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(17) (a) S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, **74**, 1154 (1952); (b) J. D. Roberts, C. C. Lee, and W. H. Saunders, *ibid.*, **76**, 4501 (1954); (c) G. J. Karabatsos and C. F. Orzech, *ibid.*, **84**, 2838 (1962); (d) P. S. Skell and M. Starer, *ibid.*, **84**, 3962 (1962); (e) A. A. Aboderin and R. L. Baird, *ibid.*, **86**, 2300 (1964).

(18) National Institutes of Health Postdoctoral Fellow.

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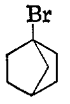
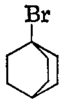
Solvolytic Reactivity of 1-Chlorobicyclo[1.1.1]pentane[1]

Sir:

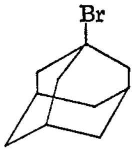
It is generally observed that the reactivity of bridgehead halides decreases markedly as the size of the bridging rings decreases.[2] Thus, the reactivities of several bridgehead halides are



10^{-13}



10^{-6}



10^{-3}

$(CH_3)_3CBr$
1

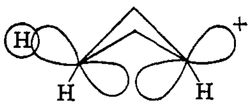
The changes in reactivity have been attributed to the difficulty in creating a planar carbonium ion at the bridgehead position, increasing deviation from planarity increasing the energy of the ion formed.[3]

A significant exception to the trend is found with 1-bromobicyclo[2.1.1]hexane, which reacts 10^7 more rapidly than 1-bromonorbornane.[4] We now wish to report that the next lower homolog, 1-chlorobicyclo[1.1.1]pentane, is three times more reactive than *t*-butyl chloride and about 10^{14} more reactive than 1-chloronorbornane.

1-Chlorobicyclo[1.1.1]pentane was prepared by the photochlorination of bicyclo[1.1.1]pentane.[5] The products were the 1-chloro derivative (25%), the 2-chloro derivative (7%), the 1,3-dichloride (5%), the 2,2-dichloride (33%), the 1,2-dichloride (5%), and 3-methylenecyclobutyl chloride (25%). The predominant attack by chlorine atoms at the bridgehead position, as contrasted to norbornane,[6] appears to result from the marked deactivation of the methylene positions as compared with cyclohexane.[7]

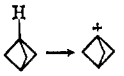
The 1-chloro derivative underwent solvolysis in 80% ethanol with rate constants of 3.03×10^{-5} sec^{-1} at 25° and 6.26×10^{-4} sec^{-1} at 50°, giving $\Delta H^{\ddagger} = 12.0$ kcal/mole and $\Delta S^{\ddagger} = +4$ eu. The products were 3-methylenecyclobutanol and its ethyl ether. Under the same conditions, the rate constant for *t*-butyl chloride was found to be 9.67×10^{-6} sec^{-1} at 25°.[8]

The high reactivity of the chloride may be attributed to the driving force for ring fragmentation, relieving considerable strain. However, the same is true with the bicyclo[2.1.1]hexane derivative which is 10^7 less reactive. An alternative explanation is derived from our examination of the energy of the cyclobutyl cation[11] using the CNDO method.[12] Here, we assume that the activated complex for the solvolysis still retains significant bonding to the leaving group, thus making appropriate a tetrahedral geometry for the reacting center. The previous calculations suggested that an equatorial leaving group would be strongly preferred over an axial leaving group because of the possibility of a cross-ring interaction with the former.



This is in good accord with the experimental observations.[9,10] An extension to the bicyclo[1.1.1]pentane case would seem favorable because of the collinear geometry of the bridgehead bonds and the extremely short cross-ring distance (1.8–1.9 A). The calculated energies for conversion of the corresponding hydrocarbon to the cation, a hydrogen atom, and an electron are indicated in Table I. It can be seen that the energy for the bicyclo[1.1.1]pentane derivative is between that of the planar and pyramidal *t*-butyl cations. The results provide an explanation for the high reactivity of the bridgehead halides and for the formation of 3-methylenecyclobutanol as the product. Considerable charge is transferred to the 3 position as a result of

Table I. Energy of Formation of Some Cations

Reaction	ΔE, au
$CH_4 \longrightarrow CH_3^+ + H\cdot + e^-$	0.9190
$C_2H_6 \longrightarrow C_2H_5^+ + H\cdot + e^-$	0.8230
$C_3H_8 \longrightarrow i\text{-}C_3H_7^+ + H\cdot + e^-$	0.7559
$i\text{-}C_4H_{10} \longrightarrow t\text{-}C_4H_9^+ + H\cdot + e^-$ (planar)	0.7004
$\longrightarrow t\text{-}C_4H_9^+ + H\cdot + e^-$ (pyramidal)	0.7766
 $+ H\cdot + e^-$	0.7299

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(1) This investigation was supported by the U. S. Army Research Office (Durham).

(2) *Cf.* R. C. Fort, Jr., and P. von R. Schleyer, *Advan. Alicyclic Chem.*, **1**, 284 (1966).

(3) P. D. Bartlett and L. H. Knox, *J. Am. Chem. Soc.*, **61**, 3184 (1939); W. von E. Doering, M. Levitz, A. Sayigh, M. Sprecher, and W. P. Whelan, *ibid.*, **75**, 1008 (1953); G. J. Gleicher and P. von R. Schleyer, *ibid.*, **89**, 582 (1967).

(4) K. B. Wiberg and B. R. Lowry, *ibid.*, **85**, 3188 (1963).

(5) We have previously reported the isolation and characterization of the 1- and 2-chlorides *via* the photochemical reaction of the hydrocarbon with *t*-butyl hypochlorite: K. B. Wiberg and D. S. Connor, *ibid.*, **88**, 4437 (1966).

(6) E. C. Kooyman and G. C. Vegter, *Tetrahedron*, **4**, 382 (1958).

(7) A comparison of the reactivity in chlorination of bicyclo[1.1.1]pentane and other hydrocarbons will be presented subsequently.

(8) As might be expected based on our results with bicyclo[2.1.1]hexyl 5-tosylate[9] and bicyclo[3.1.1]heptyl 6-tosylate,[10] 2-chlorobicyclo[1.1.1]pentane is also quite reactive ($k = 1.16 \times 10^{-3}$ sec^{-1} at 100°). However, it is not as reactive as the 1-chloro derivative.

(9) K. B. Wiberg and R. Fenoglio, *Tetrahedron Letters*, 1273 (1963).

(10) K. B. Wiberg and B. A. Hess, Jr., *J. Am. Chem. Soc.*, **89**, 3015 (1967).

(11) K. B. Wiberg, *Tetrahedron*, in press.

(12) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966).

the cross-ring interaction making attack at this position quite favorable.

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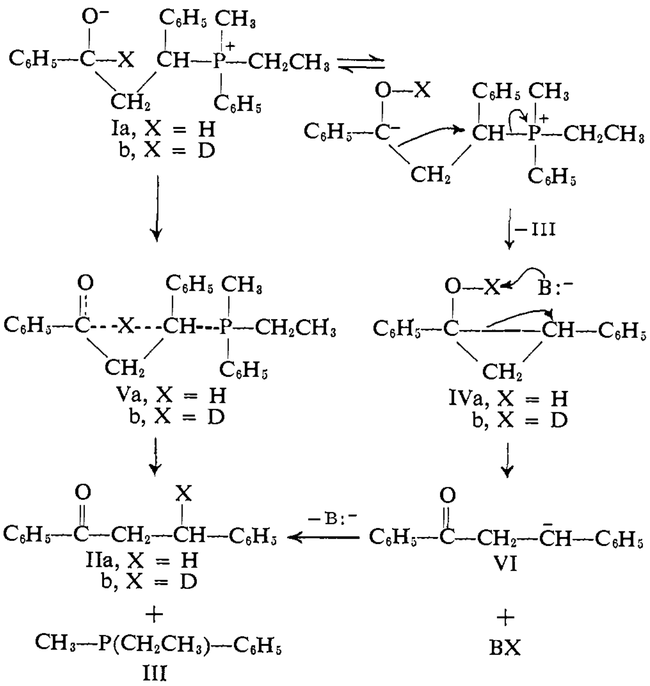
A Deuterium Tracer Study of the Thermal Decomposition of the Adduct of Lithium Iodide and Methylethylphenyl-(1,3-diphenyl-3-hydroxypropyl)-phosphonium Betaine

Sir:

The adduct of lithium iodide and methylethylphenyl-(1,3-diphenyl-3-hydroxypropyl)phosphonium betaine (I) precipitates when styrene oxide is added to an ether solution of methylethylphenylbenzylidenephosphorane prepared from methylethylphenylbenzylphosphonium iodide and phenyllithium.[1] When I, which is a typical intermediate of the Wittig reaction of a phosphonium ylide with an epoxide, an important method of synthesis of cyclopropanes under favorable conditions, is heated to a temperature of 190–200° in decalin suspension, a number of products are formed, but the major ones are benzylacetophenone (IIa) and methylethylphenylphosphine (III). Three mechanisms have been given consideration[2–4] for this decomposition reaction, and one of them, that involving 2,4-diphenyloxetane as an intermediate, was eliminated from further consideration by the results of a ^{14}C tracer study.[2]

The two remaining mechanistic possibilities consist of (1) the formation of 1,2-diphenylcyclopropanol (IVa) as an intermediate and (2) a direct 1,3-hydride shift by way of transition state Va. Although it is clear that the same deuterated product, IIb, would be obtained from Ib by either mechanism (B:⁻ could be a second molecule of I or else some other base, such as $C_6H_5\overset{O^-}{\overset{|}{C}}HCH_2C_6H_5$, known to be present in trace amounts[2]), it is also obvious that the mechanism involving IVb as an intermediate would lead to dilution of deuterium content in the product, IIb, if a suitable Brønsted acid containing ordinary hydrogen were added to Ib prior to the decomposition step.[5] Also, deuterium would undoubtedly be found α to the carbonyl group of II if the anion VI were formed as an intermediate.[6]



Benzaldehyde-*d*, prepared by the reaction of 1-benzoyl-1,2-dihydroquinaldonitrile with D_2SO_4, was converted to styrene-α-*d* oxide by the method of Corey and Chaykovsky[7] and converted to Ib as described above. The sample of IIb obtained by the decomposition of Ib was converted to hydrocinnamanilide by reaction with hydrogen azide and sulfuric acid, and the anilide was then hydrolyzed to give hydrocinnamic acid, the mass spectrum of which has been analyzed, at least to some extent.[8] Finally, the decomposition of Ib was carried out in the presence of 1 equiv of triphenylcarbinol, and IIb was isolated and converted to hydrocinnamic acid as cited above. The most pertinent mass spectral data of the various samples of hydrocinnamic acid are given in Table I.[9] Within the limits of experimental error, the mass spectra of hydrocinnamic acid derived from samples of IIb, produced from Ib either in the presence or in the absence of triphenylcarbinol, were identical. It was also apparent that no deuterium was present in the $-CH_2CO_2H$ portion of the hydrocinnamic acid derived from IIb by observation of the *m/e* peaks at 59 (attributable to $^+CH_2CO_2H$) and 60 (attributable to $^+CH_2CO_2H$ containing a normal abun-

Table I. Mass Spectral Data of Hydrocinnamic Acid and of Hydrocinnamic-α-*d* Acid

	m/e	*I* ± 0.6	Ratio of *I* values
Hydrocinnamic acid	151	4.0	4.0/32.0 = 0.16
	150	32.0	
Hydrocinnamic-α-*d* acid	151	16.5	16.5/33.8 = 0.490
derived from IIb from	150	33.8	
experiment without	92	58.2	58.2/146.5 = 0.400
$(C_6H_5)_3COH$ present	91	146.5	
Hydrocinnamic-α-*d* acid	151	12.5	12.5/23.5 = 0.530
derived from IIb from	150	23.5	
experiment with	92	35.8	35.8/81.5 = 0.439
$(C_6H_5)_3COH$ present	91	81.5	

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(1) W. E. McEwen, A. Blade-Font, and C. A. VanderWerf, *J. Am. Chem. Soc.*, **84**, 677 (1962).

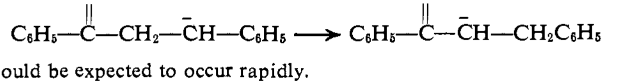
(2) W. E. McEwen and A. P. Wolf, *ibid.*, **84**, 676 (1962).

(3) I. Tomoskozi, *Tetrahedron*, **19**, 1969 (1963).

(4) S. Trippett, *Quart. Rev.* (London), **17**, 427 (1963).

(5) Hydrogen–deuterium exchange between alcohol functional groups has been found to attain equilibrium in less than 2 min at elevated temperatures: H. Kwart, L. P. Luhn, and E. L. Banister, *J. Am. Chem. Soc.*, **76**, 5998 (1954). Thus, the exchange IVb + ROH ⇌ IVa + ROD would certainly occur to a significant extent under the conditions of the experiments undertaken in this study.

(6) The conversion



$$C_6H_5-\overset{O}{\overset{\|}{C}}-CH_2-\bar{C}H-C_6H_5 \longrightarrow C_6H_5-\overset{O}{\overset{\|}{C}}-\bar{C}H-CH_2C_6H_5$$

would be expected to occur rapidly.

(7) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 866 (1962).

(8) "Mass Spectral Data," Dow Chemical Co., Midland, Mich.

(9) The *m/e* peak at 91 (attributable to $C_6H_5CH_2^+$) is the prinicpal one in the mass spectrum of hydrocinnamic acid. The peak at *m/e* 150 is that of the molecular ion $[C_6H_5CH_2CH_2CO_2H]^+$. The peaks at *m/e* 92 and 151, derived from deuterated hydrocinnamic acid, are attributable mainly to $C_6H_5CHD^+$ and $[C_6H_5CHDHC_2CO_2H]^+$, respectively, although there are also minor contributions to these peaks arising from small concentrations of naturally occurring ^{13}C in the samples.