Chloromethyl phenyl sulfoxide is highly resistant to the reaction with potassium iodide in acetone at 50°; even after 60 hr no potassium iodide was consumed, and the sulfoxide was recovered quantitatively. Comparison of this result with those reported[5,6] for some chlorides in the same condition led us to conclude that chloromethyl phenyl sulfoxide is less reactive than *n*-butyl chloride by a factor of at least 10^2, this factor being as high as 10^7 when compared with phenacyl chloride (Table I). Preliminary experiments showed that chloromethyl phenyl sulfoxide is less reactive than *n*-butyl chloride toward piperidine in boiling benzene, too.

Table I. Relative Rates of Alkyl Chlorides in the Reaction with Potassium Iodide in Acetone at 50°

RCl	Relative rates
$CH_3CH_2CH_2CH_2Cl$	1^a
$PhCOCH_2Cl$	$105{,}000^b$
$PhSOCH_2Cl$	$<0.01^c$
$PhSO_2CH_2Cl$	$<0.01^{c,d}$

[a] $k = 0.0933$ l. mol^{-1} hr^{-1} (0.0955[5]); the value reported by Conant[5] is for $0.4343k$. [b] See ref 5. [c] No reaction occurred in 60 hr at 60°. [d] No reaction was observed in 12 hr at 56° or after 10 weeks at 0°.[6] With chloromethyl *p*-tolyl sulfone the relative rate was estimated to be <0.02.[6]

The present results appear quite interesting. The inertness of chloromethyl phenyl sulfone was successfully shown by Bordwell and Cooper[6] to be due to a steric blocking of the attacking reagent by the sulfonyl group; *i.e.*, this molecule has a structural resemblance to neopentyl chloride. The inertness of chloromethyl phenyl sulfoxide, however, is hardly rationalized in terms of this kind of steric blocking. On the other hand, electronic effects of carbonyl, sulfinyl, and sulfonyl groups are known to be almost the same. Thus the marked retarding effect of the sulfinyl group[7] seems quite interesting but remains unexplained.

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[5] J. B. Conant and W. R. Kirner, *J. Am. Chem. Soc.*, **46**, 232 (1924); J. B. Conant, W. R. Kirner, and R. E. Hussey, *ibid.*, **47**, 488 (1925).

[6] F. G. Bordwell and G. D. Cooper, *J. Am. Chem. Soc.*, **73**, 5184 (1951).

[7] Even if the lack of enhanced reactivity may be explained according to the postulate of Bartlett and Trachtenberg,[8] the retarding effect, taking *n*-butyl chloride as standard, cannot be explained.

[8] P. D. Bartlett and E. N. Trachtenberg, *J. Am. Chem. Soc.*, **80**, 5808 (1958).

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Received May 28, 1968

Secondary Isotope Effects for Solvolyses Leading to Classical Norbornyl Cations

Sir:

During a recent study of the solvolysis of *exo*-norbornyl-3,3-d_2 bromide and its *endo* counterpart, it was found that the secondary isotope effect for the former was significantly smaller than that of the latter (k_H/k_D = 1.04 *vs.* 1.16 per D).[1] The magnitude of a secondary isotope effect is a sensitive function of the characteristics of the transition state, and it is diminished by such factors as participation by solvent[2] or strong resonance interactions in the transition state.[3] Since a neighboring group that provides assistance during a solvolysis reaction functions as an "internal solvent," a similar perturbation of the secondary isotope effect would be expected. By applying this criterion we concluded[1] that *exo*-norbornyl bromide solvolyzes with assistance and that the transition state that leads to the norbornyl cation is best formulated as one that is delocalized and nonclassical.[4]

To expand the experimental foundation upon which these conclusions are based, we have now measured the secondary isotope effects that arise during the solvolysis of the *exo*- and *endo*-*p*-nitrobenzoates of 2-phenylnorbornan-2-ol. The labeled compounds were prepared by exchanging norcamphor in deuteriotrifluoroacetic acid, allowing the dideuterio ketone to react with phenylmagnesium bromide to give the *endo* alcohol, and inverting the configuration of the alcohol with hydrochloric acid to produce the *exo* alcohol.[5,6] The *p*-nitrobenzoates, which contained 1.87 atoms of deuterium, were solvolyzed in 60% dioxane, and the rate constants are summarized in Table I.

Table I. Solvolysis of the *exo*- and *endo*-*p*-Nitrobenzoates of the 2-Phenylnorbornan-2-ols[a]

Compound	Temp, °C	$k \times 10^4$, sec^{-1}	k_H/k_D
endo-*p*-Nitrobenzoate	62.50	0.288 ± 0.002	1.15 ± 0.02
endo-*p*-Nitrobenzoate-3,3-d_2		0.250 ± 0.002	
exo-*p*-Nitrobenzoate	39.50	3.47 ± 0.02	1.18 ± 0.02
exo-*p*-Nitrobenzoate		2.94 ± 0.02	

[a] Rate constants were measured in duplicate or triplicate, and the errors represent the deviations from the mean value of a series of constants. The observed constants are in excellent agreement with the values calculated from Brown's data.[6]

Several important conclusions can be drawn from these results. From a comparison of the values of these isotope effects with those that have been reported for the α-phenylethyl system,[3] it is apparent that the electronic characteristics of the solvolysis transition states in both of these diverse systems must be similar; *i.e.*, the transition state that leads to the phenylnorbornyl cation must be classical regardless of whether the exiphile (leaving group) departs from an *exo* or an *endo* position.[7] Therefore, the magnitude of the secondary isotope effect is not a property of the geometry of the exiphile but is rather a reflection of the electronic nature of the transition state that leads to the cation.

Since the transition states for the solvolysis of the *p*-nitrobenzoates of *exo*- and *endo*-2-phenylnorbornanols and *endo*-norbornyl bromide are classical, *the dramatic contrast in secondary isotope effects that is observed during the ionization of exo- and endo-norbornyl bro-*

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[1] J. P. Schaefer, M. J. Dagani, and D. S. Weinberg, *J. Am. Chem. Soc.*, **89**, 6938 (1967).

[2] K. T. Leffek, J. A. Llewellyn, and R. E. Robertson, *Can. J. Chem.*, **38**, 2171 (1960).

[3] V. J. Shiner, Jr., W. E. Buddenbaum, B. L. Murr, and G. Lamaty, *J. Am. Chem. Soc.*, **90**, 418 (1968).

[4] S. Winstein and D. Trifan, *ibid.*, **71**, 2953 (1949); **74**, 1147, 1154 (1952).

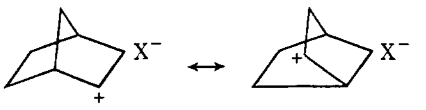
[5] D. C. Kleinfelter and P. von R. Schleyer, *J. Org. Chem.*, **26**, 3740 (1961).

[6] H. C. Brown, F. J. Chloupek, and M. H. Rei, *J. Am. Chem. Soc.*, **86**, 1248, 1246 (1964).

[7] K. Takeuchi and H. C. Brown, *ibid.*, **90**, 2693 (1968).

mides indicates that there is a fundamental electronic difference in the transition states that are involved. In view of the fact that this difference is in the direction that one would expect if participation during the ionization step occurred, we are forced to conclude that our findings provide compelling support for Winstein's[4] suggestion that the transition states for the solvolysis of simple *exo*-norbornyl compounds are nonclassical.[8]

This conclusion is based on the following argument. For a classical norbornyl cation that arises from the solvolysis of an *exo*-oriented exiphile, the secondary isotope effect (k_H/k_D) is approximately 1.18 ± 0.02 for two deuterium atoms. If the charge at C_2 is delocalized between C_1 and C_2 in the transition state, the magnitude of the effect would be diminished by a factor of $(1.18)^n$, where n is the fraction of the charge associated with C_2. For a transition state in which the resonance forms



are equal contributors, only one-half of the electronic charge would reside on C_2. The isotope effect that would be associated with a transition state approximating this situation would therefore be $(1.18)^{1/2}$ or 1.085; this value corresponds exactly to what was observed for the solvolysis of *exo*-norbornyl bromide.[1,10]

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[8] Brown[9] has argued that, because parallels exist between the solvolysis rates of compounds that lead to classical norbornyl cations, the stereochemical fate of these cations, and the behavior of the parent norbornyl systems, these data cannot logically be used as a foundation for postulating nonclassical behavior for the parent system. Unfortunately, the perturbations that result from the conversion of a secondary system to a tertiary system introduces additional factors (*e.g.*, new steric effects) that cloud the interpretation of data and cast doubt upon the validity of arguments based upon the analogous behavior of secondary and tertiary systems. The difference in secondary isotope effects for these two systems clearly demonstrates that tertiary norbornyl systems should not be used as models for the norbornyl cation.

[9] A summary of H. C. Brown's arguments along with numerous references to his papers can be found in *Chem. Eng. News*, **45**, 86 (Feb 13, 1967).

[10] It would be erroneous to conclude that the excellent agreement between the observed isotope effect and that calculated on the basis of the above model requires that in the transition state for solvolysis of simple *exo*-norbornyl derivatives the norbornyl fragment must be completely symmetrical. A transition state in which bridging was only one-third complete could not be distinguished from the above model due to the experimental uncertainties that are involved in the isotope effects.

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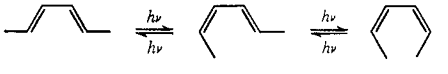
Mechanism of the Photochemical Valence Tautomerization of 1,3-Butadienes

Sir:

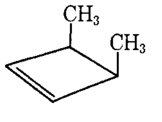
Irradiation of 1,3-butadiene is known to give rise to cyclobutene (1a) and bicyclo[1.1.0]butane (1b), the former being the major product.[1] While the experimental evidence strongly suggests that both processes occur from the excited singlet state of 1,3-butadiene,[2a] the difference between the two reaction pathways has never been satisfactorily explained. On the basis of a study of the photoisomerization of the stereoisomers of 2,4-hexadiene, we propose that (1a) is a concerted process, while (1b) is most probably a stepwise reaction.[2b]

(1)

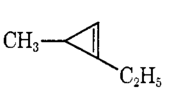
The photoisomerizations of *trans,trans*-, *cis,trans*-, and *cis,cis*-2,4-hexadienes were studied in ether solution at 2537 Å. The stereoisomerizations indicated by (2) rapidly led to a photostationary state in which the concentrations corresponded to *trans,trans* 35.7%; *cis,trans* 30.5%; *cis,cis* 33.7%. At the same time, four other isomers (mol wt by mass spectrometry = 82) were also formed more slowly. The most important of these amounted to 33% of the hexadiene that disappeared. Its ir (strong absorptions at 727, 2950, and 3020 cm^{-1}) and nmr spectra (τ 3.98 (2 H), singlet; ~7.1 (2 H), multiplet; 9.02 (6 H), doublet (J = 7 cps) with fine structure) when considered together with the fact that it isomerized cleanly at 180° to give *cis,-trans*-2,4-hexadiene showed that it was *cis*-3,4-dimethylcyclobutene (I). The stereochemistry of the thermal decomposition of this molecule has already been demonstrated by Winter[3] to be conrotatory.



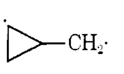
(2)



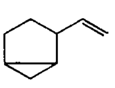
I



II



III



IV

The second isomer which accounted for about 5% of the hexadiene that disappeared had infrared absorptions at 1775 and 1725 cm^{-1} (m) as well as at 1375 and 1360 cm^{-1} (m). The nmr spectrum consisted of a broad (half-width 4 cps) absorption (1 H) at τ 3.45, an octet at 7.5 (2 H), and a complex absorption from 8.5 to 9.1 (7 H). In the 100-Mc spectrum,[4] the last absorption could be resolved into an octet (1 H) at τ 8.6, a symmetric triplet at 8.86 (3 H), and a doublet at 8.99 (3 H). Decoupling experiments showed that the absorptions at τ 7.5 and 8.86 could be attributed to the CH_2 and CH_3 of an ethyl group while the proton at τ 8.6 and the three protons at 8.99 could be due to a >$CHCH_3$ group. The lone proton at τ 3.45 was coupled to all of these protons with coupling constants which ranged from 1.8 cps for the CH proton to 1.0 cps for the CH_3 of the ethyl group. The presence of an ethyl and a methyl group left only three carbons to account for. Two of these presumably formed the ends of an olefinic group while the third carbon was not olefinic. The infrared absorption at 1775 cm^{-1} is quite close to the C=C stretching frequency in 1,3-dimethylcyclopropene[5] of 1773 cm^{-1}. The structure which would fit all of these data is that of 1-ethyl-3-methylcyclopropene (II).

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[1] R. Srinivasan, *J. Am. Chem. Soc.*, **85**, 4045 (1963).

[2] (a) R. Srinivasan, *Advan. Photochem.*, **4**, 113 (1966). (b) It is assumed that the same mechanism is operative in the valence tautomerization of all linear 1,3-dienes.

[3] R. E. K. Winter, *Tetrahedron Letters*, 1207 (1965). We thank Dr. Winter for supplying us with the spectral data for I for comparison.

[4] We thank Dr. C. S. Yannoni of this laboratory for these spectra.

[5] G. L. Closs, *Advan. Alicyclic Chem.*, **1**, 74 (1966).