

general, of chemiluminescence excitation than those containing no sp^2 carbon. However, our results are insufficient to determine the cause of the only weak light emission from dioxetanes such as IV that contain no sp^2 carbon. The possible explanations include: (a) the dimerization of IV to form a cyclic peroxide analogous to IX, (b) that IV forms no complex prior to decomposition and the singlet excited products undergo intersystem crossing preferentially to energy transfer, or (c) a nonconcerted decomposition of IV. All three would lead to a short lifetime of the highly energetic dioxetane molecule. Further experimental work is required to elucidate these points.

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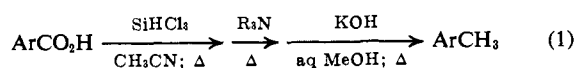
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A New and Convenient Method for the Reduction of an Aromatic Carboxyl to a Methyl Group

Sir:

A reasonable number of methods are available for the reduction of carboxylic acids to either alcohols¹⁻⁵ or aldehydes.^{6,7} However, there exists no simple procedure whereby complete reduction of the carboxyl moiety to a methyl group can be effected.⁸

We are hereby reporting such a procedure which appears to be general for many aromatic acids. The overall transformation can be depicted by eq 1. The



yield of reduction product for a representative series of aromatic acids is quite good (Table I).

While the sequence shown in eq 1 involves essentially three steps, all of these can be carried out sequentially without any purification of intermediates.

In a typical experiment, 0.6 mol of trichlorosilane and 0.1 mol of 3,5-dimethylbenzoic acid in 80 ml of

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(8) (a) Such a transformation can be achieved by reduction of the acid to the alcohol with lithium aluminum hydride and conversion of the alcohol to the tosylate, followed by a second reduction either with lithium aluminum hydride or Raney nickel and hydrogen. See N. G. Gaylord, "Reduction with Complex Metal Hydrides," Interscience, New York, N. Y., 1956, p 855. Benzylic-type alcohols can also be reduced directly with hydrogen under pressure in the presence of various catalysts. See, for example, R. L. Shriner and R. Adams, *J. Amer. Chem. Soc.*, **46**, 1683 (1924). (b) Benzoic acid can be reduced to toluene with rhenium-type catalysts and hydrogen at high temperatures and pressures. See ref 2 and H. S. Broadbent and D. W. Seegmiller, *J. Org. Chem.*, **28**, 2347 (1963).

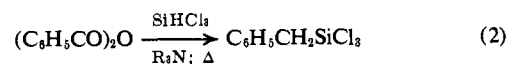
Table I. Reduction of Aromatic Acids to Substituted Benzenes^{a, b}

Starting acid	Product ^{c, d}
Benzoic	Toluene (78)
<i>m</i> -Toluic	<i>m</i> -Xylene (82)
<i>p</i> -Toluic	<i>p</i> -Xylene (74)
3,5-Dimethylbenzoic	Mesitylene (82)
<i>p</i> -Chlorobenzoic	<i>p</i> -Chlorotoluene (94)
<i>p</i> -Bromobenzoic	<i>p</i> -Bromotoluene (94)
Phthalic	<i>o</i> -Xylene (64)

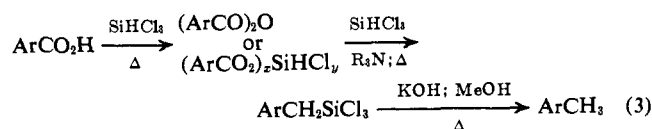
^a In every case, the same reaction conditions as those outlined in the text for entry 4 were employed, except that only 0.05 mol of phthalic acid was used. ^b In each case, approximately 0.2 mol of amine hydrochloride was isolated. ^c Products were identified by matching ir spectra with those of authentic samples. ^d The values in parentheses are the percentage yield of isolated product, based upon the weight of starting acid.

acetonitrile were refluxed 1 hr. After cooling, 0.264 mol of tri-*n*-propylamine was added so that the temperature did not rise above 15°. After the mixture was refluxed for 16 hr it was diluted to 850 ml with diethyl ether and filtered to remove the amine hydrochloride. The distillate was concentrated to remove the ether and acetonitrile, whereupon 50 ml of methanol was added to the nonvolatile oily residue and the solution refluxed for 1 hr. One mole of potassium hydroxide dissolved in a solution of 95 ml of methanol and 25 ml of water was then added slowly, and the resulting suspension refluxed for 19 hr. It was then diluted with 600 ml of water and extracted with pentane. The latter was washed with 50 ml of 2 *N* hydrochloric acid. Removal of the solvent and distillation gave 0.082 mol (82%) of mesitylene.

While exact mechanistic details of the reduction must remain speculative at this time, certain observations have been made which are suggestive of the overall pathway. If one uses benzoic acid as the substrate and interrupts the reaction after the first step (refluxing with trichlorosilane in acetonitrile), an excellent yield of benzoic anhydride (74%) can be realized after distilling the residue.⁹ It was noted, also, that benzoic anhydride like benzoic acid¹⁰ undergoes reductive silylation in the presence of trichlorosilane and tri-*n*-propylamine, forming benzyltrichlorosilane (eq 2).



It is well established that silanes, like benzyltrichlorosilane, are cleaved by aqueous base,¹¹ forming toluene as one of the products in this case. If one can generalize from benzoic acid to all the examples in Table I, the overall reduction process can be depicted by eq 3.



(9) It is quite possible that such anhydrides are formed thermally during this distillation from the aryloxy- or acyloxysilanes (in the case of aliphatic acids) which are present. Further work will be needed to ascertain whether benzyltrichlorosilane is being formed from benzoic anhydride or the benzoyloxysilanes.

(10) R. A. Benkeser and J. M. Gaul, *J. Amer. Chem. Soc.*, **92**, 720 (1970).

(11) C. Eaborn, "Organosilicon Compounds," Butterworths, London, 1960, pp 143-146.

It may well be that the above procedure will be restricted to aromatic acids only. Octanoic acid was not reduced to *n*-octane by the procedure described, although it is of interest that the anhydrides of certain aliphatic acids could be isolated by distillation⁹ from the mixture after the first step of the reaction sequence.

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Electronic Structure of Ferricenium Ion

Sir:

The ground-state electronic configurations for ferrocene and the ferricenium ion have been formulated through a combination of theoretical and experimental effort.¹⁻⁵ Noteworthy among the recent work is an electron spin resonance study⁵ of $\text{Fe}(\text{cp})_2^+$ in various compounds at 20°K, establishing a ${}^2E_{2g}(a_{1g})^2(e_{2g})^3$ ground state.⁶ The lowest excited state, ${}^2A_{1g}(a_{1g})^1(e_{2g})^4$, previously has been assumed to lie 16,200 cm^{-1} above the ${}^2E_{2g}$ state.^{3,4} In this communication we report the results of detailed magnetic susceptibility studies which provide further characterization of the ground electronic state of the ferricenium ion and evidence from low-temperature spectra that the electronic transition at 16,200 cm^{-1} is of the charge-transfer type.

The anisotropic *g* values ($g_{\parallel} = 4.36$ and $g_{\perp} = 1.30$) extracted from the esr spectrum⁵ of the ferricenium ion at 20°K can be quantitatively interpreted by taking into account spin-orbit coupling and the effect of low-symmetry crystal fields on a ${}^2E_{2g}$ ground state. Employing as a basis set the wave functions for the resulting pair of Kramers doublets,⁷ we have diagonalized the $\hat{L} + 2\hat{S}$ matrix, yielding the energy levels in a magnetic field and thus the theoretical expression for the temperature dependence of the susceptibility. In this treatment the extent of the temperature dependence of the effective magnetic moment of the ferricenium ion is primarily determined by a parameter (δ) which gauges the magnitude of the distortion from D_5 symmetry. The theoretical curves of μ_{eff} vs. *T* for two different values of δ show clearly (Figure 1) that the magnetic moment associated with the ${}^2E_{2g}$ state is expected to be strongly dependent on temperature.

We have measured the magnetic susceptibilities of four crystalline ferricenium salts from 300 to 42°K using a vibrating sample magnetometer. The experi-

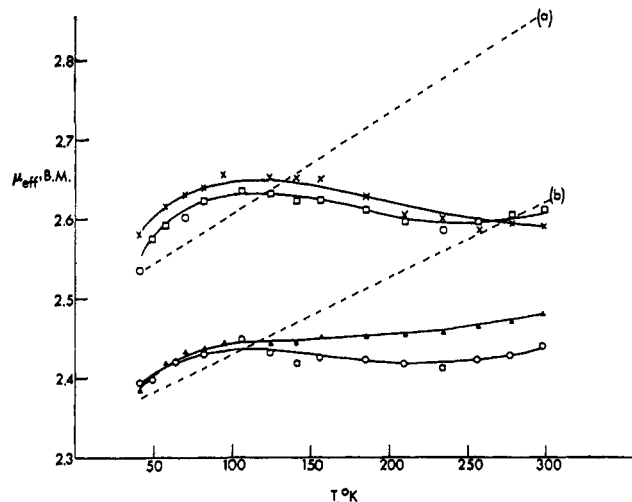


Figure 1. Curves of the effective magnetic moment (μ_{eff}) vs. temperature for four ferricenium salts: X, $[\text{Fe}(\text{cp})_2](\text{PF}_6)$; □, $[\text{Fe}(\text{cp})_2](\text{picrate})$; Δ, $[\text{Fe}(\text{cp})_2](\text{I}_3)$; O, $[\text{Fe}(\text{cp})_2](\text{BF}_4)$. The dashed lines (a) and (b) are theoretical curves for a ${}^2E_{2g}$ ground state experiencing low-symmetry crystal fields (δ) of 200 and 350 cm^{-1} , respectively.

mental μ_{eff} vs. *T* curves are displayed in Figure 1. The most striking result is that the magnetic moment of the ferricenium ion in these compounds is relatively independent of temperature and definitely does not exhibit the behavior predicted for it on the basis of a ${}^2E_{2g}$ state with a temperature-independent δ . Thus the ${}^2E_{2g}$ theoretical susceptibility expression can be modified to account for two possibilities: (a) temperature dependence of the low-symmetry crystal field, $\delta(T)$, or (b) thermal population of the ${}^2A_{1g}$ state ($\mu_{\text{eff}} \approx 1.73$ BM). We have found that either of these modifications separately is capable of explaining the experimental data, the former requiring δ to vary typically from ~ 150 cm^{-1} at 42°K to ~ 350 cm^{-1} at 300°K and the latter requiring⁸ $\Delta E[{}^2A_{1g} - E'({}^2E_{2g})] \approx 350$ cm^{-1} . We are undertaking a single-crystal magnetic susceptibility study over a temperature range in an attempt to decide the relative importance of the two factors.

Another interesting observation from Figure 1 is that the magnetic moment of the ferricenium ion is a function of the anion. This is interpreted as another indication of the great sensitivity of $\mu_{\text{eff}}({}^2E_{2g})$ to changes in the magnitude of the distortion from D_5 symmetry. Changes in the range shown can be accounted for simply by the small differences in intermolecular interactions in the four compounds investigated.

Electronic absorption spectra for ferricenium ion at 300 and 77°K are shown in Figure 2. The band at 16,200 cm^{-1} is of moderate intensity and exhibits vibrational structure at 77°K. The vibrational progression is assigned to the symmetric ring-metal stretching frequency, which is found^{9,10} at 303 cm^{-1} in ferrocene.

(8) A near degeneracy of the ${}^2E_{2g}$ and ${}^2A_{1g}$ ferricenium states is entirely consistent with one interpretation of the electronic spectrum of ferrocene. The energy difference $\Delta E({}^2A_{1g} - {}^2E_{2g})$ is equal to ${}^3\Delta\epsilon^{\text{core}}(e_{2g} - a_{1g}) + 20B$, where *B* is the Racah parameter. Our best low-temperature spectrum of ferrocene places the d-d transitions as follows: ${}^1A_{1g} \rightarrow a^1E_{1g}$, 21,800; ${}^1A_{1g} \rightarrow {}^1E_{2g}$, 24,000; ${}^1A_{1g} \rightarrow b^1E_{1g}$, 30,800 cm^{-1} . For ferrocene this gives $\Delta\epsilon^{\text{core}}(e_{2g} - a_{1g}) = -7100$ cm^{-1} and $20B = 7800$ cm^{-1} . Assuming no drastic changes occur in $\Delta\epsilon^{\text{core}}$ and *B* in going from $\text{Fe}(\text{cp})_2$ to $\text{Fe}(\text{cp})_2^+$, $\Delta E({}^2A_{1g} - {}^2E_{2g})$ is estimated to be relatively small.

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