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A ^{13}C NUCLEAR MAGNETIC RESONANCE STUDY OF CYCLOBUTADIENE-IRON TRICARBONYL-SUBSTITUTED CARBONIUM IONS

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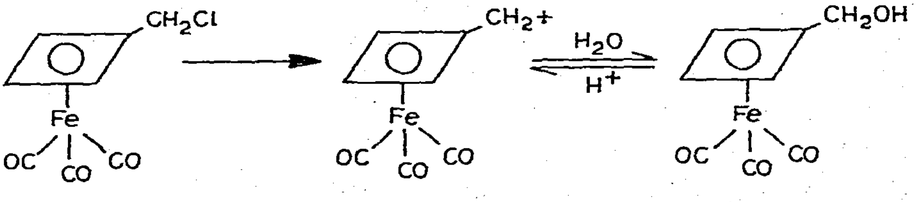
Summary

The ^{13}C NMR spectra of (hydroxymethyl)-, (α-hydroxyethyl)- and (α-hydroxybenzyl)cyclobutadieneiron tricarbonyl (in $CDCl_3$) and of their derived carbonium ions (in concentrated H_2SO_4) are reported. The data suggest extensive donation of electron density from the metal, via the cyclobutadiene unit, to the exocyclic, electron-deficient carbon atom, thus giving highly stabilized carbonium ions.

Introduction

Transition metal-stabilized carbonium ions have been the subject of much interest and research during recent years. Among such species are those whose stabilization is the result of an adjacent cyclobutadieneiron tricarbonyl substituent.

In 1966 Pettit et al. [1] reported that chloromethylcyclobutadieneiron tricarbonyl (I) solvolyzes rapidly in water or methanol solution to give the corresponding alcohol or methyl ether. The observed high reactivity was explained in terms of the intermediacy of a relatively stable carbocation, II (eq. 1). The

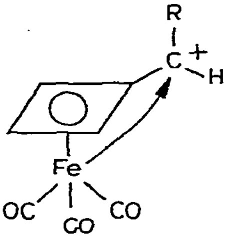


(I) (II) (III)

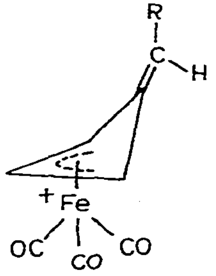
(1)

existence of II was confirmed by isolation of its hexachloroantimonate salt upon treatment of the chloromethyl derivative, I, with antimony pentachloride. This cation also was obtained upon treatment of the alcohol, III, with concentrated sulfuric acid. Its proton NMR spectrum in this solvent showed broad signals at δ 6.68, 5.91 and 5.09 ppm with respective areas of 1:2:2. These data are inconsistent with the formulation of the cation as structure II, in which the charge is localized on the carbinyl carbon atom, since the two protons on that carbon atom should in that case resonate at lowest field.

The proton NMR spectrum of the secondary carbocation derived from (α-hydroxyethyl)cyclobutadienyliron tricarbonyl was more enlightening since the resonances at δ 6.5(s), 6.2(q), 5.8 and 5.4 (*AB* pattern), and 2.8(d) ppm



(IV)



(V)

allowed a more definitive assignment. Two possible structures, IV and V, were suggested, with the latter being preferred. In IV, movement of the iron atom toward the carbonium ion center results in more effective overlap; in V, an allylic-type ligand is bound to an oxidized iron center. Analogous structures had been proposed for α-ferrocenyl carbocations [2]. Structure V is consistent with the proton NMR data, which suggest a π-allyl structure according to the low field signal. In 1971, Davis et al [3] reported an X-ray crystallographic structure determination of α,α-bis(cyclobutadieneiron tricarbonyl)benzyl tetrafluoroborate. The principal features of the structure were: (1) the carbinyl carbon atom and the three carbon atoms to which it is attached are nearly coplanar; (2) there is no significant puckering of the cyclobutadiene rings; (3) the iron atoms show no large displacements from the center of the cyclobutadiene rings; (4) the C—C distances in the cyclobutadiene rings are close to equal and similar in magnitude to those in cyclobutadieneiron tricarbonyl itself. Davis et al. also reported the proton NMR spectrum of α,α-bis(cyclobutadieneiron tricarbonyl) ethyl tetrafluoroborate in liquid SO_2 at 10°C; signals were observed at δ 5.57(s, 2H), 5.34(d, J 9 Hz, 2H), 5.22(d, J 9 Hz, 2H) and 2.70(s, 3H). On the basis of this information they concluded that the major interaction lending stability to these disubstituted cations involves interaction of a filled metal orbital with the four carbon atoms of the cyclobutadiene ring with subsequent electron transmission to the electron-deficient carbonium ion center through a π—π carbon—carbon interaction.

The applicability of the results from the crystal structure of the α,α-bis(cyclobutadieneiron tricarbonyl)benzyl cation to the $[(OC)_3Fe(C_4H_3CHR)]^+$ cations is unclear. The coplanarity of the cyclobutadiene rings of the former may or may not occur in the latter. Noteworthy is the difference in the proton NMR spectra for the two methyl derivatives. The low field signal at δ 6.5 ppm for the proton "*trans*" to the substituent in $[(OC)_3Fe(C_4H_3CHCH_3)]^+$ is shifted to higher field (δ 5.57 ppm) in $\{[(OC)_3Fe(C_4H_3)]_2CCH_3\}^+$.

Our interest in transition metal-substituted carbonium ions and their ^{13}C NMR spectra [4-6] prompted us to investigate the structure in solution of cations of type $[(OC)_3Fe(C_4H_3CHR)]^+$ (R = H, CH_3, C_6H_5) by ^{13}C FT NMR spectroscopy. In this paper we report the results of this study.

Results and discussion

In order to better understand the cyclobutadieneiron tricarbonylsubstituted carbonium ions, a measure of the electron density at the various carbon atoms and, more importantly, the change in electron density at these carbon atoms on conversion of the parent alcohol to the carbonium ion, was desired. Olah et al. [7] have used the field position of the carbon atom resonances in ^{13}C NMR as direct measures of the amount of electron density at the various carbon atoms. They indicate that the smaller the electron density residing at a given carbon atom, the less shielded it will be, and, consequently the lower the field position of its ^{13}C NMR signal. For classical, wholly organic carbonium ions the difference in chemical shifts for the carbinyl carbon atom on going from the alcohol to the corresponding carbonium ion ($-\overset{|}{\underset{|}{C}}-OH \rightarrow -\overset{|}{\underset{|}{C}}+$) is 250-300 ppm. Whether or not these findings are strictly applicable to systems involving additional stabilization by metal centers is not totally clear. While deshielding may occur due to the formation of a positive charge, such compensatory factors as the anisotropic effects of metal centers surely are contributing to the chemical shift positions of the ^{13}C NMR signals. However, it is proposed that the field position of the signals observed for the metal-substituted alcohols and carbonium ions may be interpreted as measures of the relative electron densities at the respective carbon atoms. Moreover, earlier studies [4,5,9] have used ^{13}C NMR data to interpret the stabilities of carbonium ions generated from other organometallic species. In the light of these considerations, ^{13}C NMR spectroscopy should be useful in determining a model consistent with the stability of cyclobutadieneiron tricarbonyl-substituted carbonium ions.

The data obtained from the ^{13}C NMR spectra of (hydroxymethyl)-, (α-hydroxyethyl)- and (α-hydroxybenzyl)cyclobutadieneiron tricarbonyl and their corresponding carbonium ions are summarized in Table 1*. The assignments shown in Table 1 are based on standard ^{13}C NMR correlations [11,12], off-resonance-decoupled spectra and, in the case of the alcohols, proton-coupled spectra, from which the listed coupling constants were obtained. Proton-coupled spectra of the carbonium ions in concentrated sulfuric acid solution could not be obtained due to the longer pulsing times needed to obtain the spectra. These carbonium ion solutions decompose slowly, giving carbon monoxide and paramagnetic species, thus making it difficult to maintain a strong lock signal. Off-resonance (partially coupled) decoupled spectra were obtained in all cases.

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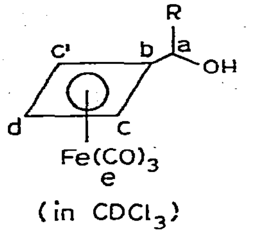
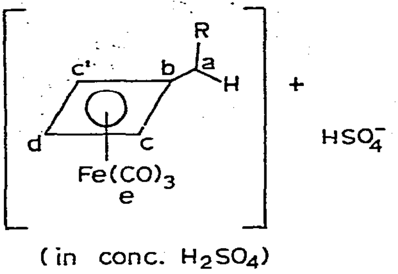
* Figures showing these spectra can be found in ref. 10.

TABLE 1

^{13}C CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR SOME CYCLOBUTADIENEIRON TRICARBONYL CARBINOLS AND THEIR DERIVED CARBONIUM IONS





R	Carbon	Alcohol[b]	J(C—H) (Hz)	Carbonium ion[b]	Δδ
H	a	58.7	145	104.5	—45.8
	b	84.5	—	98.0	—13.5
	c	64.6	192	84.6	—20.0
	d	63.1	193	109.0	—45.9
	e	214.8	—	201.0	+13.8
CH_3	a	63.8	146	133.8	—70.0
	b	90.2	—	96.6	—6.4
	c	62.6	191	78.8	—16.2
	c'[a]	62.7	191	80.4	—17.6
	d	63.1	189	106.5	—43.4
	e	214.8	—	201.8	+13.0
	CH_3	22.5	127	17.5	+5.0
C_6H_5	a	70.7	148	140.8	—70.1
	b	88.0	—	90.9	—2.9
	c	63.4	188	80.0	—16.6
	c'[a]	63.6	188	80.0	—16.4
	d	64.2	190	106.2	—42.0
	e	214.6	—	202.8	+11.8
	Ph-sub	141.9	—	129.9	+12.0
	o	129.1	161	130.9	—1.8
	m[a]	126.5	156	130.9	—4.4
	p	128.7	161	136.7	—8.0

[a] No attempt was made to distinguish between these resonances for specific assignments. [b] Field positions are reported in ppm downfield from TMS (see Experimental).

Line assignments in the case of the unsubstituted alcohol were unambiguous. First, considering only short-range coupling to hydrogen atoms attached directly to each carbon atom, the assignment is clear. Carbon atom a (cf. Table 1) gives rise to a triplet and is at highest field. Carbon atom b is quaternary; it gives rise to a relatively less intense signal at δ(C) 84.5 ppm and shows no short-range coupling. Carbon atoms c and c′ are equivalent and show one doublet centered at δ(C) 64.6 ppm which is approximately twice as intense as the signal due to the remaining carbon atom, d. Both of the signals for the ring carbon atoms bearing hydrogen substituents are split into doublets with coupling constants, $J(^1H—^{13}C)$, of 192 and 193 Hz. The magnitude of these coupling constants appears to be invariant with substitution at carbon atom a. In all cases examined, the values agreed within experimental error with the value of 191 Hz observed by Preston and Davis [13] for unsubstituted cyclobutadieneiron tricarbonyl in

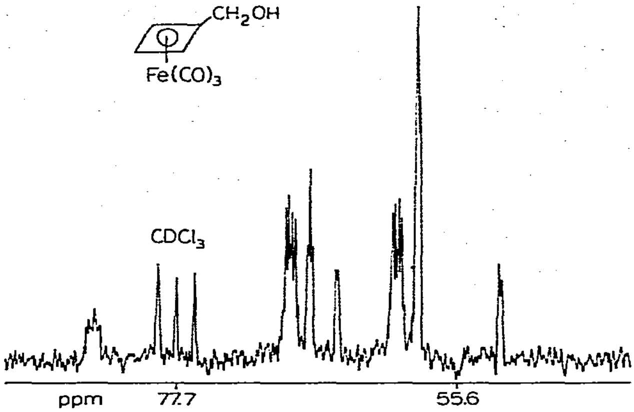


Fig. 1. ^{13}C NMR spectrum of (hydroxymethyl)cyclobutadieneiron tricarbonyl (proton-coupled).

a proton NMR experiment. In addition, the substituents on carbon atom a appear to have little effect on the position of the signal for the carbon monoxide ligand carbon atoms at δ(C) 214.8 ppm.

Interestingly, the proton-coupled spectrum of the primary alcohol complex gave a "textbook" example of long-range coupling. A section of this spectrum is reproduced in Fig. 1. Of special interest are the carbon atoms c and c′ whose ^{13}C resonance is split due to the coupling of the proton attached at carbon atom d and of the proton attached to the transannular ^{12}C (in addition to short range coupling). An eight-line pattern results. The totally coupled signal due to carbon atom d is a doublet of triplets, half of which lies under the center of the triplet arising from carbon atom a.

Assignment of lines in the ^{13}C NMR spectrum of the unsubstituted carbonium ion II is straightforward in the light of additional information from the off-resonance proton-decoupled spectrum. In the partially coupled spectrum the carbinyl carbon atom at δ(C) 104.5 ppm gives rise to a triplet, the quaternary carbon signal at δ(C) 98 ppm remains unsplit, and the resonances of the two equivalent carbon atoms c and c′ and of carbon atom d appear as doublets. The ^{13}C resonance of the carbon monoxide ligand resonance is shifted upfield by 13.8 ppm. As in the alcohols, this resonance shows only a small substituent effect and occurs at about 200 ppm.

Line assignments for the methyl- and phenyl-substituted alcohols were more difficult to make. The carbinyl carbon atom in each of these compounds is asymmetric. The signals for carbon atoms c and c′ are separated by 0.1 ppm and 0.2 ppm, respectively. Lack of free rotation about the C_a—C_b bond in the carbonium ions also results in nonequivalence of these two carbon atoms. In the spectrum of the methyl-substituted carbonium ion these signals are separated by 1.4 ppm. However, the signals are not resolved in the spectrum of the phenyl-substituted carbonium ion.

The remaining lines were assigned by analogy to the spectrum of the unsubstituted alcohol and carbonium ion. In the case of the methyl-substituted alcohol, since proton-coupled spectra give doublets for all of the carbon atoms a, c, c′ and d, their assignment is not straightforward. However, carbon atom a is sp^3 hybridized and would be expected to have C—H spin—spin coupling constants of about 140 Hz. Carbons c and c′ are very similar and should have very similar chemical shifts and lie upfield from carbon atom d. Observations with ferrocenylmethyl alcohols [4,9] show that the ring carbon atoms furthest from the substituted carbon atom have signals which lie furthest downfield. The C—H spin—spin coupling constants for the ring carbon atoms are in agreement with those already observed (vide supra). These facts speak for the assignments as shown in Table 1 and are consistent with the splitting pattern suggested for carbon atoms a, c, c′ and d. The assignment of the lines in the ^{13}C NMR spectrum of (α-hydroxybenzyl)cyclobutadieneiron tricarbonyl is based on similar arguments. The ^{13}C NMR spectra of the methyl- and phenyl-substituted carbonium ions were assigned on the basis of off-resonance proton-decoupled experiments and arguments similar to those presented above for the spectra of the alcohols.

Two interesting features are readily apparent in the study of these spectra. Noteworthy is the relatively small downfield shift, $\Delta\delta$(C), for the carbinyl carbon atom a on going from the alcohol to the respective carbonium ion. Compared to wholly organic systems, this shift is remarkably small and this indicates that the carbinyl carbon atom of the carbonium ions is less electron-deficient than those in wholly organic species, such as the trimethyl- or triphenylmethylcarbonium ions [8]. The values of this $\Delta\delta$(C) shift, however, are considerably larger than those observed previously for either the analogous ferrocenylcarbinols [4] (—CH_2OH, —26.2; —CHMeOH, —52.1; —CHPhOH, —49.4 ppm) or the corresponding methylidynetricobalt nonacarbonyl-substituted carbinols [5] (—CH_2OH, —13.5; —CHMeOH, —37.4; —CHPhOH, —35.7 ppm). It would seem, on the basis of these comparisons, that the positive charge generated at the carbinyl carbon atom when the cyclobutadieneiron tricarbonyl-substituted carbonium ion is formed is being neutralized through electron delocalization from elsewhere within the molecule. Such electron delocalization, however, occurs to a lesser extent in the present case than with the $[C_5H_5FeC_5H_4CHR]^+$ and the $[(OC)_9Co_3CCHR]^+$ ions. The fact that the carbinyl carbon atom of the ferrocenylcarbonium ions is relatively less electron-deficient than that of the cyclobutadieneiron tricarbonyl-substituted analogs may be attributed to the greater extent of electron donation to the electron-deficient center by the two relatively electron-rich cyclopentadienyl ligands in the former case*. The less electron-rich cyclobutadiene ring cannot afford the same extent of stabilization.

The second notable feature of the present study is the large downfield shift of carbon atom d on conversion of the alcohol to the carbonium ion (cf. Table 1). In all three derivatives the magnitude of this shift is 42—46 ppm, as compared to the shifts of only 3-13 ppm observed for carbon atoms c and c′. This observation may be rationalized in terms of $[(OC)_3FeC_4H_3CHR]^+$ cations stabilized in the main by metal—carbon bond hyperconjugation [14]. In the (hypothetical) unstabilized cations all four carbon atoms of the cyclobutadiene ring would be bonded more or less equally strongly to the iron atom, as is the case in neutral cyclobutadieneiron tricarbonyl complexes [15]. The occurrence of iron—carbon bond hyperconjugation in such a cation, however, would be expected to weaken

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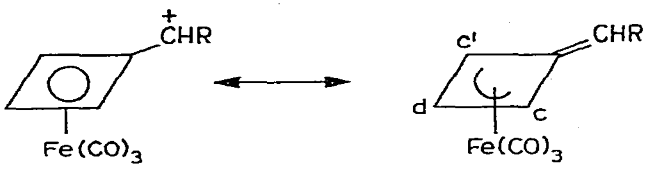
* Our ^{13}C NMR studies have shown that both of the cyclopentadienyl rings participate in the stabilization of ferrocenylmethyl carbonium ions [4].

the bonding contribution to iron of the carbon atom to which the carbonium ion center is attached. The result would be relatively stronger bonding of carbon atoms c, c′ and d to the iron atom, i.e., in essence a π-allyl bonding component would be introduced. Thus a resonance description of the $[(OC)_3FeC_4H_3CHR]^+$ cations as VIa (with implied iron—carbon bond hyperconjugation) ↔ VIb may be appropriate.



(VIa) (VIb)

The terminal carbon atoms of π-allylic ligands in transition metal complexes generally show ^{13}C NMR resonances between δ(C) 45-78 ppm and the central carbons atoms between 90-130 ppm [12]. In order to examine a system which provides a good model for the cations under discussion, the ^{13}C NMR spectrum of π-allyliron tricarbonyl bromide, π-$C_3H_5Fe(CO)_3Br$, was measured. Nesmeyanov et al. [16] reported the existence of two sets of signals in the proton NMR spectrum of this compound and attributed this to the presence of two isomers, VII and VIII (Fig. 2). The ^{13}C NMR spectrum of this complex also shows two sets of signals as shown in Table 2 and Fig. 3. The position of the signal from carbon atom d in the cyclobutadieneiron tricarbonyl-substituted carbonium ions agrees quite well with that observed for the field position of the central carbon atom in the π-allyl ligand. A molecular orbital picture of the allyl—metal bond in π-allyl-metal complexes shows two major components in the bonding [17]: forward donation from the filled ψ_1 orbital to an empty metal orbital, which causes electron density to be drained from all three carbon atoms, and interaction of the

(VII) (VIII)

Fig. 2. Isomers of π-allyliron tricarbonyl bromide.

TABLE 2

^{13}C CHEMICAL SHIFTS^a FOR π-ALLYLIRON TRICARBONYL BROMIDE

Carbon	Isomer I	Isomer II
Terminal	65.6	55.3
Central	102.5	113.5
Carbonyl	208.1	208.1
	205.6	205.6

^{a}ppm downfield from TMS.

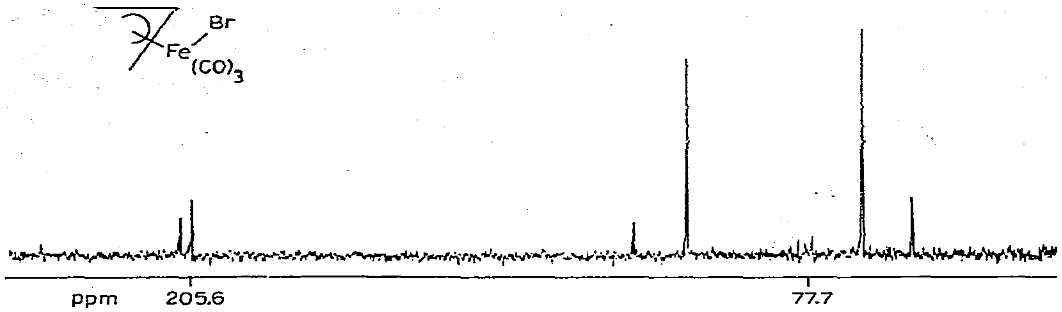


Fig. 3. ^{13}C NMR spectrum of π-allyliron tricarbonyl bromide (proton-decoupled).

lowest unoccupied ligand orbital, ψ_2 (nonbonding), with a filled metal orbital of suitable symmetry, which returns electron density to the ligand, but only to the terminal carbon atoms. This results in a net deshielding of the central carbon atom. Bonazza and Lillya [18] have suggested that the latter of these two interactions is the dominant mode of bonding in species formulated as π-allyl and π-pentadienyl carbonium ions.

Table 1 shows that $\Delta\delta(C)$ for the carbon monoxide ligand carbon atoms on conversion of the alcohols to the carbonium ions is +12-14 ppm. This observation is in agreement with the VIa ↔ VIb description of the carbonium ions. The accumulation of positive charge at the iron atom would result in a stronger Fe—CO bond (i.e., a decrease in the Fe—CO distance), which would lead to increased shielding of the carbon monoxide carbon atoms due to anisotropic effects of metal.

Experimental

General comments

The ^{13}C NMR spectra were obtained in the Fourier transform mode utilizing a modified Bruker HFX-90 spectrometer interfaced with a Digilab FTS/NMR-3 data system and are accurate to ±0.2 ppm. The field was locked using the ^{19}F signal of hexafluorobenzene contained in a capillary tube inside the sample tube. Satisfactory proton-decoupled spectra of approximately 1 *M* solutions were obtained in ca. 2000 pulses using a pulse width of 8 μsec (corresponding to a nutation angle of ca. 30°), a data acquisition time of 0.41 sec and 0.80 sec between pulses. Proton noise decoupling was achieved using a decoupling frequency corresponding to 3.39 ppm upfield from the benzene proton resonance and a decoupling bandwidth of 1200 Hz. Off-resonance decoupling was achieved by irradiating in the CW mode at a frequency corresponding to 8.28 ppm upfield from the benzene proton resonance. A greater number of pulses was required to obtain proton-coupled spectra. The field positions of the lines were computer generated or calculated by measuring the distance between lines and using the plotting parameters. All the spectra of the alcohols and of the π-allyliron complex are referenced to internal $CDCl_3$ and reported in ppm downfield from tetramethylsilane. The spectra obtained in concentrated sulfuric acid are referenced to external tetramethylsilane through the ^{19}F lock signal.

Preparation of the alcohols

(a) (Hydroxymethyl)cyclobutadieneiron tricarbonyl. To a cooled (0°C) solution of 2.0 g (9.1 mmol) of cyclobutadienecarboxaldehydeiron tricarbonyl in 20 ml of methanol was added 0.4 g (10.5 mmol) of sodium borohydride over a period of 15 min. After the reaction mixture had stirred for an additional 15 min, it was poured into water and the product extracted with ether. The combined ether extracts were washed thoroughly with water, dried ($MgSO_4$), and concentrated to yield 2.1 g (100%) of a yellow oil which crystallized upon cooling. The crude product was recrystallized from an ether/pentane mixture to produce pale yellow crystals, m.p. 45-46°C, (lit. [21] m.p. 44.5-45.5°C). NMR (CCl_4): δ 2.37 (s, 1H), 3.98 (s, 2H), 4.10 (s, 1H) and 4.14 ppm (s, 2H).

(b) (α-Hydroxyethyl)cyclobutadieneiron tricarbonyl. Acetylcyclobutadieneiron tricarbonyl (4.0 g, 17.1 mmol) was allowed to react with 0.9 g (23.7 mmol) of $NaBH_4$ in a manner similar to that above except that stirring was continued for 45 min after the addition of $NaBH_4$ had been completed. The product was isolated by the usual extraction process and weighed 3.0 g (74%). The crude product was purified by chromatography over alumina utilizing ether to elute the product. The pure compound had m.p. 34-36°C (lit. [22] m.p. 34-35.5°C). NMR ($CDCl_3$): δ 1.15 (d, 3H), 1.80 (s, 1H), 4.07 (s, 2H), 4.14 (s, 1H) and 4.28 ppm (q, 1H).

(c) (α-Hydroxybenzyl)cyclobutadieneiron tricarbonyl. In a dry 100 ml three-necked flask equipped with a reflux condenser, magnetic stirring bar, and a nitrogen inlet-outlet tube was prepared a solution of phenylmagnesium bromide from 0.5 g (20.6 mmol) of magnesium, 2.5 g (15.9 mmol) of bromobenzene and 30 ml of anhydrous ether. To the cooled (0°C) Grignard solution was added a solution of 1.7 g (7.7 mmol) of cyclobutadienecarboxaldehydeiron tricarbonyl in 20 ml of ether. After the addition was complete (15 min), the mixture was stirred for 30 min at 0°C and 30 min at reflux. Hydrolysis with saturated ammonium chloride was followed by separation of the ether layer and the usual back-extractions. The dried ether extracts were concentrated at reduced pressure. The residue (1.4 g, 61%) solidified on cooling. The product is a pale yellow solid, m.p. 62-63°C (lit. [22] m.p. 62-63°C). NMR ($CDCl_3$): δ 1.95 (s, 1H), 4.05 (s, 2H), 4.17 (s, 1H), 5.14 (s, 1H) and 7.33 ppm (s, 5H).

Preparation of π-allyliron tricarbonyl bromide

A 200 ml, three-necked flask, equipped with a gas inlet tube and magnetic stirring unit, was flushed with nitrogen, charged with 10.95 g (30.1 mmol) of diiron nonacarbonyl (ALFA/Ventron) and 50 ml of hexane. To this slurry was added 3.59 g (29.7 mmol) of allyl bromide, and the mixture was warmed to 40°C for 2 h. The mixture was allowed to cool to room temperature, filtered, and the solvent was removed under reduced pressure. The resulting residue was recrystallized from 30-60°C petroleum ether to give 1.96 g (25%) of the title compound, m.p. 91-92°C (dec); lit. [23] m.p. 86-87°C (dec).

Preparation of samples for NMR study

Preparation of the samples of the various alcohols was carried out in a dry box under an atmosphere of nitrogen. The sample alcohol was dissolved in $CDCl_3$ and filtered into a 10 mm NMR tube which was equipped with vortexing plugs and a sealed capillary containing hexafluorobenzene. The tube was capped and sealed by wrapping electrical tape about the cap. The sample of π-allyliron tricarbonyl bromide was prepared in similar manner, but an inert atmosphere was not required.

Preparation of the samples of cations required some care, as the reaction of the alcohol with concentrated sulfuric acid was exothermic, causing decomposition if the sample was not cooled. The $CDCl_3$ solvent from the above alcohol samples were evaporated in a stream of nitrogen after their ^{13}C NMR spectra had been recorded, and the remaining compound was cooled in an ice bath. Concentrated sulfuric acid, which had been degassed previously by two freeze—thaw cycles, was added under a stream of nitrogen until all of the sample appeared to be dissolved. The mixture was allowed to warm slowly to room temperature, filtered quickly (since these solutions appear to be stable in air for only short periods) and placed in an NMR tube which was equipped as described above. These solutions decomposed quickly, and difficulty is encountered in obtaining a strong lock signal in the spectrometer.

Acknowledgements

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