained by involving reactions with ions analogous to VIIa and VIIb $\leftrightarrows$ VIIa $\leftrightarrows$ VIIc (processes 2 and 3), but not by reactions with ions analogous to VIIa, IX, and VIIb (processes 2, 3′, and 4′). Moreover, in their studies on the stereochemistry of 6,2 hydride shifts, Berson and Grubb[10] showed that the 2-carboxy-3-methyl-5-norbornyl cation with a deuterium label at C-3 eventually gave a lactone product with the deuterium exclusively at C-2. Following the mechanistic scheme proposed,[10] if 6,2 hydride shifts were to proceed through ions analogous to IX which could give rise to final product, the deuterium label would have been distributed between C-2 and C-6, not exclusively at C-2. Thus it appears that IX may be a transition state for the rearrangement of VIIa to VIIb, but the solvolysis product is not formed directly from IX. If processes 1, 2, 3′, and 4′ were obtained in the solvolyses of II-2-^{14}C, the contribution from reaction with VIIa increases and that from reaction with IX decreases as the solvent is changed from HOAc to HCOOH. There is no apparent explanation for such behavior. If processes 1, 2, 3, and 4 were operative, the higher contribution of the concerted rearrange-

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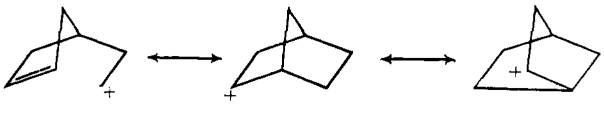
[9] S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, **74**, 1154 (1952); A. Colter, E. C. Friedrich, N. J. Holness, and S. Winstein, *ibid.*, **87**, 378 (1965).

[10] J. A. Berson and P. W. Grubb, *ibid.*, **87**, 4016 (1965).

ment (process 4) in HOAc than in HCOOH would be consistent with the more nucleophilic nature of HOAc. On these grounds, processes 1, 2, 3, and 4 may be preferable to 1, 2, 3′, and 4′.

The present results indicate that differences in the extents of isotopic rearrangements do exist in the σ and π routes to the norbornyl cation. Factors that could contribute to these differences may include the fact that the leaving groups were not the same and that unlike the earlier work,[2,7] no acetate or formate ions were added to the reaction mixtures during solvolyses of II-^{14}C. The major difference, however, is the possible involvement of the process of concerted rearrangement depicted by VIIIa or VIIIb. Such a process, if proven valid on further experimentation, could be the result of a greater contribution of Xa to the hybrid ion Xa–c produced by the π route.[11] It may also be suggested that the concerted rearrangement occurs following the formation of the Wagner–Meerwein intermediate. Since only minor secondary kinetic isotope effects were observed in the solvolyses of II-1,1-d_2[6], the hydride shift in the concerted rearrangement likely does not take place in a slow step competitive with the formation of VIIa.


Xa Xb Xc

Experimental Section

2-(Δ^3-Cyclopentenyl)-2-^{14}C-ethyl *p*-Nitrobenzenesulfonate (II-2-^{14}C). This compound was prepared from diethyl 2-^{14}C-malonate and 4-bromocyclopentene by the procedures analogous to those used in the preparation of II-1,1-d_2.[6]

Solvolytic Reactions. A solution of 3.0 g (0.01 mole) of II-2-^{14}C in 30 ml of HOAc or in 50 ml of HCOOH was heated in a water bath at 60° for 30 hr. The resulting material was extracted and worked up to give *exo*-I-OH-^{14}C in the manner described in the preceding paper.[2] The over-all yields of the alcohol were about 50 and 45%, respectively, for acetolysis and formolysis.

Degradation of *exo*-I-OH-^{14}C. Each sample of *exo*-I-OH-^{14}C was degraded to *cis*-cyclopentane-1,3-dicarboxylic acid (III), to *cis*-cyclopentane-1,3-diamine (IV), to succinic acid (V), to ethylenediamine (VI) by methods already described,[2,7] with the exception that the conversion of V to VI was effected by the Schmidt reaction instead of using the Curtius reaction.[7] The amines IV and VI were converted to their respective dibenzamides. The derivative from IV melted at 212-214° (lit.[7] mp 213-215°). *Anal.* Calcd for $C_{19}H_{20}O_2N_2$: C, 74.00; H, 6.54; N, 9.09. Found: C, 74.22; H, 6.48; N, 9.02. The dibenzamide of VI melted at 248-249° (lit.[12] mp 249°). *Anal.* Calcd for $C_{16}H_{16}O_2N_2$: N, 10.44. Found: N, 10.46.

Samples of the acids III and V and the dibenzamides of IV and VI were repeatedly recrystallized until their specific activities were constant. All calculations of isotopic rearrangements were based on the activities of these purified samples.

Acknowledgment. We wish to express our sincere appreciation to Professors P. D. Bartlett and P. von R. Schleyer for valuable comments and constructive criticisms on the work reported in this and the preceding papers.

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(11) P. von R. Schleyer, M. M. Donaldson, and W. E. Watts, *J. Am. Chem. Soc.*, **87**, 375 (1965), have obtained kinetic evidence suggesting that contribution of Xa to the hybrid ion from the σ route may be very small. In a private communication, Professor Schleyer also pointed out that in going from II to VIII, the positive charge develops far from the position of the anion. This charge separation can be reduced by the concerted hydride shift and this may be supplying the driving force for process 4.

(12) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd ed, John Wiley and Sons, Inc., New York, N. Y., 1948, p 234.

Pyrolysis and Mass Spectrum of Dibenzothiophene 5,5-Dioxide

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Contribution from the Research Department, Amoco Chemicals Corporation, and the Research and Development Department, American Oil Company, Whiting, Indiana.

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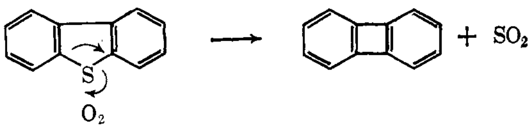
Abstract: Pyrolysis of dibenzothiophene 5,5-dioxide gave dibenzofuran, instead of the expected biphenylene. Evidently the dioxide rearranged to the sulfinate ester and eliminated SO to close the dibenzofuran ring. This decomposition closely parallels its behavior under electron impact.

Carbon–carbon bonds have been formed by elimination of sulfur dioxide from sulfones.[1] Formation of benzyne from *o*-sulfobenzoic anhydride[2] and of free aryl radicals from sulfonyl halides[3] gives additional evidence that sulfur dioxide is a good leaving group. Thermal elimination of sulfur dioxide from dibenzothiophene 5,5-dioxide could provide a direct and easy synthesis of biphenylene. To test this surmise, dibenzothiophene 5,5-dioxide was pyrolyzed at 690° under nitrogen in a Vycor tube.



All the dibenzothiophene dioxide had reacted. No biphenylene was observed. Instead, the major products, accounting for about 95% of the total, were dibenzofuran and dibenzothiophene in the ratio 6:1. The predominant reaction, therefore, involved over-all loss of SO rather than of SO_2.

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(1) M. P. Cava and A. A. Dean, *J. Am. Chem. Soc.*, 81, 4266 (1959); H. Drews, E. K. Fields, and S. Meyerson, *Chem. Ind.* (London), 1403 (1961); W. Z. Heldt, *J. Org. Chem.*, 30, 3897 (1965).

(2) S. Meyerson and E. K. Fields, *Chem. Commun.*, in press.

(3) P. J. Bain, E. J. Blackman, W. Cummings, S. A. Hughes, E. R. Lynch, E. B. McCall, and R. J. Roberts, *Proc. Chem. Soc.*, 186 (1962); E. K. Fields, *J. Chem. Soc.*, 5766 (1965).