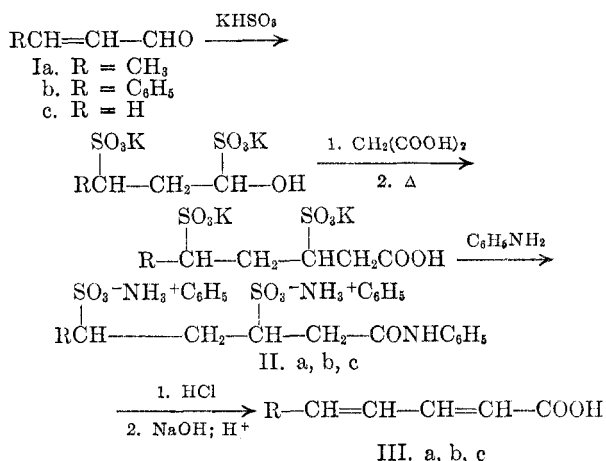


omitting the hydrochloric acid treatment, crystalline solids were obtained upon dilution with water. Thus, for example, crotonaldehyde (Ia) led to the formation of a substance, m.p. 155–156°, which gave negative qualitative tests for sulfur and nitrogen and possessed an elementary analysis corresponding to the empirical formula C_6H_6O .



We have repeated this series of reactions starting with crotonaldehyde and obtained a substance with the same melting point and elementary analysis which gave at best doubtful qualitative tests for nitrogen. In view of (1) the difficulty of accommodating a transformation of IIa to $(C_6H_6O)_n$, (2) the similarity of the melting point with that reported for sorbanilide,² and (3) the very similar elemental analysis of C_6H_6O and sorbanilide ($C_{12}H_{13}NO$), we were led to compare the two substances in spite of the dubious tests for nitrogen. Mixture melting point and infrared spectral comparison with an authentic sample of sorbanilide² proved the identity of the two substances.

The explanation for the formation of sorbanilide presumably lies in the relative rates of elimination *vs.* amide hydrolysis and the fortuitous choice of reaction time by Nottbohm. Essentially all the material not converted to sorbanilide by refluxing IIa with sodium hydroxide solution was obtained as sorbic acid by acidification of the alkaline filtrate. Attempts to characterize the product formed from IIa with hydrochloric acid were not successful.

Nottbohm also reported formation of a substance, m.p. 188°, C_9H_8O , from cinnamaldehyde (Ib). This appears likely to be the unreported anilide of 5-phenyl-2,4-pentadienoic acid. (*Anal.* Calcd. for $C_{17}H_{15}ON$: C, 81.9; H, 6.1; reported by Nottbohm¹; C, 81.8, 81.7; H, 6.2, 6.1.)

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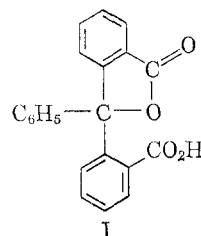
(2) O. Doebner and A. Wolf, *Ber.*, **34**, 2221 (1901) report m.p. 154–156° for sorbanilide.

The Metalation of Diphenylferrocenylcarbinol¹

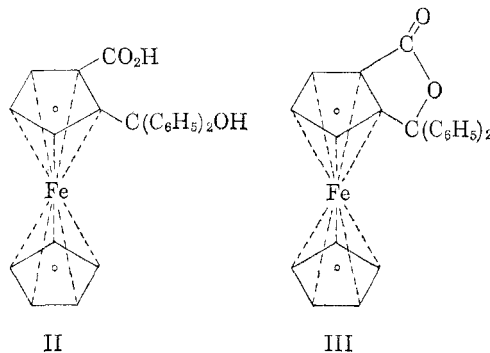
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MARVIN S. MELZER

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It is known that triphenylcarbinol can be metalated with *n*-butyllithium and then carbonated to form the lactone of triphenylcarbinol-2,2'-dicarboxylic acid² (I).



We are hereby reporting that a somewhat analogous reaction occurs with diphenylferrocenylcarbinol. Treatment of the latter compound with *n*-butyllithium, followed by carbonation with Dry Ice produced 2-carboxydiphenylferrocenylcarbinol (II) in 73% yield. When II was heated or treated with acid it readily converted to the lactone of 2-carboxydiphenylferrocenylcarbinol (III).



The structure of II was clearly indicated by its acidic nature and infrared spectrum which showed a strong carboxyl band at 5.95 μ and bands at 9 and 10 μ indicating an unsubstituted C_5 ferrocene ring. The ready conversion of II to III places the carboxyl group at the 2- rather than 3- position relative to the alcohol function.

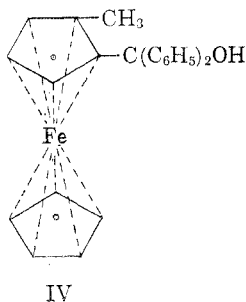
The structure of III was clearly indicated by its elemental analysis, molecular weight and infrared spectrum. The latter showed unambiguous five-

(1) This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under contract No. AF 49(638)-297. Reproduction in whole or in part is permitted for any purpose of the United States Government.

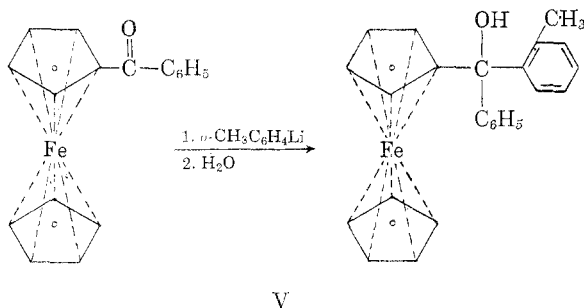
(2) (a) H. Gilman, G. E. Brown, F. J. Webb, and S. M. Spatz, *J. Am. Chem. Soc.*, **62**, 977 (1940); (b) H. Gilman and G. E. Brown, *J. Am. Chem. Soc.*, **62**, 3208 (1940).

membered ring lactone absorption at 5.6μ and ferrocene absorption at 9 and 10μ . The spectrum was devoid of $-\text{OH}$ absorption.

The metalated diphenylferrocenylcarbinol was found to react with methyl iodide producing a methylated compound, presumably with structure IV.

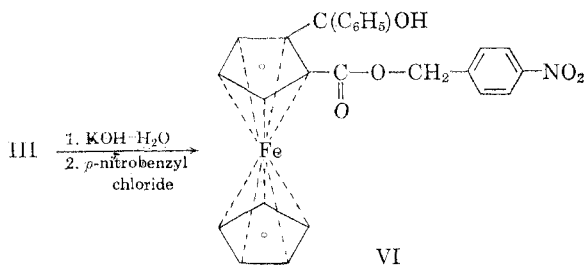


In order to prove that metalation of the diphenylferrocenylcarbinol had not occurred in one of the phenyl rings (paralleling the reaction with triphenylcarbinol) rather than in the ferrocene moiety, an authentic sample of ferrocenylphenyl-*o*-tolylcarbinol (V) was synthesized as shown below.

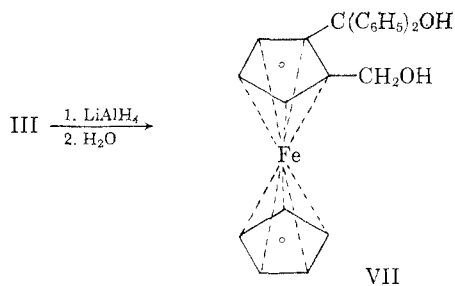


Compound V melted at 125° in contrast to 167° (the m.p. of IV) which clearly indicated that the site of metalation was in the ferrocene and not the phenyl ring.

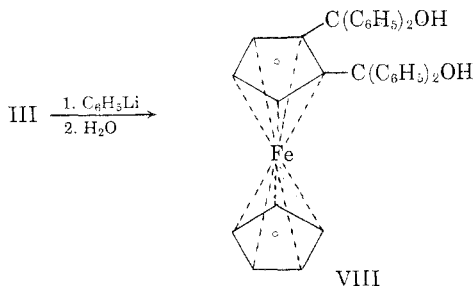
Compound III exhibited reactions which are classical for lactones. When saponified with base and treated with *p*-nitrobenzyl chloride, an ester (VI) was produced.



When treated with lithium aluminum hydride, a diol (VII) was formed in quantitative yield.



Similarly, treatment of the lactone with phenyllithium produced bis-1,2-(diphenylhydroxymethyl)ferrocene (VIII) in 97% yield.



EXPERIMENTAL

Diphenylferrocenylcarbinol. Phenyllithium was prepared in dry diethyl ether under nitrogen from 5.0 g. (0.72 g.-atom) of lithium wire and 56.5 g. (0.36 mole) of bromobenzene. A solution of 33.1 g. (0.12 mole) of benzoylferrocene³ in ether was added dropwise, and the mixture was refluxed for 24 hr. under nitrogen. Hydrolysis was effected with water, and the ether layer was separated and dried. Removal of the ether gave impure carbinol, which after crystallization from hexane melted at $130-131^\circ$. The yield was 76%.

Anal. Calcd. for $\text{C}_{23}\text{H}_{20}\text{FeO}$: C, 75.01; H, 5.47. Found: C, 75.29; H, 5.23.

2-Carboxydiphenylferrocenylcarbinol. *n*-Butyllithium (0.15 mole) in ether was added to 22.75 g. (0.062 mole) of diphenylferrocenylcarbinol also dissolved in ether. The dark yellow suspension was stirred under nitrogen at room temperature for 36 hr. and was then carbonated with Dry Ice. After the mixture had warmed to room temperature, water was added. Approximately 5 g. of the starting carbinol was recovered from the ether layer. The water layer was acidified ($\text{pH} = 1$) with hydrochloric acid and rapidly extracted with ether. The ether layer was washed extensively with water to remove the valeric acid and any residual hydrochloric acid. Evaporation of the ether yielded 13 g. (73%) of red crystals melting with effervescence at $137-139^\circ$. Recrystallization of this material from ether raised the melting point to $144-146^\circ$ (effervescence).

Anal. Calcd. for $\text{C}_{24}\text{H}_{20}\text{FeO}_3$: C, 69.92; H, 4.89; Fe, 13.55; mol. wt. 395. Found: C, 69.34, 69.46; H, 5.65, 5.63; Fe, 13.16; mol. wt. (Rast), 418.

When heated above 146° the liquid melt resolidified and melted again at $203-204^\circ$ (lactone). The acid could also be converted to the lactone by vigorous shaking with aqueous hydrochloric acid. It also reacted instantaneously with aqueous sodium bicarbonate or sodium hydroxide, forming an ether-insoluble yellow sodium salt. The free acid showed a sharp $-\text{OH}$ band at 2.9μ in the infrared, as well as a strong band at 5.95μ (carboxyl) and the typical 9 and 10μ bands of ferrocene.

(3) N. Weliky and E. S. Gould, *J. Am. Chem. Soc.*, 79, 2742 (1957).

Lactone of 2-Carboxydiphenylferrocenylcarbinol. If the carbonation product from above was allowed to remain in contact with the hydrochloric acid used to acidify the solution, brown crystals were obtained upon evaporation of the solvent. Crystallization from ether produced a solid (40% yield) which melted sharply at 200°.

Anal. Calcd. for $C_{24}H_{18}FeO_2$: C, 73.12; H, 4.57; Fe, 14.17. Found: C, 73.06; H, 4.51; Fe, 14.00.

The infrared spectrum of this product showed unambiguous five-membered ring lactone absorption at 5.6 μ , and 9, 10 μ ferrocene absorption. The spectrum was devoid of —OH absorption.

2-Methyldiphenylferrocenylcarbinol. Diphenylferrocenylcarbinol (30 g.; 0.08 mole) was metalated with *n*-butyllithium as described above. To this product was added 118 g. (0.8 mole) of dry methyl iodide in ether. After spontaneous reflux subsided, the mixture was refluxed under nitrogen for 24 hr. Hydrolysis with water was followed by separation and drying of the ether layer. Evaporation of the solvent, yielded 21 g. (69%) of amber crystals, which, after crystallization from ether, melted sharply at 167°.

Anal. Calcd. for $C_{24}H_{22}FeO$: C, 75.39; H, 5.80; Fe, 14.61. Found: C, 75.11; H, 5.81; Fe, 14.53.

The infrared spectrum of this material showed a strong —OH band at 2.8 μ , ring methyl absorption at 7.2 μ (absent in the spectrum of the parent carbinol), as well as the ferrocene absorption at 9 and 10 μ .

*Ferrocenylphenyl-*o*-tolylcarbinol.* *o*-tolyllithium was prepared by adding 85.5 g. (0.5 mole) of *o*-bromotoluene in 60 ml. of ether to 7.8 g. (1.2 g.-atoms) of lithium wire in ether under nitrogen. An ethereal solution of 18 g. (0.062 mole) of benzoylferrocene was added at a dropwise rate to the *o*-tolyllithium at room temperature. The mixture was stirred at room temperature for 24 hr. and then refluxed an additional 4 hr. After hydrolysis with water, the ether layer was separated and dried. Removal of the solvent deposited 18.0 g. (80%) of a yellow solid melting at 124–127°. This material was placed on an alumina chromatogram column, developed with benzene and eluted with ether. The analytical sample melted at 124–125°.

Anal. Calcd. for $C_{24}H_{22}FeO$: C, 75.39; H, 5.80; Fe, 14.61. Found: C, 75.59; H, 5.71; Fe, 14.83.

An infrared spectrum of this compound showed an —OH stretch at 2.9 μ , methyl compression modes at 6.9 μ (sym.) and 7.24 μ (antisym.) as well as the 9 and 10 μ peaks characteristic of ferrocene.

2-Hydroxymethyldiphenylferrocenylcarbinol. A 0.6-g. sample (0.0025 mole) of the pure lactone in ether was treated with an ethereal solution of 0.5 g. (0.013 mole) of lithium aluminum hydride under nitrogen. The amber solution rapidly changed into a yellow suspension accompanied by spontaneous reflux. When the reflux subsided, the mixture was refluxed for 24 hr. The excess hydride was destroyed with ethyl acetate and water was added. The ether layer was separated, and the solvent was removed under vacuum. A yellow solid (0.6 g.) was deposited melting in the crude state at 145°. After recrystallization from ether, the yellow crystals melted at 146°. The yield was quantitative.

Anal. Calcd. for $C_{24}H_{22}FeO_2$: C, 72.30; H, 5.55. Found: C, 72.16; H, 5.80.

The infrared spectrum of this material showed strong —OH absorption at 2.9 μ and the characteristic 9 μ and 10 μ bands of ferrocene.

bis-1,2-(Diphenylhydroxymethyl)ferrocene. Approximately 0.1 mole of phenyllithium in ether was added dropwise to an ethereal solution of 1.0 g. (0.0025 mole) of the lactone under nitrogen. Spontaneous refluxing occurred, followed by the formation of a yellow suspension. The mixture was stirred for 4 hr. at room temperature and then refluxed an additional 20 hr. After hydrolysis with water, followed by the usual work-up procedure a yield of 1.35 g. (97%) of a yellow solid melting at 190–192° was obtained. Recrystallization from ether yielded a dark yellow crystalline solid melting at 195–196°.

Anal. Calcd. for $C_{36}H_{30}FeO_2$: C, 78.55; H, 5.49; Fe, 10.15. Found: C, 78.31; H, 5.72; Fe, 9.97.

The infrared spectrum showed —OH absorption at 2.8 μ as well as the 9 and 10 μ bands of ferrocene.

p-Nitrobenzyl ester of 2-carboxyferrocenyldiphenylcarbinol. A 2.0-g. sample of the lactone (0.005 mole) was refluxed for 40 hr. in 100 ml. of 20% aqueous potassium hydroxide whereupon a brick-red suspension formed. The alkaline solution was neutralized to a pH of 7 with hydrochloric acid. Then a slurry of 3.0 g. (0.0175 mole) of *p*-nitrobenzyl chloride in 200 ml. of ethanol was added. The mixture was now refluxed for 24 hr. under nitrogen during which time a tan suspension formed. The mixture was filtered and the precipitate recrystallized from a large volume of ethanol producing 2.5 g. (93%) of a tan solid. This solid was triturated with tetrahydrofuran and filtered. The filtrate was evaporated. The residue was washed several times with ether and then recrystallized from acetone. It melted at 246°.

Anal. Calcd. for $C_{31}H_{25}FeNO_5$: C, 68.03; H, 4.58; N, 2.56; Fe 10.21. Found: C, 67.63; H, 4.81; N, 2.54; Fe, 10.27.

The infrared spectrum of this compound showed OH—absorption at 2.8 μ , carbonyl absorption at 5.85 μ , conjugated —NO₂ group at 7.4 μ and the 9 and 10 μ bands of ferrocene.

The *p*-nitrobenzyl ester was also prepared by treating 3.5 g. (0.0175 mole) of the yellow solid carbonation salt formed from the metalated ferrocenyldiphenylcarbinol with 3.0 g. (0.0175 mole) of *p*-nitrobenzyl chloride in 125 ml. of anhydrous tetrahydrofuran. After 48 hr. reflux, the mixture was treated with water, causing a brown solid to precipitate. This solid was dried and washed several times with ether. After recrystallization from acetone, the orange crystals melted at 246°, in agreement with the previous value. This yield was 3.8 g. (89%).

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The Enol Content of γ -Fluoro- β -keto Esters by Proton Magnetic Resonance

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The enol contents of a number of perfluoroalkyl β -diketones have been determined by Park and co-workers¹ using the Kurt Meyer "indirect" method. In all cases examined, the % enol was over 90% and in fact, several values of 120% were obtained. Other workers^{2,3} have reported anomalous values of 115–202% enol for β -diketones in various solvents.

In our studies of fluorine-containing β -keto esters, we were interested in determining the influence of γ -fluorine substitution on the enol content of ethyl acetoacetate (I), which has been shown to possess about 7.5% enol in the pure liquid and 6.9% in methanol at 0°.⁴ The marked dependence of the

(1) J. D. Park, H. A. Brown, and J. R. Lacher, *J. Am. Chem. Soc.*, **75**, 4753 (1953).

(2) K. Meyer, *Ber.*, **45**, 2843, 2848, 2858 (1912).

(3) J. C. Reid and M. Calvin, *J. Am. Chem. Soc.*, **72**, 2952 (1950).

(4) J. B. Conant and A. F. Thompson, Jr., *J. Am. Chem. Soc.*, **54**, 4039 (1932).