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CYCLOBUTADIENEIRON TRICARBONYL CARBOXYLIC ACIDS: SYNTHESIS AND ACIDITY

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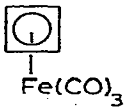
Summary

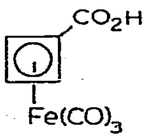
Two carboxylic acid derivatives of the cyclobutadieneiron tricarbonyl (I) system have been synthesized and their pK_a values determined. It appears that I tends to be electron withdrawing by induction and electron releasing by resonance.

Introduction

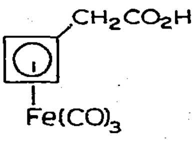
The electronic behavior of organometallic systems such as ferrocene and benzenechromium tricarbonyl has been studied in great detail. However, very little is known about the electronic character of the equally interesting cyclobutadieneiron tricarbonyl (I) system. It has been recently shown by Pettit and co-workers [1] that I can very effectively stabilize an adjacent carbonium ion. X-Ray data indicate that the major interaction leading to stabilization of the ionic center involves a π—π carbon—carbon interaction with the cyclobutadiene ring rather than direct metal—exocyclic-carbon interaction. In order to evaluate further the relative magnitude and nature of the electronic properties of I, we have synthesized carboxylic acids II and III and determined their pK_a values.



(I)



(II)



(III)

Results and discussion

The synthesis of II had been previously accomplished [2] by the alkaline hydrolysis of *S*-methyl (cyclobutadieneiron tricarbonyl)thiocarboxylate which

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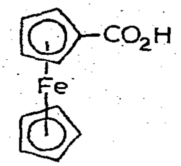
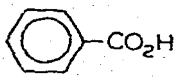
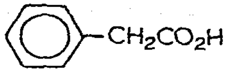
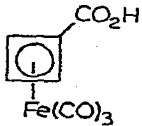
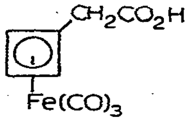
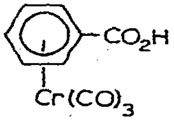
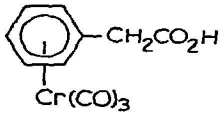
TABLE 1

pK_a VALUES OF ACIDS IN 50% ETHANOL

Acid	Apparent pK_a	Acid	Apparent pK_a
	6.11[a]		
	5.68[b]		5.64[b]
 (II)	5.01	 (III)	5.56
	4.77[b]		5.02[b]

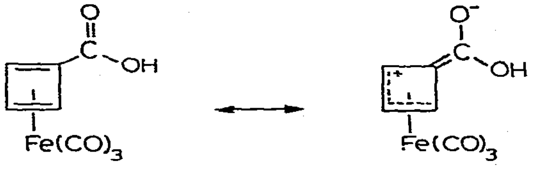
[a] Ref. 12. [b] Ref. 13.

was prepared from I, chloromethylthiol formate, and anhydrous aluminum chloride. The present synthesis involves a Hoesch type addition of trichloroacetonitrile to I. This reaction produces trichloroacetylcyclobutadieneiron tricarbonyl which in turn yields II upon alkaline hydrolysis. This procedure is more convenient than the previous synthetic pathway and proceeds in higher yields. The trichloroacetyl derivative is a postulated intermediate in the haloform reaction of methyl ketones; however, application of the haloform reaction to acetylcyclobutadieneiron tricarbonyl leads only to decomposition. This is probably due to the oxidizing nature of the reaction medium. The present scheme circumvents this difficulty.

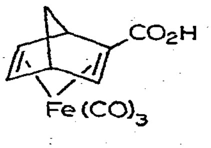
The synthesis of acid III is straightforward and involves a simple displacement of the chloride ion in chloromethylcyclobutadieneiron tricarbonyl by cyanide ion. Hydrolysis of this acetonitrile derivative leads to III.

The pK_a values of the acids (Table 1) were determined in 50% ethanol (volume/volume) at 20° by titrimetric methods. From a determination of the acidity of III, some information concerning the inductive effect exerted by the cyclobutadieneiron tricarbonyl moiety can be obtained. An examination of the pK_a values reveals that III is a slightly stronger acid than phenylacetic acid. Since it is known that the phenyl group is a weak electron withdrawing group by induction [3], the cyclobutadieneiron tricarbonyl moiety must also exert an electron withdrawing effect by induction. Its withdrawing ability is slightly greater than that of the phenyl group but not nearly as strong as that of the benzenechromium tricarbonyl group.

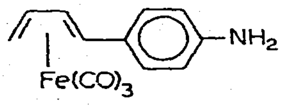
The acidity of II will be affected by both inductive and resonance effects. The inductive effect exerted by I will be influenced to a large degree by the electronegativity of the carbon atoms of the cyclobutadiene ring. Cram [4] has related the electronegativity of carbon atoms to the percentage *s* character in the carbon orbitals involved in a carbon—hydrogen bond. It has also been shown that there is a direct relationship between the magnitude of the $^{13}C—H$ coupling constants for a particular carbon—hydrogen bond and the amount of *s* character in that orbital of the carbon atom [5]. The $^{13}C—H$ coupling constant for cyclobutadieneiron tricarbonyl has been found to be 191 Hz [6] compared with 159 Hz [5] for benzene. This indicates that the ring carbon atoms of I are much more electronegative than those in benzene. Thus inductively these atoms should stabilize the carboxylate anion and increase the acidity of II compared with benzoic acid. The pK_a values confirm this increased acidity; however, the degree of acidity cannot be explained wholly on the basis of the electronegativity of the carbon atoms. For example, we have determined that benzenechromium tricarbonyl has a $^{13}C—H$ coupling constant of approximately 175 Hz. On this basis alone, II should be a stronger acid than the chromium tricarbonyl-complexed benzoic acid. Table 1 reveals that this is not true; therefore, additional factors must be involved in determining the acidity of II. One such factor would be possible resonance effects. The cyclobutadieneiron tricarbonyl system is an electron-rich system as is evidenced by the ease with which it undergoes electrophilic aromatic substitution reactions [7]. Furthermore, its ability to stabilize an adjacent carbonium ion by π-electron delocalization has been previously mentioned [1]. Therefore, a resonance structure such as IV may well contribute to the stabilization of the un-ionized form of the acid and thus weaken the acidity of II. A third factor to be considered is the electronic character of the iron tricarbonyl group. Various experiments have shown this moiety to be an electron releasing group. While bicycloheptadiene carboxylic acid exhibits a pK_a value of 7.00, its complexed form (V) has a pK_a value of 7.50 [8]. Similarly *p*-(1,3-butadiene)-aniline has a pK_a value of 3.81 while its complexed counterpart (VI) has a value of 3.90 [9]. Conversely, the chromium tricarbonyl group has been shown to be



(II) (IV)



(V)



(VI)

a strong electron withdrawing group [13]. Therefore, the combination of inductive and resonance effects produces an acid, (II), which is stronger than benzoic acid but weaker than the chromium tricarbonyl complexed benzoic acid.

In summary, cyclobutadieneiron tricarbonyl appears to exhibit a weak electron withdrawing effect by induction as well as an electron releasing effect by resonance.

Experimental

Microanalyses were performed by Chemalytics, Inc., Tempe, Arizona. IR spectra were obtained with a Perkin—Elmer model 457 Spectrophotometer and NMR spectra were determined on a Perkin—Elmer model R12B nuclear magnetic resonance spectrometer.

Cyclobutadieneiron tricarbonyl acetic acid (III)

Into a 100 ml three-necked flask, equipped with a dropping funnel, stirring bar, and a condenser capped with a nitrogen inlet-outlet tube, were placed 0.30 g of powdered NaCN and 10 ml of dimethyl sulfoxide. To this was added dropwise (15 min) a solution of chloromethylcyclobutadieneiron tricarbonyl (1.02 g) [7] in 10 ml of dimethyl sulfoxide. The mixture was stirred for 1 h and then poured into 100 ml of water. The aqueous solution was extracted with three 50 ml portions of ether. The combined ether solutions were washed with water and then dried ($MgSO_4$). After filtration and evaporation the residue was transferred to an alumina column. Elution with ether removed a yellow band which yielded the crude acetonitrile derivative as an orange oil. The crude nitrile was dissolved in 45 ml of ethanol and a solution of 5 g of NaOH in 35 ml of H_2O added. This solution was refluxed under nitrogen for 1.5 h. It was then diluted with water and extracted with ether to remove any unreacted material. The aqueous phase was then acidified with HCl and extracted with ether. These ether extracts were dried and evaporated to yield the desired acid as a pale yellow powder (yield 0.42 g, 40%), m.p. 85—86°. An analytical sample was prepared by recrystallization from petroleum ether. (Found: C, 43.66; H, 2.64. $C_9H_6FeO_5$ calcd.: C, 43.24; H, 2.42%.) NMR (acetone-d_6): δ 4.34 (2H, s), 4.27 (1H, s), 3.12 (2H, s) ppm. IR (CCl_4): 2050, 1975 (vs, metal carbonyl), 1710 cm^{-1} (s, acid carbonyl).

Cyclobutadieneiron tricarbonyl carboxylic acid (II)

A 100 ml three-necked flask was fitted with a dropping funnel, condenser equipped with a nitrogen inlet-outlet tube and a tube for the introduction of HCl gas. Into the flask was placed 25 ml of dry CH_2Cl_2 and 3.32 g of anhydrous aluminum chloride. The flask was cooled in an ice bath and 3.97 g of trichloroacetonitrile in 10 ml of CH_2Cl_2 was added dropwise from the funnel. A solution of 2.50 g of cyclobutadieneiron tricarbonyl in 10 ml of CH_2Cl_2 was then added dropwise over a period of 1 h. After stirring for an additional 0.5 h, HCl gas was slowly bubbled through the reaction mixture for 1 h. A mixture of 50 ml of concentrated HCl and 100 g of crushed ice was prepared and the reaction mixture was poured onto it. The organic layer was separated and the aqueous layer extracted with three 50 ml portions of $CHCl_3$. The combined organic layers were washed with 5% $NaHCO_3$, dried ($MgSO_4$), and concentrated to produce a dark brown oil that slowly solidified. This solid was transferred to a Soxhlet extractor and extracted with 250 ml of pentane until the extracts were colorless (0.5 h). The pentane solution was evaporated to produce the crude trichloroacetylcyclobutadieneiron tricarbonyl. The crude ketone was dissolved in 10 ml of ethanol and a solution of 3.5 g of KOH in 25 ml of H_2O was added. The solution was refluxed under nitrogen for 5 h and then poured into water and extracted with three 50 ml portions of ether. The aqueous phase was then acidified with concentrated HCl and extracted with ether. These ether extracts were dried and evaporated to yield 1.41 g (46%) of the crude acid, m.p. 148—150°. The acid may be purified by recrystallization from CH_2Cl_2 to form yellow crystals, m.p. 150—151° (lit. [2] 151—152°). NMR ($CDCl_3$): δ 4.35 (1H, s), 4.55 (2H, s) ppm. IR (CCl_4): 2075, 2007, 1991 (vs, metal carbonyl) and 1679 cm^{-1} (s, acid carbonyl).

pK_a *Measurements*

All pK_a measurements were conducted in 50% ethanol solutions by titrimetric methods at $20 \pm 1°$. Solvents were degassed and nitrogen was bubbled through the solutions during the titrations. A Beckman Zeromatic pH meter and glass electrode were used. Standardization was accomplished by the use of an aqueous ethanol buffer [10].

The weighed compound (0.5 mmol) was first dissolved in absolute ethanol (22.5 ml) and then distilled water (22.5 ml) was added. During the titration, equal amounts (0.5 ml) of 0.10 *N* NaOH and ethanol were added, and the pH values thus obtained were used to calculate the pK_a values by the method of Albert and Serjeant [11]. Table 1 lists the pK_a values of II and III and several related carboxylic acids.

Acknowledgements

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