Journal of Organometallic Chemistry, 57 (1973) 373–378

THE SYNTHESIS AND CHARACTERIZATION OF THE IRON TETRACARBONYL COMPLEX OF *cis*-1-METHYLENECYCLOPROPANE-2,3-DICARBOXYLIC ANHYDRIDE. THE FORMATION OF POSITIONAL ISOMERS

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(Received January 4th, 1973)

SUMMARY

The iron tetracarbonyl complex of Feist's anhydride exhibits a novel type of positional isomerism previously not observed for olefins. This isomerism arises from positioning of the iron tetracarbonyl moiety above or below the plane of the double bond. It is suggested that iron tetracarbonyl complexes of methylenecyclopropane can form without the ring opening that gives rise to the usual iron tricarbonyl derivatives of trimethylenemethane.

INTRODUCTION

As part of continuing investigations into the chemistry of methylenecyclopropene[1], we have prepared a derivative of *cis*-1-methylenecyclopropane-2,3-dicarboxylic anhydride, (I), (Feist's anhydride[2]), containing an iron tetracarbonyl moiety complexed to the exocyclic double bond of (I), as opposed to the iron tricarbonyl residue which is usually complexed to methylenecyclopropane[3–6] and its derivatives. This is the first report of such an iron tetracarbonyl complex containing this ligand. Previously, Emerson *et al.*[3,6] reported the synthesis of trimethylenemethane-iron tricarbonyl via the reaction of excess of diiron nonacarbonyl with 3-chloro(2-chloromethyl)propene in ether, and Noyori *et al.*[5] described similar reactions of ring-substituted methylenecyclopropanes leading to trimethylenemethaneiron tricarbonyl complexes. In none of the cases reported does the iron tricarbonyl complex possess an intact cyclopropane ring. Numerous other iron tricarbonyl complexes have been described, as well as a lesser number of iron tetracarbonyl complexes of mono- and di-olefins[7–21].

Schenck *et al.*[13] and Weiss *et al.*[12] reported the synthesis and characterization of the iron tetracarbonyl derivative of maleic anhydride, as well as a number of analogous complexes. Two general methods were used: (1) photolysis of the ligand in benzene in the presence of iron pentacarbonyl[13]; or (2) reaction between the ligand and diiron nonacarbonyl in benzene at or below 45° [12]. In neither these, nor in other reported iron tetracarbonyl complexes has there been mention of positional isomerism as observed in the complex of Feist's anhydride, (I).

Numerous examples of a similar positional isomerism are known, however;

for example, Ginsburg *et al.* have described the synthesis of several iron tricarbonyl complexes of tetraenic propellanes[22,23].

RESULTS AND DISCUSSION

cis-1-Methylenecyclopropane-2,3-dicarboxylic anhydride, (I), synthesized as described[2], exhibited a splitting of each signal in its NMR spectrum which disappeared in the iron tetracarbonyl complex. Refluxing an ether or benzene solution of (I) with a stoichiometric amount of diiron nonacarbonyl resulted in a greenish solution from which a crystalline material could be obtained. The m.p. of this product varied from sample to sample, 120–175° (dec.). TLC analysis of the reaction mixture showed two spots in a variety of solvents. Samples of crystalline material often showed a single spot, but also sometimes exhibited the two spots present in the reaction mixture.

The NMR spectrum of the initial reaction mixture was solvent dependent. Crystalline product samples usually showed two singlets in $CDCl_3$ or pyridine-d_5, having the same shifts as two of the singlets in the original reaction mixture, *viz.* $CDCl_3$: δ 2.25 (s, 1H); 2.30 (s, 1H); 3.15 (s, 1H) and 3.23 (s, 1H); pyridine-d_5; δ 2.35 (s, 2H); 3.45 (s, 1H) and 3.95 (s, 1H). If a sample of the reaction mixture exhibited all three singlets (pyridine-d_5), the area at δ 2.35 was equal to the sum of the other two singlets. In crystalline samples exhibiting single spots (TLC), the NMR spectrum exhibited two singlets of equal area; $CDCl_3$: δ 2.30 (s, 1H); 3.15 (s, 1H); pyridine-d_5 : δ 2.35 (s, 1H); 3.95 (s, 1H).

The two spots from the reaction mixture in a variety of TLC solvents exhibit similar R_f values, but are clearly two separate spots when the NMR ($CDCl_3$) has four singlets, and a single spot (one of two original R_f's) when the NMR ($CDCl_3$) shows two singlets. A pure isomer could be separated from the reaction mixture by fractional crystallization. No major differences appeared between the IR spectrum of the pure isomer and that of the mixture (90/10), and the mass spectra of both showed the same fragmentation pattern.

Material having the spectral characteristics cited above was obtained by photolysis of anhydride I in benzene or ether with added iron pentacarbonyl (5 ×). Additional products formed are currently under investigation. Isomers IIa and IIb are not formed in equal amounts, their ratio being solvent dependent, *i.e.* approximately 60/40 in ether, and approximately 75/25 in benzene. In refluxing benzene, in the absence of diiron nonacarbonyl, a portion of the pure material decomposes, but does not give the other isomer. A 90/10 isomer mixture in refluxing benzene did not change in ratio (NMR). Neither the relative rates of decomposition of the isomers, nor the effect of excess of diiron nonacarbonyl in the reaction were evaluated.

The observations reported are consistent with reaction of I with diiron nonacarbonyl leading to two iron tetracarbonyl complexes, IIa and IIb. The strongest supporting evidence is the separation of one pure product, and the change in NMR spectrum coupled with corresponding changes in the TLC's. The assignments of both IIa and IIb as iron tetracarbonyl complexes is evident from the IR, mass spectra, and elemental analyses. Schenck *et al.*[13] and Weiss *et al.*[12] have shown that iron tetracarbonyl complexes exhibit similar $Fe(CO)_4$ carbonyl stretching frequencies between 2000 and 2120 cm^{-1}, and the IR pattern is more characteristic of an iron tetracarbonyl complex than an iron tricarbonyl complex[9,10,24].

The mass spectrum provides the strongest evidence for the suggested complex. The presence of a parent peak, m/e 292, together with peaks arising from four successive losses of CO requires that the complex contain iron tetracarbonyl, and a peak at m/e 180 indicates a fragment having an iron atom complexed to the free ligand. The free ligand itself occurs at m/e 124, and undergoes fragmentation to give a peak at m/e 96. Loss of CO_2 gives m/e 52[1]. The mass spectrum also indicates the disposition of the $Fe(CO)_4$ moiety within the complex II. The m/e 82 peak may arise via attachment of the iron atom to the olefin after loss of the remainder of the molecule. This is reasonable in view of behaviour reported for analogous complexes. The mass spectra and IR indicate retention of the anhydride ring intact.

The isomers IIa and IIb are represented in Fig. 1, the $Fe(CO)_4$ moiety being respectively *anti* and *syn* to the anhydride ring. Two distinct iron tetracarbonyl complexes are feasible because two non-equivalent faces exist in the olefin. It is possible to conceive of other examples of olefins where this type of positional isomerism should occur as shown in Fig. 2. Of these structures, the presence of an asymmetric center, ($R_1 \neq R_2$, in V and VI) creates a diastereomeric olefin. Both of the $Fe(CO)_4$ complexes derivable from V are diastereomers. Such olefins have not previously been described in $Fe(CO)_4$ chemistry[25].

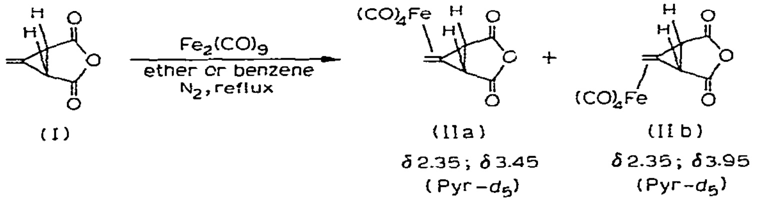

Fig. 1. Formation of positional isomers.

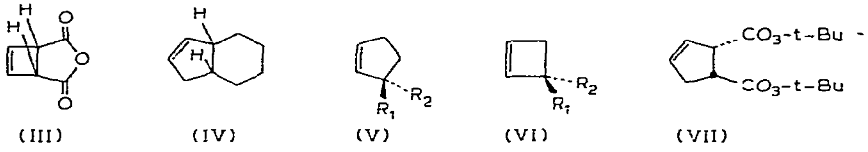

Fig. 2. Ligands capable of positional isomerism.

From steric considerations alone, the isomer possessing the $Fe(CO)_4$ moiety *anti* to the anhydride ring, IIa, should be formed in the greater quantity provided their rates of decomposition are almost equal. In the NMR spectrum, singlets at δ 2.35 and 3.45 (pyridine-d_5) should be assigned to the *anti*-isomer, IIa, and the singlets at δ 2.35 and 3.95 to the *syn*-isomer, IIb. In $CDCl_3$, the protons of the *anti*-isomer, IIa, are at δ 2.30 and 3.15. It is assumed that no interconversion of the isomers occurs during their preparation, indeed no such reports of interconversion in $Fe(CO)_4$ complexes have appeared.

Judging by what is known for similar $Fe(CO)_4$ complexes, the cyclopropyl proton singlet is at δ 2.35 (pyridine-d_5), and the vinyl protons are at δ 3.45 and 3.95. This seems likely since the "free" $Fe(CO)_4$ moiety in the *anti*-isomer, IIa, and the

$Fe(CO)_4$ moiety, buttressed by the anhydride ring in the *syn*-isomer, IIb, should cause different chemical shifts of the vinyl protons.

The absence of coupling in the cyclopropyl and vinyl protons in complexes IIa and IIb is interesting and contrasts with the coupling observed in Feist's anhydride I. The absence of coupling and the upfield shifts for each type of proton is due to the change in electron density at the double bond and to rehybridization at the *exo*-methylene carbon. The ability of the $Fe(CO)_4$ moiety to complex completely with the electrons of the double bond, so as to eliminate any allylic coupling, is thereby demonstrated.

The question arises as to why anhydride I forms a stable methylenecyclopropane–$Fe(CO)_4$ complex, whereas all other methylenecyclopropane derivatives only form an iron tricarbonyl complex containing the trimethylenemethane ligand; in the latter, the cyclopropane ring is no longer intact[3–6]. This result most likely relates to the relative stability of the $Fe(CO)_4$–olefin complex and the $Fe(CO)_3$–trimethylenemethane moiety. Since the $Fe(CO)_4$ complex involves an sp^3 carbon atom at both ends of the double bond, a considerable amount of ring strain is exerted upon the cyclopropane ring and this may be relieved by ring opening. Formation of the $Fe(CO)_3$–trimethylenemethane complex requires placing this into another anhydride ring, *e.g.* in I, the planarity required for the trimethylenemethane ligand cannot be attained. It is also possible that the anhydride ring entirely prevents opening of the cyclopropane ring, thereby stabilizing the $Fe(CO)_4$ complex. Evidence that this is so has been obtained by a study of the reactions of *cis*- and *trans*-Feist's esters with diiron nonacarbonyl[27].

EXPERIMENTAL

cis-1-Methylenecyclopropane-2,3-dicarboxylic anhydride, I, synthesized from *trans*-1-methylenecyclopropane-2,3-dicarboxylic acid (Feist's acid) by the procedure of Ettlinger and Kennedy[2,26], was characterized by its NMR spectrum: ($CDCl_3$): δ 5.9 (t, 1H, J 2.0 Hz); 3.4 (t, 1H, J 2.0 Hz), and IR spectrum $\nu(CHCl_3)$ 3060, 3010, 1860 (anhydride), 1780 (anhydride), 1360, 1215, 1095, 910, 870 and 850 cm^{-1}. The anhydride can be boiled under reflux in dry ether or benzene under nitrogen for at least 16 h without change. A solution of anhydride I in dry ether or benzene in the presence of a stoichiometric amount of diiron nonacarbonyl was boiled under reflux for 16 h. Removal of the solvent from the reaction mixture, after filtration through Florisil to remove all traces of inorganic material, left an oil whose NMR spectrum revealed the presence of unreacted starting material, in addition to four singlets ($CDCl_3$) or three singlets (pyridine-d_5). The oily material was dissolved in methylene chloride or hot pentane. Cooling of the pentane solution or addition of pentane to the methylene chloride solution followed by cooling to −20°, led to the formation of slightly greenish or yellow-green crystals, II.

The product, II, was washed free of all mother liquors, dried in vacuo, and analyzed spectrally. Crystals obtained in this manner were usually a single isomer, as seen by NMR and TLC. The other isomer could only be obtained 90% pure (NMR). The m.p. of the pure isomer was $\simeq 165°$, but could be determined accurately only with difficulty because of concomitant decomposition. Sample mixtures of both isomers exhibited m.p.'s in the range 120–175°. A typical elemental analysis was: Found:

C, 41.46; H, 1.32. $C_{10}H_4O_7Fe$ calcd.: C, 41.10; H, 1.37%. The product was obtained in 15–20% yield.

The IR spectra of the completely pure isomer and the 90/10 mixture showed no serious differences: $\nu(CHCl_3)$ 3000 w, 2910 w, 2840 w, 2100 w, 2035 s, 2010 s, 1855 w, 1785 s, 1200 w, 1095 w, 970 w, and 915 w cm^{-1}. Mass spectral data were: *m/e* (Rel. Int.): 292 (parent, 1.74), 264 (29), 236 (30), 209 (10), 108 (87), 180 (base, 100), 152 (6), 140 (7), 136 (35), 124 (12), 112 (24), 108 (40), 96 (5.2), 84 (46), 82 (39), 81 (15), 56 (90) and 52 (5).

The ease of interconversion of the two isomers was determined using the pure isomer obtained by fractional crystallization and the 90% pure isomer. Lack of any interconversion after refluxing in benzene under nitrogen was established by TLC and NMR. In each case decomposition of the isomers could be detected by a higher spectrum amplitude in the NMR. TLC solvent systems were: ethyl acetate, tetrahydrofuran, isopropanol, and varying mixtures of petroleum ether and ethyl acetate. The best solvent for the NMR is pyridine-d_5, from which the complexes can be easily recovered.

NMR spectra were recorded on a Varian A-60 and Bruker 90 MHz instruments. IR spectra were recorded on a Perkin–Elmer Grating Spectrophotometer Model 237B, and mass spectra on an Atlas MAT CH4. Elemental analyses were performed within the analytical department of this Institute.

ACKNOWLEDGEMENTS

The author wishes to thank Dr. A. Eisenstadt, Tel Aviv University, Ramat-Aviv, Israel, for helpful discussions and for a generous supply of diiron nonacarbonyl. Professor A. Efraty of Rutgers University, New Brunswick, N.J., U.S.A., made many constructive comments during the preparation of the manuscript, as did Dr. B. Green of this Institute. Generous financial support via a Weizmann Institute Senior Postdoctoral Fellowship is hereby acknowledged.

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