Ferrocenobenzosemiquinones

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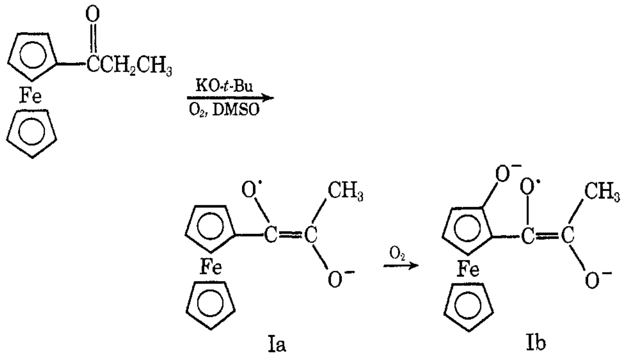
Novel paramagnetic ligands are observed by esr spectroscopy. These paramagnetic ligands are discussed in terms of oxidation chemistry and electron spin delocalization. Electron spin density is experimentally demonstrated to be on the metal by observation of Mn$^{5/2}$ splitting of 5.63 G. The role of charge separation in electron spin delocalization is briefly discussed.

The preparation of paramagnetic metallocenes *via* Scheme I has been previously reported.[1] Ia and Ib were observed by electron spin resonance spectroscopy and these species were discussed in terms of electron spin delocalization and oxidation chemistry.

SCHEME I



Using the reaction conditions in Scheme I, we have observed that 1,2-ferrocenyl diketones condense upon initial oxidation to form the corresponding quinones according to Scheme II.

SCHEME II

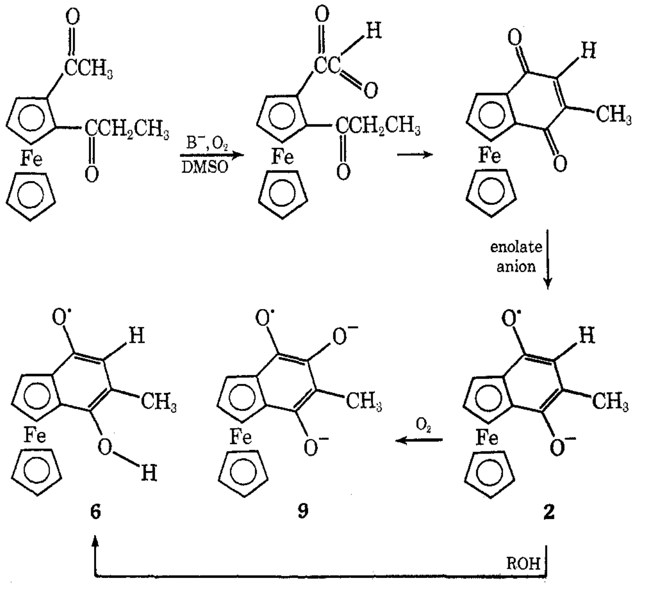
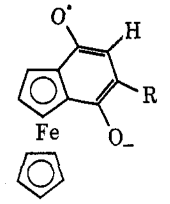
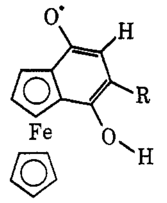
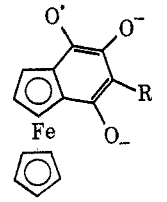
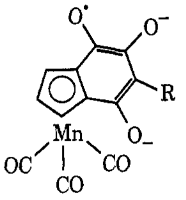


TABLE I

Compd	R	H_a	Fe ring	g
				
1[a]	H	4.05 (2 H)	0.43 (2 H)	
2	CH_3	3.47 (4 H)	0.43 (2 H)	2.00792
3	CH_2CH_3	3.54 (1 H), 2.45 (2 H)	0.43 (2 H)	2.00791
4	$CH(CH_3)_2$	3.35 (1 H), 1.67 (1 H)	0.74 (2 H)	2.00790
				
5	H	3.97 (1 H), 3.52 (1 H)	1.15 (1 H), 0.35 (2 H)	2.00785
6	CH_3	4.25 (1 H), 3.3 (3 H)	1.1 (1 H), 0.35 (2 H)	2.00785
7	CH_2CH_3	4.32 (1 H), 2.45 (2 H)	1.1 (1 H), 0.35 (2 H)	2.00785
				
8[b]	H	4.65 (1 H)	0.35 (2 H)	
9	CH_3	4.48 (3 H)	0.35 (2 H)	
10	CH_2CH_3	4.30 (2 H)	0.35 (2 H)	
				
			Cy ring	
11[c]	H	4.15 (1 H) 5.63 (Mn$^{5/2}$)	0.675 (2 H)	2.00492

[a] Produced by electrolytic reduction of the quinone and by the oxidation of 1,2-diacetylferrocene. [b] Produced by oxidation of 1,2-(α-ketotetramethylene)ferrocene and overoxidation of **1**. [c] Produced by oxidation of 1,2-(α-ketotetramethylene)cyclopentadienylmanganese tricarbonyl. Prepared by method of M. Cais, and A. Modiano, *Chem. Ind.* (*London*), 202 (1960).

Entries **1**–**10** of Table I provide proof of the reaction sequence shown in Scheme II. Examples **1** and **8** were produced by independent means. **1** was produced by reduction of the corresponding quinone and by oxidation of 1,2-diacetylferrocene (Scheme III). Figure 1 shows the esr spectrum of **1**. Entry **8** was produced by overoxidation of **1** and by oxidation of 1,2-(α-ketotetramethylene)ferrocene (Scheme IV). Figure 2 shows the esr spectrum of **8**. Figure 3 shows the esr spectrum resulting from the oxidation of 1-acetyl-2-

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[1] J. J. McDonnell and D. J. Pochopien, *J. Org. Chem.*, **36**, 2092 (1971).

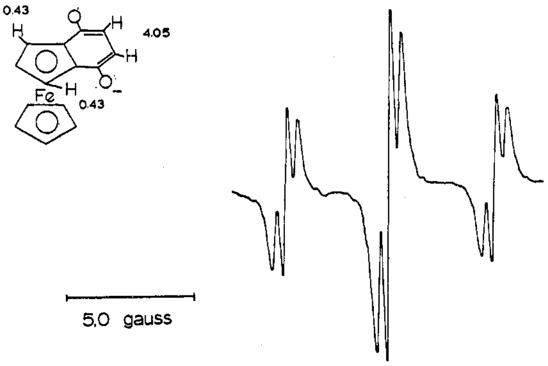


Figure 1.

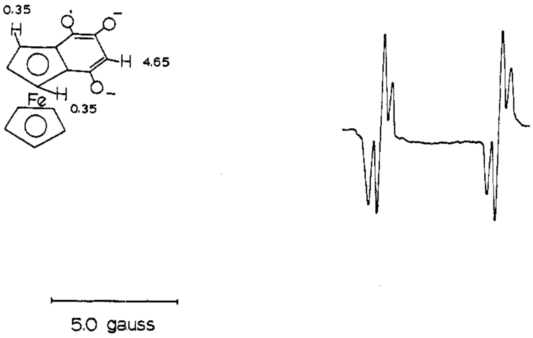
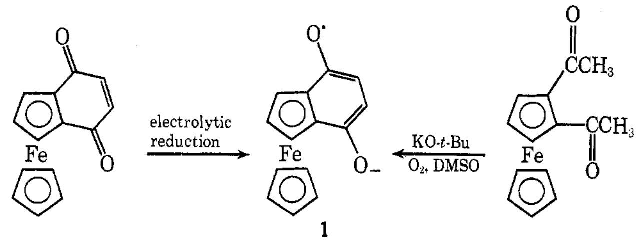


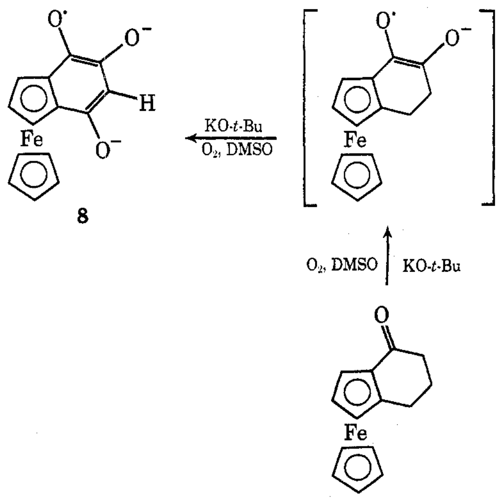
Figure 2.

SCHEME III



1

SCHEME IV



8

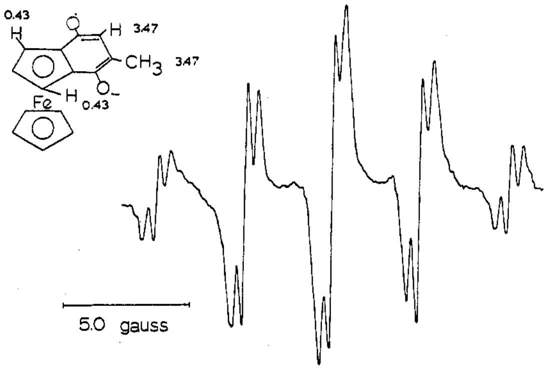


Figure 3.

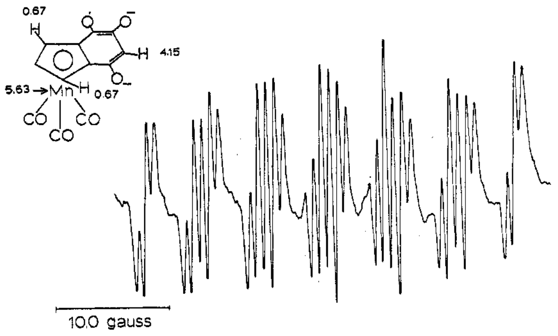
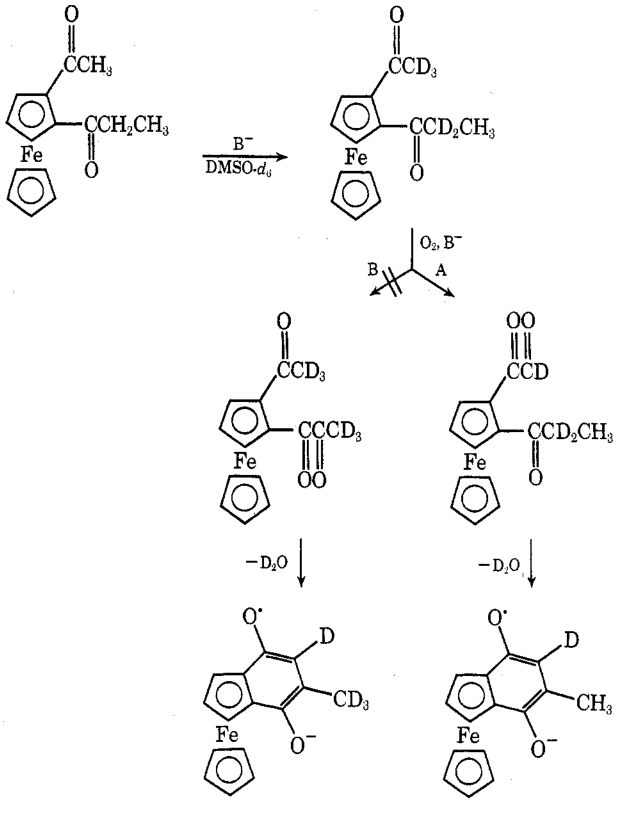


Figure 4.

propionylferrocene. This spectrum requires the assignment of hyperfine splitting constants as shown. **5**–**7** were produced by simply adding *tert*-butyl alcohol to entries **1**–**3**.

When oxidation in Scheme II is conducted in DMSO-d_6 an esr spectrum is observed which is consistant with the replacement of a hydrogen splitting of 3.47 G with a deuterium splitting of 0.53 G (Figure 3B). This would seem to require that the quinone is formed *via* initial oxidation of the acetyl group in Scheme Va. In Scheme Vb, the initial oxidation of the propionyl group would replace four large hydrogen splittings with deuterium. The latter is not observed.

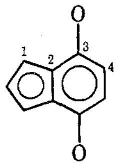
SCHEME V



Entry **11** in Table I makes it clear that some electron density resides on the metal atom. Figure 4 shows the high resolution esr spectrum of **11** and the analysis of this spectrum requires the hyperfine splitting of a $Mn^{5/2}$ nucleus of 5.63 G. The spectra of **8** and **11** show approximately equal spin distribution in the ligand. However, the g value in **8** is higher than that in **11**. It is interesting to observe that **8**, the ferrocene analog, has a higher g value than 2-hydroxy-1,4-naphthaquinone (g 2.00403)[2] and **11**, the cyclopentadienylmanganese tricarbonyl analog, has a g value much closer to that of the corresponding 2-hydroxy-1,4-naphthaquinone. g values are controlled by a delicate balance of several factors—λ coefficient of the HOMO, spin density distribution, and the spin–orbit coupling coefficient of the atoms containing free electron density.[3] The higher spin–orbit coupling constant of Fe^{2+} (400 cm^{-1}) *vs.* 305 cm^{-1} [4] for Mn^+ is qualitatively in the right direction for the observed g value change.[5]

Hückel and Hückel-McLachlan calculations[6] using a large variety of coulombic integrals for oxygen and carbon atoms as well as various bond integrals for C–C and C–O bonds in the ligand π system do not agree with the experimental spin densities. Chart I shows the results of a typical calculation. In these systems charge separation undoubtedly plays an important role in electron spin delocalization in the ligand.[7] For example, of the resonance structures (a, b, and c) shown in Chart II, a may well be the most favored on the basis of change separation. This is especially true when the coulombic interaction of the metal ion is considered. a places very little free electron density into the carbon skeleton of the five-membered ring as observed by experiment. Electron spin density could be placed on the metal by direct interaction with the p orbital of carbon atoms in the 1 and 2 position. We are in the process of developing a complete theoretical treatment in this regard.

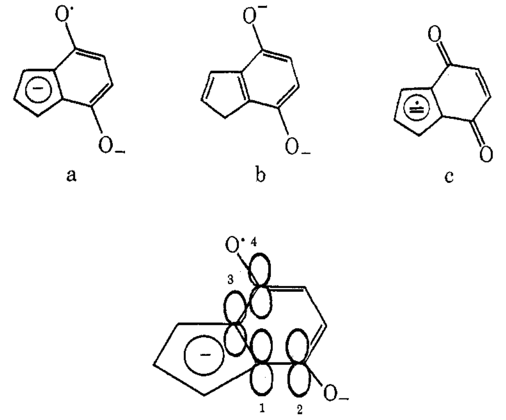
CHART I[a]



Exptl spin densities, ρ	Calcd spin densities, ρ
0.0186 (1)	0.284 (1)
0.174 (4)	0.112 (4)

[a] $\alpha_0 = \alpha_c + 5h$, $Q = -23$, $A_H = Q\rho$.

CHART II



a b c

Experimental Section

General Procedure for Electrolytic Reductions.—Radical anions were generated in a slightly modified Varian electrolytic cell; the part extending into the microwave cavity was of the flat cell type. The cell was evacuated and flushed with nitrogen several times before use. Mercury, serving as the cathode material, was filled into the cell until it reached the flat part of the cell. The solution of the substrate to be reduced was then added and the cell closed under nitrogen. Reduction was accomplished with a Heath-Kit power supply.

The solvent employed in the reductions was DMF which had been refluxed and distilled over CaH_2 in a nitrogen atmosphere. The electrolyte, tetraethylammonium perchlorate, was dried under vacuum over P_2O_5. In all cases, the solution was 0.1 M in the electrolyte and 1×10^{-3} M in the substrate. Concentrations of substrate which were greater than 1×10^{-3} M resulted in the broadening of the esr spectrum.

The radical could be regenerated several times from the same solution if the solution was shaken so as to replenish the concentration of substrate near the cathode.

General Procedure for the Preparation of Semiquinones.—The cyclization of 1,2-diacylferrocenes was achieved under conditions similar to the formation of the semidione radical anions. To 15 mg of the ferrocenyl derivative in one half of an H-cell was added 0.9 cc of dry DMSO; to a 3–4 molar excess of potassium *tert*-butoxide in the other half of the H-cell was added 0.9 cc of dry DMSO. After both of the solutions were thoroughly degassed with N_2 (5 min), the sealed H-cell was inverted and the solutions were thoroughly mixed; 2 cc of air were injected into the H-cell through a serum cap by means of a syringe. An additional needle placed through a serum cap on the other half of the H-cell allowed the air to be added without a pressure buildup. The semiquinone was then formed by shaking the contents of the cell.

Further oxidation of the semiquinone was achieved by the subsequent addition of small amounts of oxygen to the H-cell. The addition of excessive amounts of oxygen, however, resulted in the disappearance of the signal.

Protonation of the semiquinone was achieved by using a DMSO solution containing 20% *t*-BuOH in place of the dry DMSO.

Ferrocobenzoquinone was prepared by a modification of the procedure of Rinehardt.[8] To 5.0 g of 1,2-(α-ketotetramethylene)-ferrocene in 200 ml of $CHCl_3$ was added 200 g of activated MnO_2 and the mixture was stirred in the dark for 20 hr. The slurry was filtered through Celite and the MnO_2 was washed with ether until the washings were colorless. The solvent was removed under reduced pressure and the residue was taken up in 25 ml of ether to which was added 150 ml of hexane. The ether was removed under reduced pressure and the violet quinone extracted with H_2O leaving an orange hexane layer. The quinone was extracted from the salted aqueous layer with ether. The layers were separated and the organic layer was dried ($MgSO_4$). Recrystallization from ether–hexane produced 2.3 g (43.9%) of **24**: mp 152° (lit.[9] 150–151.5°); nmr ($CDCl_3$) δ 4.33 (s, 5, Fc), 5.12 (t, 1, Fc), 5.41 (d, 2, Fc), 6.69 (s, 2, Qu).

Preparation of Ketonic Precursors. 1,2-α-Ketotetramethyleneferrocene was prepared according to the method of Rinehardt:[10] mp 85° (lit.[10] mp 85.4–85.7°); nmr ($CDCl_3$) δ 2.35 (m, 6, CH_2-CH_2), 4.18 (s, 5, Fc), 4.48 (d, 2, Fc), 4.84 (t, 1, Fc).

1,2-Diacetylferrocene was prepared according to the procedure of Rosenblum and Woodward[11] in 1.9% yield: mp 105° (lit.[11] mp 106–107°); nmr ($CDCl_3$) δ 2.50 (s, 6, $COCH_3$), 4.28 (s, 5, Fc), 4.62 (t, 1, Fc), 4.88 (d, 2, Fc).

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(2) T. C. Hollocher, N. Tooney, and R. Adman, *Nature*, **197**, 74 (1963).

(3) A. J. Stone, *Mol. Phys.*, **6**, 509 (1963).

(4) T. M. Dunn, *Trans. Faraday Soc.*, 1441 (1961).

(5) H. M. McConnell and R. T. Robertson, *J. Phys. Chem.*, **61**, 1018 (1957).

(6) A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

(7) Hückel–McLachlen calculations are not well designed to accommodate charge separation.

(8) K. L. Rinehardt, A. F. Ellis, C. J. Michejda, and P. A. Kittle, *J. Amer. Chem. Soc.*, **82**, 4112 (1962).

(9) R. A. Johnson and H. C. Murray, *J. Chem. Soc. D*, 989 (1971).

(10) K. L. Rinehardt and A. J. Cury, *J. Amer. Chem. Soc.*, **79**, 3290 (1957).

(11) M. Rosenblum and R. B. Woodward, *ibid.*, **80**, 5443 (1958).

1-Acetyl-2-propionylferrocene was prepared as we previously reported:[1] mp 46°; nmr ($CDCl_3$) δ 1.17 (t, 3, CH_2CH_3), 2.47 (s, 3, $COCH_3$), 2.86 (m, 2, CH_2CH_3), 4.25 (s, 5, Fc), 4.58 (t, 1, Fc), 4.88 (d, 2, Fc).

1-Acetyl-2-butyrylferrocene.—To 15.0 g (0.1128 mol) of $AlCl_3$ in 100 ml of CH_2Cl_2 was added 9.4 g (0.0412 mol) of acetylferrocene and 12.0 g (0.0760 mol) of butyric anhydride in 250 ml of dry ($MgSO_4$) CH_2Cl_2 dropwise with stirring under N_2. After 4 hr the solution was cooled to 5° and hydrolyzed, and the layers were separated. The combined organic layer and ethereal wash of the aqueous layer were dried ($MgSO_4$) and the solvent was removed under reduced pressure. The red oil which remained was chromatographed on silica gel. Elution with 25% ether in hexane produced three bands. The first band (orange) contained a trace of acetylferrocene. The second band (orange) contained 0.23 g (1.87%) of desired compound: mp 103–103.5°; nmr ($CDCl_3$) δ 1.0 (t, 3, CH_2CH_3), 1.74 (m, 2, CH_2CH_3), 2.48 (s, 3, $COCH_3$), 2.81 (t, 2, $COCH_2$), 4.27 (s, 5, Fc), 4.61 (t, 1, Fc), 4.89 (d, 2, Fc). The third band (red) contained 8.65 g (70.3%) of 1-acetyl-1′-butyrylferrocene: mp 54°; nmr ($CDCl_3$) δ 1.01 (t, 3, CH_2CH_3), 1.72 (m, 2, CH_2CH_3), 2.34 (s, 3, $COCH_3$), 2.65 (t, 2, $COCH_2$), 4.48 (t, 4, Fc), 4.74 (m, 4, Fc.)

Anal. Calcd for $C_{16}H_{18}O_2Fe$: C, 64.45; H, 6.08. Found: C, 64.32; H, 6.12. *Anal.* Calcd for $C_{16}H_{18}O_2Fe$: C, 64.45; H, 6.08. Found: C, 64.37; H, 6.04.

1-Acetyl-2-(3-methyl)butyrylferrocene.—To 16.0 g (0.120) mol) of $AlCl_3$ in 150 ml of CH_2Cl_2 was added 12.0 g (0.0996 mol) of 3-methylbutyryl chloride and 10.0 g (0.0438 mol) of acetylferrocene in 250 ml of dry CH_2Cl_2 dropwise with stirring under N_2. After 5 hr the solution was cooled to 6° and hydrolyzed, and the layers were separated. The organic layer was washed with 2 *M* Na_2CO_3 solution. The combined organic layer and ethereal wash of the aqueous layer were dried ($MgSO_4$) and the solvent was under reduced pressure. The red oil which remained was chromatographed on silica gel. Elution with 10% ether in hexane produced five bands. The first band (yellow) and the second band (orange) contained traces of some material which was not characterized. The third band (red) contained 0.90 g (9%) of starting material. The fourth band (red) contained 0.86 g (6.29%) of **27**: mp 59–60°; nmr ($CDCl_3$) δ 1.00 [d, 6, $CH(CH_3)_2$], 2.28 (m, 1, CH), 2.49 (s, 3, $COCH_3$), 2.72 (d, 2, $COCH_2$) 4.28 (s, 5, Fc), 4.62 (t, 1, Fc), 4.90 (d, 2, Fc). The fifth band (red) contained 9.85 g (72.0%) of 1-acetyl-1′-(3-methyl)butyrylferrocene: mp 76–77°; nmr ($CDCl_3$) δ 1.01 [d, 6, $CH(CH_3)_2$], 2.28 (m, 1, CH), 2.35 (s, 3, $COCH_3$), 2.55 (d, 2, $COCH_2$), 4.51 (t, 4, Fc), 4.78 (t, 4, Fc).

Anal. Calcd for $C_{17}H_{20}O_2Fe$: C, 65.40; H, 6.46. Found: C, 65.61; H, 6.48. *Anal.* Calcd for $C_{17}H_{20}O_2Fe$: C, 65.40; H, 6.46. Found: C, 65.48; H, 6.40.

Registry No.—**1**, 12766-52-8; **2**, 12766-58-4; **3**, 12766-62-0; **4**, 12766-65-3; **5**, 12766-54-0; **6**, 12766-59-5; **7**, 12766-63-1; **8**, 12766-51-7; **9**, 12766-57-3; **10**, 12766-61-9; **11**, 12766-50-6; ferrocobenzoquinone, 12766-53-9; 1,2-α-ketotetramethyleneferrocene, 12766-55-1; 1,2-diacetylferrocene, 12766-56-2; 1-acetyl-2-propionylferrocene, 12766-60-8; 1-acetyl-2-butyrylferrocene, 12766-64-2; 1-acetyl-2-(3-methyl)butyrylferrocene, 12766-66-4.

Competitive Metal Hydride Reductions of β-Phorone with Cyclic Ketones

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Competitive reductions with lithium aluminum tri-*tert*-butoxyhydride of β-phorone, a nonconjugated enone, and a number of cyclic saturated ketones and conjugated enones having varied steric environments were studied. The nonconjugated enone was found to be less reactive than cyclic saturated ketones, but more reactive than the conjugated enones. Steric and torsional factors are involved, but apparently not in a major way, in determining relative reactivities in these experiments.

The greater reactivity toward metal hydride reduction of cyclic saturated ketones as compared with cyclic conjugated enones has been recognized, and selective reductions have been successfully carried out with steroids. For example, reduction of androst-4-ene-3,17-dione (**1**) with lithium aluminum tri-*tert*-butoxyhydride (LATH)[2] occurred at C-17 in preference to reduction at C-3.[3] A similar result with the same substrate was obtained with sodium borohydride in methanol, giving 17β-hydroxyandrost-4-en-3-one.[4] With six-membered ring ketones, similar large reactivity differences were encountered in intermolecular competition studies with lithium aluminum hydride and LATH.[5] The α,β-unsaturated ketones were consistently less reactive than their saturated competitors, even when steric or torsional[6] factors would have disfavored the latter. A similar observation was made in the reduction of the steroid prednisone-BMD with LATH.[7] The strongly hindered C-11 carbonyl group was reduced in preference to the conjugated carbonyl group at C-3. The greater selectivity of LATH over $LiAlH_4$ was also noted.[5,8]

A consideration of the steric and torsional factors conceivably involved in the reduction of various cyclohexanones and conjugated cyclohexenones led to the conclusion that these factors could not explain the observed reactivity differences between the two types of substrates, and an explanation was suggested in which the major factor was the stability of the conjugated enone system.[5] If the reduced reactivity of conjugated enones is due to the intrinsic stability of the conjugated π system, then there should be a marked difference in reactivity between conjugated and nonconjugated enones, with the latter being the more reactive.

This paper reports the results of competitive LATH reductions of the nonconjugated ketone 3,5,5-trimethylcyclohex-3-enone (β-phorone, **2**) with saturated and conjugated enone systems of varying steric com-

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[1] Undergraduate research participant, 1971–1972.

[2] Lithium aluminum tri-*tert*-butoxyhydride is also commonly called lithium tri-*tert*-butoxyaluminohydride. However, we now prefer the former name because of its similarity to the name lithium aluminum hydride.

[3] J. Fajkoš, *Collect. Czech. Chem. Commun.*, **24**, 2284 (1959).

[4] J. K. Norymberski and G. F. Woods, *Chem. Ind.* (*London*), 518 (1954).

[5] H. Haubenstock, *J. Org. Chem.*, **37**, 656 (1972).

[6] (a) M. Chérest, H. Felkin, and N. Prudent, *Tetrahedron Lett.*, 2199 (1968); M. Chérest and H. Felkin, *ibid.*, 2205 (1968). (b) For a recent and thorough discussion of stereochemical factors involved in metal hydride reductions of alkylcyclohexanones, see E. L. Eliel and Y. Senda, *Tetrahedron*, **26**, 2411 (1970).

[7] J. A. Zderic and J. Iriarte, *J. Org. Chem.*, **27**, 1756 (1962).

[8] H. Haubenstock and E. L. Eliel, *J. Amer. Chem. Soc.*, **84**, 2363 (1962).