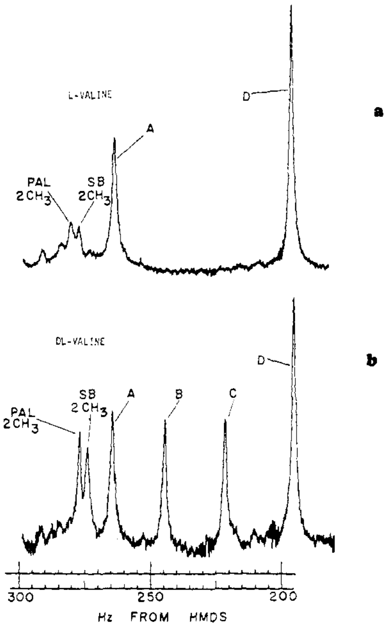

Figure 2. The 100-MHz nmr spectra of: (a) 0.102 M L-valine, 0.104 M pyridoxal, and 0.050 M Al(III) at pD 8.9; (b) 0.102 M DL-valine, 0.102 M pyridoxal, and 0.050 M Al(III) at pD 9.7. T = 30°, ionic strength adjusted to 1.0 with NaCl, HMDS = hexamethyldisiloxane in an internal capillary, PAL = pyridoxal, SB = Schiff base.

complex is prepared from the racemic amino acid and from the pure L isomer. The racemic complex has two resonances, B and C, which are absent from the pure L complex. These are assigned to the crowded and uncrowded 2-CH_3 resonances of the identical DL and LD complexes. Therefore, the doubly crowded DD and LL 2-CH_3's give rise to the resonance at A in Figure 1b. As expected, the most abundant species are the doubly uncrowded DD and LL forms. Their identical methyl groups give rise to resonance D.[7a]

Interestingly, in the DL and LD cases, crowding, and subsequent relative deshielding, at one methyl results in deshielding at the other methyl group as well. The effect is as expected because the aromatic portions of these ligands are probably quite rigid and thus steric crowding which forces one 2-CH_3 group from its favored position above an azomethine nitrogen is transmitted as a shearing force to the other azomethine nitrogen, also forcing it away from its 2-methyl group, but probably by a smaller distance than occurs at the crowded position. Accordingly, in Figures 1 and 2 the resonance at B is assigned to the crowded methyl group and the one at C is assigned to the uncrowded methyl group of the DL and LD complexes.

The relative proportions of the various species suggest that the DL and LD states are about 0.5 kcal/mol above the uncrowded DD and LL, and that the doubly crowded DD and LL states are about 0.4 kcal/mol above the DL and LD states.

Preliminary investigations of alanine, α-aminobutyric acid, norvaline, valine, and threonine indicate that similar species are also the prevalent components of these systems, and that increasing the steric requirements of the amino acid accentuates the energy separation and relative deshielding of the 2-CH_3 resonances of the various isomers. In the case of glycine, only a single peak is observed, in the region of 200 Hz, since glycine lacks optical activity and therefore cannot form distinguishible isomers.

Apparently, the ability of the unsaturated bonds to shield the methyl groups is a very sensitive function of distance and it is this effect which makes it possible to resolve these nearly isoenergetic forms. The 6-H, 4-CH, and 5-CH_2 signals for these isomers cannot be resolved.

This research is part of a continuing investigation into the structure and catalytic properties of pyridoxal systems. Further details will be forthcoming shortly.

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[7a] NOTE ADDED IN PROOF. Resonances B and C appear slowly in the optically active amino acid systems, as the result of α-proton exchange, and resulting racemization, of the bis complex.

A Carbanion Rearrangement *via* Two Homoenolate Ions

Sir:

Several reports have appeared in recent years of carbanion rearrangements that are considered to proceed *via* homoenolate ions;[1] we now wish to report on a transformation that we consider involves the rearrangement of a carbanion *via* two homoenolate ions.

Reaction of diazoacetone with diphenylketene[2] gave the enol lactone **1** (11%):[3,4] mp 49–52°; $\lambda_{max}^{CCl_4}$ 5.54, 5.92 (m) μ; δ^{CCl_4} 2.10 (d, J = 1.5 Hz, 3 H), 5.63 (q, J = 1.5 Hz, 1 H), 7.26 (s, 10 H) (the major product from this reaction was 1-acetyl-3-phenylindan-2-one[5]). Treatment of **1** with phenyllithium in ether for 20 min followed by work-up with aqueous acid gave 1,2,2-triphenyl-1,4-pentanedione (**2**)[4] (42%), mp 154.5–155.5°, 1,3,3-triphenyl-1,4-pentanedione (**3**) (4.2%), mp 152.5–154°, and 3,3-diphenylpropiophenone (**4**) (5.5%);[6] examination of the spectra of the crude reaction product failed to reveal the presence of other reaction products. The structures of compounds **2** and **3** were established by their spectra [**2**: $\lambda_{max}^{CCl_4}$ 5.79, 5.96, 7.36 (m) μ; λ_{max}^{EtOH} 239 (ε 9800), 316 mμ (ε 310); δ^{CDCl_3} 1.91 (s, 3 H), 3.71 (s, 2 H), 7.0–7.6 (m, 15 H); **3**: $\lambda_{max}^{CCl_4}$ 5.85 (sh), 5.90, 7.40 (m) μ; λ_{max}^{EtOH} 242.5 (ε 13,800), 276.5 mμ (ε 1580); δ^{CDCl_3} 2.17 (s, 3 H), 4.14 (s, 2 H), 7.1–7.5 (m, 13 H), 7.7–7.9 (m, 2 H)] and by their conversion on treatment with ethanolic aqueous potassium hydroxide to 3,4,4-triphenyl-2-cyclopentenone[4] (**5**), mp 173–179°,[7] and 3,5,5-triphenyl-2-cyclopentenone (**6**), mp 155–156.5°, respectively [**5**: $\lambda_{max}^{CCl_4}$ 5.80 (sh), 5.87 μ; λ_{max}^{EtOH} 290 mμ (ε 17,000); δ^{CDCl_3} 3.30 (s, 2 H), 6.84 (s, 1 H), 7.0–7.5 (m, 15 H); **6**: $\lambda_{max}^{CCl_4}$ 5.87 μ; λ_{max}^{EtOH} 288.5 mμ (ε 22,900);

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(1) See, for example, A. Nickon and J. L. Lambert, *J. Amer. Chem. Soc.*, **84**, 4604 (1962); A. Nickon, J. Kwasnik, T. Swartz, R. O. Williams, and J. B. DiGiorgio, *ibid.*, **87**, 1615 (1965); R. Howe and S. Winstein, *ibid.*, **87**, 915 (1965); T. Fukunaga, *ibid.*, **87**, 916 (1965); J. P. Freeman and J. H. Plonka, *ibid.*, **88**, 3662 (1966).

(2) *Cf.* P. Yates and T. J. Clark, *Tetrahedron Lett.*, 435 (1961).

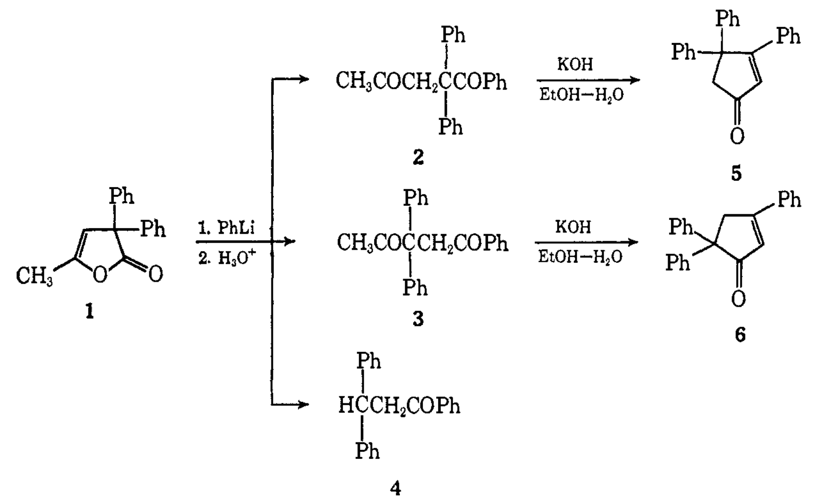
(3) Satisfactory elemental analyses have been obtained for all new compounds.

(4) First prepared by Dr. L. L. Williams, Ph.D. Thesis, Harvard University, 1961.

(5) *Cf.* A. S. Kende, *Chem. Ind.* (London), 1053 (1956).

(6) Identified by comparison with an authentic sample kindly provided by Professor R. E. Lutz, University of Virginia; *cf.* R. E. Lutz and J. O. Weiss, *J. Amer. Chem. Soc.*, 77, 1814 (1955).

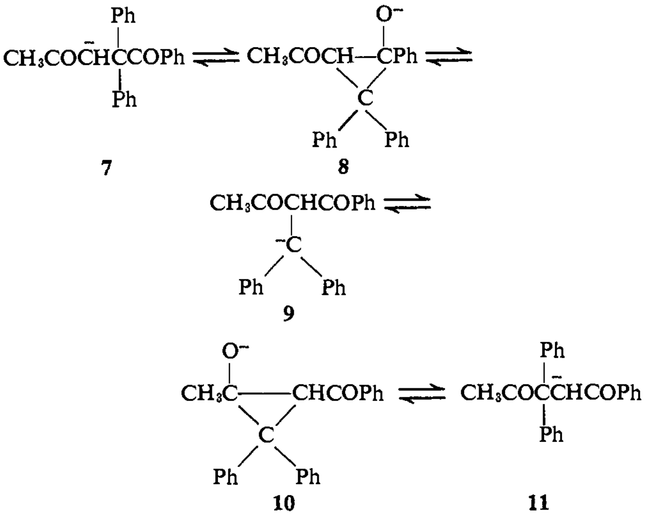
(7) The wide melting range is attributable to the presence of two dimorphs.



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

Scheme I



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[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).

[11] Province of Ontario Graduate Fellow, 1964–1965.

Total Assignment of the Proton Nuclear Magnetic Resonance Spectrum of $1,2\text{-}(CH_3)_2B_5H_7$ using Heteronuclear (^{11}B) 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 $1,2\text{-}(CH_3)_2B_5H_7$ 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-

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[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.