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ELECTRON-TRANSFER REACTIONS OF AMINES WITH α-FERROCENYLCARBONIUM IONS

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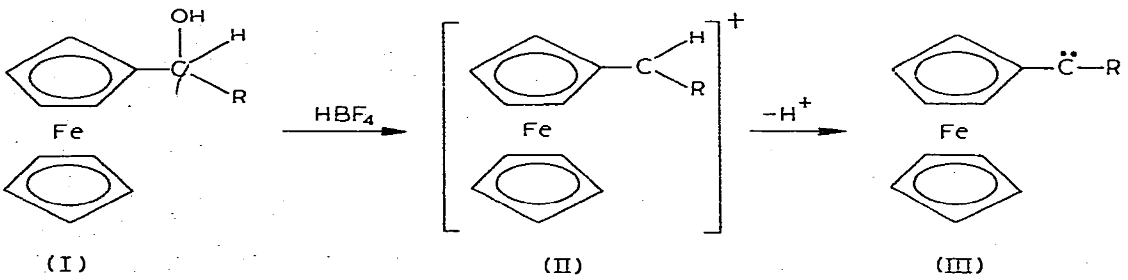
Summary

The products observed in the reactions of α-ferrocenylcarbonium ions with tertiary amines do not originate from ferrocenylcarbene intermediates. Evidence is presented in support of an electron-transfer mechanism leading to α-ferrocenylcarbinyl radicals as reaction intermediates.

Introduction

The stability of α-ferrocenylcarbonium ions [1] is of much interrest [2—6]. Much attention has been directed to the special ability of the ferrocenyl moiety to delocalize a positive charge generated on a vicinal carbon atom. That this property of the ferrocenyl groups is significantly different from that of other electron-donating substituents usually encountered in organic compounds, is evident from the easy access to isolable, highly stable secondary ferrocenylcarbonium ions, II.

Some time ago we began to investigate the possibility of using these carbonium ions as precursors for the synthesis of ferrocenylcarbenes, III. It was reasonable to expect that the mechanism involved in the stabilization of α-ferrocenylcarbonium ions might operate also in α-ferrocenylcarbenes. Further-



more, it seemed justifiable to assume that the exceptional electron-donating ability of the ferrocenyl group might lead to a carbene with enhanced nucleophillic character. Several years ago we reported [7] some preliminary results on our attempts to deprotonate II with ethyldiisopropylamine. Even though the ferrocene derivatives isolated from the above reaction could be postulated to have arisen through the formation of a ferrocenylcarbene intermediate, III, we concluded that the experimental evidence obtained by us and by others [8] * did not exclude the possible intervention of other types of intermediates. In this paper we present data which demonstrate unequivocally that the major reaction path between α-ferrocenylcarbonium ions and tertiary alkyl amines does not involve deprotonation of II to form the intermediate carbene III. Our results indicate that the amine acts as an electron-donor to the ferrocenylcarbonium ion to form radical species which lead to the observed products.

Results

The ferrocenylcarbonium ions were readily obtained as the fluoroborate salts by treating the precursor carbinols with a solution of fluoroboric acid in acetic anhydride [9], and precipitated out by the addition of a large excess of a solvent such as diethyl ether, hexane or carbon tetrachloride. The last two solvents were used in order to eliminate the possibility of oxonium salt formation in the presence of diethyl ether, such as observed [10] with tritylcarbonium ions:

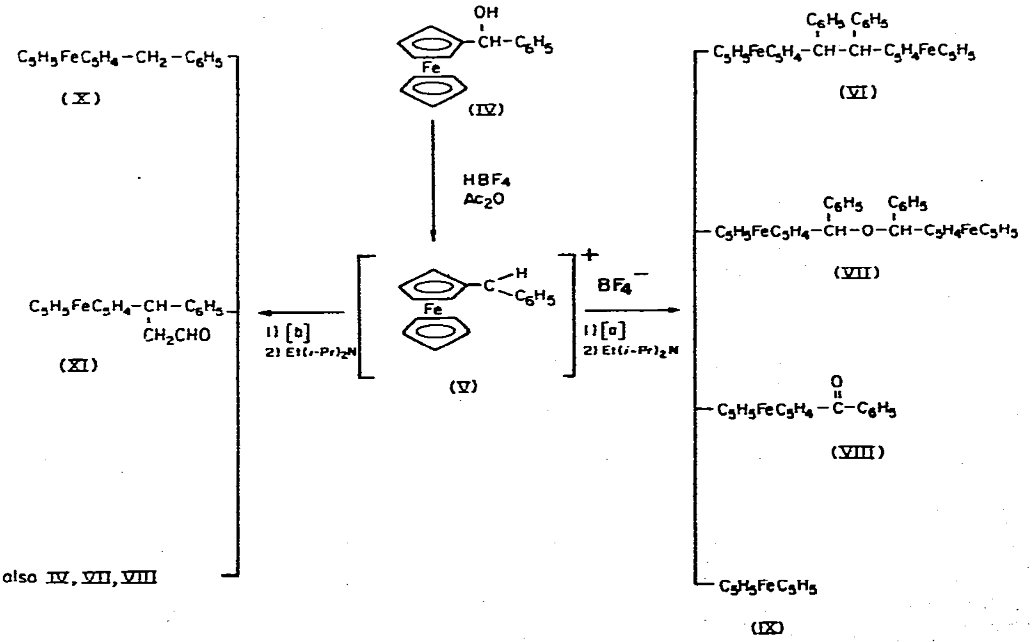


Fig. 1. Product distribution from reaction of ferrocenylphenylcarbonium fluoroborate with ethyldiisopropylamine (after precipitation of V with CCl_4 or C_6H_{12}, path a; and $(C_2H_5)_2O$, path b).

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* Reaction of $[(CH_3S)_2CH]^+BF_4^-$ with a tertiary amine has been postulated to lead to the carbene $(CH_3S)_2C$.

$$(C_6H_5)_3C^+A^- + (C_2H_5)_2O \rightleftharpoons (C_6H_5)_3C-\overset{+}{O}(C_2H_5)_2A^-$$

Ethyldiisopropylamine, EDIPA, was chosen initially for this study because it is reluctant to enter into nucleophilic alkylations [11] but is known to be sufficiently basic to exhibit good proton abstracting ability. (Subsequencty other tertiary alkylamines were found to react in similar way with our carbonium ions.)

Ferrocenylphenylcarbonium fluoroborate, V, dissolved readily in dichloromethane to form a dark reddish brown solution which changed colour instantaneously to light yellow upon addition of an equimolar quantity of EDIPA. After work up and chromatographic separation, the reaction products (Fig. 1) were identified and characterized by comparison with authentic samples, wherever possible. The yields of the products appeared to vary with the type of solvent used initially in the precipitation of the carbonium ion salt. From the above reaction of V, precipitated with either hexane or carbon tetrachloride, the product was 1,2-diferrocenyl-1,2-diphenylethane, VI, (40—50%); di(ferrocenylphenylmethyl) ether, VII (30%); benzoylferrocene, VIII (~8%) and ferrocene, IX, (8%). The carbonium ions V precipitated with diethyl ether yielded in the reaction with EDIPA: ferrocenylphenylmethane, X (33%), the starting carbinol, IV (23%), benzoylferrocene, VIII (2%) and an aldehyde which on the basis of spectral data was thought to be 3-ferrocenyl-3-phenylpropanal, XI (38%). In another experiment the product was: VII (53%); X (27%) and XI (20%). The amount of benzoylferrocene VIII increased to 66% when the reaction was carried out without first bubbling nitrogen through the solvents in order to flush out dissolved molecular oxygen. This was taken to indicate that the oxygen-containing products such as VII, VIII, XI and IV, were formed through the intervention of molecular oxygen still left in the reaction system even after various de-oxygenation procedures.

The dark blue dichloromethane solution of diferrocenylcarbonium fluoroborate, XII, became light-yellow upon addition of an equimolar amount of EDIPA. The product distribution (Fig. 2) was: diferrocenylmethane, XIII (55%); diferrocenylcarbinol, XIV (28%) and an unknown compound (~10%). When two molar equivalents of EDIPA were used, the relative yields were reversed; over 60% of XIV and only about 20% of XIII. The use of triethylamine in the reaction with XII with degassing of reactants gave yet another product distribution: 30% of XIII, 56% of XIV and 5% of a new product, (diferrocenylmethyl)-ethyl ether, XV. The same reaction carried out with prior bubbling of dry oxy-

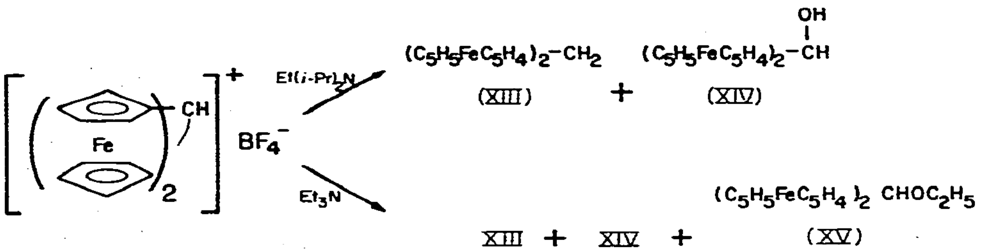
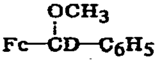
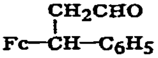
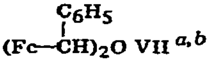
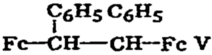


Fig. 2. Product distrubtion from reaction of diferrocenylcarbonium fluoroborate with ethyldiisopropylamine and triethylamine.

TABLE 1

MASS SPECTRUM ANALYSIS OF DEUTERIUM CONTENT IN PRODUCTS FROM REACTION BETWEEN FERROCENYLPHENYLDEUTEROCARBONIUM FLUOROBORATE AND ETHYLDIISOPROPYLAMINE ($Fc \equiv C_5H_5FeC_5H_4$)

Product	% Label (±5%)		
	d_0	d_1	d_2
 $Fc-CD(OCH_3)-C_6H_5$ XVII	6	94	
$Fc-CH_2C_6H_5$ X [b]	5	95	
 $Fc-CH(CH_2CHO)-C_6H_5$ XI [b]	13	85	2
 $(Fc-CH(C_6H_5))_2O$ VII [a,b]		5	95
 $Fc-CH(C_6H_5)-CH(C_6H_5)-Fc$ VI [a]	10	5	85

[a,b] See Fig. 1.

gen through the solvents yielded 79% of the ether XV and 15% of the carbinol XIV. This provided additional support for the explanation that molecular oxygen, even when present only in small amounts, can participate in the reaction between ferrocenylcarbonium ions and amines. The possible formation of an oxonium salt, $(C_5H_5FeC_5H_4)_2CH-{}^+O(C_2H_5)_2BF_4^-$ upon precipitation of the carbonium ion with diethyl ether (vide supra) could definitely be discounted in this case. The NMR spectrum of the fluoroborate salt did not exhibit any absorptions due to ethyl groups. Furthermore the carbonium ion salt, XII, was found by both NMR and X-ray analysis to remain unchanged even after recrystallization from methanol.[3].

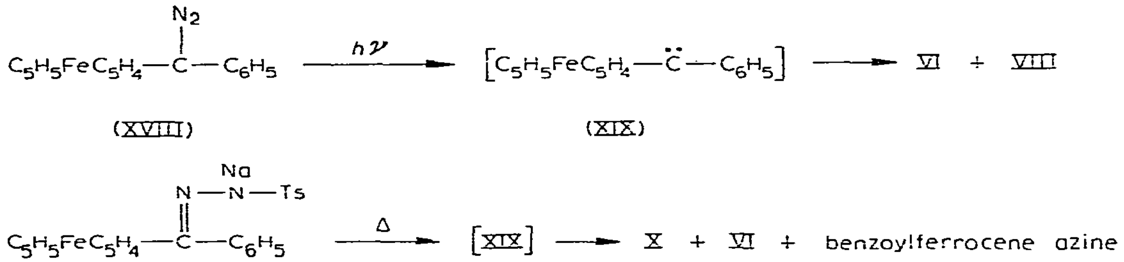
In order to determine the extent of deprotonation, if any, ferrocenylphenyldeuterocarbinol, XVI was prepared by reducing benzoylferrocene, VIII, with $LiAlD_4$. The degree of deuteration in XVI was determined by converting it into the carbonium ion salt (V analog), and subsequent reaction with methanol to give (ferrocenylphenyldeuteromethyl)methyl ether, XVII. This compound served as standard in the mass spectrum analysis. Ferrocenyldeuterocarbonium fluoroborate was treated with EDIPA and the products separated as described above. The deuterium content of the ferrocene-containing products was determined by mass spectrometry. The mass spectra were determined under conditions such that the fragmentation $[M^+] \rightarrow [M^+ - 1]$ was minimal, in order to avoid as far as possible isotopic dilution due to fragment $[M^+ - 1]$. The data summarized in Table 1 show that all the deuterium present in the starting carbonium ion salt was retained in the isolated ferrocene derivatives, thus indicating that no detectable deprotonation by the amine had occurred in the reaction.

Discussion

The reaction of tertiary amines with carbonium ions has been used extensively in organic syntheses. Typical examples are the proton-abstraction step to produce a carbon—carbon double bond in the synthesis of calicenes [12], sesquifulvalenes [13], heptafulvalene [14], and heptalene [15], and abstraction of a proton on oxygen when no proton on a carbon atom was available [16].

On the other hand, tertiary carbonium ions have been reported [17] to abstract a hydride ion from an α-carbon atom of a tertiary amine leading to a substituted methane and a quaternary ammonium or iminium salt. The tropylium cation has been used to oxidize unsaturated molecules which contain hetereoatoms. Thus, addition of carbazole to tropylium fluoroborate, $C_7H_7^+BF_4^-$ in dry acetonitrile at room temperature resulted in the immediate formation of a red, 1 : 1-charge transfer complex. Treatment with methanol yielded red violet crystals for which the radical cation structure $[\text{carbazole}]^{\dagger}BF_4^-$ was suggested [18].

The initial aim of this investigation was to produce α-ferrocenylcarbenes, III, through the deprotonation of secondary α-ferrocenylcarbonium ions, II. When a non-deoxygenated methanolic solution of ferrocenylphenyldiazomethane, XVIII, was subjected to UV irradiation to produce the ferrocenylphenylcarbene, XIX, benzoylferrocene, VIII and 1,2-diferrocenyl-1,2-diphenylethane, VI were the major products [7].



The thermal decomposition [19] of benzoylferrocene tosylhydrazone sodium salt, XX in pyridine/cyclohexene yielded benzylferocene (27%), X, the diastereoisomers of VI (15%) and benzoylferrocene azine (36%) but no addition product of the carbene XIX to cyclohexene was detected. Since products VI, VIII and X were also identified in the attempted deprotonation reaction of the carbonium ion V (Fig. 1) it appeared reasonable at first to envisage initial formation of carbene XIX. This could then react with molecular oxygen to yield either benzoylferrocene, VIII, or by abstracting a hydrogen atom to form the ferrocenylphenylcarbinyl radical it could lead to the dimer VI or through a second hydrogen atom abstraction it could produce benzylferrocene X. The labelled ferrocenylphenyldeuterocarbonium ion upon deprotonation with the tertiary amine to form the carbene XIX should have lost its deuterium, and products VI and X should have contained little or no deuterium. As the results in Table 1 show, both VI and X retained all the deuterium originally present in the α-deuteroferrocenylcarbonium ion. Furthermore, even oxygen-incorporating products such as the ether VII, and the aldehyde XI, showed practically no loss of deuterium.

The above results established unambiguously that the secondary ferrocenyl carbonium ion did not undergo deprotonation by the tertiary alkylamine and consequently the carbene mechanism hypothesis had to be excluded.

An alternative mechanism which explains the experimental findings is shown

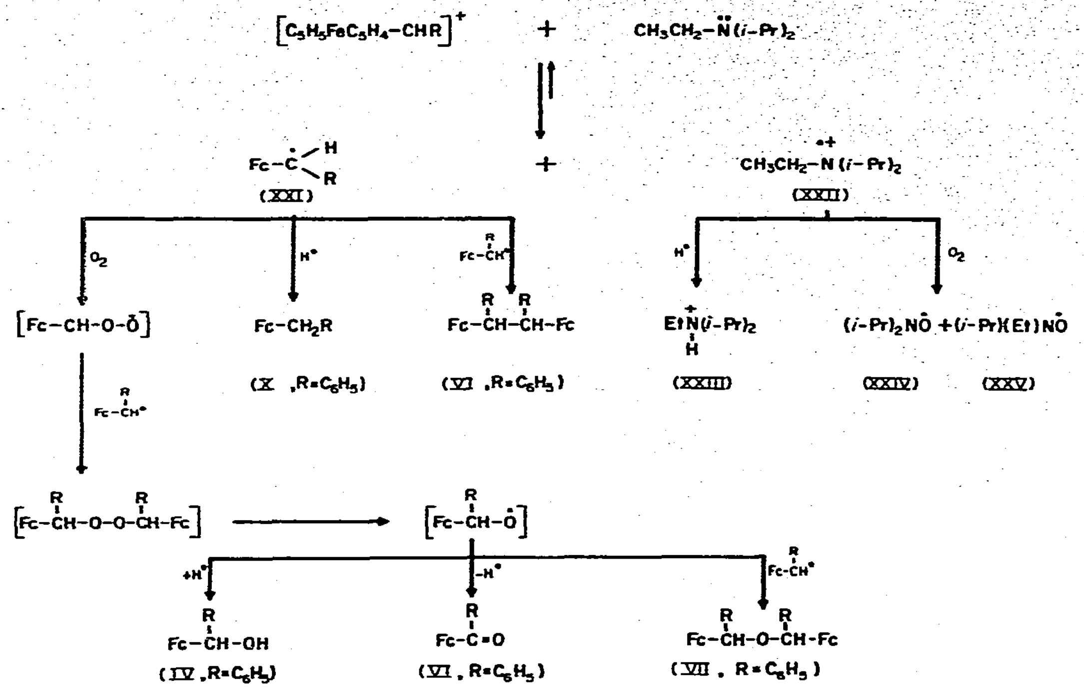


Fig. 3. Electron transfer mechanism in reaction of α-ferrocenylcarbonium ions with trialkylamines ($Fc \equiv H_5C_5FeC_5H_4$).

in Fig. 3. In this, the tertiary amine transfers an electron to the α-ferrocenylcarbonium ion to yield the α-ferrocenylcarbinyl radical, XXI and the aminium cation radical, XXII. The radical XXI could abstract a hydrogen atom from the amine (or from other such species, but not from the solvent as checked by the use of deuterated solvent) to yield the benzyl-derivative X. Or, XXI could react with itself to form the dimer VI. Reaction of radical XXI with molecular oxygen, when present, would lead to the oxygen-containing derivatives by a route such as shown in Fig. 3.

The aminium cation radical, XXII could either eliminate a proton to form a diamagnetic immonium salt, or abstract a hydrogen atom to form the diamagnetic quaternary ammonium salt, XXIII. Indeed the salt XXIII was isolated in high yields (~90%) from these reactions. During attempts to observe and identify some of the postulated radical species by ESR spectroscopy, we did not detect any spectra due to the ferrocenylcarbinyl radical XXI. However, when the reaction between a ferrocenylcarbonium ion fluoroborate, or its carbinol precursor, and ethyldiisopropylamine in dichloromethane was carried out in situ in specially designed ESR tubes, we obtained well resolved ESR spectra, such as shown in Fig. 4. The radical species with ethyldiisopropyl amine were identified as a mixture of diisopropyl nitroxide and ethylisopropyl nitroxide. The radical observed from the reaction with triethylamine was diethyl nitroxide. The concentrations of these radicals were found to depend on the degree of degassing of the system carried out prior to the mixing of the reactants. We regard this as additional support for the participation of molecular oxygen in these reactions. Recently, Barton and co-workers [20] reported that tris(*p*-bromophenyl)aminium fluoroborate in dichloromethane catalyzed the oxygenation of ergosteryl acetate in a dark reaction to give a quantitative yield of a steroidal peroxide derivative. The aminium cation radical was postulated to form a reversible adduct with oxygen which acts as the oxygen-delivering species to produce the steroidal peroxide. We suggest that the dialkylnitroxides XXIV and XXV observed in our experiments derive from the fragmentation of such an intermediate aminium cation radical—oxygen adduct. Additional

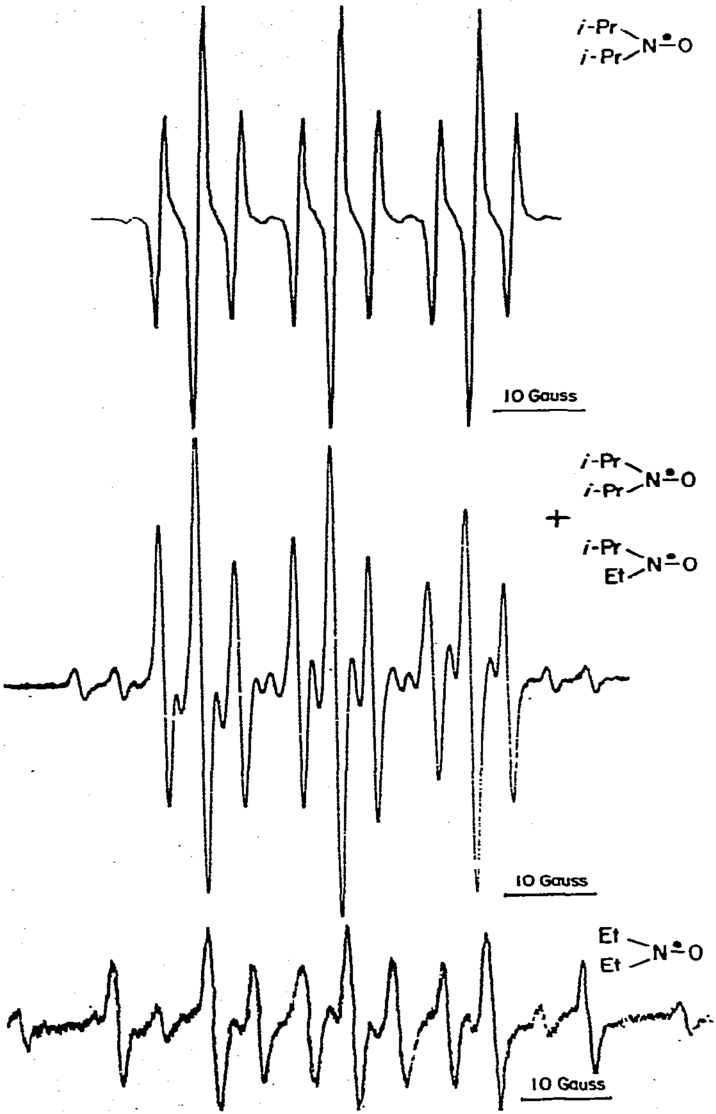


Fig. 4. ESR spectra of dialkyl nitroxide radicals formed in the reaction of ferrocenylcarbonium ions with ethyldiisopropylamine (middle) and triethylamine (bottom). ESR spectrum of diisopropyl nitroxide (top) obtained by oxidation of dissopropylamine is shown for comparison.

evidence for the electron-transfer reaction involving amines and nitroso derivatives will be presented in a separate paper [21].

Finally, our results indicate that it might be appropriate to look again at the many reported reactions of tertiary amines with carbonium ions (and similar species) in which the possibility of an initial electron-transfer step has not been considered or investigated. We note that the chemical and electrochemical oxidation of amines, leading to aminium radical cations in the initial step, has received increasing attention in recent years [22], and add that the reaction of ethyldiisopropyl amine with ferricinium fluoroborate produced a quantitative yield of ferrocene.

Experimental

IR spectra were recorded on a Perkin—Elmer model 237 grating spectrometer. NMR spectra were measured using a Varian A-60 and/or a Varian T-60 spectrometer (with TMS as internal standard). ESR spectra were recorded on a Varian E-4 spectrometer. Mass spectra were obtained using an Atlas CH-4 spectrometer. Generally, reactions were carried out under nitrogen, purified and dried by passage through BASF-Katalysator R-3-11 and molecular sieves. TLC preparative plates were prepared from Kieselgel (Merck) and the basic alumina (Merck) for column chromatography was deactivated to Grade II prior to use. Solvents, unless analytical grade, were dried and distilled.

General procedure for preparation of α-ferrocenylcarbonium salts from precursor ferrocenylcarbinols

A solution of HBF_4 (1.2 ml) (prepared by mixing 1.76 ml of conc. HBF_4 (48—52%) with 4 ml of ice-cold (acetic anhydride) was added under nitrogen to a stirred, cooled (0°C) solution of the ferrocenylcarbinol (2 mmol) in methylene chloride (3 ml). After 15 min at 0°C the mixture was cooled with dry ice/acetone and the ferrocenylcarbonium fluoroborate was precipitated by the addition of excess anhydrous diethyl ether. The supernatant layer was decanted and the precipitate was washed with an additional amount of ether followed by decantation of the supernatant. The residue was dissolved in a minimum amount of methylene chloride and repreciptated with excess diethyl ether. After decantation of the solvent the residue was dried for several hours under vacuum (oil pump) at room temperature.

In the above procedure, the diethyl ether used for precipitation of the carbonium salts could be placed by either hexane or carbon tetrachloride.

General procedure for reaction of α-ferrocenylcarbonium ion salts with amines

A three-fold molar excess of the amine was added under nitrogen to a stirred solution of the ferrocenylcarbonium ion salt in methylene chloride, at room temperature. After 15 min the solvent was evaporated under vacuum and the residue was extracted several times with either hexane, carbon tetrachloride or diethyl ether. The combined organic solvent extracts were evaporated to dryness to yield a mixture of ferrocene derivatives. This mixture was fractionated into pure products by column chromatography or by preparative thin layer chromatography. Each product was identified by its spectral properties as well as by comparison with authentic samples. The reaction of ferricinium fluoroborate (0.5 mmol) with diethyldiisopropylamine (1 mmol) under the above conditions gave a quantitative yield of ferrocene (0.5 mmol).

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