Journal of Organometallic Chemistry, 57 (1973) 363–372

THE MECHANISM OF RING OPENING IN THE REACTIONS BETWEEN *cis*- AND *trans*-FEIST'S ESTERS WITH DIIRON NONACARBONYL

IRA S. KRULL
Department of Organic Chemistry, The Weizmann Institute of Science, Rehovot (Israel)
(Received December 14th, 1972; in revised form January 2nd, 1973)

SUMMARY

The reactions between *cis*- and *trans*-Feist's methyl esters and diiron nonacarbonyl have been investigated in an attempt to interpret the mechanism of ring opening in all methylenecyclopropane derivatives in this particular reaction. It appears, on the basis of the stereoisomers actually formed from each of these esters, that the ring opening is completely stereospecific, and that it occurs in a disrotatory manner. Attempts to apply the same reaction to an analogous cyclobutene derivative have not been successful. The formation of unusual enantiomers in the reaction of the *trans*-Feist's ester is described, along with a description of the use of a chiral shift reagent to identify the enantiomers via NMR.

INTRODUCTION

The reaction of methylenecyclopropane and many of its derivatives with diiron nonacarbonyl has been studied extensively in recent years*[1]. Emerson *et al.*[1] have reported the reaction of methylenecyclopropane itself with diiron nonacarbonyl as leading to (trimethylenemethane)iron tricarbonyl and (1,3-butadiene)iron tricarbonyl. Noyori *et al.*[2a] have described the reaction of various methylenecyclopropane derivatives with diiron nonacarbonyl as resulting in similar derivatives of (trimethylenemethane)iron tricarbonyl. Noyori *et al.* have also reported the reactions of various methylenecyclopropane derivatives with lead tetraacetate[2b], palladium chloride[2c] and nickel(0)[2d], whilst Binger has described the nickel(0) catalyzed dimerization of methylenecyclopropane itself[2e]. Dowd has recently reviewed the chemistry of trimethylenemethane and its iron tricarbonyl complexes[3]. There appear no reports in the literature describing the formation and/or isolation of any iron tetracarbonyl complex of this particular ring system, other than the iron tetracarbonyl complex of Feist's anhydride**, (I)[4]. This particular complex can exist as two distinct

---

* For an excellent review of iron carbonyl chemistry, see: "The Organic Chemistry of Iron," ed. by E. K. von Gustorf and F. W. Grevels, Academic Press, New York, to be published, 1973. Of special interest for iron tricarbonyl chemistry is Chapter 13 by Prof. J. Landesberg, Adelphi University, New York, USA. The author wishes to thank Dr. Landesberg for a pre-print of his chapter.

** Feist's acid is *trans*-3-methylene-1,2-cyclopropanedicarboxylic acid.

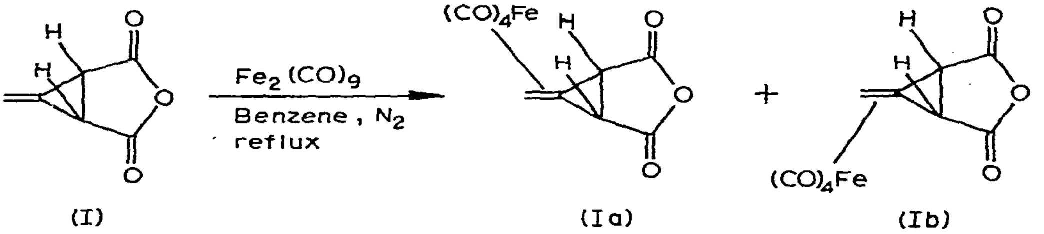

Fig. 1. The formation of positional isomers (Fe(CO)$_4$) from Feist's anhydride, (I).

positional isomers, *viz.*, (Ia) and (Ib)[4] (Fig. 1).

It appeared possible that on proceeding from the iron tetracarbonyl complex to the iron tricarbonyl complex of trimethylenemethane the iron itself might be playing a prominent role in the cyclopropane ring opening, *e.g.*, stereospecific, disrotatory, conrotatory[5]. The subject of metal catalyzed or metal assisted ring openings in strained ring systems is one of considerable current interest[6-11] and many such reactions appear to proceed stereospecifically[11].

With these factors in mind, it appeared of interest to study the reactions of certain *cis*- and *trans*-2,3-disubstituted methylenecyclopropane derivatives with diiron nonacarbonyl.

RESULTS

In the hope of understanding why Feist's anhydride, (I), forms an iron tetracarbonyl as opposed to an iron tricarbonyl complex, the reactions of *cis*- and *trans*-dimethyl esters of Feist's acid[12], *viz.*, *cis*-(II) and *trans*-(II), with diiron nonacarbonyl were studied. Both *cis*-(II) and *trans*-(II), react readily at room temperature with an excess of diiron nonacarbonyl in benzene. TLC analysis of the reaction mixtures in both cases showed that only a single material was formed from each of the esters, and that these two products were different. Purification was easily accomplished, *vide infra*, leaving materials that were analytically pure and homogeneous by TLC. On the basis of spectroscopic data, molecular weight determination by vapor pressure osmometry, and elemental analysis, it is apparent that the two products are indeed iron tricarbonyl complexes of the trimethylenemethane ring system, (Experimental Section).

NMR spectra are the most important criteria for assigning the exact structures to each of the complexes. As can be seen from Table 1, the complex arising from *cis*-(II) shows only three sharp singlets in the four solvents studied. These are not composed of accidentally degenerate signals, since they are completely solvent-independent. By contrast, the NMR spectrum of the *trans*-(II) complex is solvent-dependent (Table 1) and exhibits multiplets and an apparent singlet in the ratio 3/1/1. Furthermore, the signals appear in the same regions as observed in the *cis*-(II) complex.

In the hope of interpreting the generality of the above reactions, Feist's perester[26], *i.e.*, the di-tert-butyl perester of 1-methylenecyclopropane-*trans*-2,3-dicarboxylic acid, was reacted with an excess of diiron nonacarbonyl. No iron complex of any sort could be isolated, neither were starting materials recovered. With Feist's acid itself, *i.e.*, 1-methylenecyclopropane-*trans*-2,3-dicarboxylic acid, again no complex could be isolated, and no starting material was recovered. Attempts to extend the above reaction to a cyclobutene derivative, *viz.*, the dimethyl ester of 1,2-di-n-

TABLE 1

NMR SPECTRA OF THE $Fe(CO)_3$ COMPLEXES (III) AND (V) FORMED FROM *cis*- and *trans*-FEIST'S METHYL ESTERS, *cis*-(II) AND *trans*-(II).

Complex	*NMR spectra (solvent)*
(III)	($CDCl_3$): δ 3.7 (s, 3H, $-CO_2C\underline{H}_3$); 2.65 (s, 1H, $-C\underline{H}CO_2CH_3$); and 2.15 ppm (s, 1H, $=C\underline{H}_2$).
	(C_6D_6): δ 3.4 (s, 3H, $-CO_2C\underline{H}_3$); 2.2 (s, 1H, $-C\underline{H}CO_2CH_3$); and 1.7 ppm (s, 1H, $=C\underline{H}_2$).
	(CD_3CN): δ 3.65 (s, 3H, $-CO_2C\underline{H}_3$); 2.62 (s, 1H, $-C\underline{H}CO_2CH_3$); and 2.2 ppm (s, 1H, $=C\underline{H}_2$).
	(*Pyridine-d*$_5$): δ 3.67 (s, 3H, $-CO_2C\underline{H}_3$); 2.73 (s, 1H, $-C\underline{H}CO_2CH_3$); and 2.5 ppm (s, 1H, $=C\underline{H}_2$).
(V)	($CDCl_3$): δ 3.74 (s, 1.5H, $-CO_2C\underline{H}_3$); 3.71 (s, 1.5H, $-CO_2C\underline{H}_3$); 2.75 (s, 1H, $-C\underline{H}CO_2CH_3$); and 2.1–2.4 ppm (AB, doublet of doublets, 1H, $J_A = J_B = 3.0$ Hz, $J_{AB} = 9.0$ Hz, $=C\underline{H}_2$). δ 2.75 ppm is an apparent singlet.
	(C_6D_6): δ 3.37 (s, 1.5 H, $-CO_2C\underline{H}_3$); 3.32 (s, 1.5 H, $-CO_2C\underline{H}_3$); 2.8 (s, 1H, $-C\underline{H}CO_2CH_3$): and 2.0 ppm (s, 1H, $=C\underline{H}_2$). δ 2.8 and 2.0 ppm are apparent singlets.
	(CD_3CN); δ 3.71 (s, 1.5 H, $-CO_2C\underline{H}_3$); 3.67 (s, 1.5 H, $-CO_2C\underline{H}_3$); 2.75 (s, 1 H, $-C\underline{H}CO_2CH_3$); and 2.15–2.45 ppm (AB, doublet of doublets, 1 H, $J_A = J_B = 3.0$ Hz, $J_{AB} = 9.0$ Hz, $=C\underline{H}_2$). δ 2.75 ppm is an apparent singlet.
	(*Pyridine-d*$_5$): δ 3.68 (s, 1.5 H, $-CO_2C\underline{H}_3$); 3.63 (s, 1.5 H, $-CO_2C\underline{H}_3$); 2.95 (s, 1 H, $-C\underline{H}CO_2$-CH_3): and 2.25–2.45 ppm (AB, doublet of doublets, 1 H, $J_A = J_B = 3.0$ Hz, $J_{AB} = 6.0$ Hz, $=C\underline{H}_2$). δ 2.95 ppm is an apparent singlet.
	(CCl_4): δ 3.70 (s, 1.5 H, $-CO_2C\underline{H}_3$); 3.66 (s, 1.5 H, $-CO_2C\underline{H}_3$); 2.70 (s, 1 H, $-C\underline{H}CO_2CH_3$); 2.0–2.35 ppm (AB, doublet of doublets, 1 H, $J_A = J_B = 3.0$ Hz, $J_{AB} = 9.0$ Hz, $=C\underline{H}_2$).

propyl-*cis*-3,4-cyclobutenedicarboxylic acid*, reveal that this acid is extremely unreactive. Further attempts to bring this cyclobutene derivative into reaction with diiron nonacarbonyl are in progress.

In an attempt to study the mixture of enantiomers which should comprise complex (V), *vide infra*, arising from *trans*-(II), NMR experiments were performed using a chiral shift reagent[15]. Table 2 illustrates the results of a typical experiment utilizing a solution of tris[3-(2,2,2-trifluoro-1-hydroxyethyl)-*d*-camphorato]europium(III) complex with the complex (V)[15]. Under identical experimental conditions, *meso*-(III) shows only a gradual downfield shift of all its three singlets. If we assume complexation of the ester carbonyl with the chiral shift reagent, those protons nearest to the carbonyl ester center exhibit the greatest downfield shift, ($\Delta\delta$ 0.53 ppm), while those protons furthest from the center of complexation exhibit the least downfield shift, ($\Delta\delta$ 0.19 ppm), relative to the chemical shifts in the absence of any added reagent. No singlet splitting in *meso*-(III) could be observed when additional shift reagent was employed. In the case of *racemic*-(V), the two carbomethoxy singlets, Table 2, are gradually shifted downfield and resolved, and the resolution results eventually

---

* Kindly supplied by Prof. E. Gil-av and Dr. J. H. Leftin, Department of Chemistry, Weizmann Institute of Science.

TABLE 2

NMR SPECTRA OF THE $Fe(CO)_3$ COMPLEXES (Va) and (Vb) FORMED FROM *trans*-FEIST'S METHYL ESTER, *trans*-(II), AS A FUNCTION OF ADDED CHIRAL SHIFT REAGENT

Chiral reagent	*NMR spectrum* (*CCl_4*)
None	δ 3.76 (s, 1.5 H, $-CO_2C\underline{H}_3$); 3.73 (s, 1.5 H, $-CO_2C\underline{H}_3$); 2.73 (s, 1 H, $-C\underline{H}CO_2CH_3$); 2.34–2.13 ppm (AB pattern, doublet of doublets, 1 H, $J_A = J_B = 3.0$ Hz, $J_{AB} = 9.0$ Hz, $=C\underline{H}_2$).
3 Drops	δ 3.73 (s); 3.70 (s); 2.83 (broad singlet); 2.33–2.08 ppm (broad multiplet).
8 Drops	δ 4.02 (s) and 3.97 (s); 3.81 (apparent singlet); 3.42–3.0 (broad m); 2.34 ppm (broad s). Areas of δ 4.02 + δ 3.97 = area of δ 3.81 ppm.
12 Drops	δ 4.15 (s); 4.10 (s); 3.87 (broad singlet); 3.67–3.26 (broad absorption); 2.53–2.23 (broad s). Area of δ 4.15 = δ 4.10; areas of δ 4.15 + δ4.10 = area δ 3.87 ppm.

in the formation of two separate methoxycarbonyl areas, Table2, one being a rather broad singlet at δ 3.87 ppm, and the other consisting of two distinct sharp singlets at δ 4.15 and 4.10 ppm. The areas of the two singlets at δ 4.15 and 4.10 ppm are equal and their total area is equal to the area of the singlet at δ 3.87 ppm. The remaining signals are too broad and ill-defined to allow assignation of multiplicities or areas.

Attempts were made to influence the formation of an equal mixture of enantiomers from *trans*-(II) by changing the reaction medium to isopentyl alcohol[16] and by adding *d*-camphor (0.33 *M*) to the benzene reaction medium. No change in the relative ratio of the two enantiomers formed could be observed via the chiral shift reagent experiment.

DISCUSSION

Methylenecyclopropane derivatives and the parent ligand have been shown to form iron tricarbonyl complexes of the ring-opened trimethylenemethane system in their reactions with diiron nonacarbonyl[1,2a]. That both *cis*-(II) and *trans*-(II) form the same type of complex can be seen by the IR, mass spectra, NMR, and elemental analyses, *vide infra*. The IR pattern at 2090, 2020, and 2000 cm^{-1} is characteristic of an iron tricarbonyl complex[1,2a,13,14] and this is supported by both elemental analyses and mass spectral data. Thus the product is not an iron tetracarbonyl complex, as was found for Feist's anhydride, (I)[4]. The mass spectral results (Experimental Section) only suggest the presence of the proposed iron tricarbonyl complex, but are not entirely conclusive. Thus the presence of peaks at *m/e* 282, 254, and 226, may merely indicate the loss of three molecules of CO from the proposed complex prior to reactions which may be occurring within the mass spectrometer. The vapor pressure osmometry determination of the molecular weight for complex (III) indicates it to be the iron tricarbonyl complex however.

The formation of a single complex from *cis*-(II), *viz*., complex (III), Fig. 2, and an entirely different complex from *trans*-(II), *viz*., (Va) and/or (Vb), means that the two starting esters are undergoing ring opening in exactly the same manner, *i.e.*,

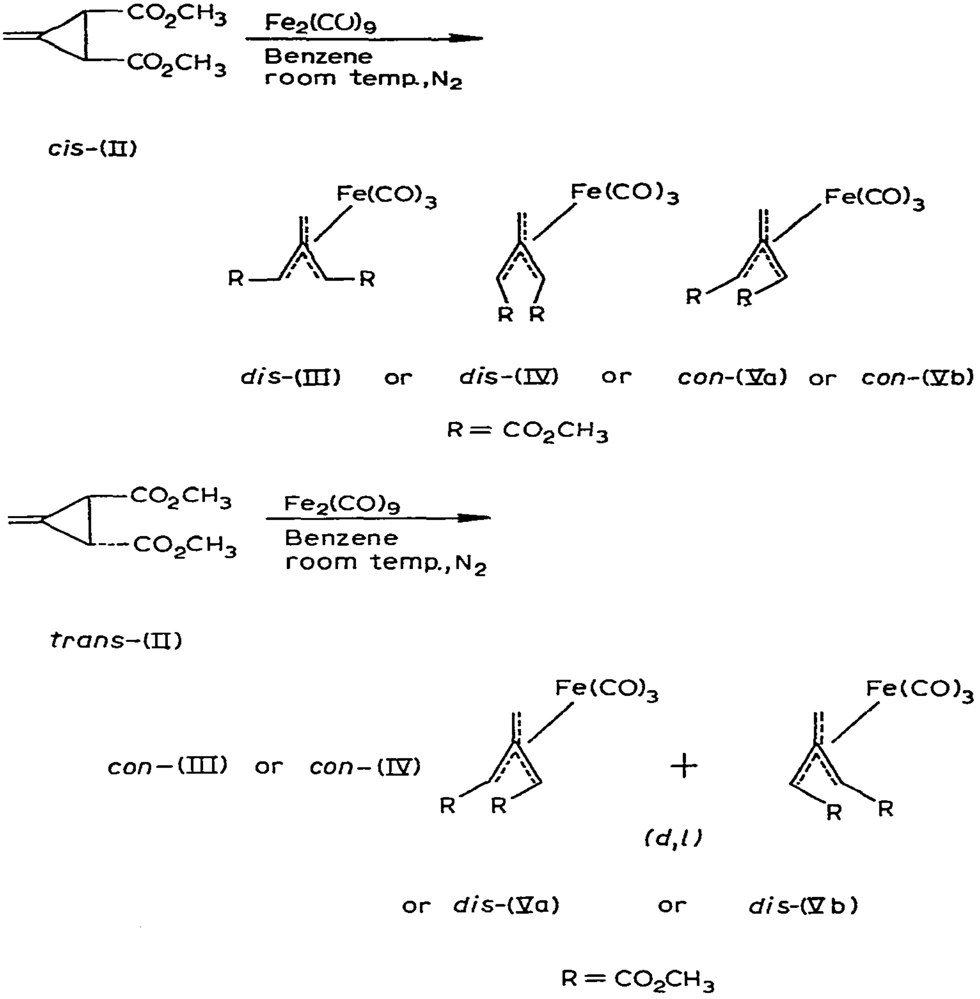

Fig. 2. The reaction of *cis*-(II) and *trans*-(II) with diiron nonacarbonyl. The possible iron tricarbonyl complexes to be expected.

stereospecifically. The strongest evidence as to the exact structure for each of the two complexes in question, arises from the NMR spectra, Table 1^{1,2a}. The chemical shift for the methoxycarbonyl groups in both complexes is approximately the same as for the chemical shift found in the starting esters. The protons adjacent to the methoxycarbonyl groups in (III) appear at about δ 2.65 ppm in three of the four solvents studied, whilst the original vinylic hydrogens appear at about δ 2.2 ppm in most cases, Table 1^{1,2a}. Complex (III) can only yield three singlets, Table 1, if it possesses a symmetrical structure, *viz.*, (III) or (IV). Complexes (III) and (IV) can only arise via a disrotatory ring opening in the starting ester, *cis*-(II). There is no apparent reason why *cis*-(II) should ring open inwards in a disrotatory manner to yield (IV), when it can ring open outwards in a disrotatory fashion, to yield (III)^{17}. In forming (IV), the two methoxycarbonyl groups must approach each other, producing a certain amount of steric repulsion. The two singlets for the protons directly attached to the trimethylenemethane system are not sharp singlets, but appear slightly broadened. This may indicate a certain amount of residual coupling.

In considering the complex anticipated from *trans*-(II), this must ring open in the same manner as *cis*-(II), as it yields an entirely different complex. The NMR spectra support complex (Va) and/or (Vb), which are really enantiomers. However, the NMR spectrum cannot by itself distinguish between (Va) and (Vb), without the use of specific chiral shift reagents[15], or optically active solvents[16]. The methoxycarbonyl groups (Table 1) appear as two distinct singlets of exactly equal area. The protons adjacent to the methoxycarbonyl groups appear as singlets(apparent), but exhibit hyperfine coupling. They cannot be separated into two distinct areas of resonance, perhaps due to a unique accidental degeneracy. The original vinyl hydrogens appear in (V) either as a singlet, C_6D_6, or as an AB pattern. This AB pattern is a perfect doublet of doublets, with additional coupling at higher amplitude and resolution (Table 1). The solvent dependence in (V) demonstrates that care needs to be taken in assigning structures via a single NMR spectrum. *A priori*, disrotatory ring opening in *trans*-(II) should occur in both possible directions, yielding an equal mixture of complexes (Va) and (Vb).

All of the above structural assignments require that the iron tricarbonyl moiety be symmetrically disposed beneath the central carbon atom of the trimethylenemethane system. This is required by the NMR spectra actually observed, and from the results of Churchill and Gold[17], X-ray analysis of (phenyltrimethylenemethane)-iron tricarbonyl shows the iron tricarbonyl moiety to be symmetrically placed beneath this central carbon atom[17].

Complex (V) is of inherent interest because it must exist as an equal mixture of the indicated enantiomers (Fig. 2). As the initial iron tetracarbonyl complex of *trans*-(II) rearranges to the iron tricarbonyl complex (V) the ring should open in either of two disrotatory fashions. The simplest way to demonstrate the presence of such enantiomers appeared to be by use a chiral shift reagent[15]. *Meso*-(III) is insensitive to the addition of the reagent as regards any separation of the original three singlets. When the same chiral reagent is added to complex (V), a gradual downfield shift of the two methoxycarbonyl singlets is observed (Table 2) and a change in the multiplicity of one of these singlets. One of the original singlets splits into two equal singlets found at δ 4.15 and 4.10, and the other singlet remains a broad singlet at 3.87 ppm. The areas of these three singlets are given in Table 2.

Enantiomers (Va) and (Vb), contain two types of methoxycarbonyl group. The group inside the trimethylenemethane system is designated R_i, and the group outside the system, R_o. The chiral shift reagent may complex with only one of these two methoxycarbonyl groups, most probably R_o, based upon its relative availability. In Table 2, the singlets at δ 4.15 and 4.10, being shifted downfield more than the remaining singlet at 3.87 ppm, may be R_o. The remaining δ 3.87 ppm is most likely R_i, both of which from (Va) and (Vb), appear at the same place. Equal areas for δ 4.15 and 4.10 ppm suggests that the two enantiomers are present in complex (V) in an exactly equal ratio. Use of an achiral NMR shift reagent, $Eu(Fod)_3$, only results in two different downfield shifts for the methoxycarbonyl singlets, but no further splitting, as above.

Attempts were made to alter the equal ratio of enantiomers observed to arise from *trans*-(V) by changing the reaction medium. When optically active isopentyl alcohol was used as the reaction solvent, there was no change in the ratio of the enantiomers (Va) and (Vb) actually formed. Use of a solution of *d*-camphor in benzene, 0.33 *M*, also did not cause any change in the (Va)/(Vb) ratio. Thus it would appear that the ring opening is completely controlled by the iron carbonyl moiety.

In the formation of the (trimethylenemethane)iron tricarbonyl complex from the reaction of any methylenecyclopropane derivative with diiron nonacarbonyl, the cyclopropane ring opening [C(2)–C(3)] occurs in a stereospecific and disrotatory manner. If the methylenecyclopropane ring system is analogous to the cyclobutene ring system, *i.e.*, $_2\pi + _2\sigma$[19], then it should exhibit the same type of metal-catalyzed ring opening. A disrotatory mode of ring opening has been found in certain silver- or copper-catalyzed cyclobutene derivatives.[1a,11,18a–c]. These processes occur in a manner opposite to the thermal ring openings found in cyclobutenes[11,18a–c,19]. Other ring openings apparently catalyzed by either $Fe(CO)_5$ or $Fe_2(CO)_9$ have been reported[18d-j]. In none of these cases has it been demonstrated that the ring opening occurs in the manner indicated above. That the ring opening in methylenecyclopropanes is actually metal catalyzed or metal assisted[11], can only be inferred from the observed stereospecificity. Nothing can yet be said about the presence or absence of concertedness. The thermal mode of ring opening, *viz.*, disrotatory *vs.* conrotatory, in methylenecyclopropane derivatives has not been reported[20]. On the basis of the above data, it may now be predicted that this will occur in a conrotatory fashion, in the absence of other thermal reactions[20].

It is of interest that methylenecyclopropane and its derivatives thermally dimerize[21a–d], in an apparently non-concerted manner, or undergo a ring-opening-isomerization sequence of degenerate rearrangements[20]. Reactions of vibrationally excited methylenecyclopropane have been reported, but these do not appear to involve a ring opening reaction analogous to that reported here*. Because of the lack of a similar reaction in the cyclobutene derivative, *vide supra*, a direct comparison between methylenecyclopropane and cyclobutene derivatives in their reactions with diiron nonacarbonyl appears not to be warranted.

EXPERIMENTAL

Both *cis*- and *trans*-Feist's methyl esters were prepared using a slight modification of the reported procedures[20]. Feist's acid[24], prepared using the modifications described by Blomquist *et al.*[12], was either refluxed overnight in absolute methanol containing a small amount of thionyl chloride (0.5 ml/100 ml, 1.0 g Feist's acid)[25], to yield the *trans*-Feist's methyl ester, *trans*-(II), or converted to Feist's anhydride, (I), using the established procedure[23]. *cis*-Feist's methyl ester, *cis*-(II), was easily obtained from Feist's anhydride, (I), by refluxing the anhydride in absolute methanol containing a trace of thionyl chloride[25]. The two esters agreed in all respects with the properties reported previously[20], and could easily be obtained pure by molecular distillation (kugelrohr) after removal of solvents by rotary evaporation. Both products are oils

---

* A discussion of the hydrocarbon products arising from the decomposition of a vibrationally excited methylenecyclopropane, formed by the addition of diazomethane to allene is given in ref. 22. None of the products found here can be readily explained as arising *via* a C(2)–C(3) ring opening anlogous to that discussed above.

at room temperature, but distillation of the pure *trans*-(II) yields a solid when the receiving flask is externally cooled. Dimethyl 1-methylenecyclopropane-2,3-*cis*-dicarboxylate, *cis*-(II), and dimethyl 1-methylenecyclopropane-2,3-*trans*-dicarboxylate, *trans*-(II), both readily undergo reactions with excess (!) of diiron nonacarbonyl* at room temperature in benzene in less than five hours[2a]. All reactions described were carried out under a stream of dry nitrogen and their progress was easily followed by analytical TLC (silica gel, aluminum plates, methylene chloride, chloroform, petroleum ether: methylene chloride, UV and iodine vapor detection).

The crude reaction mixtures were filtered using filter paper and a short column of Florisil (methylene chloride), to remove all inorganic materials. Removal of solvents by rotary evaporation left a solid from the reaction of *cis*-II, which could be purified simply be washing repeatedly with cold pentane to remove any unreacted starting material. This left complex (III), yield 60%, m.p. 94–96°, (pure by analytical TLC) which exhibited NMR spectra shown in Table 1. (Found: C, 42.75; H, 3.12. $C_{11}H_{10}FeO_7$ calcd.: C, 42.61; H, 3.25%.) IR in $CHCl_3$ (cm^{-1}); ν 3000 w; 2940 w; 2095 s; 2020 s; 2000 s; 1725 s; 1435 w; 1345 w; 1295 w; 1190 w; 1135 w; 1020 w. *M/e* (rel. int.): 308(9.8); 282(9.7); 254(67.2); 226(96.6); 198(7.3); 195(7.3); 168(100); 140(7.2); 138(7.4); 113(7.4); 110(22.7); 108(17.4); 87(17.4); 84(11.5); 67(3.7); 56(7.3); 52(15.4).

The crude reaction mixture from *trans*-(II) was seen by analytical TLC (silica gel, aluminum plates) to contain a single material (UV and iodine vapor) having an R_f value slightly greater than that of the complex arising from *cis*-(II) in all of the solvents used, *i.e.*, methylene chloride, chloroform, 1/1 petroleum ether/methylene chloride. This material is an oil, and can be distilled with some decomposition, b.p. 90–100°/0.5 mmHg. By repeated preparative TLC the *trans*-2 complex, *viz.*, (Va) and (Vb), could be easily obtained analytically pure (silica gel, aluminum plates, *vide supra*). The pure complex (V), yield 78%, exhibited NMR spectra as indicated in Table 1, and IR in $CHCl_3$ (cm^{-1}); ν 2990 w; 2930 w; 2090 s; 2020 s; 2000 s; 1720 s; 1425 w; 1300 w; 1180 w; 1155 s. *M/e* (rel. int.); 310(3.3); 307(3.3); 282(14.3); 254(36.4); 226(32.5); 195(3.4); 194(3.4); 168(61.1); 142(6.6); 140(6.8); 137(6.8); 112(27.7); 110(21.1); 108(21.3); 97(6.6); 87(61.0); 84(61.1); 81(25.7); 68(6.7); 56(100); 52(46.8). (Found: C, 42.30; H, 3.04. $C_{11}H_{10}FeO_7$ calcd.: C, 42.61; H, 3.25%.)

In the mass spectrometer, both complexes show the presence of *m/e* ions at values above that expected from the complexes alone. Ions appear as high as *m/e* 564, and at intermediate *m/e* values down to *m/e* 310. Reproducible results were obtained on two separate instruments, under similar experimental conditions**. In view of the

---

* Dr. A. Eisenstadt, Department of Chemistry, Tel Aviv University, Ramat-Aviv, Israel, has described a very simple method for the preparation of diiron nonacarbonyl from iron pentacarbonyl. The iron pentacarbonyl (50 ml) is dissolved completely in glacial acetic acid (150–200 ml), and irradiated in a standard Hanovia type photochemical immersion apparatus for about 3 h. Either a quartz or Pyrex immersion well may be used, and a 450W or 550W high pressure Mercury arc lamp. Filtration of the precipitated diiron nonacarbonyl from the reaction medium (hood) is then followed by washing with water, methanol, petroleum ether, and drying completely over calcium chloride and sodium hydroxide, *in vacuo*. Re-irradiation of the mother liquors yields additional material, yield 70%.

** The mass spectra of both complexes (III) and (V) were determined at the Weizmann Institute of science and at the Israel Institute of Technology, Haifa, Isarael. Professor A. Mandelbaum provided the latter set of mass spectra. Gratitute is hereby expressed for his assistance and for his continued constructive interest and encouragement.

correct elemental analyses, IR spectra, and separate molecular weight determination for complex (III), it is presently believed that the mass spectral results by themselves are somewhat misleading. The *m/e* 564 ion may arise by an initial loss of one molecule of CO from the iron tricarbonyl complex upon introduction into the mass spectrometer, followed by a dimerization of the resultant radicals. Such a dimer-like species would account for all of the remaining ions that appear in the mass spectra of each complex between *m/e* 564 and 310.

Concentration (0.28 *M*) of chiral and achiral shift reagents were used (*vide supra*)* in dry carbon tetrachloride, with NMR solutions of the two complexes at approximately equal concentrations. A more quantitative procedure was not employed, since only the qualitative effects of the chiral and achiral shift reagents on each of the complexes were required.

The molecular weight for *meso*-(III), was measured by vapor pressure osmometry with ethyl acetate as solvent, an average of two determinations being 338 (mol. wt. 310).

IR spectra were recorded on a Perkin–Elmer Model 237B Grating Spectrophotometer; NMR spectra were determined on a Varian A-60; and mass spectra using an Atlas MAT CH4. Microanalyses were performed in the analytical department of this Institute. The molecular weight was determined in the Plastics department using a Hitachi–Perkin–Elmer Model 115 vapor pressure osmometer.

ACKNOWLEDGEMENTS

The author wishes to express his gratitude to Dr. A. Eisenstadt of Tel Aviv University, Ramat-Aviv, Israel for a generous supply of diiron nonacarbonyl, and for his continued interest and encouragement. The continued interest and stimulating discussions of Professor A. Mandelbaum, Israel Institute of Technology, Haifa, Israel, brought the work to an early completion. Much of the work described was simplified through the expert skills and assistance of the technical staff of the Weizmann Institute of Science. Generous financial support via a Weizmann Institute Senior Post-doctoral Fellowship is hereby acknowledged.

REFERENCES

1 (a) G. F. Emerson, K. Ehrlich, W. P. Giering, and D. Ehntholt, *Trans. N.Y. Acad. Sci.*, 30 (1968) 1001;
(b) G. F. Emerson, K. Ehrlich, W. P. Giering, and P. C. Lauterbur, *J. Amer. Chem. Soc.*, 88 (1966) 3172;
(c) J. S. Ward and R. Pettit, *J. Chem. Soc. D*, (1970) 1419;
(d) K. Ehrlich and G. F. Emerson, *J. Chem. Soc. D*, (1969) 59.
2 (a) R. Noyori, T. Nishimura, and H. Takaya, *J. Chem. Soc. D*, (1969) 89;
(b) R. Noyori, Y. Tsuda, and H. Takaya, *J. Chem. Soc. D*, (1970) 1181;
(c) R. Noyori and H. Takaya, *J. Chem. Soc. D*, (1969) 525;
(d) R. Noyori, T. Odagi, and H. Takaya, *J. Amer. Chem. Soc.*, 92 (1970) 5780;
(e) P. Binger, *Angew. Chem., Int. Ed. Engl.*, 11 (1972) 309.
3 P. Dowd, *Accounts Chem. Res.*, 5 (1972) 242.
4 I. S. Krull, *J. Organometal. Chem.*, 57 (1973) 373.
5 C. L. Perrin, *Chem. Brit.*, 8 (1972) 163.
6 J. H. Leftin and E. Gil-Av, *Tetrahedron Lett.*, (1972) 3367.

---

* Kindly supplied by Prof. E. Gil-Av, Dr. V. Schurig, and Dr. M. Weinstein, Department of Chemistry, Weizmann Institute of Science.

7 J. E. Byrd, L. Cassar, P. E. Eaton, and J. Halpern, *J. Chem. Soc. D*, (1971) 40.
8 (a) P. G. Gassman and T. J. Atkins, *J. Amer. Chem. Soc.*, 93, (1971) 4597.
(b) P. G. Gassman, *et al.*, *J. Amer. Chem. Soc.*, 94 (1972) 7733, 7741, 7748, 7757.
9 (a) L. A. Paquette, R. S. Beckley, and T. McCreadie, *Tetrahedron Lett.*, (1971) 775;
(b) L. A. Paquette, *et al.*, *J. Amer. Chem. Soc.*, 94 (1972) 7761, 7771, 7780.
10 M. Sakai and S. Masamune, *J. Amer. Chem. Soc.*, 93 (1971) 4610.
11 L. A. Paquette, *Accounts Chem. Res.*, 4 (1971) 280.
12 A. T. Blomquist and D. T. Longone, *J. Amer. Chem. Soc.*, 81 (1959) 2012.
13 R. Pettit, G. F. Emerson, and J. Mahler, *J. Chem. Ed.*, 40 (1963) 175.
14 R. Pettit and G. F. Emerson, in F. G. A. Stone and R. West (Eds.), *Advances in Organometallic Chemistry*, Vol. 1, Academic Press, Inc., New York, 1964, Ch. 1, pp. 1–46.
15 (a) R. von Ammon and R. D. Fischer, *Angew. Chem., Int. Ed. Engl.*, 11 (1972) 675;
(b) G. M. Whitesides and D. W. Lewis, *J. Amer. Chem. Soc.*, 92 (1970) 6979;
(c) G. M. Whitesides and D. W. Lewis, *J. Amer. Chem. Soc.*, 93 (1971) 5914;
(d) H. L. Goering, J. N. Eikenberry, and G. S. Koermer, *J. Amer. Chem. Soc.*, 93 (1971) 5913;
(e) R. R. Fraser, M. A. Petit, and M. Miskow, *J. Amer. Chem. Soc.*, 94 (1972) 3253;
(f) R. R. Fraser, M. A. Petit, and J. K. Saunders, *J. Chem. Soc. D*, (1971) 1450;
(g) J. R. Campbell, *Aldrichimica Acta*, 4 (1971) 55.
16 (a) W. H. Pirkle and S. D. Beare, *J. Amer. Chem. Soc.*, 91 (1969) 5150, and references cited therein;
(b) M. Kainosho, K. Ajisaka, W. H. Pirkle, and S. D. Beare, *J. Amer. Chem. Soc.*, 94 (1972) 5924;
(c) W. H. Pirkle, R. L. Muntz, and I. C. Paul, *J. Amer. Chem. Soc.*, 93 (1971) 2817.
17 (a) M. R. Churchill and K. Gold, *Chem. Commun.*, (1968) 693;
(b) M. R. Churchill and K. Gold, *Inorg. Chem.*, 8 (1969) 401.
18 (a) W. Merk and R. Pettit, *J. Amer. Chem. Soc.*, 89 (1967) 4787;
(b) W. Merk and R. Pettit, *J. Amer. Chem. Soc.*, 89 (1967) 4788;
(c) E. Gil-Av and J. Shabtai, *J. Org. Chem.*, 29 (1964) 257;
(d) S. Sarel, R. Ben-Shoshan, and B. Kirson, *J. Amer. Chem. Soc.*, 87 (1965) 2517.
(e) R. Ben-Shoshan and S. Sarel, *J. Chem. Soc. D.*, (1969) 883;
(f) C. H. De Puy, V. M. Kobal, and D. H. Gibson, *J. Organometal. Chem.*, 13 (1968) 266;
(g) G. N. Schrauzer, P. Glockner, K. I. G. Reid, and I. C. Paul, *J. Amer. Chem. Soc.*, 92 (1970) 4479;
(h) R. Aumann, *Angew. Chem., Int. Ed. Engl.*, 10 (1971) 188, 189, 190;
(i) R. M. Moriarty, C-L. Yeh, and K. C. Ramey, *J. Amer. Chem. Soc.*, 93 (1971) 6709;
(j) R. Victor, R. Ben-Shoshan, and S. Sarel, *Tetrahedron Lett.*, (1970) 4253.
19 M. C. Caserio, *J. Chem. Ed.*, 48 (1971) 782.
20 W. von E. Doering and H. D. Roth, *Tetrahedron*, 26 (1970) 2825.
21 (a) W. R. Dolbier, Jr., D. Lomas, and P. Tarrant, *J. Amer. Chem. Soc.*, 90 (1968) 3594;
(b) W. R. Dolbier, Jr., D. Lomas, T. Garza, C. Harmon, and P. Tarrant, *Tetrahedron*, 28 (1972) 3185;
(c) P. Binger, *Angew. Chem., Int. Ed. Engl.*, 11 (1972) 433;
(d) P. Le Perchec and J. M. Conia, *Tetrahedron Lett.*, (1970) 1587.
22 H. M. Frey, *Trans. Faraday Soc.*, 57 (1961) 951.
23 M. G. Ettlinger and F. Kennedy, *Chem. Ind. (London)*, (1957) 891.
24 (a) F. R. Goss, C. K. Ingold, and J. F. Thorpe, *J. Chem. Soc.*, 123 (1923) 327;
(b) F. R. Goss, C. K. Ingold, and J. F. Thorpe, *J. Chem. Soc.*, 127 (1925) 460.
25 Dr. B. S. Green, private communication.
26 I. S. Krull, *Org. Prep. Proced., Int.*, in press.