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).

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The Preparation of the Octahydropentaborate(−1) Anion, B$_5$H$_8^-$, 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.

The data available at the present time suggest that the structure of the $B_5H_8^-$ anion is not greatly different from that of B_5H_9. This interpretation is based on the presence of the high-field doublet in the ^{11}B nmr spectrum, which is typical for "apex" type boron atoms, and on the facile reaction of the anion with HCl to regenerate B_5H_9 at low temperatures. The asymmetry of the low-field group in the ^{11}B nmr spectrum suggests that there are probably more than two types of "basal" boron atoms present. The exclusive formation of μ-DB_5H_8 in the reaction of LiB_5H_8 with DCl suggests that the D^+ enters directly into a bridging position by a mechanism that requires minimal hydrogen rearrangement in the activated complex. These data may be interpreted in terms of three-center bond structures 2221 or 3130 suggested by Lipscomb,[6] though other possibilities cannot be excluded.

Further investigations of these and related systems are underway and will be reported shortly.

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(6) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963.

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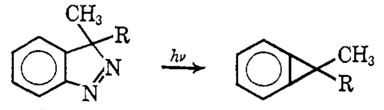
On the Mechanisms of Formation and Decomposition of Benzocyclopropenes. Electron Spin Resonance Spectral and Chemical Evidence for Triplet State Diradical Intermediates[1]

Sir:

The extension of the synthesis of cyclopropenes from 3H-pyrazoles[2] to 3H-indazoles resulted in a convenient method for the preparation of benzocyclopropene derivatives.[3] For example, irradiation of the 3H-indazoles Ia–c in hydrocarbon solvents at low temperatures gave the benzocyclopropenes IIa–c in satisfactory yields. We now wish to report the identification of diradicals which are probable reaction intermediates in the formation and in the thermorearrangements of IIa–c.

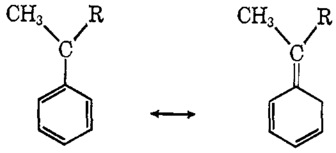


Ia, R = CN
b, R = $COOCH_3$
c, R = OCH_3

IIa, R = CN
b, R = $COOCH_3$
c, R = OCH_3

Ultraviolet irradiation (Pyrex filter) of Ia–c in pentane–isopentane glasses at 77°K in the cavity of an esr spectrometer produced spectra which can be assigned unambiguously to molecules in triplet states. In addition to the $\Delta m = 2$ transitions at half-field, six maxima were observed corresponding to the extreme values of the $\Delta m = 1$ transitions with the magnetic field vector parallel to the principal magnetic axes of the molecules.[4] All transitions were fitted to the usual triplet state spin Hamiltonian, $\mathcal{H} = g\cdot H\cdot|\beta|S + DS_z^2 + E(S_x^2 - S_y^2)$; $S = 1$.[5] The zero-field splitting parameters for the spectra obtained from Ia–c are, respectively: D/hc, 0.1069 ± 0.0005, 0.1110 ± 0.0005, 0.1217 ± 0.0008 cm^{-1}; E/hc, 0.0058 ± 0.0003, 0.0069 ± 0.0003, 0.0066 ± 0.0003 cm^{-1}. All g values are close to 2.002. The spectra produced from Ia and Ib persisted with undiminished intensities for several hours after irradiation had been discontinued, but disappeared rapidly on warming above 100°K. The spectrum obtained from Ic was considerably weaker and faded in less than 1 min after irradiation was ceased, even at 77°K.

The esr data strongly suggest the formation of triplet-state molecules with structure III in which one of the unpaired electrons is essentially localized in a σ orbital in the benzene ring plane, while the second electron is delocalized in the π system.[6] Extended Hückel calculations[7] on the corresponding benzyl radicals predict spin densities at the *ortho* positions of 9.2, 8.4, and 12.2% for IIIa–c, respectively. The observed D values are in semiquantitative agreement with these calculations. The one-center dipole–dipole interaction, represented in the carbene structure of III, makes a large contribution to the zero-field splitting.



IIIa, R = CN
b, R = $COOCH_3$
c, R = OCH_3

A sample of Ib which had been irradiated in a glass at 77°K and which exhibited a strong esr spectrum was warmed up and analyzed for products. Benzocyclopropene IIb was identified, suggesting, but not proving, that IIIb cyclizes on warming.[8]

Chemical evidence for the intermediacy of diradicals of structure III in the photolysis of indazoles was obtained when Ia was photolyzed at −70° in butadiene. Two isomeric products were isolated in 60% yield in a ratio of 1.5:1 and were assigned structures Va and Vb on the basis of mass spectral (parent peak: m/e 183.1045) and nmr evidence [resonances at δ (TMS) Va, 1.33 s (3), 2.9 m (2), 3.3 m (1), 5.3 m (2), 5.9 m (1), 7.2 m (4); Vb, 1.64 s (3), 2.7 m (1), 3.0 m (2), 5.2 m (2), 6.1 m (1), 7.2 m (4)].[9]

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(1) Supported by Grants NSF GP-1076 and GP-4214 from the National Science Foundation.

(2) G. L. Closs and W. A. Böll, *Angew. Chem.*, **75**, 640 (1963); *J. Am. Chem. Soc.*, **85**, 3904 (1963).

(3) R. Anet and F. L. Anet, *ibid.*, **86**, 525 (1964); *cf.* G. L. Closs, *Advan. Alicyclic Chem.*, **1**, 64 (1966).

(4) In the spectrum obtained from Ic only four $\Delta m = 1$ transitions were observable. The S/N ratio of the transitions corresponding to the orientation with the greatest line separation ($H \parallel z$) was too small to determine the peak positions.

(5) For a discussion of esr spectra of triplet states see: C. A. Hutchison, Jr., and B. W. Mangum, *J. Chem. Phys.*, **34**, 908 (1961); E. Wasserman, L. C. Snyder, and W. A. Yager, *ibid.*, **41**, 1763 (1964).

(6) No evidence is at present available on the geometries of III. While it is highly likely that the molecules are planar, it is unknown whether the methyl group in III has a *syn* or *anti* relationship to the *ortho* radical site.

(7) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

(8) The irradiated glasses were intensely yellow colored at 77°K and turned colorless on warming. Considering the close relationship of III with the corresponding benzyl radicals, it is very probable that the color is caused by III. The formation of III from I may well be a two step process, proceeding through an *o*-quinoid diazo compound