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The 2-Butyl Cation in Trifluoroacetic Acid. A Hydrogen-Bridged Carbonium Ion[1a]

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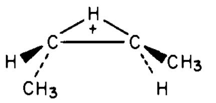
Abstract: The solvolyses of $CH_3CH_2CH(OTs)CH_3$, $CH_3CH_2CD(OTs)CD_3$ (III) and $CD_3CD_2CH(OTs)CH_3$ (XIII) have been studied in CF_3COOH and CF_3COOD. The product distributions and solvolysis rates are consistent with the intermediacy of a hydrogen-bridged 2-butyl cation. The ratio of the solvolysis rates of III to XIII is 1.1–1.2 which is consistent with anchimeric assistance by a β-H on C_3. The rate of additions of CF_3COOH to 2-butene is less than half as fast as the trifluoroacetolysis, thereby eliminating 2-butene as an intermediate in the reaction. The steady-state concentration of 2-butene is shown to be proportional to added [CF_3COONa], indicating that the trifluoroacetate anion, often used as a buffer, is a strong enough base to direct the reaction toward elimination products.

There has been considerable recent interest in the structure of simple carbocations. In particular, the possible existence of a bridging hydrogen in the ethyl cation has been the subject of several theoretical and experimental investigations. Theoretical treatments have variously favored an open or bridged ethyl cation.[2] The semiempirical and the more elaborate ab initio treatments generally favor the bridged species while simple ab initio treatments generally favor the open species.

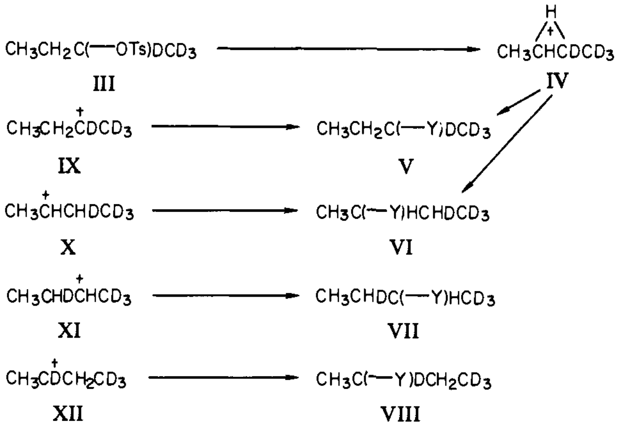
Experimental evidence is not much more conclusive. Roberts and Yancey observed only 2% rearrangement from ^{14}C-labeled ethyl cation generated by action of HNO_2 on ethylamine,[3] whereas Myhre and Evans observed up to 42% rearrangement upon generation of the 1,1-dideuterioethyl cation by action of fluorosulfuric acid on ethyl tosylate.[4] A study by Ausloos et al. has shown that the barrier for a hydride shift in the gas-phase ethyl cation must be less than 5 kcal/mol.[5] On the other hand, Jaffé and Billets have reported that $CD_3CH_2^+$ generated in an ion cyclotron resonance apparatus loses only D^+ (to form $CD_2{=}CH_2$) upon attack by base.[6]

Although the ethyl cation provides a simple model for theoretical and gas-phase studies, its relative instability greatly limits its value as a model for solution chemistry. We have, therefore, chosen the 2-butyl cation, the simplest secondary carbocation capable of symmetrical hydrogen bridging, as a model system. Semiempirical molecular orbital treatment of this ion is analogous to similar treatments of ethyl cation; 2-butyl cation is predicted to be hydrogen bridged with the two terminal methyl groups anti to each other as in I.[2i,k,7] Simple ab initio calculations (STO-3G, 4-31G) predict an open structure, while ab initio calculations that are corrected for electron correlation predict H-bridged structures.[2k] In addition, the four carbons are predicted to be coplanar, suggesting the importance of hyperconjugation of the methyls with the protonated π system.[7] Experimental evidence is again inconclusive. Acetolysis of ^{14}C-labeled 2-butyl tosylate afforded only 9% rearranged acetate[8] while proton NMR studies of 2-butyl cation in SbF_5–HSO_3F[9] and SO_2ClF–SbF_5[10] indicate a rapid interchange of the 3-hydrogen on the 2- and 3-positions. Proton–^{13}C coupling constants and ^{13}C magnetic resonance have led Olah[10] to suggest that I does not appreciably contribute to the equilibrium mixture; i.e., the scrambling is due entirely to a degenerate rearrangement involving only the open cation, II. However, recent results involving equilibrium isotope effects are now interpreted to support the bridged ion.[11]

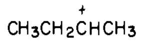


I

Scheme I



Y = trifluoroacetate



$CH_3CH_2\overset{+}{C}HCH_3$

II

Since the theoretical studies on ethyl cation do not clearly discriminate between the open and bridged ions and the experimental evidence indicates that both forms are similar in energy, it seemed reasonable that the considerable energy of solvation

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Table I. Product Distribution and Rates of Solvolysis

	products (%)[a]				$10^4k_{\text{solvolysis}}$ (±10%), M^{-1} s^{-1}		III/XIII		
tosylate	V or XV	VI or XVI	VII or XVII	VIII or XVIII	CF_3COOH	CF_3COOD	CF_3COOH	CF_3COOD	predicted[b]
III	49	45	4	2	2.91	1.68			
XIII[d]	41	35[c]	23	*c*	2.40	1.50	1.2	1.1	0.79–0.85

[a] At 37 ± 1 °C as measured by 220-MHz NMR. [b] Using values for k_H/k_D for limiting S_N1 reactions given in ref 19. [c] Total for XVI + XVIII. [d] In CF_3COOD to minimize exchange of H for D which would confuse the analysis.

Figure 1. Schematic representation of the NMR spectra of the methyl regions of the solvolysis products.

operative in solution might selectively stabilize either the bridged or the open 2-butyl cation. Trifluoroacetic acid was used as solvent in the hope that its low nucleophilicity and high ionizing power[12,13] would favor formation of the bridged cation I. A report by Schadt and Schleyer concludes that trifluoroacetic acid strongly favors aryl-assisted over solvent-assisted pathways for the solvolyses of 2-arylethyl tosylates.[13] We have suggested elsewhere that trifluoroacetic acid might stabilize carbocations by direct interaction with the trifluoromethyl group.[15] This interaction ought to result in stabilization of a more delocalized ion (i.e., a preference for a bridged ion) since no bond can be formed to the CF_3 group.

We report here evidence that indicates the existence of the bridged 2-butyl cation, I, as an intermediate in the trifluoroacetolysis of 2-butyl tosylate.

Results

The trifluoroacetolysis of 1,1,1,2-tetradeuterio-2-butyl tosylate (III) (0.5 M) at 35 °C was followed by NMR (60 and 220 MHz) (see Scheme I). Products V–VIII are easily distinguishable in the NMR spectra by the methyl resonances of the protons on the 1- and 4-positions, as shown in Figure 1. In unlabeled 2-butyl derivatives, the proton resonances on carbon 1 appear as a doublet and those on carbon 4 as a triplet at somewhat higher field. In V, the doublet from position 1 should be lacking while in VI the triplet from position 4 should be lacking. In VII the resonance corresponding to the triplet at position 4 in the unlabeled derivative should appear as a doublet, while in VIII resonance corresponding to the doublet at position 1 should appear as a singlet. Intermediacy of the bridged ion IV should lead to approximately equal amounts of V and VI. Intermediacy of the open ion IX should lead to almost exclusive formation of V if hydride shifts are slow relative to solvent trapping or a mixture of V–VIII if equilibration of the cations IX–XII occurs (see Scheme II). A similar solvolysis was performed by using 3,3,4,4,4-pentadeuterio-2-butyl tosylate (XIII) which is identical with III except that the positions of the protons and deuterons are interchanged. By analogy to III, one might expect XIII to give rise to (a) roughly equal amounts of XV and XVI if the bridged ion XIV were the predominant intermediate, (b) a mixture of XV–XVIII if equilibration of XIX–XXIII was established, and (c) only XV if no rearrangement occurred. The product distribution and rate data for the trifluoroacetolysis of III and XIII are collected in Table I.

Scheme II

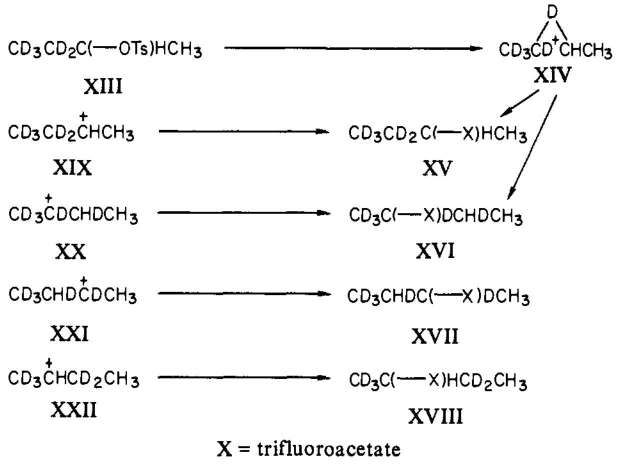

Table II. Reaction of *trans*-2-Butene (0.5 M) with Trifluoroacetic Acid (Neat) at 37 ± 1 °C as Determined by NMR

solvent	TSOH added, M	primary product	10^4k (±10%), mol^{-1} s^{-1}	k_H/k_D
CF_3COOH	0	2-butyl trifluoroacetate	1.41	
CF_3COOD	0	2-butyl trifluoroacetate	0.325	4.33
CF_3COOH	0.15	2-butyl tosylate[a]	to fast to measure	

[a] Which subsequently solvolyses.

Table III. Deuterium Incorporation in the Trifluoroacetylolysis of 2-Butyl Tosylate in CF_3COOH/CF_3COOD Mixture at 37 ± 1 °C Measured by NMR

solvent, % D	% D incorporated in product (±3%)
99	40
86	35
50	7

Roughly equimolar amounts of V and VI could be produced by an elimination–addition reaction. This possibility gains credibility by analogy to a similar mechanism reported for the H_2SO_4 solvolysis of *n*-propyl tosylate[16] and from the reports of extensive olefin formation in the trifluoroacetolysis of cyclohexyl tosylate.[17] For a test of this possibility the rates of addition of

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Table IV. The Effect of Added CF_3COONa on the Steady-State Concentration of 2-Butene

concn of 2-BuOTs, M	concn of CF_3COONa, M	$[CF_3COONa]/[2\text{-BuOTs}]_0$	steady-state fraction of 2-butene (±5%) $[2\text{-butene}]/[2\text{-BuOB}]_0$
0.42	0.39	0.93	0.13
0.58	0.66	1.12	0.15
0.62	0.90	1.44	0.20
0.55	1.01	1.83	0.25

CF_3COOH and CF_3COOD to *trans*-2-butene were measured under identical reaction conditions to those used in the solvolysis. The data are collected in Table II. The rates of addition of both acids were less than the comparable solvolysis reactions given in Table I by at least a factor of 2. In the presence of TsOH, tosylate was observed as the primary product, which proceeded to solvolyze to trifluoroacetate.

The results of a study of the extent of deuterium incorporation in 2-butyl trifluoroacetate formed from solvolysis of 2-butyl tosylate in varying CF_3COOH/CF_3COOD and CF_3COOD to *trans*-2-butene are collected in Table III. Careful integration of the 220-MHz NMR spectra of the products of the solvolysis of III indicated no loss of deuterium (<1%) whereas a similar study of the products of XIII indicated appreciable loss of deuterium (ca. 30%).

Since one of the experimental differences between the conditions of our solvolyses and those of Lambert[17a,b] is the presence of 1.1 equiv of sodium trifluoroacetate as buffer (in the latter case), we studied the effect of varying concentrations of sodium trifluoroacetate upon olefin formation during the solvolysis of 2-butyl tosylate. Olefin, as followed by NMR, was observed to increase in concentration, remain comparatively constant, and then disappear. The constant olefin level was taken to be a steady-state concentration. The data are collected in Table IV. The linear relationship between steady state olefin concentration and the ratio of added sodium trifluoroacetate to III is evident from Figure 2.

Discussion

The experimental data lead us to conclude that a bridged ion such as IV is the predominant intermediate. Three other hypotheses that (a) equilibrating or partially equilibrating open ions are the predominant intermediates, (b) the "solvolysis" is really an elimination of TsOH followed by an addition of CF_3COOH, or (c) the starting material rearranges by an internal return mechanism or elimination–addition of TsOH prior to solvolysis can be ruled out as being inconsistent with some or all of the observations as indicated in the following discussion.

Equilibration of Open Cations. Equilibration of the open ions IX–XII seems ruled out, at least for the reaction of III, by the product distribution among V–VIII. One should note that we have not explicitly taken equilibration deuterium isotope effects into account. These effects have been studied by Saunders et al., who report that ions containing β-deuteriums tend to be disfavored relative to those containing γ-deuteriums.[18] The effect of α-deuteriums remains unclear. These isotope effects would seem to favor X and XII over IX and XI. The virtual absence of VIII then argues even more strongly against equilibration of IX–XII. Furthermore, the kinetic isotope effects of Table I are clearly inconsistent with reported isotope effects for α, β, and γ deuteration in limiting S_N1 processes[19] in that the ratios of the rates of III/XIII are 1.1–1.2 while that predicted by using the values of ref 19 is 0.79–0.85.

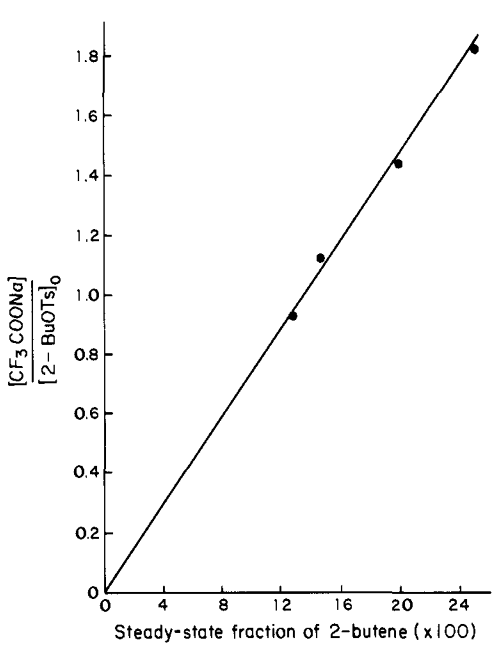

Figure 2. Relationship between steady-state olefin concentration and added CF_3COONa.

Eliminations–Additions. The fact that the rate of addition of CF_3COOH to *trans*-2-butene is significantly slower than the trifluoroacetolysis provides strong evidence against the intermediacy of 2-butene *along the solvolysis reaction path*. The rapid[20] rate of addition of TsOH to 2-butene (Table II) suggests the possibility that tosylate might be in equilibrium with 2-butene

$$\underset{\text{III}}{CH_3CH_2C(\text{—}OTs)DCD_3} \rightleftharpoons \underset{\text{XIX}}{CH_2CH\text{=}CDCD_3} + HOTs \rightleftharpoons \underset{\text{XX}}{CH_3C(\text{—}OTs)HCHDCD_3} \rightleftharpoons \text{etc.}$$

leading to a rearrangement of the tosylate. If this process occurs, some DOTs should eventually be eliminated which would lead to to some loss of the deuterium originally on C-2 to the solvent. No such loss was observed. Equilibration of III and XX should be apparent from the NMR spectra (the methyl resonances are different). The small amount of XX formed (which is attributed mostly to internal return, see below) does not support this equilibration. The apparent anomaly between the results of the unbuffered solvolyses reported here and the large fraction of olefin produced during the trifluoroacetolysis of cyclohexyl tosylate (buffered with CF_3COONa) reported by Lambert[17a,b] is removed by the evidence that the steady-state concentration of 2-butene is proportional to the concentration of added trifluoroacetate (Figure 2). Olefin formation requires removal of a proton from the intermediate ion by a base. Since, in the buffered reactions,

$$\begin{tikzcd}
\text{tosylate} \arrow[r, shift left, "R_1"] & \text{carbocation} \arrow[l, shift left, "R_{-1}"] \arrow[r, shift left, "R_2"] \arrow[d, "R_3"] & \text{olefin} \arrow[l, shift left, "R_{-2}"] \\
& \text{trifluoroacetate} &
\end{tikzcd}$$

$$R_2 = [\text{carbocation}](k_a[CF_3COO^-] + k_b[CF_3COOH] + k_c[OTs^-] + k_d[HOTs]); R_{-2} = k_{-2}[\text{olefin}]$$

trifluoroacetate is clearly the strongest base present in appreciable concentration the rate of formation of olefin from carbocation, R_2, might be dominated by $k_a[\text{carbocation}][CF_3COO^-]$. If we assume that the rates of the other processes (R_1, R_{-2}, and R_3) are largely unaffected by trifluoroacetate concentration (only a salt

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[20] A parallel behavior of HOBs and propene is CF_3COOH has been reported: Shiner, V. J., Jr.; Fisher, R. D.; Dowd, W. *J. Am. Chem. Soc.* **1969**, *91*, 7748–9.

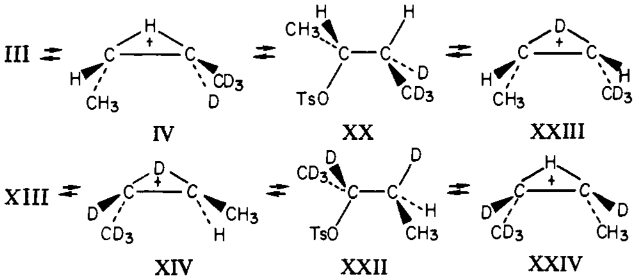
effect would be expected) and make the steady-state approximation with respect to both olefin and carbocation, the steady-state concentration of olefin will be $[\text{olefin}]_{\text{steady state}} = [\text{carbocation}]_{\text{steady state}}k_a[CF_3COO^-]/k_{-2}$. At the steady state, $d[\text{olefin}]/dt = 0$ or $R_2 = R_{-2}$, so the steady state of carbocation should be independent of R_2. Therefore, $[\text{olefin}]_{\text{steady state}}$ should be proportional to $[CF_3COO^-]$ if CF_3COONa is the base in the elimination. Figure 2 shows the experimental verification of this relationship and thereby the relative unimportance of all contributions to R_2 except $k_a[CF_3COO^-][\text{carbocation}]$. Here $[\text{olefin}]/[\text{2-butyl tosylate}]_0$ is plotted vs. $[CF_3COONa]/[\text{2-butyl tosylate}]_0$, where $[\text{2-butyl tosylate}]_0$ is the starting concentration. This result is in accord with the observation that acetate ion increases the fraction of olefin product in the acetolysis of cyclohexyl tosylate.[21]

Equilibration of Starting Tosylate via Internal Return. Internal return[22] is known to be very important for solvolyses in CF_3COOH. Evidence for internal return with rearrangement was apparent from the 220-MHz NMR spectra taken during the solvolyses of III and XIII. The rates of formation of rearranged tosylate are similar to those for solvolysis, since, during the early stages of the reaction, the peaks due to XX and XXII appeared at roughly the same rate as those due to the products. The actual rates of formation of XX and XXII are difficult to determine accurately due to the unknown rates of solvolysis for XX and XXII. In order to account for the roughly equimolar formation of V and VI from the trifluoroacetolysis of III by internal return with rearrangement followed by solvolysis, the rate of internal return would have to be many times faster than solvolysis, which is in contradiction with our observations.

$$\underset{\text{III}}{CH_3CH_2C(\text{—OTs})DCD_3} \rightleftharpoons \text{carbonium ion} \rightleftharpoons \underset{\text{XX}}{CH_3C(\text{—OTs})HCHDCD_3}$$

$$\underset{\text{XIII}}{CD_3CD_2C(\text{—OTs})HCH_3} \rightleftharpoons \text{carbonium ion} \rightleftharpoons \underset{\text{XXII}}{CD_3C(\text{—OTs})DCHDCH_3}$$

Intermediacy of a Bridged Cation. As explained previously, the roughly equimolar formation of V and VI, almost to the exclusion of VII and VIII, is strongly suggestive of a bridged ion. If the ratio of V to VI be the result of equilibration of ions IX and X, the carbocation must live several hydrogen-transfer half-lives. The β-deuterium isotope effect, k_H/k_D, for hydride transfer in ethyl cation is 2.4.[4] If this value be applicable to the present case, only slightly more than 1 half-life would be necessary for the formation of 5% VII. Furthermore, existence of the bridged ion IV as the predominant intermediate for the trifluoroacetolysis of XII is consistent with all the data reported as well as in accord with Saunders most recent results.[11] The relative amounts of V–VIII formed are readily understandable. The anomalous kinetic isotope effects of Table I become understandable if anchimeric assistance is provided by the bridging hydrogen. In such a case, substitution by deuterium at C-3 ought to have more than an ordinary effect upon the rate. There is some parallel in Shiner's studies of deuterated 2,4-dimethyl-3-pentyl brosylates[23] and 4-*tert*-butylcyclohexyl tosylates.[24] The disparity between the product distributions for reactions of III and XIII can be understood by considering the detailed processes of internal return and redissociation. For III, the bridged ion IV should form in the preferred trans geometry as indicated. Internal return leads to either III or XX. Upon redissociation, XX can form either bridged ion, IV, or XXIII, only the latter of which would lead to products other than V and VI. Formation of XXIII is clearly disfavored because it is cis rather than trans and has a deuterium rather than hydrogen bridge. Since both II and XX should dissociate almost exclusively to IV, internal return has a negligible effect upon the products. The case of XIII is rather different. The initially formed ion XIV can internally return to either XIII or XXII. Upon redissociation, XXII can form either XIV or XXIV. Since XIV is deuterium bridged and trans while XXIV is hydrogen bridged and cis, the dissociation of XXII will be much less selective than that of XX, leading to formation of significant amounts of XVII and eventually XVIII.



The fact that deuterium is incorporated during the solvolysis of 2-butyl tosylate in CF_3COOD indicates that exchange must occur somewhere during the course of the reaction. From our evidence it is impossible to determine at what stage of the reaction sequence the exchange takes place. The exchange may even occur through the involvement of a small amount of 2-butene in an elimination–addition (of TsOH) side process. If the exchange does occur through an ionic intermediate, the lack of deuterium loss for the solvolysis of III in CF_3COOH accords well with the idea that the bridging hydrogen is chemically different (i.e., exchangeable) from the other hydrogens on C-2 and C-3.

The present results are consistent with the report that trifluoroacetolysis of 2,2,6-trideuteriocyclohexyl tosylate leads to trifluoroacetate where label has been either lost or scrambled,[17] especially if one considers the possibility of the interconversion of 11 degenerate bridged cyclohexyl cations.

Experimental Section

2-Butyl Tosylates. Tosyl chloride, purified by the method of Pelletier,[25] was reacted with $CH_3CH_2CH(OH)CH_3$, $CH_2CH_2CD(OH)CD_3$, or $CD_3CD_2CH(OH)CH_3$ according to an established procedure.[26] The deuterated alcohols obtained were isotopically pure by NMR.

1,1,1,2-Tetradeuterio-2-butanol. This was prepared by action of CH_3CH_2MgBr on CD_3CDO. Ethyl bromide (15.0 g, 0.14 mol) was reacted with excess magnesium (99.9%) in dry ether. After the mixture was refluxed for 1 h and cooled, 5.0 g (0.14 mol) cold CD_3CDO in ether solution was slowly added with stirring. After the addition was complete, the mixture was refluxed for 30 min. The reflux condenser was cooled to −3 °C by using a cooling bath. The intermediate product was hydrolyzed with water and acetic acid, washed with Na_2CO_3 and NaCl, concentrated and distilled (bp 98 °C; yield, 4.06 g (49%)). The product was isotopically pure by NMR.

3,3,4,4,4-Pentadeuterio-2-butanol. This was prepared by a procedure analogous to that described above starting from CD_3CD_2Br and CH_3CHO (bp 98 °C; yield, 59%). The product was isotopically pure by NMR (>97%).

Deuteriotrifluoroacetic Acid. Deuterium oxide was slowly added (under N_2) to excess trifluoroacetic anhydride that had been cooled to −78 °C. The CF_3COOD was distilled from the unreacted anhydride (bp 73 °C; yield, 100%). The deuterium content as measured by NMR was generally 97–98%.

Reaction Rate Measurements. The reagents (tosylate or *trans*-2-butene and trifluoroacetic acid) were mixed in a cooled test tube and transferred to an NMR tube. All reactions were unbuffered except where specifically indicated. The NMR spectra (60 and 220 MHz, probe temperate 37 °C) were repeatedly scanned and integrated during the course of the reaction, using the methyl of the tosylate group (which shifts very slightly during the reaction) as an internal standard. Infinity readings were taken at least 24 h later. Rate constants were calculated by using a computer program written for that purpose. When necessary

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(because D/H exchange and/or internal return to rearranged tosylate caused significant deviation from a simple first-order kinetic plot), the rates were extrapolated to zero time.

Product Distributions. These were determined from integration of the 220-MHz spectra with the use of a curve resolver where necessary. The curve resolver was necessary to establish the relative amounts of VI and VIII, for example, since the small difference in chemical shift of the methyl groups of VI and VIII (due to the adjacent deuterium) causes some overlapping of the singlet of VIII with the upfield peak of the doublet of VI. The stability of the products was evident from the constant ratio with which the products were formed.

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The Surface of Silica as a Medium for the Radical and Ionic Decomposition of Diacyl Peroxides

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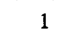
Abstract: The rates of decomposition of β-phenylpropionyl peroxide **1**, β-phenylisovaleryl peroxide **2**, and β-phenylisovaleryl *p*-nitrobenzoyl peroxide **3** are much higher on silica surfaces than they are in solution. The products formed on silica surfaces are derived from both radical and ionic precursors except in the case of **3**, for which the reaction may be entirely ionic. The relationships between the medium effects on the rates and on the products suggest that the ionic and radical parts of the reaction branch from a common polar intermediate.[1a,b,e] Both the ionic and radical products differ significantly from those formed in solution. In the neophyl radical, adsorption inhibits the migration of phenyl to form phenyl-*tert*-butyl radical. In the ionic reaction, there is extensive migration of methyl in competition with phenyl, in contrast to the behavior of neophyl derivatives in solvolysis[9] reactions. Dihydrocoumarin, from **1**, and dimethyldihydrocoumarin, from **2** and **3**, are not formed at all in solution. Esters, which are often formed via carboxy inversion and related reactions when polar diacyl peroxides decompose in solution, appear to arise from electron transfer in radial-pair precursors. There is no evidence of carboxy inversion compounds or carbonic acid esters in the physically adsorbed products, although some RO—C(=O)$^+$ groups (1–2%) appear to be trapped by the silica. Rearranged and unrearranged neophyl cations are trapped more extensively as silyl ethers. Other ion-derived products are one of the phenylisobutylenes, several phenylbutenes, and the carboxylic acids. Coadsorbed oxygen or acetonitrile alters the product distribution partly by trapping radicals and partly by site preemption[3] effects.

In the decomposition of certain diacyl peroxides, although some of the products can be assigned to radical-pair precursors, others found in the same reaction mixture require ion-pair precursors. Both the proportion of ionic products and the decomposition rate are increased by polar solvents or by suitable polarizable or polar substituents. Even though the proportion of radical products in the fast reactions decreases, the net rate of radical production is often observed to increase. It has therefore been proposed that the radical and ionic branches of the reaction share a common rate-determining step whose transition state is rather polar.[1]

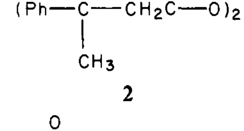
In this paper we report an unusual medium effect and novel products in the decomposition of bis(β-phenylisovaleryl) peroxide (**2**). Peroxide **2**, with its polarizable neophyl group, is a borderline member of the class of polar diacyl peroxides. The related compound **3**, with a much better anionic leaving group, has been shown to give the carboxy inversion (ionic) reaction in solution.[2] Peroxide **1**, with its less polarizable β-phenylethyl group, should be less susceptible to the ionic mode of decomposition. A few experiments with **1** and **3** are included for comparison.

Our attention was drawn to peroxide **2** by the discovery that the rate of its decomposition on a silica surface is about 70 times



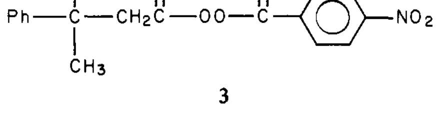
$(\mathrm{PhCH_2CH_2C(=O)—O})_2$

1



$(\mathrm{Ph—C(CH_3)_2—CH_2C(=O)—O})_2$

2



3

Table I. Products from Peroxide 1 (Mol %)[a]

	in benzene[b]	on P_0 silica		
		c	with O_2[d]	$h\nu$[e]
R_1COOH	13.1	48.4	45.1	28.4
R_1COOH		0.8[f]	0.7[f]	
R_1COOR_1	12.8	18.2	25.1	2.88
lactone L_1	0	0.63	3.30	0.0
R_1OH	trace	2.04	7.37	trace
R'_1OH	trace	trace		trace
R_1OSi[g]		4.4	7.28	0.5
R'_1OSi[g]		2.4		trace
R_1H	76	9.3	2.5	18.7
R_1R_1	18.7	3.92	9.26	14.8
styrene[h]	0[h]	0.4	1.89	0[h]
dibenzyl	18.5			

[a] Means of several analyses in most cases. [b] 0.1 M at 55 °C. [c] Means of runs at 2.66 and 5.1 wt % at 55 °C. This corresponds to about 0.1 monolayer. The differences were small. [d] 6.0 wt % at 55 °C, with coadsorbed O_2. [e] 6.25 wt % at 25 °C, photochemical. [f] Extracted after acid hydrolysis of the silica. [g] Alcohol extracted after acid hydrolysis of the silica. [h] No attempt was made to isolate the polymer.

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