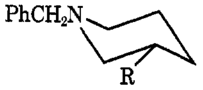
more stable rotomer or rotomers have a methyl or phenyl group in a pseudoaxial arrangement for **7c**, **7d**, and **7e**.



	R	$\Delta\delta$
7a,	R = CH_3	s
b,	R = CH_3CH_2	s
c,	R = $PhCH_2$	12.9
d,	R = $(CH_3)_2CH$	6.7
e,	R = $(CH_3)_3C$	13.0

The appearance of the diastereotopic protons of the methylene group of an *N*-benzyl substituent as an AB quartet in the nmr spectrum of an alkylated piperidine or piperazine has been shown to be positive evidence for a 2-equatorial alkyl, a 3-axial alkyl or a large 3-equatorial alkyl substituent. The appearance of the methylene signal as a singlet is evidence for the absence of these conformational features.

Acknowledgment.—The nmr spectra were determined with a Joel MH-100 obtained from Grants NSF GP 29176 and NIH 5S05-FR-07108. The authors also wish to express appreciation to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of the research. Appreciation is also expressed to Dr. H. C. Brown for a generous sample of 3-*tert*-butylpyridine and to Dr. O. Frank Beumel and Foote Mineral for *n*-butyllithium used in this research.

[8] This research was abstracted from the thesis of L. N. P submitted to the Graduate School of the University of New Hampshire in partial fulfillment of the Ph.D. degree. Martin Luther King and Petroleum Research Fund Fellow, 1969–1972.

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Fundamental Studies of Substituted Ferrocenes. VII.[1] Proton Magnetic Effects in Trimethylsilylferrocene

Summary: Specific deuterium labeling of trimethylsilylferrocene shows that the upfield two-proton apparent triplet at δ 4.07 ppm can be assigned to the 2,5-position protons and thus the downfield two-proton apparent triplets at δ 4.30 ppm can be assigned to the 3,4-position protons.

Sir: In a previous publication[2] we had advanced the hypothesis based on chemical shift data that the response of a ferrocene ring to an electron-donating substituent (typified by an amino group) was "principally manifested at the 3,4 positions," care being taken at that time to avoid use of the term resonance. Since then other monosubstituted ferrocenes containing electron-donating substituents have been shown to exhibit similar pmr behavior.[1,3] We now propose that this phenomenon be interpreted as a resonance effect[4] and offer as proof the herein documented observation of electron withdrawal from the 3,4 positions of trimethylsilylferrocene as determined by pmr. Since the trimethylsilyl group in several instances has been found to participate in (p–d) π-electron withdrawal[5] (although in most instances the result is not marked), our proposal amounts to suggesting that correct assignment of chemical shifts according to two distinct π-resonance effects in an unknown system constitutes satisfactory identification of such effects in said system.

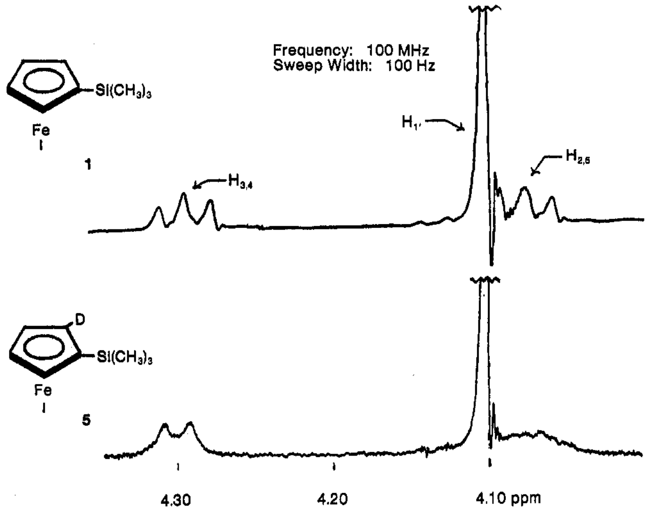

Figure 1.

Trimethylsilylferrocene (**1**) possesses chemical shift shielding values for the $H_{2,5}$ and $H_{3,4}$ proton resonances in accordance with resonant electron withdrawal by the trimethylsilyl group from the 3,4 positions. The pmr spectrum of **1** exhibits two unsymmetrical triplets[6,7] for the homoannular proton resonances. Assignments for these resonances have been made on the basis of comparative spectra of trimethylsilylferrocene and 2-deuteriotrimethylsilylferrocene ($CDCl_3$) as shown in Figure 1. Attenuation of the resonance at δ 4.07 ppm and the change in splitting of the resonance of δ 4.30 ppm from a triplet to a doublet with introduction of a deuterium at the 2 position permits equivocal assignment of the resonance at high field to the $H_{2,5}$ protons and that at low field to the $H_{3,4}$ protons.

The deuterated trimethylsilylferrocene was prepared by the series of reactions shown in Scheme I. Treatment of chloroferrocene (**2**) with *n*-butyllithium under conditions reported[8,9] to give metalation of chloroferrocene and now documented to provide 2 metalation,[1] followed by addition of trimethylchlorosilane, afforded 2-chlorotrimethylsilylferrocene (**3**) as an oil. Sodiation of **3** with dispersed sodium and deuterolysis of the sodiated intermediate (**4**) with excess deuterium oxide produced trimethylsilylferro-

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[1] Part VI: D. W. Slocum, W. E. Jones, and C. R. Ernst, *J. Org. Chem.*, **37**, 4278 (1972).

[2] D. W. Slocum, P. S. Shenkin, T. R. Engelmann, and C. R. Ernst, *Tetrahedron Lett.*, 4429 (1971).

[3] D. W. Slocum, B. P. Koonsvitsky, and C. R. Ernst, *J. Organomet. Chem.*, **38**, 125 (1972).

[4] Other effects such as field, inductive, and (for pmr) anisotropy would be expected to be strongest at the 2,5 positions.

[5] M. E. Freeburger and L. Spialter, *J. Amer. Chem. Soc.*, **93**, 1894 (1971).

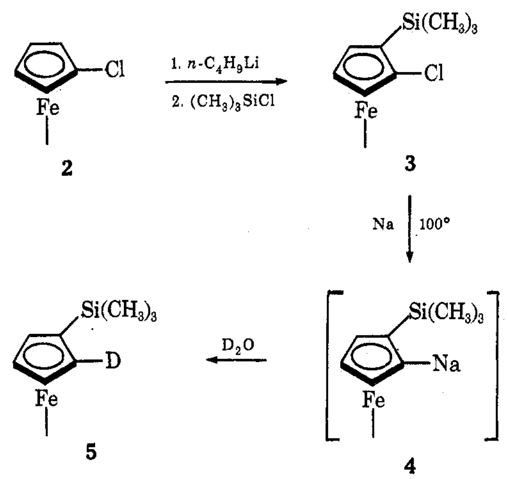
[6] M. D. Rausch and M. Mark, *J. Org. Chem.*, **28**, 3225 (1963).

[7] M. I. Levenberg and J. H. Richards, *J. Amer. Chem. Soc.*, **86**, 2634 (1964).

[8] J. Huffman, L. Keith, and R. Ausbury, *J. Org. Chem.*, **30**, 1600 (1958).

[9] A. N. Nesmeyanov, *Dokl. Akad. Nauk SSSR*, **176**, 598 (1968).

SCHEME I



cene[10] containing a total of 0.88 deuterium atom as analyzed by the falling drop method.

Trimethylsilylferrocene has been the only monosubstituted ferrocene studied to date which exhibits enhanced deshielding of the 3,4-position protons with respect to the 2,5-position protons. Since earlier studies[2] have demonstrated that resonance effects in the ferrocene system detected by pmr spectroscopy are manifested chiefly at the 3,4 positions, the observation of significant deshielding of the $H_{3,4}$ protons in **1** can be attributed to a resonance withdrawal by the d orbitals on silicon from the 3,4 positions.[11]

Acknowledgment.—Thanks are due for a graduate followship from Southern Illinois University for C. R. E and support by the donors of the Petroleum Research Fund, administered by the American Chemical Society. Appreciation is expressed to Mr. Joseph Nemeth, University of Illinois, for the falling drop analysis.

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[10] M. Rausch, M. Vogel, and H. Rosenberg, *J. Org. Chem.*, **23**, 900 (1958).

[11] A referee has pointed out that the sequence of chemical shifts in trimethylsilylferrocene is the same as that in the α-ferrocenyl carbonium ion as initially assigned by Cais, *et al.*[12] However, the carbonium ion is a charged intermediate or transition state where charge delocalization would be expected to override secondary ground-state effects as described herein. Interestingly, this ground-state effect in **1** can now be explained as a simple resonance interaction without recourse to arguments involving ring/metal atom movement.[13]

[12] M. Cais, J. J. Dannenberg, A. Eisenstadt, M. I. Levenberg, and J. H. Richards, *Tetrahedron Lett.*, 1695 (1966).

[13] For a recent summary and criticism of this concept, *cf.* J. Feinberg and M. Rosenblum, *J. Amer. Chem. Soc.*, **91**, 4324 (1969).

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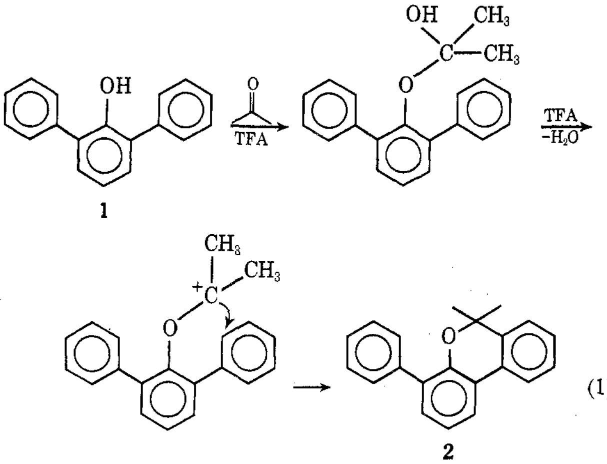
NOVEMBER 11, 1972

A New Reaction of 2-Phenylphenols with Carbonyl Compounds Yielding Dibenzopyrans

Summary: A new synthesis of dibenzopyrans, fluorenols, and indenofluorenols is described.

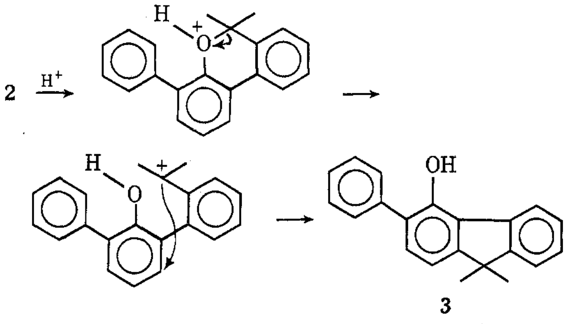
Sir: The acid-catalyzed condensation of carbonyl compounds with phenols to yield bisphenols is a well-known reaction of broad scope.[1] However, it was reported by Kahovec and Pospisil[2] that 2,6-diphenylphenol (**1**) did not react with acetone in the presence of conventional acid catalysts such as hydrogen chloride. This observation was confirmed in our laboratory, but, when **1** was combined with acetone under more strongly acidic conditions, for example, in refluxing trifluoroacetic acid (TFA) (H_0 −3.0),[3] a new condensation reaction occurred yielding 4-phenyl-6,6- dimethyl-6*H*-dibenzo[*b*,*d*]pyran (**2**): mp 79–80°; 64%; *m/e* 286 (M^+), 271 $(M^+ - 15)$; nmr ($CDCl_3$) δ 1.55 (s, 6, CH_3), 6.90–7.80 ppm (m, 12, ArH); ir (KBr) 1360 and 1380 (*gem*-dimethyl), 700 cm^{-1} (monosubstituted aryl); satisfactory analysis for $C_{21}H_{18}O$. It is assumed that the reaction proceeds *via* the reversible formation of the phenol hemiacetal of acetone. Protonation and loss of water from the hemiacetal generates a carbonium ion which attacks either of the flanking phenyl groups to form the pyran **2** as shown in eq 1.



(1)

The threshold of acidity (H_0) required for pyran formation was approximately −3.0. No reaction occurred with hydrogen chloride, formic acid (H_0 −2.2),[4] formic-hydrochloric acid, or 50:50 (v/v) formic-trifluoroacetic acid mixtures.

Prolonged refluxing of **2** in TFA rearranged this tertiary benzylic ether to 9,9-dimethyl-3-phenyl-4-fluorenol (**3**) (eq 2): mp 106–107°; ir (KBr) 3540, 703 cm^{-1}; nmr ($CDCl_3$) δ 1.50 (s, CH_3), 5.68 (s, 1, ArOH), 7.00–8.15 ppm (m, 11, Ar H); *m/e* 286 (M^+), 271 $(M^+ - 15)$; analyzed for $C_{21}H_{18}O$.



(2)

The rearrangement regenerated an *o*-phenylphenol which in the presence of acetone reacted further to form the indenodibenzopyran (**4**): mp 112–113°; nmr ($CDCl_3$) δ 1.47 (s, 6, CH_3), 1.73 (s, 6, CH_3), 6.93–8.25 (m, 10, Ar H); *m/e* 326 (M^+), 311 $(M^+ - 15)$;

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[1] H. Schnell and H. Krimm, *Angew. Chem., Int. Ed. Engl.*, **2**, 373 (1963).

[2] J. Kahovec and J. Pospisil, Collect. *Czech. Chem. Commun.*, **34**, 2843 (1969).

[3] H. H. Hyman and R. A. Garber, *J. Amer. Chem. Soc.*, **81**, 1847 (1959).

[4] R. Stewart and T. Mathews, *Can. J. Chem.*, **38**, 602 (1960).