Table II. Total Energies (hartrees) and Potential Barriers (kcal mol^{-1}) for Substituted Propanes

Substituent (X)	Energy III	Energy IV	Barrier
CH_3	−155.46457	−155.45878	3.63
H	−116.88512	−116.87924	3.69
F	−214.33172	−214.32621	3.46
OH	−190.70912	−190.70356	3.49
CN	−207.43037	−207.42457	3.64

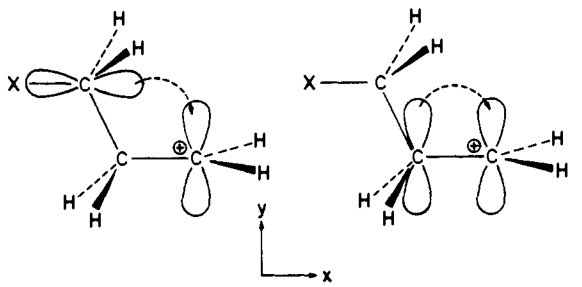
terminal methyl groups in the similarly substituted *propanes*, III *vs.* IV (Table II). Indeed, in these propanes, the barrier is effectively independent of the substituent X.

To gain insight into the mechanism of these effects it is instructive to look at some aspects of the electron distribution as, for example, the Mulliken gross population[9] of the "empty" 2p orbital at the positive carbon center (which we shall call the 2p(C^+) orbital) shown in Table III. We can see that in the *eclipsed* forms of the 1-propyl cations, the 2p(C^+) populations are approximately the same as in the ethyl cation and virtually invariant with respect to X. On the other hand, the 2p(C^+) populations in the *perpendicular* conformations are significantly greater than in the ethyl cation and strongly dependent on the substituent X, the populations being greatest (X = CH_3) and least (X = CN) in the cases where the barriers are greatest and least, respectively. These results suggest that (i) the CH_2X group does *not* interact with the 2p(C^+) orbital in the *eclipsed* conformation and (ii) the dominant effect producing the barrier is preferential stabilization of the *perpendicular* conformation through interaction of the CH_2X group with the 2p(C^+) orbital, leading to its increased population.

Table III. Populations of the 2p(C^+) Orbital in Substituted 1-Propyl Cations and the Ethyl Cation

Substituent (X)	Conformation I	Conformation II
CH_3	0.148	0.113
H	0.135	0.113
F	0.143	0.113
OH	0.132	0.116
CN	0.125	0.110
Ethyl cation	0.112	0.112

Analysis of overlap and atomic populations[9] (not reported in detail here) indicates that this interaction takes place by two mechanisms, *viz.*, (a) overlap of the $2p_x$ orbital on C_3 with the 2p(C^+) orbital on C_1 (see V) and (b) increased overlap population (compared with the ethyl cation) of the $2p_y$ orbital on C_2 with the 2p(C^+) orbital on C_1 (see VI). In the *eclipsed* conformation (II), (a) cannot occur at all because of symmetry restrictions and, for the same reason, the CH_2X group cannot contribute directly to (b) either. This is reflected in overlap populations of the 2p(C^+) orbital in this conformation which are effectively independent of the substituent X. On the other hand, in the *perpendicular* form, the two effects (a and b) both occur and are magnified when X is electron releasing (*e.g.*, X = CH_3) and diminished when X is electron withdrawing (*e.g.*, X = CN), leading to higher and lower barriers, respectively.



V VI

The classical approach to the calculation of the effect of substituents on carbonium ions is based on the Kirkwood–Westheimer model in which the cation is represented as a point charge.[10] This model, of course, predicts that the substituents, X, should not influence the rotational barrier (the energy difference between I and II). In contrast, the present quantum mechanical calculations predict that the effect of a γ substituent should depend significantly on the conformation at the cation center. Experimental tests are underway to differentiate between these predictions.

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[9] R. S. Mulliken, *J. Chem. Phys.*, 23, 1833 (1955).

[10] *Cf.* G. J. Gleicher, J. L. Jackson, P. H. Owens, and J. D. Unruh, *Tetrahedron Lett.*, 833 (1969), and private communication from Professor Gleicher.

[11] Princeton University Fellow, 1968–1969; American Cyanamid Fellow, 1969–1970.

* Address correspondence to either of these authors.

Leo Radom, John A. Pople*
Department of Chemistry, Carnegie-Mellon University
Pittsburgh, Pennsylvania 15213

Volker Buss,[11] Paul v. R. Schleyer*
Department of Chemistry, Princeton University
Princeton, New Jersey 08540

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The Stereochemistry of SN1 Displacement at a Vinylic Carbon

Sir:

It has been reported recently that the SN1 solvolysis of two vinylic halides, namely of the 1,2-dianisyl-2-phenylethenyl[1a] and the 1-cyclopropylpropen-1-yl system,[1b] entails complete randomization of configuration. Presumably, a linear vinylic cation is formed as an intermediate, which on nucleophilic attack affords the cis and trans isomer with equal probability.[1]

The findings of Rappoport and Bergman raise the question whether complete "racemization" is a general feature of SN1 solvolysis of vinylic systems, perhaps as a consequence of the ready accessibility of either face of the vinyl cation in an intramolecular scrambling process or whether the special stability of the two systems studied merely allowed attainment of a symmetric solvation shell before covalent collapse to the products occurred.

In order to answer these questions we sought to study a vinylic system which would give rise to a less stable

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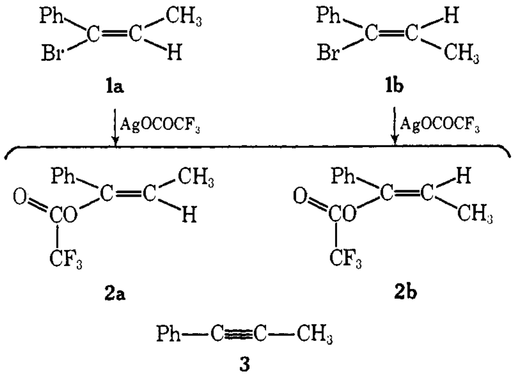
[1] (a) Z. Rappoport and Y. Apeloig, *J. Amer. Chem. Soc.*, 91, 6734 (1969); (b) D. R. Kelsey and R. G. Bergman, *ibid.*, 92, 228 (1970).

vinylic cation and yet undergo heterolysis under mild conditions so as to preclude equilibration of the products. Accordingly, we chose 1-phenylpropen-1-yl bromide (**1**) as a model and synthesized both cis (**1a**) and trans isomer (**1b**) by conventional methods.[2]

The reaction of various vinylic halides related to **1a** and **1b** with silver nitrate in ethanol has been reported to proceed at 130° *via* a free-radical path and to be accompanied on occasion by explosions.[4] Therefore, we were surprised to find that a suspension of silver trifluoroacetate in isopentane does react with **1** and also with 1-phenylethenyl bromide, *even at room temperature.* Clearly, our special combination of silver salt and solvent represents a most powerful electrophilic system, which has proved of general utility for generating carbonium ions on a preparative scale, *e.g.*, allylic cations from the corresponding halides at a temperature as low as −78°.[5]

Scheme I



In order to determine which of the isomers of the pairs **1a** + **1b** and **2a** + **2b** are thermodynamically the more stable, we have kept pure **1a** and pure **1b** at room temperature for periods up to 6 weeks. While **1b** does not change during this period, **1a** is converted into **1b** to the extent of *ca.* 30%. More importantly, in the presence of catalytic amounts of HBr, a mixture of **1a** and **1b**, initially present in a ratio of 6:1, changes its isomer ratio to 0.95:1 after 3 weeks. Similar results and configurational assignments have been obtained by Fahey[6] for the corresponding chlorides and acetates, and it seems reasonable to conclude that **2b** is also more stable than **2a**. At any event, appropriate control experiments exclude any equilibration of products in the reaction of principal concern, *viz.*, the silver ion induced heterolysis of both *cis*- (**1a**) and *trans*-1-phenylpropen-1-yl bromide (**1b**) (*cf.* Scheme I).

It can be seen immediately (*cf.* Table I) that this reaction involves overall *retention of configuration.* Interestingly, the degree of net retention is the same for **1a** *as well as* **1b**, *i.e.*, *ca.* 13%. This result makes it unlikely that we are dealing with an SN2 type displacement in which carbon–bromine heterolysis is assisted nucleophilically by trifluoroacetate ion from the rear. Furthermore, since 1-phenylpropyne (**3**) is formed in almost the same amount from **1a** and **1b**, an E2 elimination can be similarly ruled out. If such a reaction were to occur, the trans isomer **1b** should give rise to more acetylene **3** than the cis form **1a**.[7]

Table I. Products from the Reaction of Stereoisomeric 1-Phenylpropen-1-yl Bromides **1a** and **1b** with Silver Trifluoroacetate at 25°

	Products, %[a]	
Starting material and exptl condn	**3**[b]	Ratio **2a**:**2b**
1a, isopentane, stirring for 1 day[c,d]	57	1.28[e] 1.31[e] 1.35[f]
1b, isopentane, stirring for 3 days[c,d]	53	0.76[e] 0.79[f]
1a, diethyl ether, 3 days[c,g]	57	1.9[f]

[a] The error in the product ratio **2a**:**2b** is *ca.* $\pm 2\%$ when determined by integration of glc peaks and $\pm 5\%$ in the nmr determination. The percentage of **3** was estimated by comparison of its three-proton methyl singlet at τ 8.04 with the two quartets of **2a** and **2b**; while all experiments indicated similar amounts of **3** being formed, the absolute error in **3** could be $\pm 10\%$. [b] Interestingly, under the same conditions 1-phenylethenyl bromide and iodide give rise to only about 25% phenylacetylene. [c] 1 *M* vinylic bromide, 1.2 *M* $AgOCOCF_3$. [d] 1 *M* tri-*n*-butylamine present. [e] Glc determination. [f] Nmr determination. [g] The trans isomer **1b** does not react under these conditions.

The observed retention of configuration is striking and suggests that the vinyl cation is generated on the surface of the silver salt and then held by interaction with trifluoroacetate ion present in the crystal lattice. Formation of covalent trifluoroacetate is accomplished by attack on the cation from two directions, frontside attack from the surface being preferred to attack from the rear by a factor of 1.3. In this manner one can rationalize most easily why both **1a** and **1b** show the same degree of retention.

In diethyl ether the reaction is homogeneous and the large proportion of retained product from **1a** (>30% net retention) can be explained by a double inversion process involving an intermediate oxonium ion.[8] Un-

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(2) Treatment of *trans*-1-phenylpropene with bromine in carbon tetrachloride gave a 5:1 mixture of *erythro*- and *threo*-1-phenyl-1,2-dibromopropane which on elimination of hydrogen bromide with alcoholic potassium hydroxide afforded **1a** and **1b** in a ratio of 4:1; pure samples of each isomer were obtained by preparative glc on a Hewlett-Packard Model 776 chromatograph using a 20 ft × $^3/_4$ in. column containing Carbowax 20M at 125° and a flow rate of 0.4 l./min. The stereochemical assignment of **1a** and **1b** rests on the mechanism of synthesis,[3a] the greater reactivity of the cis isomer **1a** (*cf.* Scheme I), and the nmr spectra; note that the olefinic proton in the trans isomer **1b** (and also in **2b**) not only resonates at lower field as expected,[3] but also that the phenyl protons in **1b** (and in **2b**) appear as a many-line, complex pattern which is diagnostic for a trisubstituted olefin with the olefinic proton situated cis to a phenyl group.[3a,b] In contrast, the phenyl protons trans to the olefinic proton, *e.g.*, in **1a** and **2a**, appear as a broad singlet, and we have observed the same phenomena in *cis*-1-phenylpropen-1-yl iodide (**4a**) and its trans isomer **4b**, which we prepared stereospecifically by treatment of **1a** and, respectively, **1b** with magnesium in ether followed by addition of iodine (*cf.* H. Normant, *Advan. Org. Chem.*, **2**, 1 (1960)): nmr of **1a** τ 2.6–2.9 (5 H, broad singlet), 3.89 (1 H, quartet, J = 7.7 Hz), 8.58 (3 H, doublet); **1b**, τ 2.3–2.9 (5 H, complex), 3.78 (1 H, quartet, J = 6.8 Hz), 8.07 (3 H, doublet); **2a**, τ 2.5–2.6 (5 H, broad singlet), 4.28 (1 H, quartet, J = 7.5 Hz), 8.22 (3 H, doublet); **2b**, τ 2.3–2.7 (5 H, complex), 4.02 (1 H, quartet, J = 7.2 Hz), 8.31 (3 H, quartet); **4a**, τ 2.5–3.0 (5 H, broad singlet), 4.11 (1 H, quartet, J = 6.8 Hz), 8.12 (3 H, doublet); **4b**, 2.5–3 (5 H, complex), 3.57 (1 H, quartet, J = 7.7 Hz), 8.55 (3 H, doublet).

(3) (a) R. C. Fahey and C. Schubert, *J. Amer. Chem. Soc.*, **87**, 5172 (1965); (b) M. Barbieux, N. Defay, J. Pecher, and R. H. Martin, *Bull. Soc. Chim. Belg.*, 73, 716 (1964); (c) U. E. Matter, C. Pascual, E. Pretsch, A. Pross, and S. Sternhell, *Tetrahedron*, **25**, 691, 2023 (1969); (d) S. W. Tobey, *J. Org. Chem.*, **34**, 1281 (1969).

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(5) H. M. R. Hoffmann and G. F. P. Kernaghan, to be published; see also H. M. R. Hoffmann, D. R. Joy, and A. K. Suter, *J. Chem. Soc. B*, 57 (1968); H. M. R. Hoffmann and D. R. Joy, *ibid.*, 1182 (1968); H. M. R. Hoffmann and N. F. Janes, *ibid.*, *C*, 1456 (1969).

(6) R. C. Fahey and D. J. Lee, *J. Amer. Chem. Soc.*, **88**, 5555 (1966).

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(8) See H. Weiner and R. A. Sneen, *ibid.*, **87**, 287 (1965); a referee

Table II. Products from the Reaction of Trifluoroacetic Acid and Hydrogen Bromide with 1-Phenylpropyne (**3**) at 25°

Exptl condn[a]	Product ratio
CF_3CO_2H, isopentane	**2a**:**2b** = 1.53
CF_3CO_2H, CH_2Cl_2	1.48
CF_3CO_2H, CH_2Cl_2, $(C_2H_5)_4N^+\,O^-COCF_3$	1.13
HBr,[b] CH_2Cl_2	**1a**:**1b** = 2.8
HBr,[b] CH_2Cl_2, $(C_2H_5)_4N^+Br^-$	0.65

[a] 0.9 *M* 1-phenylpropyne, CF_3CO_2H, and tetraethylammonium salts being used. [b] 50 ml of solvent saturated with HBr.

fortunately, experiments in solvent dioxane, which is even more nucleophilic, were not successful owing to formation of a complex with the silver salt.

It is interesting to note that the steric consequence of SN1 displacement of the cis isomer **1a** and of the electrophilic addition of trifluoroacetic acid to **3** (*cf.* Table II) is nearly the same, the ratio **2a**:**2b** being 1.3 and 1.5, respectively. Such a result is reasonable if a vinylic cation–trifluoroacetate pair of similar configuration is involved in both reactions. As expected[9] added trifluoroacetate ion (and added bromide ion even more so) leads to an increase in trans addition product, undoubtedly *via* nucleophilic intervention during the ion-pair stage of the reaction.

Our results can also be compared with those of Rappoport[1a] and Bergman[1b] who not only used solvents of high ionizing power such as 80% ethanol, acetic acid, and dimethylformamide, but also vinylic halides which reacted readily with silver acetate in acetic acid. Since these conditions do not suffice to ionize the 1-phenylpropen-1-yl bromides **1a** and **1b**, it becomes clear that the vinylic cations produced in the earlier studies were more stable than ours and in the polar solvents used had an excellent chance of forming cis and trans isomers in the same ratio from reactant of either geometry. To our knowledge, the reactions reported here represent the first examples of a stereoselective heterolysis of vinyl halides and we conclude that vinyl halides like saturated alkyl halides and tosylates are subject to similar environmental influences in SN1 reactions.

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has suggested that a tight ion pair might be involved, since even a single inversion had not been observed previously for displacements on vinyl carbon. However, the large amount of retention of configuration leads us to prefer our suggestion.

(9) R. C. Fahey, *Top. Stereochem.*, 3, 237 (1968).

* Address correspondence to this author.

George F. P. Kernaghan, H. M. R. Hoffmann*
William Ramsay and Ralph Forster Laboratories
University College, London WC1H OAJ, England

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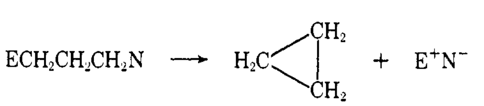
Kinetics of Acetolysis of ω-Tosyloxyalkyltrimethyltins. Evidence for σ Participation in Cyclopropane Formation from 3-Tosyloxypropyltrimethyltin

Sir:

Many cyclization reactions can be formally represented as α,ω eliminations. For example, methods for preparing cyclopropanes include dehydrotosylation,[1] dehydrobromination,[2-4] dechloroboronation,[5-7] and debromosilylation.[8] If the overall elimination reaction is envisioned as shown in eq 1, the product-forming



(1)

step can result from one of at least four processes: (a) intramolecular nucleophilic displacement by the carbanion formed by ionization of the E–C bond; (b) intramolecular electrophilic displacement by the carbonium ion formed by ionization of the C–N bond; (c) an intramolecular free-radical displacement by a radical formed by homolysis of either the C–N or C–E bond; (d) a concerted process in which ring formation and elimination occur simultaneously. Mechanism a might be observed in the base-induced eliminations and mechanism b may be involved in the aluminum chloride catalyzed dechlorosilylation[8] of 3-chloropropyltrimethylsilane. We wish to report kinetic evidence for mechanism d.

We have prepared four ω-tosyloxyalkyltrimethyltins, $(CH_3)_3Sn(CH_2)_nOTs$, with $n = 3$–6, by addition of trimethyltin hydride to the appropriate unsaturated alcohols,[9] followed by reaction with *p*-toluenesulfonyl chloride. Each had the expected elemental analysis, nmr spectrum, and infrared spectrum.

When 3-tosyloxypropyltrimethyltin was heated in biphenyl solution it decomposed at about 125° yielding 82% cyclopropane and 77% trimethyltin tosylate, along with small amounts of tetramethyltin and dimethyltin ditosylate formed, presumably, by disproportionation of trimethyltin tosylate. The other three tosyloxyalkyltrimethyltins required temperatures around 230° for decomposition. In each case alkenes were the major products.

5-Tosyloxypentyltrimethyltin yielded 10% cyclopentane in the hydrocarbon product. *n*-Propyl tosylate also decomposed at 230° yielding a substantial amount of propylene.

Solvolysis of 3-tosyloxypropyltrimethyltin in anhydrous acetic acid containing sodium acetate at 65° yielded cyclopropane as the only volatile product, and trimethyltin acetate isolated in 80% yield. The other three homologs were solvolyzed in the same system at 120°. From the butyl, pentyl, and hexyl analog, respectively, there was obtained 0.46, 0.52, and 0.51 mol of methane and 0.53, 0.48, and 0.50 mol of ω-acetoxyalkyltrimethyltin.

Despite the apparent complexity of the reactions of the higher homologs, the kinetics of the acetolysis of the four tosylates were measured spectrophotometrically[10,11] in the presence of sodium acetate. First-order

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(2) A. C. Knipe and C. J. M. Stirling, *J. Chem. Soc. B*, 808 (1967).

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