

Table I. Ionization Potentials of Ferrocenes and Bis(1-substituted-borabenzene)iron^a

Compound	Ia	Iv
Ferrocene		6.88 ¹¹
1,1'-Diacetylferrocene	7.05	7.41
4a	7.04	7.67
4b	7.22	7.73
4c	7.16	7.67

^aIa and Iv are ± 0.05 eV. Calibration relative to HXe/ ϕ .

3.5 (dt, $J = 13, 2$ Hz, 2 H); 2.9 (brd, $J = 13$ Hz, 2 H). Interesting, although the mass spectrum of **6d** has a strong peak for the molecular ion (m/e , 156 for $C_5H_6^{11}B^{79}Br$), the base peak occurs at m/e 76, which corresponds to a loss of HBr to the parent borabenzene ($C_5H_5B^+$).⁷ Treating **6d** with excess *tert*-butyllithium followed by ferrous chloride produces bis(1-*tert*-butylborabenzene)iron (**4c**) in an overall yield of 28%: Mp, 144–145°; ¹H NMR (CDCl₃), τ 8.85 (s, 18 H), 5.65 (d, $J = 9$ Hz, 4 H), 4.60 (m, 4 H), 4.40 (t, $J = 5.5$ Hz, 2 H); ¹¹B NMR (CDCl₃) δ -24.6; mass spectral m/e , 322 (M⁺, C₁₈H₂₈¹¹B₂⁵⁶Fe); uv (C₂H₅OH) λ_{max}^{nm} 214 (35000), 274 (2170), 312 (1320), 362 (660). **4b** has also been produced analogously from **2d** with methyllithium and presumably the synthesis could be extended to other 1-substituted analogs by varying the alkyl lithium. Compounds **4a** and **4b** have recently been reported by Herberich.³ Thus this synthesis provides a point of convergence for the two methods for producing borabenzene.

Like the previously reported complexes, data indicate that the 1-substituted-borabenzene is a η^6 -ligand.¹⁻³ π -Boron coordination to iron is suggested by the air-stability of **4** in contrast to their pyrophoric conjugate acids **6** and by the large upfield shift of **4** relative to **6** in the ¹¹B NMR spectra. Similarly the ¹H NMR chemical shift values show a considerably smaller range than those of η^5 -cyclohexadienyl iron complexes.⁷

The ⁵⁷Fe Mössbauer spectrum of **4a** has been measured. The isomeric shift relative to Na₂Fe(CN)₅NO·2H₂O is identical with that of ferrocene, 0.72 mm/sec, while the quadrupole splitting is 1.97 mm/sec, somewhat smaller than that of ferrocene (2.40 mm/sec). A similar reduction in the magnitude of the quadrupole splitting has been observed for ferrocenes with strongly electron withdrawing substituents.⁹ This suggests 1-phenylborabenzene withdraws somewhat more electron density from the iron than do the cyclopentadienyl rings of ferrocene, although the equality of the isomeric shift makes it improbable that there is any large electronic difference at iron.

The ionization potentials of **4** have been measured by He(I) ionization. See Table I. The vertical ionization potentials are approximately 0.8 eV greater than ferrocene¹⁰ and indeed are similar to those of the electron withdrawing ferrocene 1,1'-diacetylferrocene.

Friedel-Crafts acetylation of **4b** with acetylchloride, aluminum chloride in methylene chloride at 0° gave a 20% yield of a monoacetyl product, **7b**: mass spectral m/e , 280 (M⁺, C₁₄H₁₈¹¹B₂⁵⁶FeO); ir (CDCl₃) 1662 cm⁻¹; ¹H NMR, τ 9.35 (s, 3 H), 9.13 (s, 3 H), 7.63 (s, 3 H), 5.90 (d, $J = 8$ Hz, 1 H), 5.50 (d, $J = 9$ Hz, 1 H), 5.34 (d, $J = 9$ Hz, 1 H), 4.8–4.3 (m, 5 H), 4.08 (d, $J = 6$ Hz, 1 H). Since only three α -protons are observed as higher field doublets, the acetyl group must occupy the 2-position. Bis(1-*tert*-butylborabenzene)iron was recovered unchanged upon attempted acetylation even at higher temperatures.

The four α -protons of **4b** exchange when treated with trifluoroacetic acid-*d*₁ at 25°. No further exchange was found even after 24 hr at reflux. Exchange is slower in CF₃CO₂D-benzene mixtures. In competition experiments ferrocene

reacts more rapidly than **4b**, which exchanges at approximately the same rate as mesitylene. Thus on an approximate reactivity scale, ferrocene is three orders of magnitude more reactive than **4b**.¹²

The lower reactivity of the **4b** relative to ferrocene is consistent with its higher ionization potential. On the other hand the low reactivity of the β and γ positions relative to the α position may reflect a lower stability of the corresponding intermediates for substitution. Perhaps boron-cross-conjugated diene-iron complexes, which must be intermediates for substitution at the β and γ positions, are of higher energy than the terminal boron-conjugated diene-iron complex which would be the intermediate for α -substitution.¹³

Acknowledgments. This work was partially supported by grants from the National Science Foundation. We would also like to thank Professor Herberich for discussing his work with us prior to publication.

References and Notes

- (1) G. E. Herberich, G. Greiss, and H. F. Heil, *Angew. Chem., Int. Ed. Engl.*, **9**, 805 (1970); G. E. Herberich and G. Greiss, *Chem. Ber.*, **105**, 3413 (1972).
- (2) G. E. Herberich and H. J. Becker, *Angew. Chem., Int. Ed. Engl.*, **12**, 764 (1973); **14**, 184 (1975).
- (3) G. E. Herberich, *Chimia*, **26**, 475 (1972); G. E. Herberich, H. J. Becker, and G. Greiss, *Chem. Ber.*, **107**, 3780 (1974).
- (4) A. J. Ashe, III, and P. Shu, *J. Am. Chem. Soc.*, **93**, 1804 (1971).
- (5) A. J. Ashe, III, and P. Shu, Abstracts, 165th National Meeting of the American Chemical Society, Dallas, Texas, April 1973, No. ORGN 53.
- (6) Satisfactory combustion analyses have been obtained on all new compounds.
- (7) However, see R. Van Veen and F. Bickelhaupt, *J. Organomet. Chem.*, **43**, 241 (1972).
- (8) D. Jones, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4458 (1962).
- (9) A. V. Lesikan, *J. Chem. Phys.*, **40**, 2746 (1964); R. A. Stukan, S. P. Gubln, A. N. Nesmeyanov, V. I. Gol'danskii, and E. F. Makarov, *Theor. Exp. Chem. (USSR)*, **2**, 581 (1966).
- (10) In parallel to these observations, it has been reported that the ionization potential of 3 is 1 eV greater than that of cobaltocene. G. E. Herberich, G. Greiss, H. F. Heil, and J. Muller, *Chem. Commun.*, 1328 (1971).
- (11) S. Evans, M. L. H. Green, B. Jewitt, A. F. Orchard, and C. F. Pygall, *J. Chem. Soc., Faraday Trans. 2*, 1847 (1972).
- (12) See A. N. Nesmeyanov, D. N. Krysanov, V. N. Setkina, N. V. Kislyakova, and N. S. Kochetkova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1932 (1962). Apparently the relative rates of acetylation parallel those of deuterium exchange: see H. C. Brown and G. Marino, *J. Am. Chem. Soc.*, **81**, 5611 (1959); M. Rosenblum, J. O. Santer, and W. G. Howells, *ibid.*, **85**, 1450 (1963).
- (13) A similar effect is observed with tricarbonyl(diene)iron complexes: R. E. Graf and C. P. Lilly, *J. Am. Chem. Soc.*, **94**, 8282 (1972).
- (14) A. P. Sloan Fellow, 1973–1976.

Arthur J. Ashe, III,*¹⁴ Elizabeth Meyers
Paul Shu, Thomas Von Lehmann

Department of Chemistry, University of Michigan
Ann Arbor, Michigan 48104

J. Bastide

Physikalisch-Chemisches Institut der Universität Basel
4056 Basel, Switzerland
Received June 23, 1975

Zeugmatographic High Resolution Nuclear Magnetic Resonance Spectroscopy. Images of Chemical Inhomogeneity within Macroscopic Objects¹

Sir:

Two- and three-dimensional images of objects, including living organisms, may be generated from their NMR signals in magnetic field gradients.^{2,3} These "zeugmatographic" techniques may be combined with high resolution pulsed Fourier transform NMR spectroscopy to make possible noninvasive nondestructive spatially resolved chemical analyses of the interiors of objects.

We describe here one simple illustrative example of such

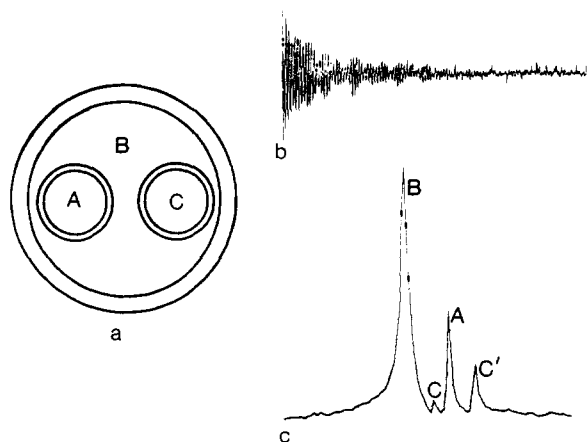


Figure 1. (a) A cross-sectional diagram of the composite sample. The outer 15 mm o.d. tube contains sulfuric acid (B), one inner 5 mm o.d. tube contains water (A), and the other contains *p*-(CH₃)₃CC₆H₄NO₂; (b) a 4-MHz free induction decay (FID) of the proton resonance signals from the entire sample after a nonselective 5 msec 90° pulse in a homogeneous static magnetic field. The segment shown is 500 msec in length; (c) the Fourier transform power spectrum of (b). The peak labels correspond to those in (a), with C being the collapsed group of aromatic hydrogen peaks and C' the *tert*-butyl peak. The chemical shift difference between B and C' is about 10 ppm, or 40 Hz.

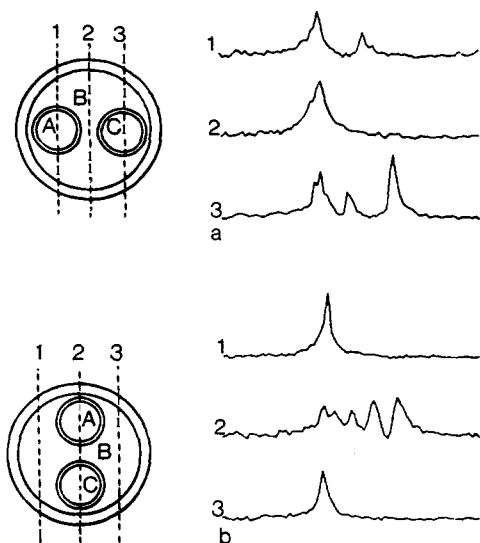


Figure 2. Spectra of the object in Figure 1a produced by selective excitation in a field gradient: (a) excitation in an *x*-gradient, to give the spectra of compounds present near several planes of constant magnetic field perpendicular to the *x* axis; (b) excitation in an *x*-gradient, after rotation of the object by 90°.

an experiment, and suggest some possible extensions and useful applications. Our test sample is diagrammed in Figure 1, which also shows the results of a conventional high resolution pulsed Fourier transform experiment on this non-spinning complex object. If a magnetic field gradient is imposed on the sample during the radiofrequency pulse, resonance will occur only in a limited region,^{3a,4} such as that near line 1 in Figure 2a. If the gradient is then removed, the free induction decay of the remaining transverse magnetization in the selectively excited region may be Fourier transformed to give a spectrum such as 1 in Figure 2a, in which only the signals from material near one constant field plane appear. Repetition of this sequence with a slight change in magnetic field (or radiofrequency), as shown in Figure 3, will give information on the materials present in another slice of the sample. One-dimensional projections of the distributions of each resolvable chemical species may thus be

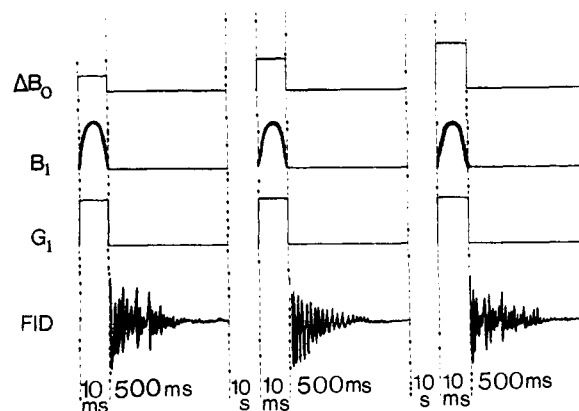


Figure 3. A schematic pulse sequence capable of generating free induction decays (FID) that may be transformed to give spectra such as those in Figure 2. An offset field pulse ΔB_0 is stepped to cause the B_1 excitation pulses to generate signals in a succession of locations 1, 2, 3 ... in gradient G_1 . The pulses are all off during the FID so that each spectrum has the same origin in frequency space.

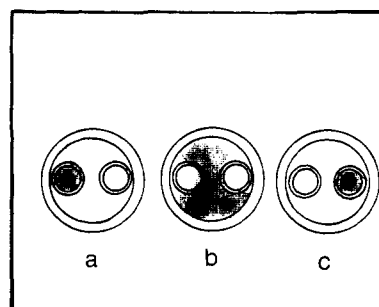


Figure 4. Proton NMR zeugmatograms of the individual chemical species in the object shown in Figure 1. Each was reconstructed by a multiplicative ART-type⁸ algorithm from six 32-point projections, at 30° intervals, each derived from 18 selective 7 msec half-width Gaussian pulse excitations in a 0.25 G cm⁻¹ gradient. The images are displayed by a 16 gray level overprinting program: (a) the distribution of water in one inner tube; (b) the distribution of sulfuric acid in the outer tube; (c) the distribution of *p*-*tert*-butylnitrobenzene in the other small tube, as derived from the intensities of the *tert*-butyl resonance. All data were obtained from the integrals of phase-corrected absorption mode transforms.

assembled. Rotation of the object, as in Figure 2b (or the gradient), will give additional projections from which the two- or three-dimensional distributions of each compound may be reconstructed,^{2a} as shown in Figure 4.

This technique is potentially applicable to any chemical components of an object that show resolved NMR signals in a homogeneous magnetic field, and may be extended to studies in solids by the application of line-narrowing techniques.⁵⁻⁷ Spatial resolutions of better than 0.1 mm will be difficult to achieve because of the limited sensitivity of nuclear magnetic resonance, and the upper limits on sample size will probably depend upon magnet technology. In addition to studies of chemical systems, biological applications, such as the differentiation between fat and other tissues in organisms, are under investigation.

Acknowledgment. This investigation was supported by Public Health Service Research Grant No. CA-15300 from the National Cancer Institute, and by the Gulf Oil Foundation.

References and Notes

- (1) Presented in part at the 169th National Meeting of the American Chemical Society, Philadelphia, Pa., April 8, 1975.
- (2) (a) P. C. Lauterbur, *Nature (London)*, **242**, 190 (1973); (b) P. C. Lauterbur, Proceedings of the First International Conference on Stable Isotopes in Chemistry, Biology, and Medicine, May, 1973, AEC Publication CONF-

- 730525; (c) P. C. Lauterbur, *Pure Appl. Chem.*, **40**, 149 (1974).
 (3) (a) W. S. Hinshaw, *Phys. Lett. A*, **48**, 87 (1974); (b) P. C. Lauterbur, W. V. House, Jr., D. M. Kramer, C.-N. Chen, and R. Dias, Proceedings of the 18th Ampere Congress, Vol. 1, Nottingham Ampere Committee, Department of Physics, The University of Nottingham, England, 1974, p 27; (c) P. Mansfield, P. K. Grannell, and A. A. Maudsley, *ibid.*, p 431; (d) W. S. Hinshaw, *ibid.*, p 433; (e) J. M. S. Hutchison, J. R. Mallard, and C. C. Goll, *ibid.*, p 283.
 (4) A. N. Garraway, P. K. Grannell, and P. Mansfield, *J. Phys. C*, **7**, L457 (1974).
 (5) (a) J. S. Waugh, C. H. Wang, L. M. Huber, and R. L. Vold, *J. Chem. Phys.*, **48**, 662 (1968); (b) J. S. Waugh, L. M. Huber, and U. Haeberlen, *Phys. Rev. Lett.*, **20**, 180 (1968); (c) U. Haeberlen and J. S. Waugh, *Phys. Rev.*, **175**, 453 (1968).
 (6) A. Pines, M. G. Gibby, and J. S. Waugh, *J. Chem. Phys.*, **59**, 569 (1973).
 (7) (a) P. Mansfield, P. K. Grannell, A. N. Garraway, and D. C. Stalker, Proceedings of the First Specialized "Colloque Ampere", Institute of Nuclear Physics, Krakow, Poland, 1973, p 16; (b) P. Mansfield and P. K. Grannell, *J. Phys. C*, **6**, L422 (1973); (c) P. Mansfield, P. K. Grannell, and A. A. Maudsley, Proceedings of the 18th Ampere Congress, Nottingham, England, Vol. 2, 431 (1974).
 (8) G. T. Herman, A. Lent, and S. W. Rowland, *J. Theor. Biol.*, **42**, 1 (1973).

Paul C. Lauterbur,* David M. Kramer
 Waylon V. House, Jr., Ching-Nien Chen

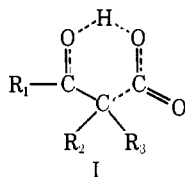
Department of Chemistry
 State University of New York at Stony Brook
 Stony Brook, New York 11794

Received July 28, 1975

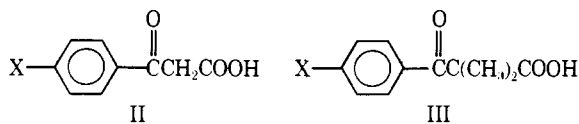
The Nature of the Transition State for the Decarboxylation of β -Keto Acids

Sir:

Although it is generally accepted that the mechanism for the decarboxylation of β -keto acids involves unimolecular decomposition through a cyclic transition state (I), the timing of the hydrogen transfer relative to carbon-carbon bond cleavage is highly controversial.¹⁻⁶ Particularly perplexing



is the report² that hydrogen isotope effects vary from 0.8 to 2.8 (k_H/k_D) for the decomposition of ring substituted benzoylacetic acids in benzene, suggesting that hydrogen transfer is part of the reaction coordinate in some systems but not in others, or that the degree of hydrogen transfer varies markedly with substituent. In addition, substituent effects on the decarboxylation of a series of ring substituted benzoylacetic acids (II) in water ($\rho = 0.03$)⁶ and in benzene (ρ



- a, X = H
 b, X = NO₂
 c, X = Cl
 d, X = CH₃O

$= -1.0$)² have been interpreted⁶ in terms of a transition state with significant charge separation in benzene and a nonpolar transition state in water. Although the observed substituent effects seemed to demand such an explanation, this unusual conclusion, coupled with the highly variable hydrogen isotope effects, prompted us to investigate these reactions further. We now wish to report that (1), contrary to a previous report,² enolization of benzoylacetic acid (IIa) in benzene is extensive and complicates the interpretation of

Table I. Substituent Effects and Hydrogen Isotope Effects in the Decarboxylation of Substituted α,α -Dimethylbenzoylacetic Acids at 47.7°a

Substituent	$10^4 k_H$ (sec ⁻¹) ^b	$10^4 k_D$ (sec ⁻¹) ^b	k_H/k_D ^{b,c}
<i>p</i> -CH ₃ O	2.72 ± 0.07	2.47 ± 0.12	1.14 ± 0.02
H	5.09 ± 0.27	4.34 ± 0.34	1.20 ± 0.02
<i>p</i> -Cl	4.18 ± 0.26	3.47 ± 0.17	1.20 ± 0.02
<i>p</i> -NO ₂	6.29 ± 0.41	4.40 ± 0.14	1.41 ± 0.04

^a Rates were measured spectrophotometrically in 0.200 *N* HCl and 0.185 *N* DCl solutions. At these acid concentrations, the rates of decarboxylation are independent of acid concentration and represent decomposition of the un-ionized acid. The synthesis of these compounds has been described (M. W. Logue, *J. Org. Chem.*, **39**, 3455 (1974)). ^b Errors are standard deviations. ^c Isotope effects were determined by running H's and D's simultaneously in order to minimize systematic errors.

the experimental results for decarboxylation of β -keto acids in nonpolar solvents and (2) hydrogen isotope effects for the decarboxylation of ring substituted α,α -dimethylbenzoylacetic acids (IIIa-d), which cannot enolize, are uniformly small ($k_{H_2O}/k_{D_2O} = \text{ca. } 1.3$) and vary only slightly with substituent (Table I).

Ultraviolet spectra of benzoylacetic acid (IIa) in benzene ($\lambda_{\text{max}} 289$, $\epsilon 6600$),¹⁰ as well as cyclohexane ($\lambda_{\text{max}} 287$, $\epsilon 11300$) suggest extensive enolization in these solvents,⁷ whereas the uv spectrum of IIa in 0.2 *N* aqueous HCl ($\lambda_{\text{max}} 249$, $\epsilon 13400$, and $\lambda_{\text{max}} 285$ (s), $\epsilon 2800$) suggests little or no enolization. Further evidence for this interpretation is provided by the fact that the uv spectra of α,α -dimethylbenzoylacetic acid (IIIa) in water ($\lambda_{\text{max}} 248$, $\epsilon = 10700$, and $\lambda_{\text{max}} 280$ (s), $\epsilon 900$), benzene ($\lambda_{\text{max}} 282$, $\epsilon 750$),¹⁰ and cyclohexane ($\lambda_{\text{max}} 242$, $\epsilon = 12500$, and $\lambda_{\text{max}} 280$, $\epsilon 900$) are virtually identical. In addition, IIa adds ca. 85% of the theoretical¹¹ amount of bromine practically instantaneously in benzene solution.

The existence of this complicating side reaction, earlier believed to be absent, means that the previously measured² substituent effects and isotope effects do not refer solely to the decarboxylation process. Consequently, conclusions regarding the nature of the transition state for decarboxylation in benzene are unreliable. Use of dimethylbenzoylacetic acids (III) as substrates would obviate this problem; however, dimerization of these acids in nonpolar solvents¹⁵ presents an additional complication. Thus, in view of other available evidence (solvent effects¹ and substituent effects), we prefer a nonpolar transition state in all solvents.

The uniformly small isotope effects which we observed in the decarboxylation of α,α -dimethylbenzoylacetic acids in water suggest that the hydrogen is not undergoing translation in the reaction coordinate. These low isotope effects stand in marked contrast to the isotope effects of 2.4-4.8 (extrapolated to 50°) observed in the thermal decarboxylation of 2,2-dimethyl-3-phenylbut-3-enoic acids.¹⁸ We interpret these low isotope effects in terms of the model proposed by Swain and Schowen in which proton transfer between electronegative elements accompanying heavy atom reorganization is not part of the reaction coordinate.^{19,20} Application of this concept to the decarboxylation of β -keto acids predicts that the transition state should involve a proton in a stable potential well during cleavage of the carbon-carbon bond and, consequently, low isotope effects are expected. The transition state for decomposition of these acids would then look like IV with the wavy lines representing a

