Organometallic Studies. XVII.[1] A Novel Approach to the Synthesis of the Benzopentalene System[2]

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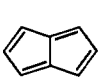
The benzopentaleneironcyclopentadienyl π-complex VIII obtained as a transient cation from the acid solvolysis of 2,3-ferrocoindenol (VII) appears to undergo an extremely fast internal oxidation–reduction process, resulting in the formation of the cation radical XI which then dimerizes to the ferricenium-type dication XII.

Introduction

Benzopentalene (II) and its parent compound pentalene (I) have engaged the attention of both theoretical and experimental chemists ever since Armit and Robinson[3] first suggested that pentalene might be an



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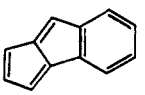


II

aromatic hydrocarbon.[4] Even though this interest has prompted a large number of investigators to attempt the synthesis of these compounds, both pentalene and benzopentalene still remain a challenge to the ingenuity of the synthetic organic chemist.

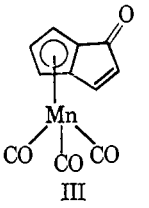
The information which has accumulated in the literature, as a result of both the many experimental attempts and the various theoretical treatments,[4] could be taken to indicate that a novel experimental approach using starting materials other than the classical type of organic compounds and some recently developed techniques, such as for example that of photochemistry, might ultimately lead to the preparation of these elusive compounds, nonsubstituted pentalene and benzopentalene.

We have chosen as starting materials for our synthesis work π-bonded organometallic compounds, and this communication describes our work on the benzopentalene system. Details of the work on the pentalene system will be published in a subsequent communication.[2]

Results and Discussion

The failure of many investigators to isolate pentalene or benzopentalene[4] from reaction sequences which should have succeeded had these two compounds been aromatic-like in their nature has provided much circumstantial evidence for the growing belief that one might be dealing with compounds which are in fact cyclic polyolefins with a great tendency to form polymerized derivatives. Indeed, the experimental literature on this subject is full of statements such as "a polymeric, untractable material only was obtained." An obvious analogy exists between the efforts to obtain I and II and those which have been aimed at synthesizing cyclobutadiene. The theoretically reasoned prediction, in 1956, of Longuet-Higgins and Orgel[5] that cyclobutadiene should be stabilized, and thus amenable to synthesis, in the form of a transition metal complex, induced us to extrapolate the same reasoning to the case of pentalene and subsequently to that of benzopentalene.

In the course of our work on the pentalene system, it became necessary to learn something about the dimerization tendency of the cyclopentadienone derivative[2] III, and a suitable model was sought which would be free of such dimerization complications. What seemed to us a suitable model compound, 2,3-ferrocoindenone (VI) had been reported briefly in the literature.[6] It occurred to us that VI would not only be the right model compound for testing the reaction sequence



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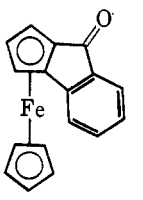


VI

envisaged in the pentalene work, but it could serve at the same time as starting material for attempting to arrive at the analogous benzopentalene–metal complex.

An improved method was developed for the synthesis of VI in gram quantities. Reduction of VI with lithium aluminum hydride in ether or, simpler still, with sodium borohydride in alcohol solution afforded the crystalline alcohol VII. The latter shows great tendency to be oxidized back to the ketone VI either during column chromatography or when left in solution in the presence of air. Acid solvolysis of 2,3-ferrocoindenol (VII) was expected to give the carbonium ion VIII which, it was hoped, would precipitate as a stable salt in the presence of a suitable anion, such as BF_4^-. The expectation for the stability of the carbonium ion VIII was based on the demonstrated high stability[7] of α-ferrocenylcarbonium ions (IX) and th

(1) Part XVI: M. Cais and N. Maoz, *J. Organometal. Chem.*, in press.

(2) Parts of the work reported herein were presented at the following meetings: (a) M. Cais, A. Modiano, N. Tirosh, A. Eisenstadt, and A. Rubinstein, 19th International Congress of Pure and Applied Chemistry, London, July 10–17, 1963, Abstracts of Papers, AB 4-12, p. 166; (b) M. Cais, A. Raveh, and A. Modiano, Meeting of the Israel Chemical Society, Beer Sheva, Dec. 1963; *cf. Israel J. Chem.*, 1, 228 (1963); (c) M. Cais, A. Modiano, N. Tirosh, and A. Eisenstadt, 8th International Conference on Coordination Chemistry, Vienna, Sept. 7–11, 1964; *cf.* Proceedings, ref. 1c, p. 229.

(3) J. W. Armit and Robinson, *J. Chem. Soc.*, **127**, 828 (1922).

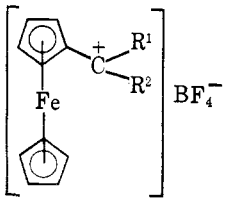
(4) For reviews and leading references see (a) E. D. Bergmann in "Non-Benzenoid Compounds," D. Ginsburg, Ed., Interscience Publishers, Inc., New York, N. Y., 1959; (b) M. E. Vol'pin, *Usp. Khim.*, **29**, 298 (1960); (c) E. Le Goff, *J. Am. Chem. Soc.*, **84**, 1505 (1962); (d) T. J. Katz, M. Rosenberger, and R. K. O'Hara, *ibid.*, **86**, 249 (1964).

(5) H. C. Longuet-Higgins and L. Orgel, *J. Chem. Soc.*, 1969 (1956).

(6) D. E. Bublitz, W. E. McEwen, and J. Kleinberg, *J. Am. Chem. Soc.*, **84**, 1845 (1962).

(7) See ref. 8a for leading references.

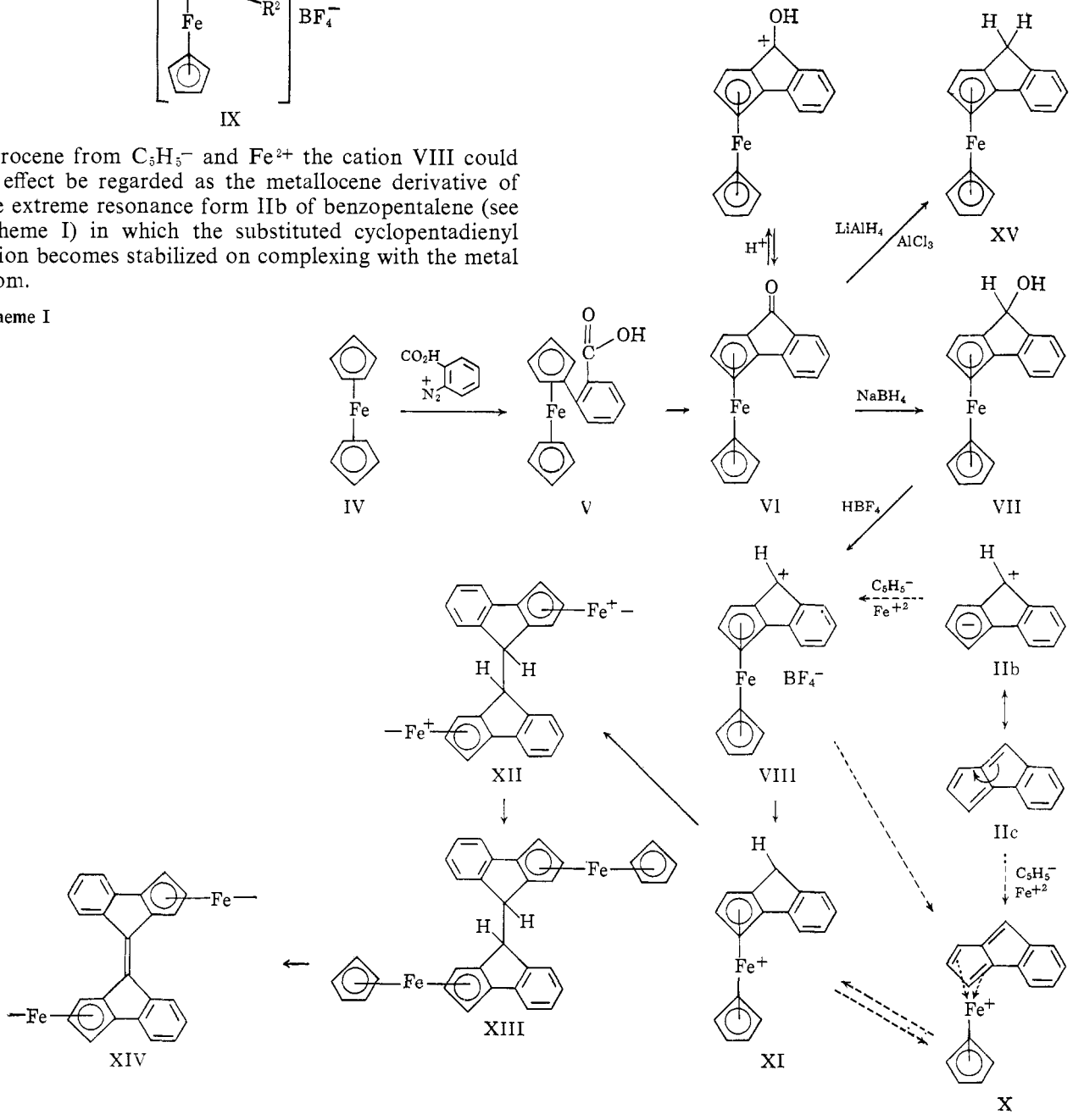
actual isolation of stable fluoroborate salts of such ions.[2,8,9] By direct analogy to the formation of



IX

ferrocene from $C_5H_5^-$ and Fe^{2+} the cation VIII could in effect be regarded as the metallocene derivative of the extreme resonance form IIb of benzopentalene (see Scheme I) in which the substituted cyclopentadienyl anion becomes stabilized on complexing with the metal atom.

Scheme I



Treatment of the alcohol VII with fluoroboric acid afforded an almost quantitative yield of a green salt which analyzed correctly for the elemental composition required of the salt VIII. However, on attempting to measure the n.m.r. spectrum of this salt it was immediately apparent that a strongly paramagnetic species was present in the solution of the salt, which caused considerable over-all broadening of the n.m.r. spectrum. In fact, no n.m.r. signal could be obtained at all on measuring solutions of this salt. If measurement of the n.m.r. spectrum of the alcohol VII in deuteriochloroform was followed by addition of gaseous hydrogen chloride to the n.m.r. tube containing the alcohol solution, the latter changed color instantaneously from orange-brown to dark green and the n.m.r. signals of the alcohol VII disappeared completely. This result was in direct contrast to that obtained[8a] when a similar experiment was carried out with carbinols from which one expected the formation of cation IX. In the latter case only slight displacements of the proton resonance signals could be observed.[8a]

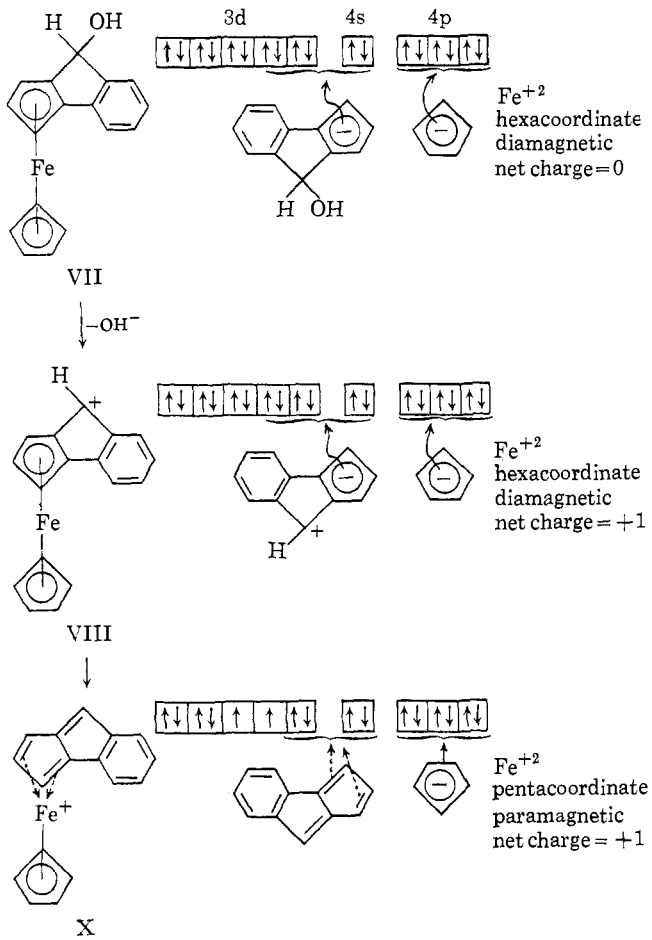
The most attractive explanation for the formation of a paramagnetic species in the acid solvolysis of the alcohol VII seemed to be that the carbonium ion intermediate VIII underwent an electronic rearrangement leading to the formation of the benzopentalene complex X with most of the positive charge being localized

(8) (a) M. Cais and A. Eisenstadt, *J. Org. Chem.*, 30, 1148 (1965); (b) M. Cais and A. Eisenstadt, *Rev. Roumaine Chim.*, in press; (c) M. Cais and E. Eisenstadt, 2nd International Symposium on Organometallic Chemistry, Madison, Wis., Aug. 30–Sept. 3, 1965.

(9) J. E. Mahler, D. H. Gibson and R. Pettit, *J. Am. Chem. Soc.*, 85, 3959 (1963), and preceding papers have isolated stable salts of π-pentadienyliron tricarbonyl cations by an analogous acid solvolysis of the respective alcohols.

on the metal atom. This structure would incorporate the less extreme resonance form of benzopentalene (IIa) which would at the same time be stabilized by a π-dieneiron-type complex. Furthermore, this change of the cyclopentadienyl anion form to the fulvene-type structure would require the concomitant change of the Fe^{II} atom from hexacoordinate to pentacoordinate bonding, thus giving rise to a structure expected to show paramagnetic properties equivalent to two unpaired electrons.

This change can be conveniently illustrated by the following pictorial representation.



The magnetic susceptibility of the fluoroborate salt (in powder form), obtained from the solvolysis of the alcohol VII, was found[10] to be $\chi_g^{294.5°K} = 5.1 \times 10^{-6}$ c.g.s.u. The results of temperature-variation measurements of the magnetic susceptibility of the powdered salt, as shown in Figure 1, can be taken to indicate that the compound is pure and of one species. In other words there is no indication of an equilibrium mixture nor does there appear to be any appreciable content of diamagnetic material.

The magnetic moment, calculated from the above data obtained at room temperature, for the molecular formula $(C_{17}H_{13}Fe)^+BF_4^-$ corresponding to X is $\mu_{eff} = 2.2$ B.M. A solution of the fluoroborate salt in dimethyl sulfoxide was found (by the Gouy method) to

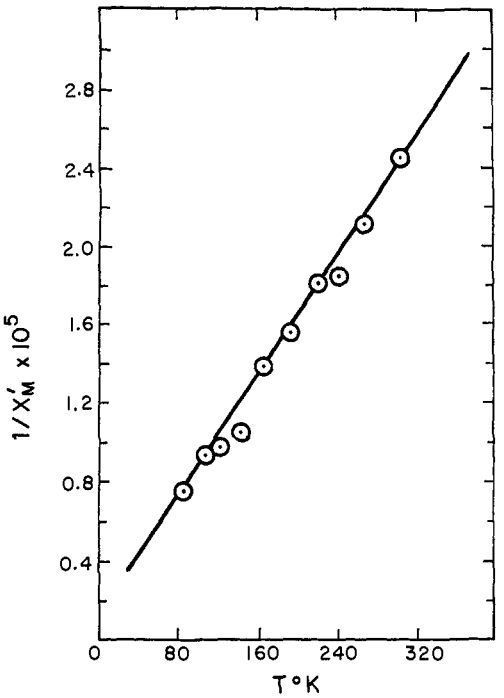


Figure 1. Magnetic susceptibility of the fluoroborate salt XII (least squares fit is $y = 0.1028 + 0.007729x$).

follow the Curie–Weiss law down to 200°K., whence the solid started to precipitate out of the eutectic solution. A magnetic moment of $\mu_{eff} = 2.2$ B.M. was also obtained from measurements of solutions of the fluoroborate salt in both dimethyl sulfoxide and methylene chloride at room temperature. Thus, the magnetic moment appears to be independent of the dielectric strength of the solvent, and one may take this to indicate the absence of spin–spin interaction in solution. The same conclusion can be drawn from the results of the temperature-dependence measurements of the solid salt.

The data for the magnetic susceptibility measurements could not be reconciled with a structure such as X which should have a $\mu_{eff} \approx 2.8$–3 B.M., corresponding to two unpaired electrons. In fact, the value of 2.2 B.M. is practically identical with that obtained for a number of ferricenium salts measured[10] under the same conditions as those for the fluoroborate salt VIII.[11] Since the value of 2.2 B.M. for the ferricenium salts corresponds to one unpaired electron per Fe atom, the same must be true for the fluoroborate salt VIII.

A structure of the fluoroborate salt which would have one unpaired electron per Fe atom could be arrived at as shown in Scheme I. The carbonium ion VIII could undergo an internal oxidation–reduction process whereby one of the nonbonding d_{2g} electrons of the Fe atom in VIII would be transferred to the positive carbon atom to form the radical cation XI. Dimerization of XI would then form the dimeric dication XII in which, even though the molecular formula would require two unpaired electrons, each iron atom would have the same electronic configuration as the

(10) We are greatly indebted to Mr. Peter R. Woolliams, University College, London, England, for the magnetic susceptibility measurements and for much valuable discussion. We also wish to thank Professor S. Kirschner, Wayne State University, Detroit, Mich., for helpful discussions of the magnetic susceptibility results.

(11) Values reported[12] for ferricenium salts are in the range $\mu_{eff} = 2.34$ B.M.

(12) For tables of magnetic moments of cyclopentadienyl and arene metal compounds, see G. Wilkinson and F. A. Cotton in "Progress in Inorganic Chemistry," Vol. 1, F. A. Cotton, Ed., Interscience Publishers, Inc., New York, N. Y., 1959.

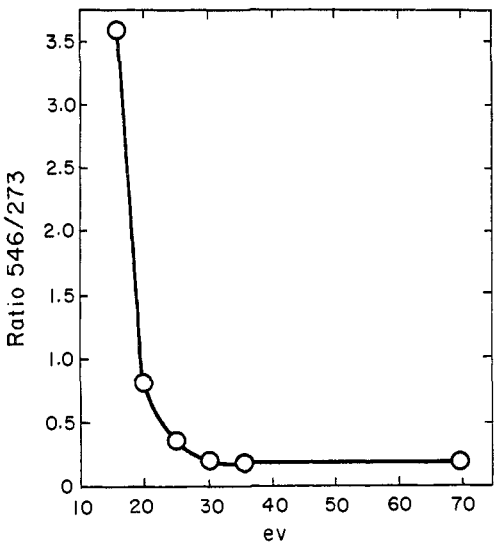


Figure 2. Variation of the intensity ratio of ions (*m/e* 546)/(*m/e* 273) with the electron beam energy.

metal atom in the ferricenium cation, namely one unpaired electron per iron atom. The magnetic moment calculated for this dimer dication corresponds to μ_{eff} = 3.14 B.M. (corrected for diamagnetic susceptibility[13]) in agreement with experimental values found for compounds having two unpaired electrons per molecule.[14]

An *intramolecular* oxidation–reduction process involving α-metallocenylcarbonium ions has already been postulated by several authors.[15] On the other hand the α-ferrocenylphenylcarbonium ion IX (R^1 = H, R^2 = C_6H_5) has been isolated by us[8a] as the diamagnetic fluoroborate salt, no evidence having been found of any significant *inter-* or *intramolecular* oxidation–reduction processes during the acid solvolysis of the corresponding carbinol derivative.[16] However, in order to find evidence for the dimeric structure XII, it became desirable to determine the molecular weight of the fluoroborate salt. Cryoscopic measurements of solutions of the fluoroborate salt in dimethyl sulfoxide were inconclusive because they gave values of $i \approx 4$ whereas structure VIII would require $i \approx 2$ and the dimer XII should give $i \approx 3$. Moreover ΔT appeared to increase with time, which might mean that some kind of solvent–solute reaction was slowly taking place during the measurements. Recourse was then made to mass spectrometry.[17]

The extremely low volatility of the fluoroborate salt required prolonged heating of the sample before a spectrum could be recorded.[18] The ion having the

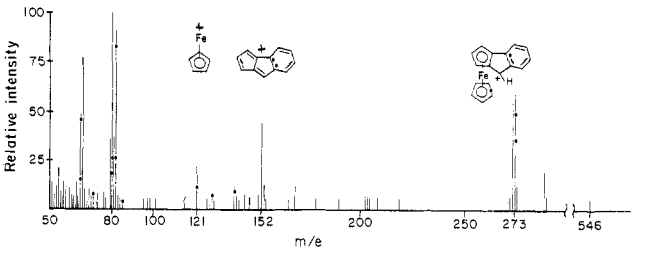


Figure 3. Mass spectrum of dimer XIII.

m/e value 273 corresponds to the mass of the cation VIII, which probably arises from the splitting of ion *m/e* 546 into two equal fragments. The presence of ion *m/e* 546, which corresponds to the dimeric structure XIII, provides corroborative evidence[19] that the fluoroborate salt has in fact the dimeric structure XII. In order to investigate the possibility that the ion *m/e* 546 might have arisen from recombination of two ions *m/e* 273, the mass spectrum was recorded at several different electron beam energies.[18] As can be seen from Figure 2 the ratio of the intensity of the peak of ion *m/e* 546 to the intensity of the peak of ion *m/e* 273 increases with lowering of the electron beam energy. This is rather conclusive evidence that ion *m/e* 273 arises from fragmentation of ion *m/e* 546 (Figure 3).

One could also infer from this result that the initial sample contained very little, if any, material which upon ionization would give rise to the molecular ion *m/e* 273.

Additional circumstantial evidence for XII being the most likely representation of the structure of the fluoroborate salt can be obtained from analyzing the results of reduction experiments with this salt. Very fast reduction appears to take place upon mixing an acetone solution of the salt with an aqueous solution of ascorbic acid, the color of the solution changing immediately from dark green to light brown.[20] The reaction product appeared to consist of two major components which were very different in their behavior on chromatography. The less polar component consisted of high-melting orange brownish crystals whose ultraviolet and infrared spectra were very similar to those of 2,3-ferrocoindene (XV) (Figures 4 and 5) obtained from the reduction of the ketone VI with lithium aluminum hydride–aluminum chloride. This together with molecular weight, n.m.r., and mass spectra data confirmed structure XIII as the most likely one for this compound. The second more polar component has not been characterized yet, though the analytical data correspond to a molecular formula isomeric to XIII.

Rather similar results, leading to the isolation of XIII, were obtained on reducing the fluoroborate salt with zinc powder. The same compound, XIII,

(13) The diamagnetic corrections were made using the data given by B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960.

(14) Values reported[12] for cyclopentadienylmetal derivatives with two unpaired electrons per molecule are in the range $\mu_{eff} \cong 2.80$–3.16 B.M.

(15) (a) K. L. Rinehart, Jr., C. J. Micheda, and P. A. Kittle, *J. Am. Chem. Soc.*, **81**, 3162 (1959); (b) A. Berger, W. E. McEwen, and J. Kleinberg, *ibid.*, **83**, 2274 (1961).

(16) We should like to refrain, at present, from speculating on the causes as to why an internal oxidation–reduction should take place with the carbonium ion VIII and not do so with the analogous carbonium ion IX. The possible *antiaromaticity* of the cyclopentadienyl cation in VIII will be discussed in a subsequent publication.

(17) We wish to thank Dr. A. Mandelbaum, of this department, for the mass spectra measurements and for helpful discussions in the interpretation of the spectra.

(18) The measurements were recorded on a Type Atlas CH 4 mass spectrometer. Ionization energy was maintained at 70 e.v. and the ionization current at 20 μa. The sample was introduced into the ion source by means of a direct inlet system and heated under the electron beam until sufficient pressure could be obtained.

(19) The possibility that such dimerization might take place during the prolonged heating of the sample in the inlet system of the mass spectrometer cannot be ruled out completely.

(20) This type of reduction is fully analogous to the reduction of the ferricenium cation to ferrocene. A carbonium ion such as VIII would be expected to react with one of the nucleophilic centers of ascorbic acid rather than undergo a one-electron reduction to a radical species. Reaction of the carbonium ion IX with ascorbic acid gave indeed a compound which analyzed correctly for the product expected from the nucleophilic attack reaction: M. Cais and A. Eisenstadt, unpublished results.

was also obtained when a 2-min.-old solvolysis reaction mixture was poured into water, without first isolating the fluoroborate salt through precipitation with ether. Had the carbonium ion VIII been present in the reaction mixture in a significant amount, the carbinol VII should have been the major reaction product.

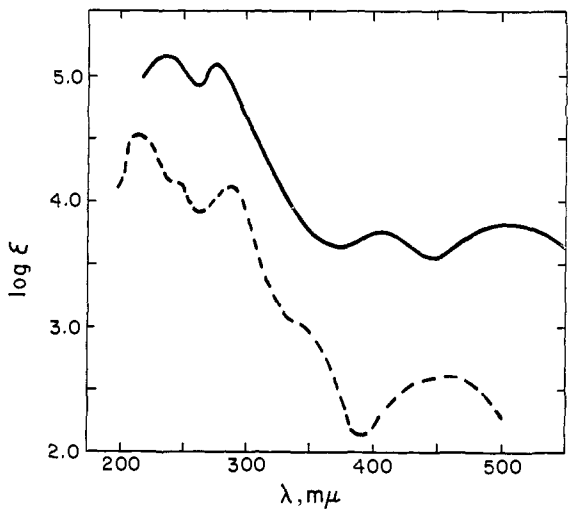


Figure 4. Ultraviolet spectra (in ethanol) of: ———, 2,3-ferrocoindenone (VI); and – – – –, 2,3-ferrocoindenol (VII).

A rather different result was obtained when the above experiment was repeated but the 2-min.-old solvolysis reaction mixture was poured into excess sodium ethoxide–ethanol solution. In addition to XIII, a significant amount of a dark blue solid compound was isolated which we believe to have the fulvalene-type structure XIV.[21] The major obstacle to the successful isolation of the carbonium ion VIII appears to be the extremely rapid[22] intramolecular oxidation–reduction reaction VIII → XI. We are currently investigating the possibility of preventing this internal oxidation–reduction reaction, and thus achieve the isolation of the carbonium ion VIII, by the introduction of an electron-withdrawing group in the second, unsubstituted cyclopentadienyl ring of the alcohol VII, thereby increasing the oxidation potential of the metal atom.[25,26] Alternatively, by attempting to replace the Fe atom with Ru or Os in the alcohol VII, we are trying to make use of the reported fact that ruthenocene and osmocene undergo oxidation with much greater difficulty than does ferrocene.[25,26]

(21) For comparison purposes the analogous compounds have been prepared from the ketone VI and the lithium derivatives of cyclopentadiene, indene, and fluorene: M. Cais and A. Modiano, to be published.

(22) An attempt was made to observe the changes VII → VIII → XI → XI → XII by a rapid-mixing and flow technique as described by Sutin and co-workers.[23] Even though the apparatus used[23] was suitable for studying reactions with half-times down to about 5 msec. by means of the stopped-flow technique, it was not possible to obtain evidence for the presence of any of the intermediates in the reaction VII → XII.[24]

(23) G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963).

(24) We wish to thank Professor N. Sutin, Brookhaven National Laboratory, Upton, N. Y., for carrying out these experiments for us while on sabbatical leave at the Weizmann Institute of Science, Rehovot, Israel.

(25) T. Kuwana, D. E. Bublitz, and G. Hoh, *J. Am. Chem. Soc.*, **82**, 5811 (1960).

(26) G. L. Hoh, W. E. McEwen, and J. Kleinberg, *ibid.*, **83**, 3949 (1961).

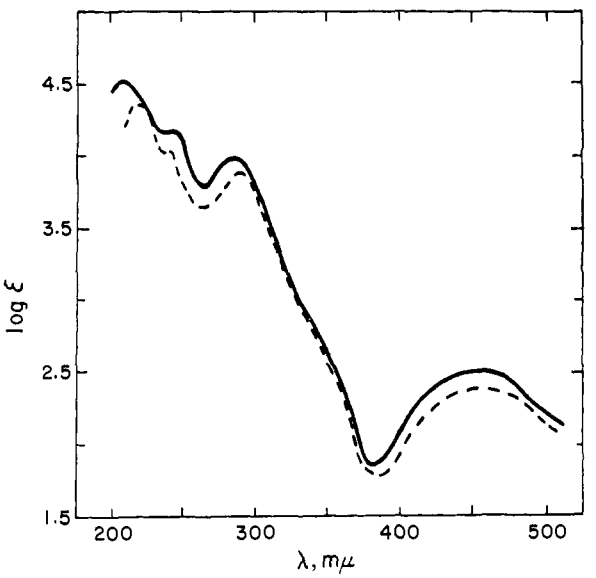


Figure 5. Ultraviolet spectra (in ethanol) of: ———, 2,3-ferrocoindene (XV); and – – – – –, the dimer XIII.

Experimental Section[27]

Synthesis of 2,3-Ferrocoindenone (VI). A suspension of *o*-anthranilic acid diazonium fluoroborate[28] (11.8 g., 0.05 mole) in acetone (50 ml.) was added dropwise at room temperature to a stirred solution of ferrocene (9.3 g., 0.05 mole) in acetone (100 ml.). After completing the addition the solution was stirred at room temperature for 1 additional hr. and then the solution was concentrated under vacuum (water pump) to a volume of about 50 ml. The residual solution was mixed with an aqueous solution of 1 *N* sodium hydroxide (200 ml.) and filtered to remove the unreacted ferrocene (2.9 g.). The alkaline filtrate was acidified with concentrated hydrochloric acid solution and the reddish oil which separated was extracted with methylene chloride (three 100-ml. portions). The combined methylene chloride extracts were washed with water till neutral, dried (Na_2SO_4), and evaporated to dryness to obtain 10.2 g. of a dark oil. This was shown to contain a significant amount of *o*-ferrocenylbenzoic acid by reacting the crude oil (9.7 g.) with excess diazomethane. After the usual work-up and chromatography on neutral alumina, methyl *o*-ferrocenylbenzoate (4.5 g.) was obtained as a reddish brown oil, b.p. 150–153° (0.15 mm.) *Anal.* Calcd. for $C_{18}H_{16}FeO_2$: C, 67.52; H, 5.04; Fe, 17.44. Found: C, 67.70; H, 5.20; Fe, 17.27. The infrared spectrum ($\nu_{C=O}$) showed 1725 $cm.^{-1}$.

Oxalyl chloride (10 ml.) was added in three portions to a solution of crude *o*-ferrocenylbenzoic acid (10.2 g.) in methylene chloride (150 ml.) and the mixture was allowed to stand overnight.

After removing the solvent (water pump) and all traces of unreacted oxalyl chloride (oil pump), the

(27) Melting points were determined on a Kofler block-type instrument and are uncorrected. The ultraviolet spectra were measured on a Cary Model 14 recording spectrophotometer. The infrared spectra were measured in chloroform solution, unless otherwise stated, on a Perkin-Elmer Infracord Model 137 spectrophotometer. The n.m.r. spectra were measured on a Varian Model A-60 spectrometer, with tetramethylsilane as internal standard.

(28) J. Frederick, J. Dippy, and F. R. Williams, *J. Chem. Soc.*, 1466 (1934).

residue was dissolved in methylene chloride (150 ml.) and stirred with anhydrous aluminum chloride (15 g.) for 1 hr. at room temperature. After the addition of iced water (~300 ml.) the reaction mixture was extracted twice with methylene chloride. Removal of the solvent yielded 10 g. of a dark solid. This was chromatographed on neutral alumina (200 g.). Elution with benzene (400 ml.) yielded 1.3 g. of a yellow oily material, b.p. ~80° (0.05 mm.), which on the basis of elemental analysis and the similarity of the infrared spectrum to that of methyl *o*-ferrocenylbenzoate is considered to be the ethyl ester of *o*-ferrocenylbenzoic acid. *Anal.* Calcd. for $C_{19}H_{18}FeO_2$: C, 68.29; H, 5.43; mol. wt., 334. Found: C, 68.25; H, 5.76; mol. wt., 323 (cryoscopic), 334 (mass spectrometer). The infrared spectrum ($\nu_{C=O}$) showed 1725 cm.$^{-1}$.

Further elution with methylene chloride (300 ml.) yielded the main product, *2,3-ferrocoindenone* (2.5 g.), as red-violet crystals, m.p. 104–105° (lit.[6] m.p. 105–106.2°). The spectroscopic data showed infrared ($\nu_{C=O}$) 1700 cm.$^{-1}$ ($CHCl_3$); ultraviolet $\lambda_{max}^{ethanol}$ 235 mμ (ϵ 14,000), 276 (12,900), 407 (5450), 512 (6200); n.m.r., substituted benzene protons complex multiplet centered at τ 2.5 (relative intensity 4), substituted cyclopentadienyl protons multiplet centered at 5.00 (intensity 3), and unsubstituted cyclopentadienyl protons singlet at 5.82 (intensity 5).

Elution with an additional 400 ml. of methylene chloride yielded 1.1 g. of a mixture of two compounds, which shows ketonic carbonyl absorption in the infrared spectrum at 1690 cm.$^{-1}$ but was not further characterized in the present work.

Synthesis of 2,3-Ferrocoindenol (VII). The ketone VI (1.65 g., 0.006 mole) in methanol (50 ml.) was reduced with sodium borohydride (*1* g.). The red-violet color of the ketone disappeared within 10–15 min., and thin layer chromatography showed the reaction to be complete. The solvent was removed under vacuum (water pump) and after adding water (~10 ml.) the mixture was extracted with petroleum ether (b.p. 40–60°). The organic solvent extracts were washed twice with water, dried (sodium sulfate), and evaporated to dryness to yield VII (1.6 g.) as a solid yellow compound, m.p. 90–91° (hexane). *Anal.* Calcd. for $C_{17}H_{14}FeO$: C, 70.37; H, 4.86; Fe, 19.25. Found: C, 70.27; H, 4.96; Fe, 18.92. Spectroscopic data showed infrared (ν_{OH}) 3700 cm.$^{-1}$; ultraviolet $\lambda_{max}^{ethanol}$ 212 mμ (ϵ 33,000); 243 (13,050), 289 (12,300), 345 (980), 459 (369), $\lambda_{max}^{conc\ H_2SO_4}$ 238 mμ (ϵ 11,530), 260 (11,170), 304 (10,150), 360 (3916), 412 (2356), 502 (620), 543 (689), 586 (308), 754 (330); $\lambda_{max}^{70\%\ HClO_4}$ 206 mμ (ϵ 25,200), 252 (19,000), 265 (12,600), 305 (11,900), 354 (4870), 410 (2510), 496 (537), 592 (387); n.m.r., complex multiplet at τ 2.67 (benzene protons), doublet at 4.8 (methine proton), multiplet at 5.58 (substituted cyclopentadienyl protons), singlet at 5.8 (unsubstituted cyclopentadienyl protons), doublet at 7.82 (hydroxyl proton), with intensities in the ratio 4:1:3:5:1.

The reaction of VII (0.26 g.) with acetic anhydride (1.5 ml.) in pyridine (2 ml.) gave, after the usual work-up, 0.25 g. of crude *2,3-ferrocoindenyl acetate*. Distillation under vacuum at 90° (0.01 mm.) and crystallization from petroleum ether (b.p. 40–60°) gave the analytical sample, m.p. 90–91°. *Anal.* Calcd. for $C_{19}H_{16}FeO_2$: C, 68.72; H, 4.81; Fe, 16.82. Found: C, 68.78; H, 4.89; Fe, 16.66.

Synthesis of 2,3-Ferrocoindene (XV). A solution of 2,3-ferroindenone (500 mg.) in dry tetrahydrofuran (5 ml.) was added dropwise to a suspension of lithium aluminum hydride (75 mg.) and anhydrous aluminum chloride (250 mg.) in tetrahydrofuran (10 ml.). The reaction mixture was then refluxed, under stirring, for 5 hr. and then worked up in the usual manner. Chromatography of the crude product on basic alumina and elution with hexane–benzene (4:1) yielded 150 mg. of yellow crystals, m.p. 72–73°. *Anal.* Calcd. for $C_{17}H_{14}Fe$: C, 74.15; H, 5.10; Fe, 20.75; mol. wt., 275. Found: C, 74.03; H, 5.20; Fe, 20.65; mol. wt., 270. Spectroscopic data showed infrared, no OH or C=O absorptions; ultraviolet $\lambda_{max}^{ethanol}$ 212 mμ (ϵ 34,200), 241 (15,800), 286 (10,600), 345 (615), 456 (362); n.m.r. (measured with Varian Model HR 60 spectrometer), complex multiplet at τ 2.85 (benzene protons), 6.49 (methylene protons), 5.55–5.85 (cyclopentadienyl protons).

Solvolysis of 2,3-Ferrocoindenol (VII). A solution (5 ml.) of fluoroboric acid in acetic anhydride (prepared by adding 4 ml. of 40% aqueous fluoroboric acid to 18 ml. of acetic anhydride at ice bath temperature) was added to a solution of 2,3-ferrocoindenol (1 g.) in acetic anhydride (2.5 ml.), and the reaction mixture was allowed to stand at room temperature for 15 min. This was then poured into 250 ml. of anhydrous diethyl ether and the dark green precipitate (1.1 g.) was collected by rapid filtration. Further purification was effected by dissolving the green salt in acetone and reprecipitating with ether. The green powdery material did not melt when heated up to 360°. *Anal.* Calcd. for $[(C_{17}H_{13}Fe)^+BF_4^-]_2$: C, 56.72; H, 3.64; B, 3.00; F, 21.12. Found: C, 56.51; H, 3.79; B, 2.87; F, 21.03. The infrared spectrum (in KBr) exhibited bands at 3150, 1580, 1510, 1440, 1080–1000, 850, and 765 cm.$^{-1}$. The ultraviolet spectrum of the salt in concentrated sulfuric acid, taken within 2 min. of the making up of the solution, showed bands at $\lambda_{max}^{H_2SO_4}$ 255 mμ (ϵ 7920), 305 (5932), 356 (4324), 495 (2710), 544 (2599), 585 (2220), 754 (831). This spectrum is practically the same as the spectra obtained from a solution of 2,3-ferrocoindenol in concentrated sulfuric or perchloric acids (see previous experiment and Figure 6). The changes in the ultraviolet spectrum of sulfuric acid solutions of the alcohol as a function of time are shown in Figure 7. The same changes as a function of time were observed with the fluoroborate salt in sulfuric acid. The magnetic susceptibility of the fluoroborate salt measured in powder form by the Gouy method was $\chi_g^{294.5°K} = 5.1 \times 10^{-6}$ c.g.s.u.[10] This corresponds to $\mu_{eff} = 3.14$ B.M. for the dimeric structure or $\mu_{eff} = 2.2$ B.M. per Fe atom. The same value (2.2 B.M.) was obtained on carrying out the measurements in dimethyl sulfoxide solution (Gouy method) or in dimethyl sulfoxide and methylene chloride solutions by n.m.r.[10] On attempting to measure the e.s.r. spectrum either at room temperature or at liquid nitrogen temperature no true paramagnetic signal could be observed.[10,29]

(29) We wish to thank Professor S. Fujiwara, The University of Tokyo, Tokyo, Japan, and Dr. Horsefield of Varian Associates, Zürich,

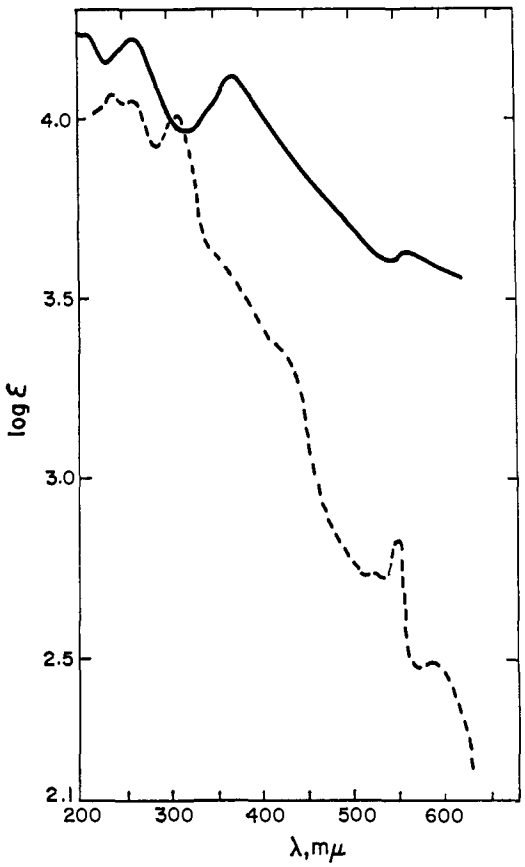


Figure 6. The ultraviolet spectra (in concentrated H_2SO_4) of: ———, 2,3-ferrocoindenone (VI); and - - - - - - - - 2,3-ferrocoindenol (VII).

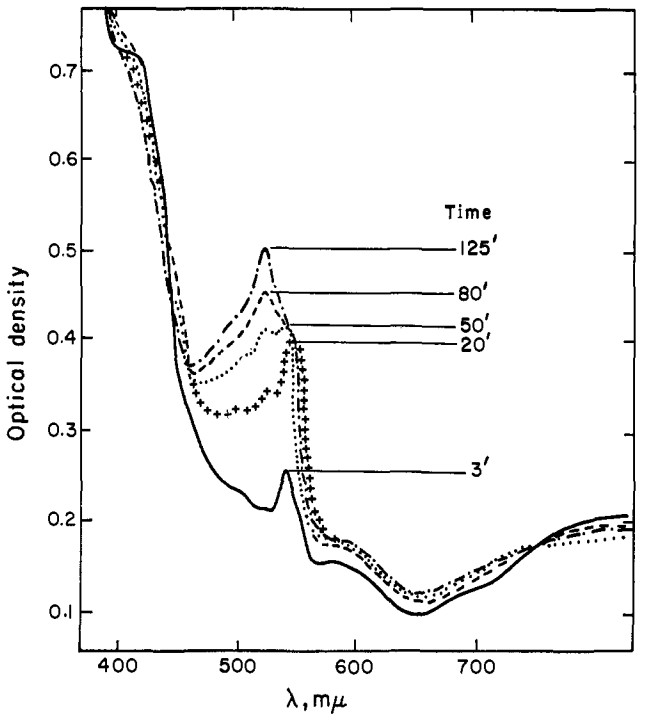


Figure 7. The change in the ultraviolet spectrum of a solution of 2,3-ferrocoindenol (VII) in concentrated H_2SO_4 as a function of time.

The temperature dependence of the magnetic susceptibility of the fluoroborate salt is shown in Figure 1.

The mass spectrum exhibited the following major *m/e* values: 48 and 49 (BF_2^+), 56 (Fe^+), 121 ($C_5H_5Fe^+$), 152 ($C_{12}H_8^+$), 273 ($C_{17}H_{13}Fe^+$, VIII?), 288 ($C_{17}H_{12}FeO^+$) (probably due to slight impurity), and 546 [$(C_{17}H_{13}Fe)_2^+$, XII?].

Reduction of the Fluoroborate Salt with Ascorbic Acid. The fluoroborate salt (234 mg.), dissolved in acetone (6 ml.), was mixed with a solution of ascorbic acid (126 mg.) in water (1 ml.). The reaction mixture was stirred at room temperature for 15 min. and, after dilution with excess water, was extracted with methylene chloride. The methylene chloride solution was washed with water, dried (sodium sulfate), and evaporated to dryness to yield 178 mg. of a brown solid. This was taken up in a minimum volume of methylene chloride, poured into excess ether, and filtered to collect 48 mg. of the starting fluoroborate salt. The filtrate was evaporated to dryness to yield 129 mg. of a material which upon trituration with a very small amount of ether yielded 40 mg. of orange brownish crystals which did not melt when heated up to 360°. The mother liquor from the triturate was evaporated to dryness to yield 80 mg. of a dark brown solid.

The orange brownish crystals were recrystallized from benzene to yield the analytical sample, which was shown by thin layer chromatography to contain a single compound. This is considered to be the dimer bi(2,3-ferrocoindenyl) (XIII). *Anal.* Calcd. for ($C_{17}H_{13}Fe)_2$: C, 74.75; H, 4.78; Fe, 20.45; mol. wt., 546. Found: C, 75.18; H, 4.73; Fe, 20.35; mol. wt., 574. The infrared spectrum, both in $CHCl_3$ and in KBr, exhibited a large number of absorption bands, some of which were as follows: (in $CHCl_3$ solution) 3120 (w), 3070 (w), 2940 (w), 1730 (w), 1670 (vw), 1623 (m), 1505 (mw), 1475 (mw), 1458 (mw), 1315 (mw), 1315 (mw), 1110 (s), 1040 (m), 1017 (ms), 1004 (s), and 888 (m) $cm.^{-1}$; the ultraviolet spectrum was very similar to that of 2,3-ferrocoindene $\lambda_{max}^{ethanol}$ 218 mμ (ε 22,500), 242 (10,300), 289 (7910), 345 (619), and 459 (234); the n.m.r. spectrum τ 2.48, 5.38, 5.72, 6.22, and 6.58.

The following major *m/e* values were observed in the mass spectrum: 80, 121 ($C_5H_5Fe^+$), 152 ($C_{12}H_8^+$), 273 ($C_{12}H_8FeC_5H_5^+$), and 546 (molecular ion).

The brown solid (80 mg.), obtained from the mother liquor of the triturate, was chromatographed over neutral alumina. Elution with hexane–benzene (3:2) yielded another 20 mg. of the dimer XIII. Further elution with methylene chloride–methanol (99:1) yielded 40 mg. of a dark brown crystalline material which did not melt when heated up to 360°. The infrared spectrum of this compound (in KBr) was similar to but not identical with that of the dimer XIII. *Anal.* Found: C, 74.63; H, 4.75.

In view of the observations from the zinc reduction experiment (*vide infra*), one should bear in mind that this compound might be an artifact from the chromatography purification.

Reduction of the Fluoroborate Salt with Zinc Powder. A mixture of the fluoroborate salt (400 mg.), dissolved in a minimum amount of glacial acetic acid, and excess zinc powder was stirred at room temperature in an inert atmosphere (helium) for 30 min. After adding

Switzerland, who measured the e.s.r. spectrum of the fluoroborate salt with the same negative results.

excess water, the reaction mixture was filtered, the solid precipitate was washed several times with methylene chloride, and the combined brown-colored methylene chloride filtrate and washings were washed with water till neutral, dried (magnesium sulfate), and evaporated to dryness to yield 300 mg. of a brown, solid material. Thin layer chromatography showed at least five different compounds. Chromatography of the crude product (300 mg.) on basic alumina and elution with petroleum ether, followed by benzene and then chloroform, allowed the recovery of a total of 280 mg. of material (collected in 14 fractions). The hexane–benzene (3:2) fraction yielded 78 mg. of pure orange brownish crystals whose physical constants turned out to be identical with those of the dimer XIII obtained in the ascorbic acid reduction. All the other chromatography fractions consisted of mixtures (several spots on t.l.c.) which could not be separated into the pure components even after repeated chromatography on various absorbents. There was reason to believe that chemical changes were taking place on the column during the chromatographic purification.

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Selective Reductions. VII. Reaction of Lithium Trimethoxyaluminohydride with Selected Organic Compounds Containing Representative Functional Groups[1]

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Contribution from the Richard B. Wetherill Laboratory of Purdue University, Lafayette, Indiana. *Received August 20, 1965*

The stoichiometry of the reaction of excess lithium trimethoxyaluminohydride with 56 selected organic compounds containing representative functional groups under standardized conditions (tetrahydrofuran solution, 0°) was examined in order to define the characteristics of the reagent for selective reductions. Compounds containing active hydrogen, such as alcohols, thiols, and amines, rapidly liberate the theoretical quantity of hydrogen. Aldehydes and ketones utilize 1 mole of hydride in undergoing reduction to the alcohol, although cinnamaldehyde utilizes 2. Carboxylic acids, anhydrides, acid chlorides, esters, and lactones utilize hydride corresponding to reduction to the alcohol stage. Epoxides react much slower than with lithium aluminum hydride, suggesting that the reagent should be useful for reduction of many functional groups in the presence of the epoxide structure. Moreover, in the case of unsymmetrical epoxides the products exhibit a high stereoselective opening of the ring. Nitriles and amides utilize hydride corresponding to reduction to the amine. Cyclohexanone oxime and pyridine do not react under the standard conditions, but nitro compounds, azobenzene, azoxybenzene, and picoline N-oxide are reduced. Disulfides and sulfoxides undergo reduction, but sulfones, sulfonic acids, and cyclohexyl tosylate are relatively inert. Consequently, in its behavior the reagent resembles lithium aluminum hydride much more closely than it does lithium tri-t-butoxy-aluminohydride previously explored with this series of compounds. However, there are significant differences which should lead to useful applications. In particular, the presence of only a single reactive hydrogen should make possible a number of selective reductions which are impractical with lithium aluminum hydride because of the presence of four hydrogens which exhibit variable reducing capabilities in the reduction.

Introduction

The addition of 3 moles of an alcohol to 1 mole of lithium aluminum hydride in an appropriate solvent provides a simple, convenient means of preparing derivatives which exhibit reducing properties significantly different from those of the parent reagent.[3,4] For example, lithium tri-*t*-butoxyaluminohydride, prepared in this manner, has proven to be a valuable reagent for the selective reduction of acid chlorides to aldehydes,[3,5] for the stereospecific reduction of steroidal ketones,[6] and for certain selective reductions in complex molecules.[7–9] A systematic survey of the characteristics of this reagent has revealed that it is an exceedingly mild reducing agent, approaching sodium borohydride in its behavior.[10]

The addition of 3 moles of ethyl alcohol to lithium aluminum hydride produces a product which is not homogeneous.[4,11] Nevertheless, this material has proven to be valuable for the preparation of aldehydes

(1) Based upon a thesis submitted by P. M. Weissman in Aug., 1964, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Graduate Research Assistant on Research Grant DA-ARO(D)-31-124-117 supported by the U. S. Army Research Office (Durham).

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