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

Kenneth B. Wiberg, Van Zandt Williams, Jr.
Department of Chemistry, Yale University
New Haven, Connecticut
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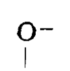
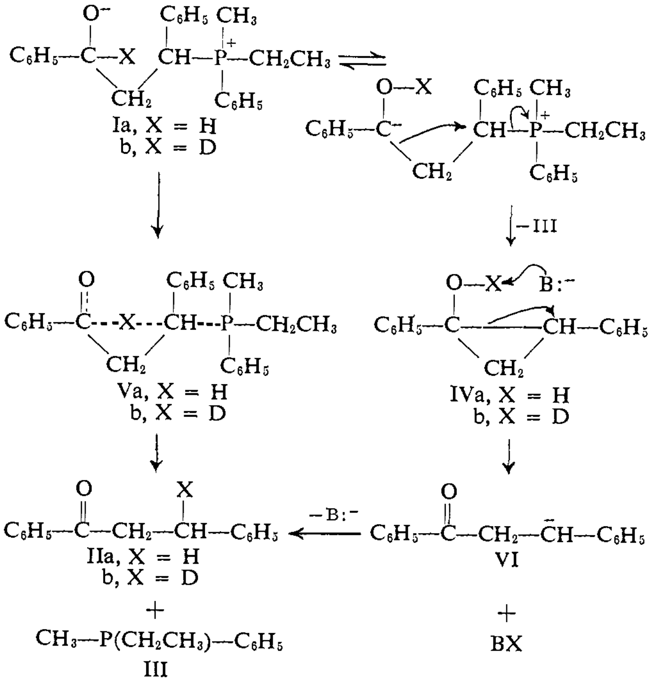
A Deuterium Tracer Study of the Thermal Decomposition of the Adduct of Lithium Iodide and Methylethylphenyl-(1,3-diphenyl-3-hydroxypropyl)-phosphonium Betaine

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  $C_6H_5\overset{O^-}{C}HCH_2C_6H_5$, 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).

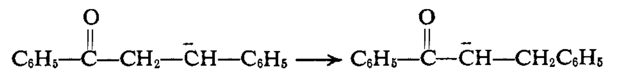
(2) W. E. McEwen and A. P. Wolf, *ibid.*, **84**, 676 (1962).

(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 $IVb + ROH \rightleftharpoons IVa + ROD$ 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.

dance of ^{13}C). Thus, the conclusion can be reached that benzylacetophenone (II) and methylethylphenylphosphine (III) arise from I by way of the transition state V.

Trippett[4] has raised the question as to whether a cation effect would be operative in the decomposition of I. This has now been explored. Methylethylphenylbenzylidenephosphorane was prepared from methylethylphenylbenzylphosphonium iodide by the action of phenylsodium in ether solution. This was treated with styrene oxide to give I and sodium iodide. The ether was evaporated, decalin was added to the residue, and the mixture was heated. No benzylacetophenone (II) and methylethylphenylphosphine (III) were produced. The products of the reaction were methylethylphenylphosphine oxide and the mixture of hydrocarbons reported previously.[1] These results can be explained on the basis that, in the lithium iodide adduct of I, the presence of a strong and largely covalent bond between lithium and oxygen decreases the nucleophilicity of the oxygen to a sufficient extent that it does not readily attack the positive phosphorus atom, the key step in the production of the phosphine oxide and hydrocarbon mixture.[1,2,10]

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[10] E. Zbiral, *Monatsh.*, **94**, 78 (1963).

Jon W. Wolfe, William E. McEwen
Department of Chemistry, University of Massachusetts
Amherst, Massachusetts 01002
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The Preparation of the Octahydropentaborate(−1) Anion, $B_5H_8^-$, and of μ-Monodeuterio-pentaborane(9)

Sir:

Pentaborane(9), B_5H_9, has been found to react with methyl- or *n*-butyllithium in ether solvents at low temperatures to form the solvated lithium salt of $B_5H_8^-$, the first example of a boron hydride anion containing five boron atoms.[1] Reaction of the lithium salt with hydrogen chloride regenerates B_5H_9 in good yield, and reaction with deuterium chloride produces μ-DB_5H_8 exclusively.

In a typical experiment a solution of 3.2 mmoles of *n*-butyllithium and 5.02 mmoles of B_5H_9 in diethyl ether was warmed from −78 to −30° over a 1-hr period. The ether, butane, and excess B_5H_9 were then evaporated at −30° and separated by high-vacuum fractional condensation[2] following treatment with excess BF_3 (to complex the ether) to yield 3.14 mmoles of butane and 1.64 mmoles of recovered B_5H_9 (thus 3.38 mmoles of B_5H_9 was consumed). The nonvolatile solvated LiB_5H_8 remained in the reaction flask as a colorless, viscous oil. The LiB_5H_8 was then redissolved in ether and allowed to react with excess HCl for 1 hr at −78°. Excess BF_3 was added and the volatile components were separated to yield 2.58 mmoles of regenerated B_5H_9 (82% based on butane produced in the initial reaction) which was identified by its 0° vapor pressure of 66.0 mm (identical with the starting B_5H_9) and its infrared spectrum.

In a similar experiment DCl was used in place of HCl, and a 72% yield of μ-DB_5H_8 was isolated and identified by its mass spectrum (sharp cutoff at *m/e* 65 corresponding to $^{11}B_5H_8D^+$ compared to an equally sharp cutoff at *m/e* 64 for $^{11}B_5H_9^+$). Infrared and nmr spectra allowed assignment of the deuterium position.

The ^{11}B nmr spectrum (32.1 Mc) of LiB_5H_8 (obtained at several temperatures from −45° to ambient) consists of an unresolved low-field group (area = 4) with peaks discernible at δ 11.8, 15.9, and 19.2 ppm ($BF_3 \cdot O(C_2H_5)_2 = 0$), and a high-field doublet (area = 1) at δ 53.0 ppm, $J = 165$ cps. When the nmr sample tube was warmed to room temperature the solution rapidly turned yellow, and after about 10 min the LiB_5H_8 spectrum had completely disappeared and was replaced by peaks corresponding to BH_4^- and other unrecognizable species.

Comparison of the ^1H nmr spectrum (100 Mc) of μ-DB_5H_8 with that of B_5H_9 under identical conditions indicated that there was a decrease of intensity only in the bridge hydrogen region of μ-DB_5H_8. The calculated ratio of the terminal hydrogen region to the bridge hydrogen region in B_5H_9 is 1.144; the observed ratio is 1.15 ± 0.01. For μ-DB_5H_8 the calculated ratio is 1.50; the observed ratio is 1.48 ± 0.02. The ^{11}B nmr spectrum of μ-DB_5H_8 was identical with that of B_5H_9, except that the resolution of the low-field doublet in the spectrum of μ-DB_5H_8 (B^{2-5}–H) was a little better, as would be expected with a decrease in the number of bridge hydrogen couplings.

The gas-phase infrared spectrum of μ-DB_5H_8 (10-cm cell, 31-mm pressure) showed a very strong BH stretching mode at 2600 cm^{-1}, but no absorption in the BD stretching region[3] at 1950–2000 cm^{-1}, even after a sample had stood several hours at room temperature in the liquid phase. This very slow exchange between bridge and terminal hydrogens was previously observed by Koski, *et al.*, in the course of B_2D_6–B_5H_9 exchange reaction studies.[4]

In the presence of weak Lewis bases such as tetrahydrofuran μ-DB_5H_8 will undergo intramolecular deuterium–hydrogen exchange between bridge and terminal positions in the base (B^{2-5}) of the B_5 pyramid (within the limits of ^{11}B nmr detection). The mass spectrum cutoff at *m/e* 65 is as sharp after equilibration as before, indicating that no measurable intermolecular exchange occurs. Previously, Onak, Gerhart, and Williams[5] found that treatment of 1-DB_5H_8 with the strong Lewis base 2,6-dimethylpyridine resulted in rapid equilibration of the deuterium atom with all the hydrogen positions in B_5H_9. The differing results in these cases suggest that at least two mechanisms of internal hydrogen exchange are possible in B_5H_9 and that the mechanism depends on the strength of the Lewis base catalyst employed.

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[1] The high thermal stability of the previously reported $[(C_2H_5)_3NH^+][(C_2H_5)B_5H_7^-]$ (W. V. Hough, L. J. Edwards, and A. F. Stang, *J. Am. Chem. Soc.*, **85**, 831 (1963)) suggests that it probably has a structure different from that of the LiB_5H_8 reported here.

[2] R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

[3] H. J. Hrostowski and G. C. Pimentel, *J. Am. Chem. Soc.*, **76**, 998 (1954); I. Shapiro and J. F. Ditter, *J. Chem. Phys.*, **26**, 798 (1957).

[4] W. S. Koski, J. J. Kaufman, and P. C. Lauterbur, *J. Am. Chem. Soc.*, **79**, 2382 (1957), and references therein.

[5] T. P. Onak, F. J. Gerhart, and R. E. Williams, *ibid.*, **85**, 1754 (1963), and references therein.