CH₃COCH₂CCOPh structures and reactions — compound **2** → (KOH, EtOH–H₂O) → **5**

Starting material **1** → (1. PhLi; 2. H₃O⁺) →

CH₃COCCH₂COPh **3** → (KOH, EtOH–H₂O) → **6**

HCCH₂COPh **4**

δ^{CDCl_3} 3.83 (d, J = 1.5 Hz, 2 H), 6.63 (t, J = 1.5 Hz, 1 H), 7.0–7.9 (m, 15 H)].[8] That **3** arises *via* rearrangement of the anion **7** was shown by the observations that (i) the yield of **3** relative to **2** increases with longer reaction times, and (ii) treatment of **2** with sodium hydride and methanol in ether gave a mixture of **5** and **6**, while **5** is not converted to **6** under these conditions.

This novel rearrangement is considered to proceed *via* the homoenolate ions **8** and **10** as shown in Scheme I. This scheme also accounts for the formation of **4**,

Scheme I
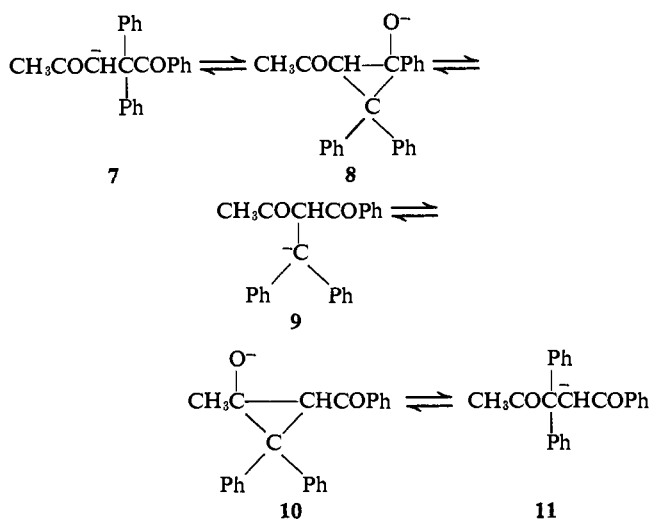
which is considered to arise by hydrolytic cleavage of 2-acetyl-3,3-diphenylpropiophenone formed *via* the ion **9**. An alternative route for the rearrangement involving two 1,2-phenyl migrations[9] is considered unlikely, both because the intramolecular conversion of **7** to **11** in this manner requires in addition a 1,2-hydrogen migration to an anionic center, which is symmetry forbidden,[10] and also because no reaction product is ob-

served in which a single 1,2-phenyl migration has occurred.

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Total Assignment of the Proton Nuclear Magnetic Resonance Spectrum of 1,2-(CH₃)₂B₅H₇ using Heteronuclear (¹¹B) Multiple Resonance Decoupling[1]

Sir:

Perhaps the most important structural feature found in polyboron hydrides is the presence of reasonably stable hydrogen bridge bonds. Yet, very little useful proton magnetic resonance information has been available for making needed bridge hydrogen correlations. This, in part, is attributed to the broad diffuse nature of the bridge hydrogen resonances, and their overlap with other features of the spectra. In addition to this, certain compounds have an equal number of chemically different bridge, terminal, or substituent protons and this has led to ambiguous assignments.[2] We wish to report a method that has enabled us to assign with certainty the complete spectra of a number of boron hydrides and their derivatives.[3] The technique used to assign 1,2-(CH₃)₂B₅H₇ is typical and is presented here.

The decoupled spectra were recorded at 100 MHz using a Varian HA-100 spectrometer[4] equipped with an NMR Specialties heteronuclear decoupler, Model HD-60, modified for use on the HA-100. This system allows the simultaneous irradiation of more than one boron environment by using several audiofrequency oscillators in parallel.

All spectra in Figure 1 were field-swept from low to high field on identical spectrometer power, gain, and re-

(8) The fact that the carbonyl-stretching band in the infrared spectrum of **5** is split while that in the spectrum of **6** is unsplit is in accord with recent observations showing that Fermi resonance splitting of the carbonyl-stretching bands of 3-phenyl-2-cyclopentenones occurs only when both the C-2 and C-5 positions are unsubstituted: P. Yates, G. D. Abrams, and L. L. Williams, *Tetrahedron Lett.*, in press; *cf.* P. Yates and L. L. Williams, *J. Amer. Chem. Soc.*, **80**, 5896 (1958).

(9) *Cf.* E. Grovenstein, Jr. and L. C. Rogers, *ibid.*, **86**, 854 (1964), and earlier papers; H. E. Zimmerman and A. Zweig, *ibid.*, **83**, 1196 (1961); H. E. Zimmerman and F. J. Smentowski, *ibid.*, **79**, 5455 (1957).

(10) *Cf.* N. F. Phelan, H. H. Jaffé, and M. Orchin, *J. Chem. Educ.*, **44**, 626 (1967); R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.* **87**, 2511 (1965).

(1) We are indebted to the National Science Foundation for Grant GP-7911 in support of this study.

(2) (a) T. Onak, G. B. Dunks, I. W. Searcy, and J. Spielman, *Inorg. Chem.*, **6**, 1465 (1967); (b) D. F. Gaines and T. V. Iorns, *J. Am. Chem. Soc.*, **90**, 6617 (1968); (c) A. B. Burg and H. Heinen, *Inorg. Chem.*, **7**, 1021 (1968); (d) A. B. Burg, *J. Am. Chem. Soc.*, **90**, 1407 (1968).

(3) Details submitted for publication.

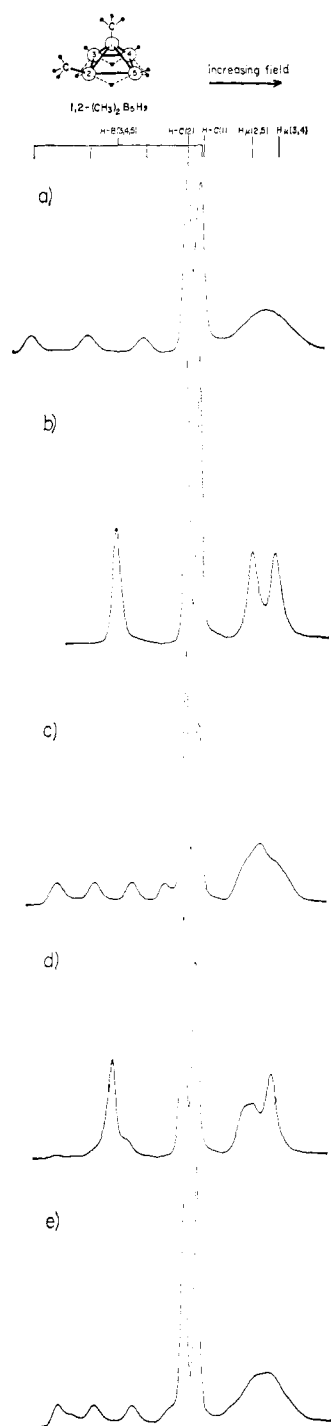(4) This instrument was obtained through Grant GP-8347 from the National Science Foundation.

1,2-(CH₃)₂B₅H₉

a)

b)

c)

d)

e)

Figure 1. Proton nmr spectra of 1,2-(CH₃)₂B₅H₇, 100 MHz: (a) undecoupled spectrum; (b) totally decoupled spectrum using three decoupling frequencies rf (X, Y, Z); (c) effect of rf(X) only; (d) effect of rf(Y) only; (e) effect of rf(Z) only. All spectra field-swept from low to high field.

corder settings to enable direct comparison to be made between the effects of various decoupling experiments (*vide infra*). Comparison undecoupled spectra were run between decoupling experiments to check instrument stability.

Briefly, the technique used was to scan manually through the frequency range of one oscillator and observe the effects on the spectrum. After determining a region of maximum perturbation, the oscillator was carefully tuned to provide the optimum desired decou-

pling effect. After determining the effect of one oscillator, others were added at the specified frequency differences (Table I) to produce total decoupling. However, the essence of this method is to observe the individual effects of the separate irradiating frequencies and to establish patterns of interdependence.

Table I. Correlation between ¹¹B Resonance Chemical Shifts and Decoupling Radiofrequencies for 1,2-(CH₃)₂B₅H₇

Boron atom	2	3, 5	4	1
Chemical shift, ppm^a	−1.1	13.2	17.6	43.6
Corresponding frequency difference (constant field)			835 Hz ← →	
			976 Hz ← →	
		1436 Hz ← →		
Applied frequency difference^b		Y^c ← 900 → Z		
	X ← 1400 → Z			

^{a} Measured at 32.1 MHz relative to ¹¹BF₃O(Et)₂ = 0.0. ^{b} In the HR mode, magnetic field variations modify the decoupling frequencies calculated for a constant field (line 3 of table). At most, this will be within 150 Hz [(12.05 − 7.66) ppm × 32.1 MHz ≤ 150 Hz] of these calculated values. Since the irradiating band width is 700 Hz, the applied frequency differences are insensitive to such corrections. ^{c} Because of decoupling frequency band width,^{b} Y decouples B(3,4,5).

¹H chemical shifts and coupling constants were obtained in separate experiments using TMS as internal standard (Varian A-60 and HA-100 spectrometers). Decoupled spectra were run at a constant temperature of 20°, maintained by the regular variable-temperature inserts, to prevent sample overheating and any consequent spurious thermal effects from the strong rf decoupling field.

The undecoupled proton nmr spectrum of 1,2-(CH₃)₂-B₅H₇ (Figure 1a) exhibits an unresolved bridge region which should theoretically contain two equal areas resulting from different types of hydrogens. The complete assignment of this spectrum depends, firstly, upon the resolution and subsequent assignment of these resonances, and secondly, upon an assignment of the two equal area methyl resonances.

To aid in accomplishing this proton nmr assignment, advantage was taken of the known unambiguous ¹¹B nmr spectrum. From a knowledge of the chemical shifts of the various boron environments it was possible to predict effective decoupling frequencies. Table I lists the boron (¹¹B) chemical shifts and the corresponding frequency differences for 1,2-(CH₃)₂B₅H₇. From these it is evident that the boron resonances cover a substantial frequency range of over 1400 Hz. In separate experiments, it has been determined that, at the operating power, the decoupler unit radiofrequency has a band width of approximately 700 Hz. Thus, it is apparent that in compounds of this type at least two oscillators are required to cover the whole 1400-Hz range spanned by the boron resonances. In the case of 1,2-(CH₃)₂-B₅H₇, three were necessary to attain total decoupling (Figure 1b), one each for the high-field, B(1), intermediate-field, B(3,4,5), and low-field, B(2), resonances.

The results are displayed in Figure 1 and details are tabulated in Table II. Figure 1 shows the undecoupled ¹H spectrum and its totally decoupled counterpart ob-

Table II. The Effect of Various ^{11}B Decoupling Frequencies on the Proton Spectrum of 1,2-$(CH_3)_2B_5H_7$

Decoupling radiofrequency	Boron atom irradiated	"Sharpening factor" [a] for methyl proton resonance 1[b]	2[c]	Other effects
Rf(X)	B(2)—CH$_3$	1.4	2.1	Predominant effect on low-field bridge proton resonance. Little effect on terminal basal proton resonance
Rf(Y)	B(3,4,5)—H	1.4	1.8	Decouples base terminal protons and high-field bridge resonance. Little effect on low-field bridge resonance
Rf(Z)	B(1)—CH$_3$	2.7	1.5	Little effect on terminal or bridge proton resonance
Rf(X) + rf(Y) + rf(Z)	B(1→5)	3.2	2.4	Spectrum totally decoupled

[a] Sharpening factor $= (H_1/H_0) \times (W_0/W_1)$, where H_0 and W_0 = height, width at half-height of methyl resonance without applied ^{11}B decoupling; H_1 and W_1 = height, width at half-height of methyl resonance with applied ^{11}B decoupling. [b] 1 = high-field methyl resonance (shown to be apex). [c] 2 = low-field methyl resonance (shown to be basal).

tained by using three audiooscillators (X, Y, Z) which generated the corresponding decoupling radiofrequencies, rf(X, Y, Z). The effect of each individual frequency [rf(X → Z)] is also shown. Thus, for example, Figure 1d illustrates the effect of irradiating the basal borons B(3,4,5) which results in the collapse of the quartet (H–^{11}B) and the concomitant appearance of a single peak. A simultaneous sharpening in the high-field bridge resonance is also noted.

The gross perturbations engendered in the thermal and bridge proton resonances are easily observed (Figure 1b–d), but the effect of ^{11}B irradiation upon the methyl resonances is a little less obvious. For purposes of comparing these effects we have defined a "sharpening factor" (Table II) which allows direct comparison between high- and low-field resonances. Careful examination of these data and the spectra allows the establishing of interdependence between the particular irradiating rf field and simultaneous effects on one or more regions of the spectrum. Thus it is seen that the low-field methyl and the low-field bridge resonances are decoupled by rf(X) (Figure 1c); similarly interrelated are the terminal proton and the high-field bridge resonances (Figure 1d), whereas the high-field methyl peak appears to be predominantly independent, Figure 1e. These effects undoubtedly result from the proximity of these proton environments to the irradiated boron atoms. These results provide confirmation of the boron assignments and enable the proton resonances to be assigned. Details are presented in Table III.

Table III. ^{1}H Nmr Chemical Shift Values and Coupling Constants for 1,2-$(CH_3)_2B_5H_7$

Proton environment[a]	τ, ppm[b]	J, Hz[c]
H···B(3,5) [d] H···B(4)	7.66	156
Hμ (2,5)	11.45	~30[e]
Hμ (3,4)	12.05	~30[e]
H···C(1)	9.95	
H···C(2)	9.60	

[a] B(3,4,5) are basal borons; Hμ = bridge hydrogen, Hμ (2) designates bridge proton between boron atoms 2 and 3, etc. [b] To avoid negative values, τ (TMS = 10.00) is used rather than δ. [c] H–^{11}B coupling only. [d] No chemical shift difference discernible. [e] Cannot be accurately determined due to lack of fine structure.

It is apparent from the data in Table II and by observation of the spectra that there is some overlap of effect.

For example, although the primary effect of rf(X) is to decouple boron atom B(2), thus sharpening the base methyl resonance and the low-field bridge resonance, it also has some effect upon the rest of the spectrum causing a slight sharpening in the apex methyl resonances and altering the coupling constants of the basal B–H resonances. This is almost certainly due to the band width of the irradiating field (vide supra) but may be also due, in part, to small long-range coupling effects.

Despite this slight element of uncertainty, it is encouraging to note the success of this method in that it has enabled the broad bridge proton resonance to be decoupled and assigned. The definitive assignment of the methyl proton resonances has also been possible; and further, from these and other experiments on various pentaborane derivatives,[3] conclusions have been made regarding the effect of substituents upon the chemical shift of the bridge resonances. Thus taking the values in pentaborane as a standard for reference, a basal methyl or ethyl group shifts the resonance due to the adjacent equivalent protons, Hμ (2,5), downfield by ca. 0.7 ppm, without substantially affecting the far bridge resonance, Hμ (3,4). A base chlorine atom caused a similar downfield shift of ca. 1.5 ppm, again without great effect upon the far resonance. In polysubstituted derivatives these affects appear to be additive.

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Organometallic Conformational Equilibria. VIII. Spin Saturation Labeling Studies of the Epimerization and Isomerization Mechanism of 1,2,3-*Trihapto*-(3-acetyl-2-methyallyl)[(S)-α-phenethylamine]-chloropalladium(II)[1]

Sir:

Crystallization of 1,2,3-*trihapto*(3-acetyl-2-methallyl)[(S)-α-phenethylamine]chloropalladium(II)[2] from carbon tetrachloride results in the isolation of only one

(1) Part VII: J. W. Faller and M. J. Incorvia, *J. Organometal. Chem.*, in press.

(2) This nomenclature has been suggested by Cotton.[3] The Greek prefix *hapto* indicates the number and location of carbon atoms connected to the metal atom.

(3) F. A. Cotton, *J. Am. Chem. Soc.*, **90**, 6230 (1968).