

- compares favorably with the value of 0.871 for the relative acetolysis rates of  $\alpha, \alpha\text{-}^2\text{H}_2$ - and  $\alpha, \alpha\text{-}^1\text{H}_2\text{-}\beta$ -(3-cyclopentenyl)ethyl *p*-nitrobenzenesulfonates at 40 °C reported by Lee and Wong.<sup>54</sup>
- (54) C. C. Lee and E. C. W. Wong, *J. Am. Chem. Soc.*, **86**, 2752 (1964).
- (55) Approximately 30 half-lives for 1-OBs and  $\beta, \beta\text{-}^2\text{H}_2$ -1-OBs; 27 half-lives for  $\alpha, \alpha\text{-}^2\text{H}_2$ - and  $\alpha, \alpha, \beta, \beta\text{-}^2\text{H}_4$ -1-OBs.<sup>56</sup>
- (56) Estimated from the Winstein–Grunwald *mY* relation<sup>21,57</sup> and the solvolysis constants of 1-OBs in anhydrous acetic acid (25 °C by  $^1\text{H}$  NMR<sup>2</sup>),  $k_1 = 9.1 \times 10^{-4} \text{ s}^{-1}$ , and in 90/10 v/v dioxane/water (25 °C by UV<sup>58</sup>),  $k_1 = 2.0 \times 10^{-4} \text{ s}^{-1}$ .
- (57) E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948).
- (58) Unpublished data of S. P. Jindal.
- (59) Greater than  $10^6$  half-lives.
- (60) (a) L. F. and M. Fieser, "Reagents for Organic Synthesis", Wiley, New York, N.Y., 1968, p 142; (b) W. G. Dauben and G. H. Berezin, *J. Am. Chem. Soc.*, **85**, 468 (1963).
- (61) Brexan-2-one and numerous ketonorbornanes are known to homoenolize under sufficiently vigorous conditions:<sup>12</sup> typically when treated with po-

- tassium *tert*-butoxide in anhydrous *tert*-butyl alcohol for several hours at 185–250 °C,<sup>3</sup> but such exchange is neither expected nor observed under the much milder conditions which we have employed; cf. (a) A. Nickon and J. L. Lambert, *J. Am. Chem. Soc.*, **84**, 4604 (1962); (b) A. Nickon, J. H. Hammons, J. L. Lambert, and R. O. Williams, *ibid.*, **85**, 3713 (1963); (c) R. Howe and S. Winstein, *ibid.*, **87**, 915 (1965); (d) T. Fukunaga, *ibid.*, **87**, 916 (1965); (e) A. Nickon and J. L. Lambert *ibid.*, **88**, 1905 (1966); (f) A. Nickon, J. L. Lambert and J. E. Oliver, *ibid.*, **88**, 2787 (1966); (g) A. Nickon, J. L. Lambert, R. O. Williams, and N. H. Werstuck, *ibid.*, **88**, 3354 (1966); (h) D. H. Hunter, A. L. Johnson, J. B. Stothers, A. Nickon, J. L. Lambert, and D. F. Covey, *ibid.*, **94**, 8582 (1972).
- (62) G. A. Abad, S. P. Jindal, and T. T. Tidwell, *J. Am. Chem. Soc.*, **95**, 6326 (1973), have demonstrated that the *exo*-hydrogen at C-3 in noncamphor undergoes base-catalyzed exchange about 680 times as rapidly as the *endo*.
- (63) Approximately 6 half-lives for the starting brosylate  $\alpha, \alpha\text{-}^2\text{H}_2$ -1-OBs; approximately 0.1 half-life for the returned *exo*-2-brendyl brosylate,  $^2\text{H}_2$ -3-OBs.

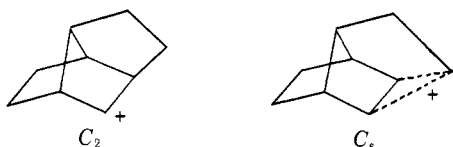
## Formolysis and Acetolysis of $\alpha\text{-}^{13}\text{C}\text{-}\beta$ -(*syn*-7-Norbornenyl)ethyl *p*-Bromobenzenesulfonate. $\pi$ -Route Generated 2-Brexyl Cation, a Nonclassical Norbornyl Type<sup>1</sup>

Robert S. Bly,\* Ruta K. Bly,\* John B. Hamilton, John N. C. Hsu, and Patricia K. Lillis

Contribution from the Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208. Received August 21, 1975

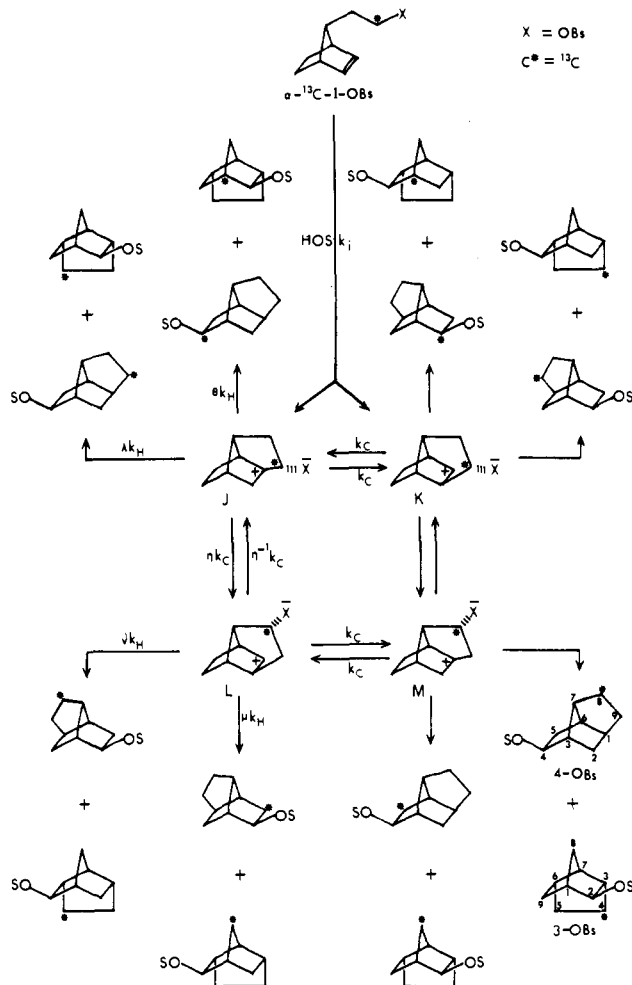
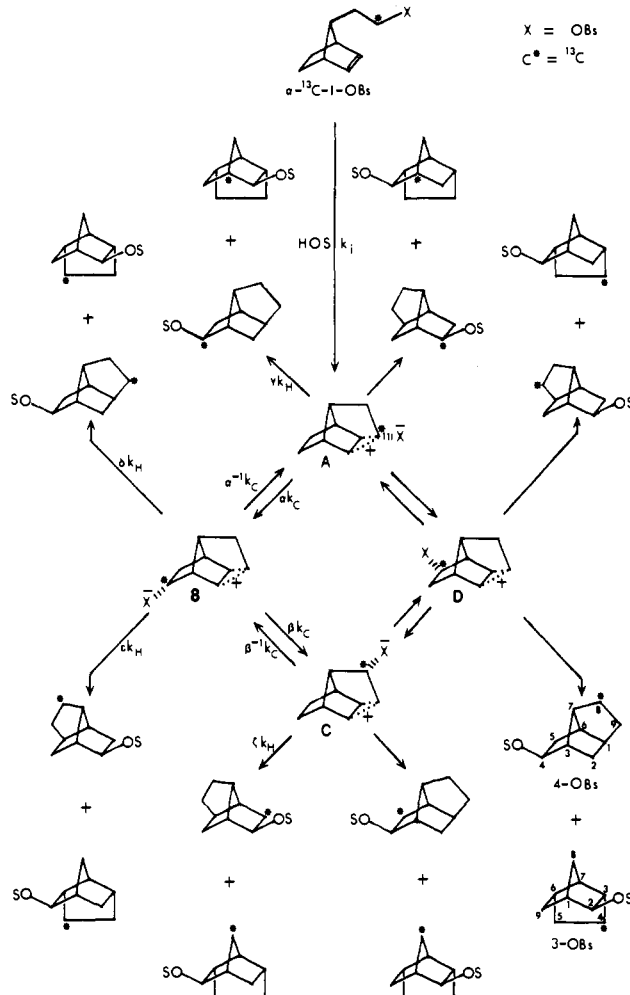
**Abstract:** The solvolysis of  $\alpha\text{-}^{13}\text{C}\text{-}\beta$ -(*syn*-7-norbornenyl)ethyl brosylate in buffered solutions at 25 °C produces mixtures of *exo*-2-brendyl and *exo*-4-brexyl derivatives specifically labeled with carbon-13. Analysis by quantitative FT  $^{13}\text{C}\{^1\text{H}\}$  NMR reveals the following carbon-13 distributions; 2-brendyl acetate: C-1 (79%), C-4 (6%), C-5 (8%), C-8 (7%); 4-brexyl acetate: C-4 (77%), C-5 (8%), C-8 (6%), C-9 (8%); 2-brendyl formate: C-1 (58%), C-4 (13%), C-5 (14%), C-8 (15%); 4-brexyl formate: C-4 (59%), C-5 (15%), C-8 (12%), C-9 (14%). Formolysis of returned, carbon-13 labeled *exo*-2-brendyl brosylate, isolated from the acetolysis of  $\alpha\text{-}^{13}\text{C}\text{-}\beta$ -(*syn*-7-norbornenyl)ethyl brosylate, produces *exo*-2-brendyl and *exo*-4-brexyl formates specifically labeled with carbon-13 as follows: 2-brendyl: C-1 (77%), C-4 (6%), C-5 (9%), C-8 (8%); 4-brexyl: C-4 (79%), C-5 (7%), C-8 (6%), C-9 (8%). These results confirm previous conclusions based upon deuterium scrambling studies that  $\pi$ -route generated 2-brexyl cations undergo at least one Wagner–Meerwein automerization prior to an irreversible hydrogen shift, that these carbon and hydrogen shifts occur in the ion pair, and that they are influenced by the counterion. Kinetic models suggest that the  $\pi$ -route generated 2-brexyl cations may possess  $C_s$  symmetry and therefore be charge delocalized.

In the preceding paper<sup>2a</sup> we reported the use of deuterium labeling to demonstrate that the solvolysis of  $\beta$ -(*syn*-7-norbornenyl)ethyl brosylate (1-OBs) generates a 2-brexyl cation which can undergo at least one Wagner–Meerwein automerization prior to product formation. By the formolysis of returned 2-brendyl brosylate ( $^2\text{H}_2$ -3-OBs) isolated from the acetolysis of  $\alpha, \alpha\text{-}^2\text{H}_2$ -1-OBs we were further able to show that the product-forming hydrogen (deuterium) shifts are effectively irreversible and to infer that both they and the carbon shifts which precede them occur at the same ion pair stage. Finally, we were able to establish that the ratio of automerization to hydrogen (deuterium) shift is dependent upon the solvolysis medium, decreasing in the order: formic acid > 90% acetone–water > acetic acid. We were unable, however, to distinguish between alternate reaction paths involving 2-brexyl cations of  $C_2$  or  $C_s$  symmetry; cf. Schemes IX and X, respec-



tively, in the preceding paper.<sup>2a</sup> This distinction is important because, as illustrated, the local symmetry of the intermediates is expected to reflect the electronic nature of the ions themselves. Its significance transcends the present problem, for it is relevant to the structure of  $\pi$ -route generated norbornyl cation itself.<sup>3</sup>

Kinetic models,<sup>2a,b</sup> developed to approximate the observed deuterium distributions in the *exo*-4-brexyl products from the solvolyses of  $\alpha, \alpha\text{-}^2\text{H}_2$ -,  $\beta, \beta\text{-}^2\text{H}_2$ -, and  $\alpha, \alpha, \beta, \beta\text{-}^2\text{H}_4$ -1-OBs suggest that these alternate "classical" and "nonclassical" 2-brexyl cation reaction paths could be differentiated if each of the four methylenic carbons in the starting material could be uniquely recognized in the final products.<sup>2a,c</sup> Since our method of deuterium assay does not discriminate either between the C-4 and C-5 positions of the *exo*-2-brendyl or the C-8 and C-9 positions of the *exo*-4-brexyl products, we decided to reexamine the solvolyses using a carbon-13 label instead; cf. Schemes I and II. We report here the preparation of  $\alpha\text{-}^{13}\text{C}\text{-}\beta$ -(*syn*-7-norbornenyl)ethyl brosylate ( $\alpha\text{-}^{13}\text{C}\text{-}1\text{-OBs}$ ) and the analysis of its C-13 labeled brendyl and brexyl solvolysis products by Fourier transform,  $^{13}\text{C}$  nuclear magnetic resonance (FT  $^{13}\text{C}$  NMR).

Scheme I. "C<sub>2</sub>" 2-Brexyl Initial Ion FormulationScheme II. "C<sub>3</sub>" 2-Brexyl Initial Ion Formulation

## Methods and Results

**Synthesis and Solvolyses.** The desired brosylate,  $\alpha$ - ${}^{13}\text{C}$ -1-OBs, was prepared from *syn*-7-norbornenylcarbonyl brosylate (6-OBs)<sup>4</sup> and  ${}^{13}\text{C}$ -enriched sodium cyanide<sup>5</sup> in the manner detailed previously for the nonenriched material, 1-OBs.<sup>2a</sup> Solvolyses were conducted at 25 °C in buffered, anhydrous solutions of acetic and formic acids for greater than 10 half-lives.<sup>2a</sup> The  ${}^{13}\text{C}$ -containing *exo*-2-brendyl ( ${}^{13}\text{C}$ -3-OS) and *exo*-4-brexyl ( ${}^{13}\text{C}$ -4-OS) products were isolated and separated as before.<sup>2a</sup>

**Product Analysis by FT  ${}^{13}\text{C}$  NMR. Carbon-13 Spectral Assignments in the Starting Material and Products.** The natural abundance FT  ${}^{13}\text{C}$  NMR spectra, recorded as detailed in the Experimental Section, of  $\beta$ -(*syn*-7-norbornenyl)ethanol (1-OH), of *exo*-2-brendyl (3-) and *exo*-4-brexyl (4-) acetates (-OAc) and formates (-OCOH), obtained from the solvolyses of 1-OBs, and of their reduction products *exo*-2-brendanol (3-OH) and *exo*-4-brexanol (4-OH) are recorded in Table I. Included for comparison are spectra of *exo*-2-norbornyl formate<sup>6</sup> (12-OCOH), *exo*-2-norborneol (12-OH),<sup>6</sup> and *syn*-7-methylnorbornene (13).<sup>6</sup> Individual peak assignments were made as follows.

**Brendyl Derivatives.** In the spectrum of the brendyl formate (3-OCOH, Figure 1) the resonances at  $\delta_c$ <sup>7</sup> 160.0 and 86.1 ppm are assigned to the carbonyl and functionalized carbon (C-2), respectively, on the basis of their large chemical shifts.<sup>8</sup> (The resonance of the functionalized position in the spectrum of *exo*-2-brendanol (3-OH) appears at 87.7 ppm.) In accord with the expected reaction course developed to accommodate the

solvolyses of  $\alpha$ , $\alpha$ - ${}^2\text{H}_2$ -1-OBs<sup>2a</sup> (cf. Schemes I and II), formolysis of  $\alpha$ - ${}^{13}\text{C}$ -1-OBs produces a  ${}^{13}\text{C}$ -enriched *exo*-2-brendyl formate ( ${}^{13}\text{C}$ -3-OCOH) whose proton-decoupled ( ${}^{13}\text{C}\{\text{H}\}$ )<sup>8</sup> spectrum (Figure 1) exhibits four greatly enhanced resonances (a doublet and three triplets after off-resonance decoupling, cf. Table I). The only triplet in the spectrum of the nonenriched formate which is *not* enhanced is that at  $\delta_c$  34.9 ppm. This signal is therefore ascribed to the methylene carbon, C-9. Of the isotopically enriched resonances, the doublet at  $\delta_c$  40.8 is attributed to C-1 as it is the only methine carbon expected to exhibit an enhanced absorption in the  ${}^{13}\text{C}$ -labeled *exo*-2-brendyl formate ( ${}^{13}\text{C}$ -3-OCOH), cf. Schemes I and II.

The only resonances that are more shielded in norbornyl alcohol (12-OH) than in norbornyl formate (12-OCOH) are due to the functionalized (C-2) and methano-bridge (C-7) carbons, respectively.<sup>6</sup> The conversion of brendyl formate (3-OCOH) to *exo*-2-brendanol (3-OH) causes similar upfield shifts (" $\Delta$  values") in the resonances at  $\delta_c$  78.0 (C-2) and 36.5 ppm. The latter, by analogy with the norbornyl case, is attributed to the methano-bridge carbon, C-8; cf. Table I. This assignment is supported by the  ${}^{13}\text{C}\{\text{H}\}$  spectrum in natural abundance of  ${}^2\text{H}_2$ -3-OAc isolated from the acetolysis of  $\beta$ , $\beta$ - ${}^2\text{H}_2$ -1-OBs and having therefore  $\sim$ 70% of the *gem*-di-deuterio label at the C-8 position.<sup>2a,d</sup> The  ${}^{13}\text{C}\{\text{H}\}$  NMR of this latter material, in contrast to that of unlabeled 2-brendyl acetate (3-OAc), which exhibits a sharp singlet at  $\delta_c$  36.7 (Table I), shows a signal of greatly diminished intensity at this frequency. We attribute this decrease in intensity to the two nonequivalent deuteriums at C-8 which, by splitting the  ${}^{13}\text{C}$ -8 resonance into a multiplet, shifting it upfield slightly and

Table I. Carbon-13 NMR Spectra of Brendyl, Brexyl, and Norbornenyl Derivatives<sup>a</sup>

Compd	Resonant nucleus												
	a	b	c	d	e	f	g	h	i	>C=O	α	β	-CH=
3-OAc <sup>b</sup>	41.0	86.5	49.9	46.9	38.5	35.2	36.7*	29.4*	32.6*				
3-OCOH <sup>b</sup>	40.8* (d)	86.1 (d)	49.6 (d)	46.8 (d)	38.3 (d)	34.9 (t)	36.5* (t)	29.1* (t)	32.4* (t)	160.0 (d)			
3-OH <sup>b,c</sup>	43.7	84.7	51.8	46.9	38.5	35.3	36.2	29.7	32.8				
	Δ <sup>d</sup>	1.4	-2.2	-0.1	-0.2	-0.4	0.3	-0.6	-0.4				
4-OAc <sup>b</sup>	45.4	78.4*	33.2*	45.4	39.4	28.5	44.1	22.6*	32.9*				
4-OCOH <sup>b</sup>	45.8 (d)	78.0* (d)	[33.1* (t)]	45.3 (d)	39.3 (d)	28.3 (t)	44.1 (d)	22.6* (t)	[32.9* (t)]	160.0 (d)			
4-OH <sup>b,c</sup>	48.8	76.0	36.0	45.4	39.5	29.0	43.5	22.9	33.2				
	Δ <sup>d</sup>	-3.0	[-2.9]	-0.1	-0.2	-0.7	0.6	-0.3	[-0.3]				
12-OCOH <sup>b</sup>	41.9	77.0	39.7	35.8	28.3	24.4	35.4				30.8 (t)	62.5* <sup>f</sup> (t)	132.7 (d)
12-OH <sup>b,e</sup>	44.5	74.4	42.4	35.8	28.8	24.9	34.6				12.5		132.4
	Δ <sup>d</sup>	-3.6	-2.7	0.0	-0.5	-0.5	0.8						
1-OH <sup>b</sup>				45.9 (d)	25.8 (t)		57.1 (d)						
13 <sup>c</sup>				47.8	25.9		54.7						

<sup>a</sup> Chemical shifts are expressed in ppm downfield from Me<sub>4</sub>Si; C<sub>6</sub>D<sub>6</sub> = 128.0 ppm; multiplicities (d = doublet, t = triplet) are shown in parentheses, uncertain assignments are enclosed in brackets and asterisks indicate enhanced signals in the isotopically enriched sample. <sup>b</sup> This work. <sup>c</sup> Multiplicities identical with those of the formate. <sup>d</sup> Chemical shift difference between formate and alcohol; positive sign indicates an upfield shift. <sup>e</sup> Reference 6. <sup>f</sup> Estimated to contain ~90% <sup>13</sup>C at this position.<sup>5</sup>

canceling the NOE,<sup>8c</sup> render the <sup>2</sup>H<sub>2</sub><sup>13</sup>C-8 signal indistinguishable from the background noise in dilute solution.

Of the two remaining <sup>13</sup>C-enriched triplets in <sup>13</sup>C-3-OCOH, (δ<sub>c</sub> 34.4 and 29.1), we ascribe the former to C-4 and the latter to C-5 by analogy with the relative chemical shifts of the C-5 and C-6 positions, respectively, in norbornyl formate (**12-OCOH**).<sup>6,9</sup>

The nonenhanced doublets, δ<sub>c</sub> 49.6, 46.8, and 38.3 ppm, respectively, in the FT <sup>13</sup>C NMR of <sup>13</sup>C-3-OCOH have been tentatively assigned to C-3, C-7, and C-6 by comparison of their relative chemical shifts and "Δ values" with those of the equivalent norbornyl carbons, C-3, C-4, and C-5; cf. Table I. The <sup>13</sup>C resonances of *exo*-2-brendyl acetate (**3-OAc**) were assigned by analogy with those of the formate, **3-OCOH**; cf. Table I.

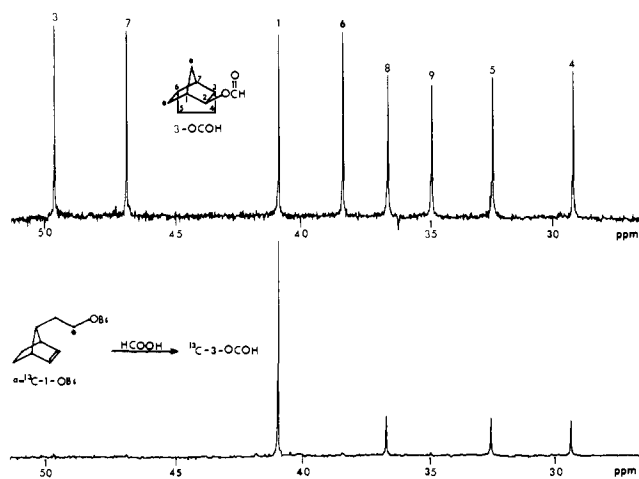
**Brexyl Derivatives.** The deshielded signals at δ<sub>c</sub> 160.0 and 78.0 ppm are assigned, respectively, to the carbonyl and functionalized position, C-4, as before. The only methylene carbon which is not expected to show <sup>13</sup>C-enrichment in the labeled product, <sup>13</sup>C-4-OCOH (Schemes I and II), is C-2; the resonance at 28.3 ppm—the only nonenhanced triplet—is assigned to it. Of the three enhanced triplets in the spectrum of <sup>13</sup>C-4-OCOH, we attribute the most deshielded, δ<sub>c</sub> 33.1, to C-5 by analogy with the equivalent C-3 position in norbornyl formate (**12-OCOH**).<sup>6</sup> The assignment is not unambiguous because of the close proximity of this signal to that of the enhanced triplet at δ<sub>c</sub> 32.9. Although the relative areas of these two overlapping resonances cannot be measured accurately, vide infra, the deshielded signal (δ<sub>c</sub> 33.1) appears slightly more intense in agreement with the expectation (Schemes I and II) that its intensity should approximate that of C-8 (δ<sub>c</sub> 36.5 ppm) in the spectrum of enriched brendyl formate (<sup>13</sup>C-3-OCOH), its generic twin. In general accord with the assignment of one of the two resonances at δ<sub>c</sub> 33.1 and 32.9 to the C-5 position is the fact that the natural abundance <sup>13</sup>C{H} NMR of <sup>2</sup>H<sub>2</sub>-4-OAc, isolated from the acetolysis of β,β-<sup>2</sup>H<sub>2</sub>-1-OBs and therefore containing 71% 5,5-<sup>2</sup>H<sub>2</sub>-4-OAc,<sup>2a,d</sup> exhibits only a single resonance in this range, vide supra. The enhanced triplets at 32.9 and 22.6 ppm are assigned to the C-9 and C-8 positions, respectively, from "γ effect" considerations which predict a lower field absorption for C-9. This assignment is in accord with the relative chemical shifts of the corresponding positions in the parent hydrocarbon brexane.<sup>10</sup>

The remaining four singlets in the FT <sup>13</sup>C{H} NMR of brexyl formate (**4-OCOH**), viz. those at δ<sub>c</sub> 45.8, 45.3, 44.1, and 39.3 ppm, are not enhanced in the labeled ester, <sup>13</sup>C-4-OCOH, and appear as doublets when decoupled off resonance. We attribute them to C-3, C-6, C-7, and C-1, respectively, by comparison of their relative chemical shifts and "Δ values" with those of the equivalent positions, C-1, C-4, C-7, and C-5, in the norbornyl derivatives **12-OCOH** and **12-OH**; cf. Table I.

The <sup>13</sup>C-chemical shift assignments for the acetate **3-OAc** follow as before from those of the formate **3-OCOH**.

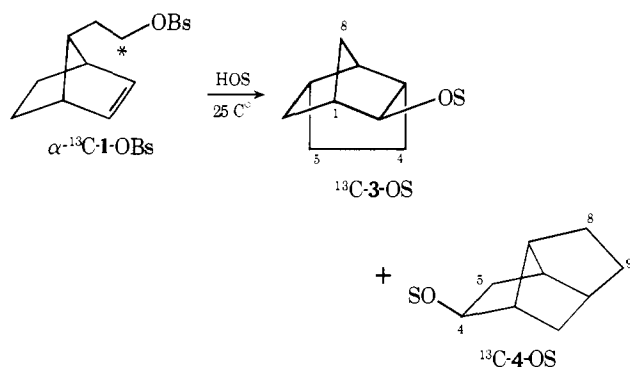
**β-(syn-7-Norbornenyl)ethanol.** The six singlets in the FT <sup>13</sup>C{H} NMR of the nonenriched alcohol **1-OH**—three triplets and three doublets in the off-resonance decoupled spectrum—are assigned as follows. The one-carbon triplet at 62.5 ppm, which appears as an enhanced singlet in the <sup>13</sup>C{H} spectrum of α-<sup>13</sup>C-**1-OH** is obviously due to C-2. The most deshielded two-carbon doublet, δ<sub>c</sub> 132.7, is assigned to C-2 and C-3 while the most shielded two-carbon doublet, δ<sub>c</sub> 45.9, is attributed to the bridgehead positions, C-1 and C-4, in accord with similar signals in *syn*-7-methylnorbornene (**13**),<sup>6</sup> Table I. The remaining one-carbon doublet (δ<sub>c</sub> 57.1) must then be due to C-7, the sole two-carbon triplet (δ<sub>c</sub> 25.8) to C-5 and C-6, and the remaining one-carbon triplet (δ<sub>c</sub> 30.8) to C-β; cf. Table I.

**Intensity Measurements on the Spectra of Enriched Solvolysis Products.** The FT <sup>13</sup>C{H} NMR spectra of pure samples

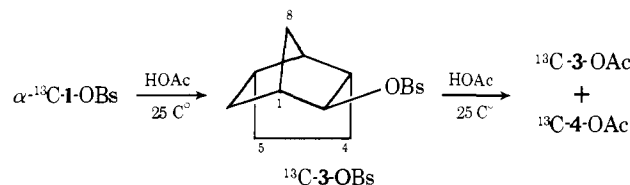


**Figure 1.** (Upper) The FT  $^{13}\text{C}\{\text{H}\}$  NMR of *exo*-2-brendyl formate (3-OCOH) from the formolysis of nonenriched  $\beta$ -(*syn*-7-norbornenyl)ethyl *p*-bromobenzenesulfonate (1-OBs). (Lower) The FT  $^{13}\text{C}\{\text{H}\}$  NMR of  $^{13}\text{C}$ -enriched *exo*-2-brendyl formate ( $^{13}\text{C}$ -3-OCOH) from the formolysis of  $\alpha$ - $^{13}\text{C}$ - $\beta$ -(*syn*-7-norbornenyl)ethyl *p*-bromobenzenesulfonate ( $\alpha$ - $^{13}\text{C}$ -1-OBs). Note that the vertical scale is different in the two spectra.

of enriched *exo*-2-brendyl ( $^{13}\text{C}$ -3), Figure 1, and *exo*-4-brexyl ( $^{13}\text{C}$ -4-) acetates (-OAc) and formates (-OCOH), isolated from the solvolysis mixtures of  $\alpha$ - $^{13}\text{C}$ -1-OBs, were determined under conditions (cf. Experimental Section) which had previously been demonstrated to provide signals of equal integrated intensity (i.e., peak areas identical to within  $\pm 1.2\%$ )<sup>11</sup> for each of the noncarbonyl positions in the natural-abundance FT  $^{13}\text{C}\{\text{H}\}$  NMR spectrum of the *exo*-2-brendyl formate (3-OCOH). The areas of the four enhanced signals, measured with an integrating polar planimeter and normalized to 100%, are equal to the fractions of the corresponding  $^{13}\text{C}$ -labeled formates present in the formolysis mixture. A comparable analysis was performed on the enriched *exo*-2-brendyl acetate ( $^{13}\text{C}$ -3-OAc) and on *exo*-4-brexyl formate ( $^{13}\text{C}$ -4-OCOH)



and acetate ( $^{13}\text{C}$ -4-OAc); cf. Table I. Finally, comparable determinations of  $^{13}\text{C}$  scrambling were made on the brendyl and brexyl products from the re-acetolysis of returned  $^{13}\text{C}$ -labeled brendyl brosylate ( $^{13}\text{C}$ -3-OBs) isolated originally from the acetolysis of  $\alpha$ - $^{13}\text{C}$ -1-OBs.



## Discussion

To test the ability of the alternate reaction mechanisms of Schemes I and II to fit our carbon-13 scrambling data, analogous kinetic models, cf. Kinetic Appendix, were developed

**Table II.** Observed and Predicted Carbon-13 Distribution in *exo*-2-Brendyl and *exo*-4-Brexyl Esters from the Solvolysis of  $\alpha$ - $^{13}\text{C}$ - $\beta$ -(*syn*-7-Norbornenyl)ethyl Brosylate at 25 °C

Solvent	Compound	Position of $^{13}\text{C}$ Label	Percent of total $^{13}\text{C}$		Obsd <sup>d</sup>	
			MCIE model <sup>a,b</sup>	MCIE model <sup>a,c</sup>		
HCOOH	<i>exo</i> -2-Brendyl	C-1	58.6	58.5	58	
		C-4 <sup>e</sup>	6.0	13.1	13	
		C-5 <sup>e</sup>	17.2	13.4	14	
		C-8	18.2	15.0	15	
	<i>exo</i> -4-Brexyl	C-4	58.6	58.5	59	
		C-5	18.2	15.0	15 <sup>f</sup>	
		C-8	6.0	13.1	12 <sup>f</sup>	
		C-9	17.2	13.4	14	
		Solvent parameter, $Q^g$		16.42	18.13	
		$k_C/k_H = r$		1.65	4.85	
Mean deviation (%)		3.4	0.4			
Maximum deviation (%)		7.0	1.1			
Standard deviation (%)		2.3	0.4			
HOAc	<i>exo</i> -2-Brendyl	C-1	79.2	78.3	79.5 (77.5)	
		C-4 <sup>e</sup>	1.4	6.8	5.5 (6.3)	
		C-5 <sup>e</sup>	9.7	7.1	7.6 (8.6)	
		C-8	9.7	7.9	7.4 (7.6)	
	<i>exo</i> -4-Brexyl	C-4	79.2	78.3	77.0 (78.7)	
		C-5	9.7	7.9	8.3 (6.7)	
		C-8	1.4	6.8	6.4 (6.4)	
		C-9	9.7	7.1	8.3 (8.2)	
	Solvent parameter, $Q^g$		28.06	30.73		
	$k_C/k_H = r$		0.794	2.32		
Mean deviation (%)		2.4	0.9			
Maximum deviation (%)		5.0	1.3			
Standard deviation (%)		1.5	0.4			

<sup>a</sup> Assumes all  $^{13}\text{C}$  isotope effects are negligible, cf. ref 20. <sup>b</sup> Cf. Scheme I and Kinetic Appendix, eq 1. <sup>c</sup> Cf. Scheme II and Kinetic Appendix, eq 2. <sup>d</sup> Values in parentheses are from the reacetolysis of returned  $^{13}\text{C}$ -2-brendyl brosylate isolated from the acetolysis of  $\alpha$ - $^{13}\text{C}$ -1-OBs at 25 °C; cf. ref 2a,g. <sup>e</sup> Footnote 9. <sup>f</sup> Poorly resolved, see text. <sup>g</sup> Cf. ref 2a,b.

and optimized in the manner described previously.<sup>2a,b</sup> From the correlations in Table II it is evident that the multiple counterion effect (MCIE), classical 2-brexyl cation mechanism (Scheme I) with its counterion perturbation factors proportioned as detailed earlier,<sup>2a,b</sup> cannot reconcile our carbon-13 results. The MCIE, nonclassical mechanism (Scheme II) does so quite precisely.

Does it follow then that  $\pi$ -route generated 2-brexyl cations are nonclassical? A referee has pointed out that our  $^{13}\text{C}$ -labeled formolysis data—the comparable acetolysis results were not available to him—are compatible with “a large counterion effect [acting only on the hydrogen (or deuterium) shift that occurs from C- $\alpha$  in the first 2-brexyl ion pair] combined with an otherwise completely degenerate 2-brexyl ion”. His suggestion, if correct, would imply that we could not rule out classical 2-brexyl cations as intermediates in the solvolysis of  $\beta$ -(*syn*-7-norbornenyl)ethyl derivatives. We have utilized the kinetic models developed earlier (Kinetic Appendix) to examine this implication by allowing only  $\theta$  in the classical model (Scheme I) or  $\gamma$  in the nonclassical model (Scheme II) to have values other than 1.0.<sup>2a,b</sup> The ability of the resulting SCIE models to reconcile our deuterium and carbon-13 scrambling data is compared with that of our original MCIE nonclassical model (Scheme II:  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\epsilon$ , and  $\zeta \neq 1.0$ ) to do so in Table III. Since the two nonclassical cation models are able to reproduce our data only slightly better than the SCIE classical model, it is evident that a clear choice among the three cannot be made on this basis alone. If the referee's suggestion regarding the nature of the counterion effect is correct, we cannot distinguish unequivocally between classical and nonclassical 2-brexyl intermediates on the basis of our present data.

**Table III.** Comparison of the Single and Multiple Counterion Effect Models for Deuterium and Carbon-13 Scrambling Data from the Solvolysis of  $\alpha,\alpha\text{-}^2\text{H}_2$ ,  $\beta,\beta\text{-}^2\text{H}_2$ ,  $\alpha,\alpha,\beta,\beta\text{-}^2\text{H}_4$ , and  $\alpha\text{-}^{13}\text{C}$ - $\beta$ -(*syn*-7-Norbornenyl)ethyl Brosylates at 25 °C

Solvent	Starting material (1-OBs)	Formate or acetate product <sup>a</sup>	Percent of product			Obsd <sup>f</sup>
			Predicted by the			
			SCIE C <sub>2</sub> model <sup>b,c</sup>	SCIE C <sub>s</sub> model <sup>b,d</sup>	MCIE C <sub>s</sub> model <sup>b,e</sup>	
HCOOH	$\alpha,\alpha\text{-}^2\text{H}_2$	2,4- <sup>2</sup> H <sub>2</sub> -4	37.4	41.7	41.4	45
		5,5- <sup>2</sup> H <sub>2</sub> -4	20.5	18.7	19.0	19
		8,8+9,9- <sup>2</sup> H <sub>2</sub> -4	42.1	39.6	39.6	36
	$\beta,\beta\text{-}^2\text{H}_2$	2,4- <sup>2</sup> H <sub>2</sub> -4	8.8	8.3	9.2	10
		5,5- <sup>2</sup> H <sub>2</sub> -4	57.2	59.9	59.1	56
		8,8+9,9- <sup>2</sup> H <sub>2</sub> -4	34.1	31.8	31.7	34
	$\alpha,\alpha,\beta,\beta\text{-}^2\text{H}_4$	2,4,5,5- <sup>2</sup> H <sub>4</sub> -4	53.3	56.3	56.1	53
		8,8,9,9- <sup>2</sup> H <sub>4</sub> -4	46.7	43.7	43.9	47
	$\alpha\text{-}^{13}\text{C}$	1- <sup>13</sup> C-3	53.2	56.8	57.1	58
		4- <sup>13</sup> C-3	15.3	14.7	14.4	13
		5- <sup>13</sup> C-3	16.1	14.7	14.7	14
		8- <sup>13</sup> C-3	15.3	13.8	13.9	15
		4- <sup>13</sup> C-4	53.2	56.8	57.1	59
		5- <sup>13</sup> C-4	15.3	13.8	13.9	15
		8- <sup>13</sup> C-4	15.3	14.7	14.4	12
		9- <sup>13</sup> C-4	16.1	14.7	14.7	14
		Mean deviation (%)	2.5	2.1	1.9	
		Maximum deviation (%)	7.6	3.9	3.6	
		Standard deviation (%)	2.4	1.2	1.2	
	Solvent parameter, <i>Q</i>	24.89 <sup>g,h</sup>	75.04 <sup>i</sup>	13.70 <sup>j</sup>		
	$k_{\text{C}}/k_{\text{H}} = r$	38.8 <sup>h</sup>	15.6	3.20		
	$k_{\text{H}}/k_{\text{D}} = l$	1.90	1.84	1.88		
	HOAc	$\alpha,\alpha\text{-}^2\text{H}_2$	2,4- <sup>2</sup> H <sub>2</sub> -4	60.3	63.8	63.3
5,5- <sup>2</sup> H <sub>2</sub> -4			12.0	10.7	11.1	11
8,8+9,9- <sup>2</sup> H <sub>2</sub> -4			27.6	25.4	25.5	23
$\beta,\beta\text{-}^2\text{H}_2$		2,4- <sup>2</sup> H <sub>2</sub> -4	5.2	4.7	5.4	8
		5,5- <sup>2</sup> H <sub>2</sub> -4	74.6	76.9	76.6	71
		8,8+9,9- <sup>2</sup> H <sub>2</sub> -4	20.1	18.4	18.0	21
$\alpha,\alpha,\beta,\beta\text{-}^2\text{H}_4$		2,4,5,5- <sup>2</sup> H <sub>4</sub> -4	70.5	72.7	72.7	70
		8,8,9,9- <sup>2</sup> H <sub>4</sub> -4	29.5	27.3	27.3	30
$\alpha\text{-}^{13}\text{C}$		1- <sup>13</sup> C-3	72.5	75.5	75.7	79.5
		4- <sup>13</sup> C-3	8.3	8.6	8.3	5.5
		5- <sup>13</sup> C-3	10.8	8.6	8.6	7.6
		8- <sup>13</sup> C-3	8.3	7.2	7.4	7.4
		4- <sup>13</sup> C-4	72.5	75.5	75.7	77.0
		5- <sup>13</sup> C-4	8.3	7.2	7.4	8.3
		8- <sup>13</sup> C-4	8.3	8.6	8.3	6.4
		9- <sup>13</sup> C-4	10.8	8.6	8.6	8.3
		Mean deviation (%)	2.7	2.2	2.1	
		Maximum deviation (%)	7.0	5.9	5.6	
		Standard deviation (%)	2.0	1.5	1.5	
Solvent parameter, <i>Q</i>		39.70 <sup>k,l</sup>	110.0 <sup>m</sup>	23.51 <sup>n</sup>		
$k_{\text{C}}/k_{\text{H}} = r$		6.75 <sup>l</sup>	5.13	1.57		
$k_{\text{H}}/k_{\text{D}} = l$		1.73	1.74	1.80		

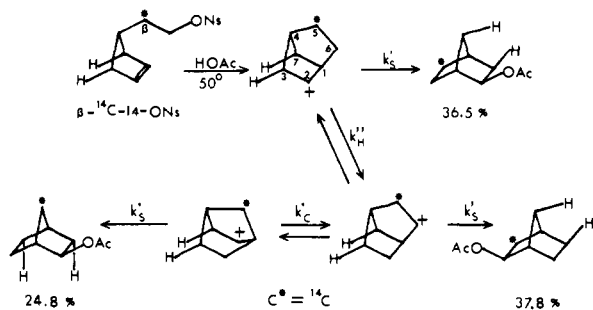
<sup>a</sup> *exo*-2-Brendyl (3); *exo*-4-brexyl (4). <sup>b</sup> Assumes all <sup>13</sup>C and secondary <sup>2</sup>H isotope effects are negligible. <sup>c</sup> Scheme I;  $\eta$ ,  $\lambda$ ,  $\mu$ , and  $\nu \equiv 1.0$ , cf ref 2a,g. <sup>d</sup> Scheme II;  $\alpha$ ,  $\beta$ ,  $\delta$ ,  $\epsilon$ , and  $\zeta \equiv 1.0$ ; cf ref 2a,b. <sup>e</sup>  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ ,  $\epsilon$ , and  $\zeta \neq 1.0$ . <sup>f</sup> For deuterium data, see ref 2a, for carbon-13 data see Table II. <sup>g</sup>  $\theta = 3.29$ . <sup>h</sup> For best fit of carbon-13 data only,  $Q = 29.86$ ,  $\theta = 4.18$ , and  $r = 113$ . <sup>i</sup>  $\gamma = 3.25$ . <sup>j</sup>  $\alpha = 0.729$ ,  $\beta = 1.12$ ,  $\gamma = 1.24$ ,  $\delta = 1.00$ ,  $\epsilon = 0.979$ , and  $\zeta = 1.02$ . <sup>k</sup>  $\theta = 6.70$ . <sup>l</sup> For best fit of carbon-13 data only,  $Q = 47.73$ ,  $\theta = 9.84$ , and  $r = 13.1$ . <sup>m</sup>  $\gamma = 5.62$ . <sup>n</sup>  $\alpha = 0.581$ ,  $\beta = 1.22$ ,  $\gamma = 1.45$ ,  $\delta = 1.00$ ,  $\epsilon = 0.964$ , and  $\zeta = 1.03$ .

Is it reasonable to assume a counterion effect which acts on a single hydrogen (or deuterium) shift? We think not. We have demonstrated through the formolysis of returned 2-brendyl brosylate (<sup>2</sup>H<sub>2</sub>-3-OBs) isolated originally from the acetolysis of  $\alpha,\alpha\text{-}^2\text{H}_2\text{-1-OBs}$  that the hydrogen (deuterium) shifts are effectively irreversible under solvolysis conditions.<sup>2a</sup> Our present carbon-13 scrambling studies (Table II) show clearly that both the acetates and the returned brosylate from the acetolysis of  $\alpha\text{-}^{13}\text{C-1-OBs}$  have essentially identical carbon-13 distributions. This finding confirms our previous inference that *all carbon and hydrogen or deuterium shifts occur in the same ion pair*.<sup>2a,g</sup> It is, therefore, unreasonable to suggest that a gegenion which is present throughout the entire label-scrambling process strongly affects the rate of a single hydrogen or deuterium shift without influencing that of any other shift.

A second reason for believing the SCIE classical model to be inadequate is that it appears to lead to inconsistent predic-

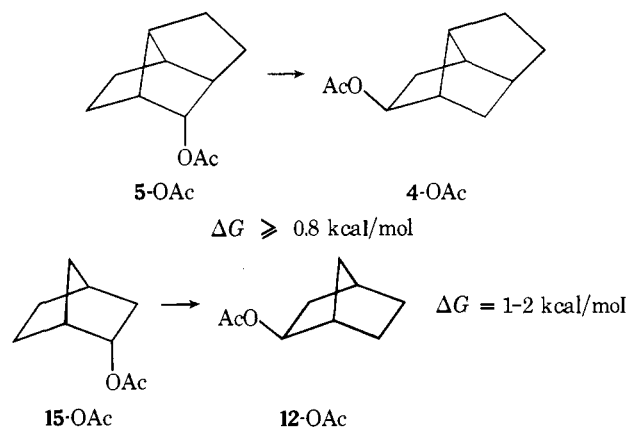
tions when extended to  $\pi$ -route generated 2-norbornyl cations. Collins and Lietzke<sup>12</sup> have pointed out that the <sup>14</sup>C scrambling observed by Lee and Lam<sup>3b</sup> in the acetolysis of  $\beta\text{-}^{14}\text{C-}\beta\text{-(3-cyclopentenyl)ethyl } p\text{-nitrobenzenesulfonate}$  ( $\beta\text{-}^{14}\text{C-14-ONs}$ ) may be accommodated by a solvolytic mechanism which involves only classical norbornyl cations, Scheme III, where  $k_{\text{C}}'/k_{\text{H}}'' = 0.022$  and  $k_{\text{C}}'/k_{\text{C}}' = 0.33$ . If the SCIE classical 2-brexyl cation model (Scheme I;  $\eta$ ,  $\lambda$ ,  $\mu$ , and  $\nu = 1.0$ ) is valid for the acetolysis of a  $\beta\text{-(syn-7-norbornenyl)ethyl brosylate}$  (1-OBs) it must also apply to the acetolysis of 14-ONs since the two processes are comparable even to the position of the gegenion in the initial ion pair.<sup>3e,f,13</sup> If the migration of a hydrogen from C- $\alpha$  is accelerated by the counterion in the 2-brexyl ion pair (Scheme I) it must be similarly accelerated in the 2-norbornyl ion pair (Scheme III). To rationalize our carbon-13 scrambling data from the acetolysis of  $\alpha\text{-}^{13}\text{C-1-OBs}$  the single counterion effect, classical 2-brexyl cation model

Scheme III. Classical 2-Norbornyl Cation Model for the Acetolysis of  $\beta$ - $^{14}\text{C}$ - $\beta$ -(3-Cyclopentenyl)ethyl *p*-Nitrobenzenesulfonate

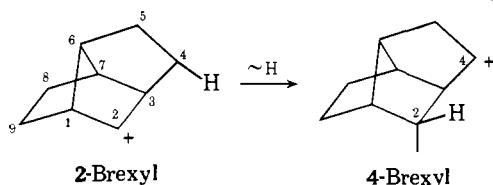


requires a counterion perturbation factor,  $\theta$ , of 9.8 and an “unperturbed”  $k_C$  to  $k_H$  ratio of 13.1 (cf. Table II, footnote 1). When a similar counterion-perturbation factor is assumed in the classical 2-norbornyl cation model (Scheme III) the “unperturbed”  $k_S'$  to  $k_H'$  ratio becomes  $0.022 \times 9.8$  or 0.22. Thus, the comparable, “unperturbed”  $k_C'$  to  $k_H'$  ratio of the Collins-Lietzke model would be 0.22/0.33 or 0.67. Since Wagner-Meerwein automerizations of  $\pi$ -route generated classical 2-brexyl and 2-norbornyl cations should occur at comparable rates under comparable conditions,  $k_C$  is expected to approximate  $k_C'$ . Thus, the uniform application of the SCIE model to these two systems suggests that the rate of 2,6-hydrogen shift in a  $\pi$ -route generated 2-norbornyl cation (Scheme III) exceeds that of the comparable shift in a classical 2-brexyl cation (Scheme I) by a factor of 13/0.67 or  $\sim 19$  times.

Equilibration studies have led Swartz to estimate that 2-brexyl acetate (**5-OAc**) is at least 0.8 kcal/mol less stable at 25 °C ( $\Delta G$ ) than *exo*-4-brexyl acetate (**4-OAc**).<sup>14a</sup> Since *endo*-2-norbornyl acetate (**15-OAc**) is about 1–2 kcal/mol less stable than its *exo* isomer (**12-OAc**),<sup>15</sup> it is likely that the difference in stability of **4-** and **5-OAc** reflects only the added



strain of the *endo*-like acetoxy group in **5-OAc** and that the 2-brexyl cation itself is not more stable than the 4-brexyl.<sup>16</sup> Thus, there is no a priori reason to expect that an “unperturbed” 4,2-hydrogen shift in a  $\pi$ -route generated, classical 2-brexyl cation would be any less rapid than the comparable



6,2-hydrogen shift in a  $\pi$ -route generated, classical 2-norbornyl cation (Scheme III). To the extent that 4-brexyl cation is charge delocalized,<sup>2a,h</sup> the 4,2-shift should be the more rapid since Swartz estimates that 2-brexyl cation is  $\sim 2.3$  kcal/mol more stable than 4-brexyl.<sup>14a</sup> Thus, the single counterion effect model rigorously applied to  $\pi$ -route generated 2-brexyl and

2-norbornyl systems appears to give inconsistent predictions of the relative rates of comparable carbon and hydrogen shifts.

A final, though less compelling, reason to prefer the multiple counterion effect model is that it reflects the expectation that the “unperturbed”  $k_C$  to  $k_H$  ratio should vary little from one solvent to another. Since the initial 2-brexyl cations, be they classical or nonclassical, are effectively “captured” by an internal nucleophile, irreversibly migrating hydrogen (or deuterium), the major impact of the solvent itself upon the brexyl and the brexyl product distributions should be through its solvating ability rather than its nucleophilicity. The MCIE model reflects this better than does the SCIE model; cf. Table III.

It is our contention that the carbon-13 scrambling data reported here argue strongly for the formation of charge-delocalized 2-brexyl cations of  $C_s$  symmetry during the solvolysis of  $\beta$ -(*syn*-7-norbornenyl)ethyl derivatives. It is likely that the 2-norbornyl cations formed in the solvolyses of  $\beta$ -(3-cyclopentenyl)ethyl derivatives are also charge delocalized.<sup>3,17</sup> We emphasize that these conclusions pertain only to ions generated solvolytically via the “ $\pi$  route”—it does not follow from our data that 2-brexyl<sup>18</sup> or 2-norbornyl cations<sup>15</sup> produced via the “ $\sigma$  route” are necessarily charge delocalized.

#### Experimental Section<sup>2e,19</sup>

**1- $^{13}\text{C}$ -2-(*syn*-7-Norbornenyl)acetonitrile (1- $^{13}\text{C}$ -7)<sup>2f</sup>** was prepared by heating under reflux 3.00 g (8.7 mmol) of *syn*-7-norbornenylcarbonyl *p*-bromobenzenesulfonate (**6-OBs**)<sup>4</sup> with 0.44 g (8.7 mmol) of  $^{13}\text{C}$ -enriched sodium cyanide<sup>5</sup> in 100 ml of *N,N*-dimethylformamide for 24 h. The workup was identical with that utilized for the preparation of the nonlabeled material described previously.<sup>2a</sup> The yield of isolated product was 81%.

**$\alpha$ - $^{13}\text{C}$ - $\beta$ -(*syn*-7-Norbornenyl)ethanol ( $\alpha$ - $^{13}\text{C}$ -1-OH)** was prepared from 1- $^{13}\text{C}$ -7 in the manner described previously for 1-OH<sup>2a</sup> except that in order to conserve material the individual intermediates  $^{13}\text{C}$ -**8** and  $^{13}\text{C}$ -**9** were not isolated and distilled. The overall yield of distilled alcohol,  $\alpha$ - $^{13}\text{C}$ -1-OH, was 40%. The FT  $^{13}\text{C}\{\text{H}\}$  NMR spectrum of this material, *vide infra* and Table I, exhibited a sharp singlet at  $\delta_c$  62.5 ppm.<sup>7</sup>

**Solvolysis of  $\alpha$ - $^{13}\text{C}$ - $\beta$ -(*syn*-7-Norbornenyl)ethyl *p*-Bromobenzenesulfonate ( $\alpha$ - $^{13}\text{C}$ -1-OBs).** Solutions containing 0.020 M brosylate (prepared as described earlier from  $\alpha$ - $^{13}\text{C}$ -1-OH<sup>2a</sup>) were solvolyzed in buffered, anhydrous formic acid at 25 °C for 15 min or in buffered anhydrous acetic acid for 20 h. The pure,  $^{13}\text{C}$ -labeled brexyl and brexyl products were isolated as before.<sup>2a</sup> The volatile acetates and formates were analyzed quantitatively for carbon-13 distribution by FT  $^{13}\text{C}$  NMR as described below.

The returned, carbon-13 labeled *exo*-2-brexyl brosylate ( $^{13}\text{C}$ -**3-OBs**) recovered from the acetolysis mixture<sup>2a</sup> was subjected to reacetolysis as before,<sup>2a</sup> and the resulting carbon-13 labeled brexyl ( $^{13}\text{C}$ -**3-**) and brexyl ( $^{13}\text{C}$ -**4-**) acetates (**-OAc**) were separated and purified, and the carbon-13 distribution in each was analyzed quantitatively by FT  $^{13}\text{C}$  NMR, *vide infra*.

**$^{13}\text{C}$  Nuclear Magnetic Resonance Spectra. Chemical Shift Determinations.** The chemical shift assignments were made on the basis of spectra determined with an XL-100-15 spectrometer operating at 25 MHz in the Fourier transform mode.<sup>19</sup> Dilute solutions of the individual compounds in perdeuteriobenzene were run at probe temperature ( $\sim 35$  °C) in 5-mm tubes with the spectrometer locked on the deuterium resonance of the solvent. In all cases a flip angle of 49° was employed with an acquisition time of 0.4 s and a zero pulse delay. The spectral width was 5000 Hz;  $\sim 10^4$  transients were observed. Signal positions were measured relative to the  $^{13}\text{C}$  resonance of the solvent which was assumed to occur 128.0 ppm<sup>8</sup> downfield from that of tetramethylsilane (0.0 ppm). All  $^{13}\text{C}$  chemical shifts,  $\delta_c$ , are reported relative to tetramethylsilane.

Spectral assignments were made as described in the Results from comparisons of the chemical shifts and multiplicities of the individual nuclei in the coupled, the off-resonance decoupled and the proton-decoupled spectra of  $\beta$ -(*syn*-7-norbornenyl)ethanol (**1-OH**), *exo*-2-brexyl formate (**3-OCOH**), and *exo*-4-brexyl formate (**4-OCOH**); cf. Table I.

**Quantitative Intensity Measurements.** Although suitable for identification purposes and chemical shift assignments, the qualitative FT  $^{13}\text{C}\{\text{H}\}$  NMR spectra do not suffice for quantitative analysis. It is apparent in the proton-decoupled, natural-abundance spectra that differences in relaxation time and/or Overhauser enhancement of the individual nuclei lead to signals of unequal intensity. To circumvent this potential source of error, that portion of each spectrum necessary for the  $^{13}\text{C}$ -scrambling analysis was redetermined on a CFT-20 spectrometer<sup>19</sup> operating at 20 MHz in the Fourier transform mode. All spectra were run on 0.5 ( $^{13}\text{C}$ -enriched) to 1.0 M (natural abundance) samples of gas chromatographically pure compounds in per-deuteriobenzene solution contained in an 8-mm tube. The spectrometer was locked on the deuterium resonance of the solvent; each sample was thermostated at 10 °C throughout a run.

The proton-decoupled, natural-abundance spectrum of *exo*-2-brendyl formate (3-OCOH) was recorded at a spectral width of 500 Hz using a normal pulse sequence (decoupler on at all times) to gain maximum advantage from the Overhauser enhancements, a 90° pulse, an acquisition time of 5.0 s, and a pulse delay of 32.0 s. A total of 2391 transients were observed. A separate 180°- $\tau$ -90° pulse sequence was used to demonstrate that the 32-s pulse delay was greater than  $5T_1$  for each of the observed nuclei.<sup>20</sup> Nuclear Overhauser enhancement factors were shown to be  $2.995 \pm 0.041$  for each of the four nuclei whose intensity was of interest by use of the NOE suppressed gated decoupling technique.<sup>21</sup> To demonstrate that the natural-abundance spectrum of *exo*-2-brendyl formate (3-OCOH) recorded under these conditions does, in fact, exhibit signals of equal intensity<sup>11</sup> for each of the observed nuclei, the peak area of each expanded signal was measured with a Geotec compensating polar planimeter. All were identical to within a standard deviation of  $\pm 1.2\%$ .

The  $^{13}\text{C}$ -enriched *exo*-2-brendyl formate ( $^{13}\text{C}$ -3-OCOH) FT  $^{13}\text{C}\{\text{H}\}$  NMR spectrum was determined in a similar manner for 1075 transients using a spectral width of 500 Hz, a 90° pulse width of 17  $\mu\text{s}$ , an acquisition time of 8.192 s and a pulse delay of 29.0 s. Integrated areas<sup>11</sup> for the enriched nuclei were measured from the expanded peaks as before; cf. Tables I and II. We estimate the computed  $^{13}\text{C}$  distribution in the enriched *exo*-2-brendyl formate to be accurate to within 1.5% of the reported value (relative total peak area) for each of the four enriched positions.

The FT  $^{13}\text{C}\{\text{H}\}$  NMR of the enriched *exo*-4-brexyl formate was acquired in a similar manner using a spectral width of 2000 Hz, a 90° pulse, an acquisition time of 2.0 s, and a 33-s pulse delay. A total of 2675 transients were observed. Carbon-13 distributions were estimated as before; cf. Tables I and II. Unfortunately, because of the wider spectral width necessary to observe all the enhanced resonances, fewer data points per peak are available for analysis, and the wave forms of the extremely narrow resonances due to C-8, C-5, and C-9 (Table I) are incompletely defined or, in the case of the latter two resonances, resolved. The  $^{13}\text{C}$  distribution data for the brexyl formate is therefore somewhat less definitive and precise than that of the brendyl derivative.

Quantitative FT  $^{13}\text{C}\{\text{H}\}$  NMR spectra of the carbon-13 enriched brendyl and brexyl acetates were acquired under conditions comparable with those used for the corresponding formates. The intensity measurements in the case of  $^{13}\text{C}$ -4-OAc are slightly more precise than those of the formates since the resonances of the C-5 and C-9 positions are better resolved in the acetate; cf. Table I.

**Acknowledgment.** We are indebted to Professor Paul D. Ellis of the University of South Carolina for his considerable help with the  $^{13}\text{C}$  nuclear magnetic resonance measurements and their interpretation, to Professor J. B. Stothers, University of Western Ontario, for his willingness to disclose his own assignments of related compounds in the brendyl and brexyl series prior to their publication,<sup>24</sup> to Dr. Clair Collins of the Oak Ridge National Laboratories for his thoughtful criticism and helpful suggestions, to the University of South Carolina for making available funds for the purchase of the CFT-20 spectrometer and last, but certainly not least, to Dr. Albert P. Zens, a former graduate student in the Department of Chemistry, for his careful and painstaking measurement of many of the carbon-13 distributions reported here.

### Kinetic Appendix

If  $^{13}\text{C}$ -isotope effects are ignored,<sup>22</sup> kinetic equations to

describe the solvolysis of  $\alpha$ - $^{13}\text{C}$ -1-OBs according to the multiple-counter-ion-effect  $C_2$ - or  $C_s$ -initial 2-brexyl cation model, Schemes I and II, respectively, in terms of the  $k_C$  to  $k_H$  ratio,  $r$ , and the solvent parameter,  $Q$ , may be deduced from those derived previously for the solvolyses of  $\alpha, \alpha$ - $^2\text{H}_2$ -1-OBs<sup>2b</sup> by simply replacing each  $k_D$  by  $k_H$ . Thus, the differential equations for the MCIE  $C_2$  and  $C_s$  formulations are respectively,<sup>23</sup>

$$dJ/dt = -[(1 + \eta)k_C + (\lambda + \theta)k_H]J + k_C K + \eta^{-1}k_C L + 0.5k_i S_0 e^{-k_i t}$$

$$dK/dt = k_C J - [(1 + \eta)k_C + (\lambda + \theta)k_H]K + \eta^{-1}k_C M + 0.5k_i S_0 e^{-k_i t}$$

$$dL/dt = \eta k_C J - [(1 + \eta^{-1})k_C + (\mu + \nu)k_H]L + k_C M$$

$$dM/dt = \eta k_C K + k_C L - [(1 + \eta^{-1})k_C + (\mu + \nu)k_H]M \quad (1)$$

and

$$dA/dt = -(2\alpha k_C + 2\gamma k_H)A + \alpha^{-1}k_C B + \alpha^{-1}k_C D + K_i S_0 e^{-k_i t}$$

$$dB/dt = \alpha k_C A - [(\alpha^{-1} + \beta)k_C + (\delta + \epsilon)k_H]B + \beta^{-1}k_C C$$

$$dC/dt = \beta k_C B - (2\beta^{-1}k_C + 2\zeta k_H)C + \beta k_C D$$

$$dD/dt = \alpha k_C A + \beta^{-1}k_C C - [(\alpha^{-1} + \beta)k_C + (\delta + \epsilon)k_H]D \quad (2)$$

where the counterion perturbation factors  $\eta - \nu$  ( $C_2$ ) or  $\alpha - \zeta$  ( $C_s$ ) are defined as described previously.<sup>2b</sup> The corresponding equations for the single-counter-ion-effect  $C_2$  and  $C_s$  models are easily derived from eq 1 and 2, respectively, by setting  $\eta$ ,  $\lambda$ ,  $\mu$ , and  $\nu$  or  $\alpha$ ,  $\beta$ ,  $\delta$ ,  $\epsilon$ , and  $\zeta$  equal to 1.0.

### References and Notes

- Portions of this work have been reported at (a) the 167th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1974, Abstract ORGN 29, and (b) Meeting in Miniature of the Florida Section of the American Chemical Society, Tallahassee, May 1974, Abstract 42.
- (a) R. S. Bly, R. K. Bly, J. B. Hamilton, and S. P. Jindal, preceding paper in this issue. Note that structures common to this and the present paper are numbered similarly. (b) Footnote 34. (c) Table II. (d) Table I. (e) Footnote 36. (f) Footnote 37. (g) Footnote 13. (h) Footnote 5.
- (a) R. G. Lawton, *J. Am. Chem. Soc.*, **83**, 2399 (1961); (b) P. D. Bartlett and S. Bank, *ibid.*, **83**, 2591 (1961); (c) P. D. Bartlett, *Justus Liebig's Ann. Chem.*, **653**, 45 (1962); (d) C. C. Lee and E. W. C. Wong, *J. Am. Chem. Soc.*, **86**, 2752 (1964); *Can. J. Chem.*, **43**, 2254 (1964); (e) P. D. Bartlett, S. Bank, R. J. Crawford, and G. H. Schmidt, *J. Am. Chem. Soc.*, **87**, 1288 (1965); (f) P. D. Bartlett and G. D. Sargent, *ibid.*, **87**, 1297 (1965); (g) C. C. Lee and L. K. M. Lam, *ibid.*, **88**, 2834 (1966); (h) G. A. Olah, A. M. White, J. R. DeMember, A. Commeyras, and C. Y. Lui, *ibid.*, **92**, 4627 (1970).
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- Private communication from Professor J. B. Stothers, University of Western Ontario.
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- (23) The brackets conventionally used to denote concentration have been omitted.
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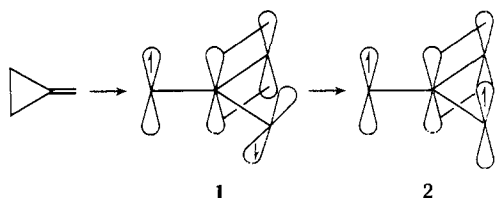
## Synthesis and Thermal Rearrangements of 3-(2'-Methylprop-1'-enylidene)tricyclo[3.2.1.0<sup>2,4</sup>]oct-6-ene

Donald H. Aue\* and Michael J. Meshishnek

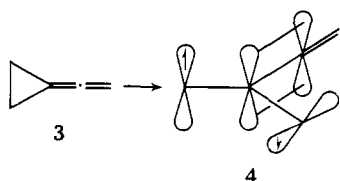
Contribution from the Department of Chemistry, University of California, Santa Barbara, California 93106. Received March 9, 1976

**Abstract:** The synthesis of the title compound **10** via a carbenoid route is reported. The thermal rearrangement of **10** in the gas phase has been studied and found to give three isomeric products, **11**, **12**, and **13**, which were characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. A kinetic study indicated that **11** and **12** are primary products and are formed in parallel first-order reactions which are not subject to catalysis. The third product, **13**, was found to be formed from **12**, in a process which is surface catalyzed. Formation of **11** is proposed to occur by a ten-electron ( $\pi_s^2 + \sigma_a^2 + \pi_a^2 + \pi_s^2 + \sigma_s^2$ ) concerted mechanism to give a divinylcyclopropane **23** which then undergoes Cope rearrangement to **11**. Formation of **12** is interpreted in terms of C-2-C-4 cleavage of **10** to a substituted trimethylenemethane, **35**, followed by addition of this diradical to the proximate double bond to give **12**. The rate of rearrangement of the related methylenecyclopropane **8b** was determined and compared with rates for other methylenecyclopropanes and alkenylidenecyclopropanes. The rates are interpreted in terms of initial formation of orthogonal trimethylenemethane diradicals in the case of unconstrained systems. Formation of near planar diradicals from **10** and **8b** is only ca. 4 kcal/mol less favorable than for the orthogonal diradicals of comparable structure.

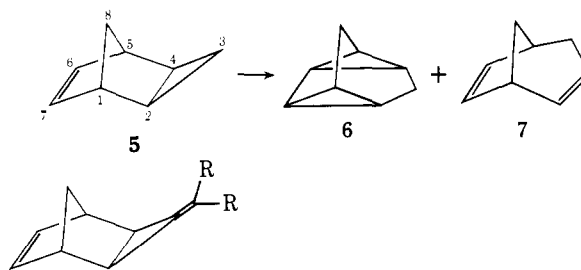
The geometry of trimethylenemethane diradicals has been the subject of considerable experimental and theoretical concern in recent years.<sup>1-5</sup> While calculations<sup>3</sup> and ESR experiments<sup>1</sup> both indicate that the ground state is a planar triplet **2**, the geometry of the singlet diradical is less clear. Some



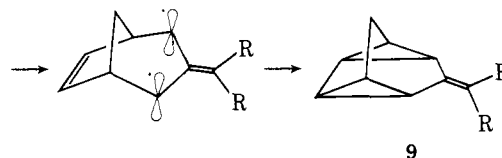
calculations indicate that the singlet prefers an orthogonal (or bisected) geometry **1** by 20-30 kcal/mol,<sup>4</sup> but more recent calculations indicate that the planar singlet may be only 3-6 kcal/mol less stable than the orthogonal singlet diradical **1**.<sup>5</sup> Gajewski's experiments on the racemization of optically active *trans*-2,3-dimethylmethylenecyclopropane indicate that the transition state leading to the planar singlet diradical is only 2 kcal/mol higher in energy than that leading to the chiral orthogonal form.<sup>6a,7</sup> Other rearrangements of methylenecyclopropanes and alkenylidenecyclopropanes (**3**) have usually been interpreted in terms of orthogonal diradicals **1** and **4**.



Cleavage of methylenecyclopropane or alkenylidenecyclopropane rings in the tricyclo[3.2.1.0<sup>2,4</sup>]oct-6-ene system (**5**)



- 8a**, R = H  
**8b**, R = CH<sub>3</sub>  
**8c**, R = (CH<sub>2</sub>)<sub>5</sub>



cannot readily give rise to orthogonal diradical intermediates because the geometric constraints at the developing radical centers force the initial diradical to be planar, as from **8**. If the ring opening in a system such as **8** must proceed through a near-planar transition state,<sup>9</sup> then the activation energy for the process should indicate the stability of such a planar diradical. These activation energies could then be correlated with those of geometrically unconstrained methylenecyclopropanes and alkenylidenecyclopropanes to indicate whether the orthogonal