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REACTIONS OF DICYCLOPROPYLACETYLENE WITH IRON CARBONYLS

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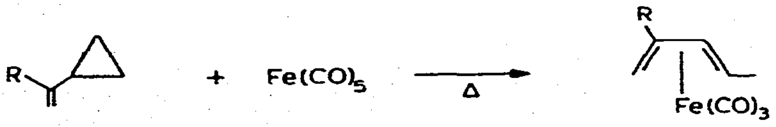
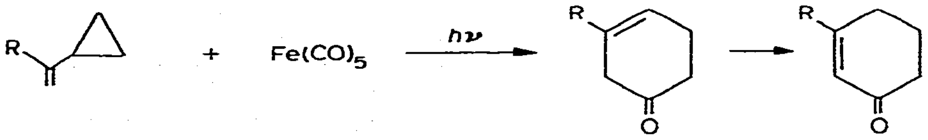
Summary

Dicyclopropylacetylene has been brought into reaction under photolytic conditions with $Fe(CO)_5$ and under thermal conditions with $Fe_2(CO)_9$ and with $Fe_3(CO)_{12}$. It was possible to obtain primarily monoacetylene adducts or bis(acetylene) adducts by modification of the reaction conditions. In addition to products normally obtained from reactions of acetylenes with iron carbonyls, products derived from cyclopropane ring opening were important. Of particular interest are products which resulted from ring opening and carbonyl insertion to yield cyclopentenone derivatives. Experiments were attempted to show the interrelationships between the various products obtained.

In previous studies carried out in this laboratory, we characterized some reactions between iron carbonyl and systems in which cyclopropyl groups are conjugated with C—C π-electron units. When the substrate was a cyclopropylethylene, thermal reaction with $Fe(CO)_5$ yielded butadienes resulting from ring-opening and a hydrogen shift (eqn. 1) [1], while the photochemical reaction led to cyclohexenones derived from ring-opening coupled with carbonyl insertion (eqn. 2) [2]; with cyclopropylacetylene the products of the photochemical reaction were benzoquinone precursors originating from the insertion of carbonyls between two molecules of acetylene while leaving the cyclopropane ring itself intact (eqn. 3) [3]. We showed that the latter reaction is general for a number of terminal acetylenes.



(1)



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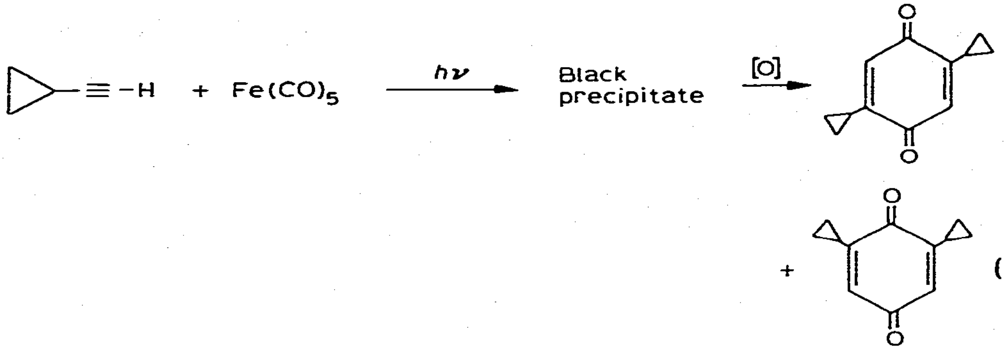

(3)

Here we report the results of a study in which dicyclopropylacetylene (I) was subjected to the action of $Fe(CO)_5$ under photolytic conditions similar to those of the earlier studies and also to $Fe_2(CO)_9$ and to $Fe_3(CO)_{12}$ under thermal conditions. There is a wealth of literature on the subject of acetylene reactions with iron carbonyls [4] and we will try to place our own results into the framework of the existing information with regard to factors which appear to govern the reaction course.

Results

Reactions of I with iron carbonyl at comparable concentrations

When I (~0.05 *M*) and $Fe(CO)_5$ (~0.1 *M*) were irradiated in hexane solution, reaction went rapidly to completion, and work-up gave a complex mixture derived largely from incorporation of two acetylene groups into an organometallic species. The components were separated and the major product under these conditions was the $(C_8H_{10})_2COFe_2(CO)_6$ complex II. Of the other products significant yields were obtained of the ferrole $(C_8H_{10})_2Fe_2(CO)_6$ (III), the trimer $(C_8H_{10})_3COFe_2(CO)_5$ (IV), an orange-red complex of formula $(C_8H_{10})_2COFe_2(CO)_6$ (V), and minor amounts of dicyclopropylmaleoyltetracarbonyliron (VI), tetracyclopropylbenzoquinone (VII), a green complex of formula $(C_8H_{10})_2Fe_3(CO)_8$ (VIII), and a red complex of formula $(C_8H_{10})_2COFe_2(CO)_6$ (IX) (see eqn. 4 and Table 1).

The products in which all cyclopropane rings remain unopened (II, III, IV, VI, VII) were easily identified by analogy to compounds previously prepared * [3—5]. IR and NMR analyses, though, indicated that three of the products (V, VIII, and IX) resulted from opening of one or more of the rings. Their struc-

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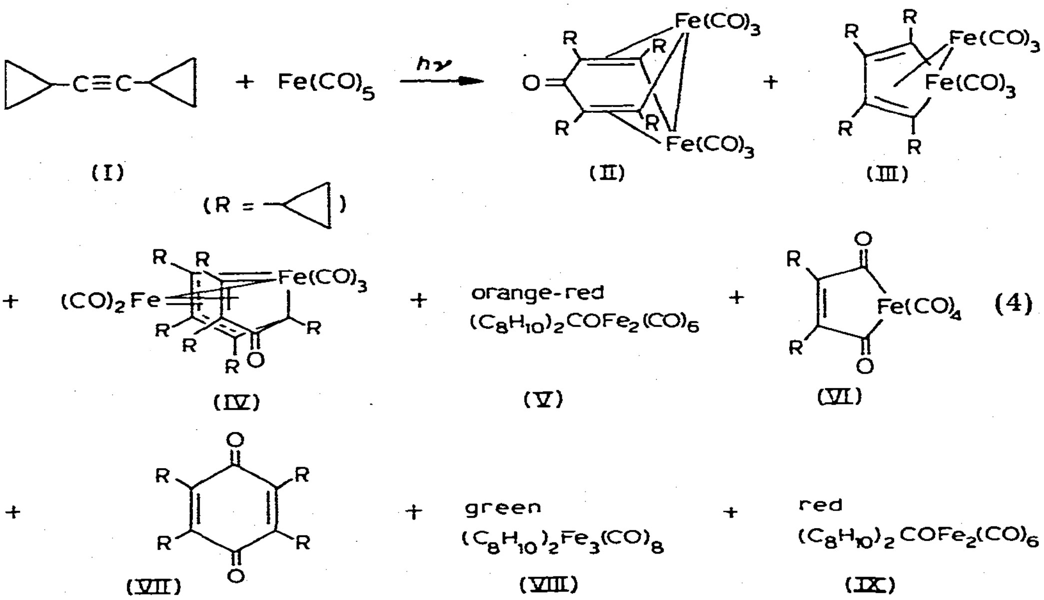
* The structure VI was unequivocally assigned by X-ray determination. (Prof. F.H. Herbstein, Technion, Haifa, Israel). The mass spectra, both by electron impact and field desorption, gave highest weight of (*M* — CO). C, H analyses fall between agreement with $C_8H_{10}Fe(CO)_5$ and $C_8H_{10}Fe(CO)_6$ formulae.

tures will be discussed in the next section.

A similar distribution of the major products (II—V) was obtained when I (~0.1 *M*) was refluxed in pentane with $Fe_2(CO)_9$ (~0.14 *M*), though most of the minor products were not detected (see Table 1). However, when I (0.1 *M*) was treated with $Fe_3(CO)_{12}$ (0.12 *M*) the major product was the orange-red complex V, with significant amounts of the green complex VIII and the ferrole III (see Table 1). Only minor amounts of II and IV were obtained, along with other unidentified products.



Reactions of iron carbonyl with I in low concentration

Because most of the products obtained from reaction of comparable concentrations of I and iron carbonyl incorporate two molecules of I it was desirable to limit the accessibility of I in order to stop the reaction in its earlier stages.

TABLE 1

PRODUCT YIELDS (%) FROM REACTIONS OF DICYCLOPROPYLACETYLENE (I) WITH IRON CARBONYLS IN COMPARABLE CONCENTRATIONS

Product	Iron carbonyl		
	$Fe(CO)_5/h\nu$	$Fe_2(CO)_9/\Delta$	$Fe_3(CO)_{12}/\Delta$
II	47	42	trace
III	6	8	6
IV	8	22	trace
V	13	16	48
VI	<1		
VII	trace		
VIII	<1		7
IX	<1		

Indeed when I (~0.01 *M*) and $Fe(CO)_5$ (~0.05 *M*) were irradiated under conditions similar to those of the earlier experiment, mainly monoacetylene products were isolated. The dominant isolable product was a violet complex of formula $C_8H_{10}Fe_2(CO)_7$ (X), with lesser amounts of a red complex $C_8H_{10}COFe_2(CO)_6$ (XI), the monomer VI observed in the previous reaction, and at least three other less stable monomers (eqn. 5). Again the parallel reaction of I (0.02 *M*) with $Fe_2(CO)_9$ (0.14 *M*) gave a similar distribution of products to the exclusion

$$\mathrm{I} + Fe(CO)_5(xs) \xrightarrow{h\nu} \underset{(\mathrm{X})}{\overset{\text{violet}}{C_8H_{10}COFe_2(CO)_6}} + \underset{(\mathrm{XI})}{\overset{\text{red}}{C_8H_{10}COFe_2(CO)_6}} + \mathrm{VI} + \text{others} \quad (5)$$

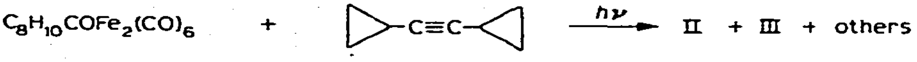
though of VI. In the thermal reaction of I with $Fe_3(CO)_{12}$ comparable dilution of the concentration of I did not lead to monomeric products but rather gave the already observed products III, V and VIII which incorporate two acetylenes.

IR and NMR analyses of complexes X and XI indicate that both cyclopropane rings of the original acetylene I have opened in the course of the reaction. Furthermore, their spectral properties are similar to each other and to complex V, the bis(acetylene) product also derived in part from cyclopropyl ring opening (see Experimental section). A discussion of their possible structures will be given in the following section.

Chemical behaviour of products from I and iron carbonyls

A number of questions arose during this study concerning the origin of some of the products and the possible relationship between them. In an attempt to elucidate this problem the following reactions were carried out.

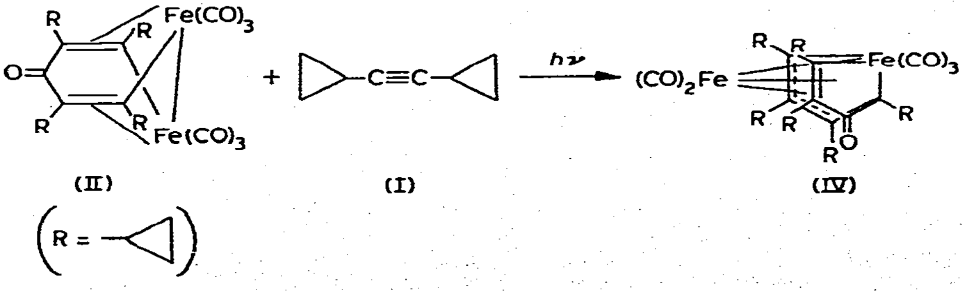
Photochemical reaction of X with an excess of I gave immediately a product mixture from which only II and III but no ring-opened products could be identified (eqn. 6), though in the absence of I, complex X did not undergo photoreaction to any significant extent. There was also no photoreaction of XI in the presence of added I.



(X) (I)

(6)

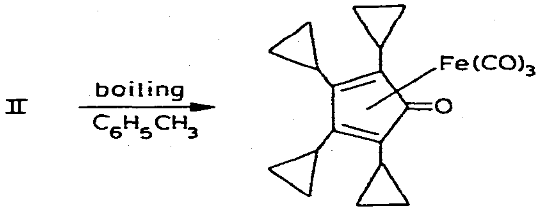
Complex II alone was quite photostable, but in the presence of I the photochemical reaction yielded IV predominantly and in good yield (eqn. 7).



(II) (I) (IV)

(7)

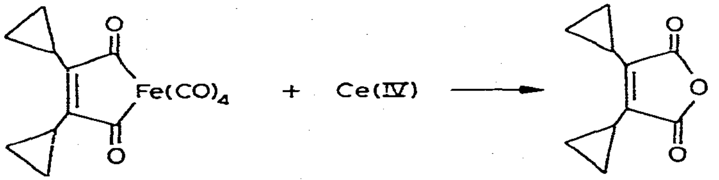
Thermal decomposition of II gave slowly and in good yield tetracyclopropylcyclopentadienone—Fe(CO)$_3$, (XII, eqn. 8) *, a product not detected in the above experiments but isolated as the major product in the high temperature neat reaction between I and Fe$_3$(CO)$_{12}$ [7].



(XII)

The ferrole III was recovered unchanged after extended reflux with Fe$_3$(CO)$_{12}$ in benzene and after irradiation at room temperature with Fe(CO)$_5$.

Oxidation of VI with ceric ion yielded dicyclopropylmaleic anhydride (XIII, eqn. 9). Previous workers effected this type of reaction by oxidation of an analogous complex with nitric acid [5b].



(9)

(VI) (XIII)

Discussion

It is clear that reactions of acetylenes with iron carbonyls may take a number of pathways depending upon the type of substitution, the nature of the reagent and the reaction conditions. We have observed, for example, that on irradiation with Fe(CO)$_5$ in solution, terminal acetylenes give precursors to benzoquinones (eqn. 3) [3], 3-hexyne gives products analogous to II and IV in addition to direct formation of tetraethylbenzoquinone and its tricarbonyliron complex [3], while tolane gives analogs of II and IV, but instead of benzoquinone type products, five-membered ring products of the ferrole of type III and the cyclopentadienone—Fe(CO)$_3$ complex of type XII are important [4a]; while dicarbomethoxyacetylene under these conditions gives predominantly the precursor of the trimer, hexacarbomethoxybenzene [3]. Trimerization is also the main pathway when tolane is heated neat at high temperature (~280°C) [8], yet at reflux temperature in benzene * [6] the products resemble those of

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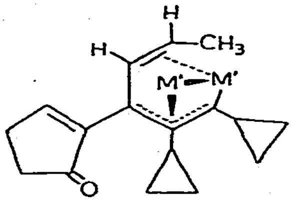
* Photochemical reaction of tolane with Fe(CO)$_5$ gave the analogous II-type product after short reaction time at ambient temperature; but on extended irradiation in refluxing benzene, the major product was the analogous XII-type complex [6].

the photochemical reaction with $Fe(CO)_5$. We have shown that when I was heated neat at ~180°C with $Fe_3(CO)_{12}$ the major products were the cyclopentadienone—$Fe(CO)_3$ (XII) and hexacyclopropylbenzene (XIV) [7]. Neat photoreaction of some dialkylacetylenes with $Fe(CO)_5$ gave benzoquinone—$Fe(CO)_3$ complexes as the only reported products [9].

If we consider only the photochemical reaction of acetylenes with $Fe(CO)_5$ in solution (see Scheme 1) we find similarity between the reactions of I, of tolane, and of dialkylacetylenes in the common formation of complexes of types II and IV, and between I and tolane by the ferrole product resulting from both.

The major deviation, of course, is the ability of I to undergo further reaction by ring-opening processes. At this point the reactions of I find models in the reactions of vinylcyclopropanes with iron carbonyls. Of the products obtained in which ring-opening has occurred (V, VIII, IX, X, XI) only the structure of complex V has so far been unequivocally assigned by X-ray analysis, as shown below [10].



M' = $Fe(CO)_3$

(V)

It can be seen that opening of one of the cyclopropane rings has been coupled with carbonyl insertion leading to cyclopentenone formation while the opening of a second ring occurs with a hydrogen shift and metal coordination to the resulting open chain. The latter process finds analogy in the $Fe(CO)_5$-induced thermal reaction of vinylcyclopropanes (eqn. 2) [1]. The former process differs, however, from the photochemical reaction of vinylcyclopropanes (eqn. 1) [2] by the formation of a five-membered ring rather than a six-membered one. This is an apparent result of the extra unsaturation at the original C—C π-linkage of I. The structural data point to only weak interaction of iron with the olefinic double bond, also borne out by the rather large value of J for the *cis* hydrogens (~9.0 Hz) *.

There is striking resemblance between complexes V and XI on comparison of their spectral data (see Experimental section), particularly their ν(CO)(metal) absorptions, which are almost superimposable in shape and position, and their ^{13}C and ^1H spectra especially for resonances attributed to cyclopentenone sources. Deviations between them are pronounced in the ketonic CO absorption (V, ~1721 cm^{-1}; XI, ~1656 cm^{-1}) and in the NMR pattern of the side chain hydrogens which infers a CH—C—CH—CH_3 linkage for XI rather than a C—CH—CH—CH_3 linkage as in V. We propose the structure XIa for this monoacetylene—iron complex. Its outstanding feature is the proposed coordination (weak by analogy to V) of iron to the cyclopentenone carbonyl group and is substantiated by the

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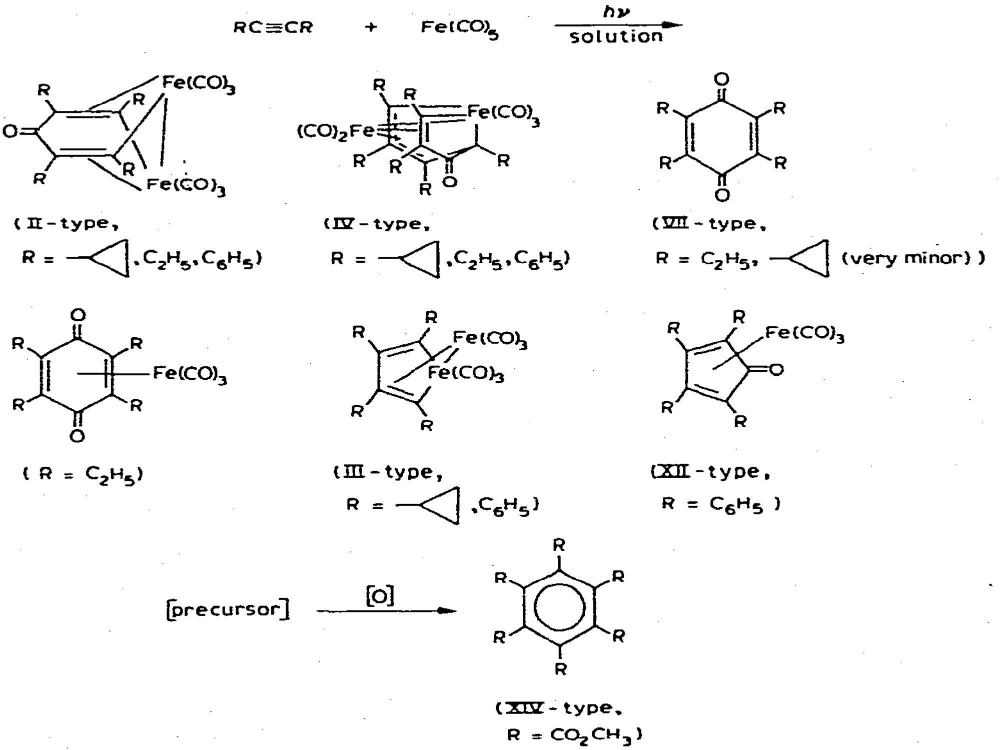
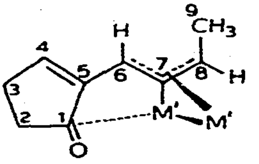
* Coordination of iron carbonyl to C—C π-electron systems generally decreases the H-couplings, J_{cis} and J_{trans} [11].

SCHEME 1. Product chart from photoreactions of various acetylenes (RC≡CR) with $Fe(CO)_5$ (R = cyclopropyl, C_2H_5, C_6H_5 or CO_2CH_3)



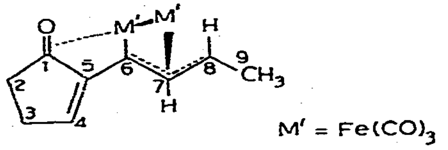
lowered carbonyl absorption in the IR. The "transoidal" relationship between C(6) and H(8) is inferred from the J value of ~9 Hz observed for their coupling in the high resolution CMR spectrum. It is also assumed that the *trans*-relationship between iron and methyl is preferable on steric grounds. Molecular models indicate that the bond distances and angles are not much different between V and the proposed structure XIa.



M' = $Fe(CO)_3$

(XI a)

The violet complex X differs slightly from both V and XI in the metal carbonyl region of the IR, and the very low absorption of the ketonic CO (~1631 cm^{-1}) suggests as in XI its coordination to iron. The presence of a cyclopentenone unit and a CH_3—CH—CH—C linkage is inferred from the PMR spectrum, giving this material a skeletal arrangement related to complex V without the second molecule of dicyclopropylacetylene. With the evidence available we tentatively assign the structure Xa to this compound. The main features of this structure in contrast to those of V and XI are the through-bond (and through-space) distances between the π-double bond and the iron coordinated to it, and the *trans*-relationship between the "allyl" hydrogens on C-7 and C-8. This relationship was made on the assumption that the preferred conformation of the CH_3 group is that of "*trans*" to the carbon chain, and that the observed coupling between H-7 and H-8 ($J \sim 9.4$ Hz) fits better their *trans* orientation in the π-allyl system.



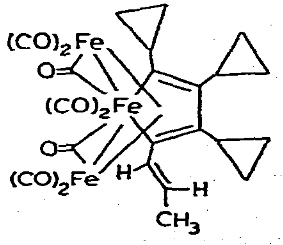
$M' = Fe(CO)_3$

(Xa)

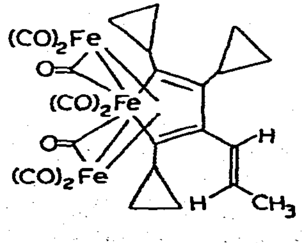
Attempts at converting X into V or XI were not successful. Rather, on irradiation with excess I, complex X appears to serve as a ready source of iron carbonyl which can react with I to give already observed products not involved with ring-opening pathways (eqn. 6). The possibility that such an experiment does not properly duplicate the reaction conditions where X is formed in the presence of excess I will be tested in another study.

Otherwise, it is strongly indicated that complexes V, X and XI are derived from a common precursor which reacts rapidly in the presence of excess I to give V and which in dilute solution results in the isomeric monoacetylene complexes X and XI.

While the structure of the green complex VIII has not yet been determined, there is evidence supporting a ferrole skeleton on which one of the four original cyclopropane rings has opened to a *trans*-propenyl moiety and in which the ferrole iron is linked to two additional irons by bridging carbonyls (see VIIIa and VIIIb). Simpler analogs of the type $(acetylene)_2Fe_2(CO)_8$ are known from reactions of disubstituted acetylenes (e.g., tolane, 3-hexyne), and similarities are seen on comparison of their CO absorptions in the IR spectrum with those of VIII. The presence of residual cyclopropanes is deduced from the IR and the NMR spectra (see Experimental section). The *trans*-propenyl group ($CH_3CH_A{=}CH_B$-) is identified in the NMR spectrum by the lowfield shifts at δ (ppm) 5.20 dd (H_B), 4.65 dq (H_A) and methyl resonance at 1.47 dd. The rather large $J(H_AH_B)$ value (~15 Hz) would indicate a structure in which this olefinic group is not coordinated or is only weakly coordinated to iron [11].



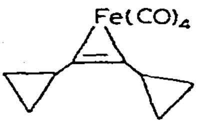
(VIII a)



(VIII b)

The presence of ring opened products from I again draws attention to the apparent difference in reaction pathways between terminal and disubstituted acetylenes, since under the conditions of the photoreaction of I, cyclopropylacetylene reacted like any other terminal-acetylene (eqn. 3).

One is tempted to invoke the intermediacy of a ferracyclopropene complex XV, itself a form of vinylcyclopropane, which should be prone to metal-induced cyclopropane ring-opening followed by carbonyl and/or metal insertion on reaction with additional iron carbonyl to yield the observed products.



(XV)

Experimental section

Melting points were determined on a Thomas Hoover Capillary Melting Point Apparatus and are uncorrected. IR spectra were measured on a Perkin—Elmer 237 Grating Infrared Spectrophotometer. Proton magnetic spectra were taken in this laboratory on a Jeol C-60H spectrometer ($CDCl_3$ solution, TMS standard) and ^{13}C NMR spectra were carried out in the laboratory of Prof. W. von Philipsborn, the University of Zürich (C_6D_6 or $CDCl_3$ solution, TMS standard). Mass spectra were measured on an MAT CH-5 spectrometer.

All new compounds gave satisfactory C—H analyses (A. Bernhardt, Mikroanalytisches Laboratorium, Elbach über Engelskirchen, West Germany, and the Hebrew University Microanalytical Laboratory, Jerusalem, Israel).

The presence of the cyclopropyl group was recognized in the IR spectrum by its characteristic absorptions at ~3080 and ~1030 cm^{-1}.

Materials

Pentacarbonyliron was obtained from the Badische Anilin und Sodafabrik, West Germany. Dicyclopropylacetylene [12], $Fe_2(CO)_9$ [13] and $Fe_3(CO)_{12}$ [14] were prepared according to published procedures.

Photochemical reactions of dicyclopropylacetylene (I) with $Fe(CO)_5$

Irradiations were carried out for ¾ h under nitrogen in pentane or hexane solution using a Philips HPK-125 lamp in a water-cooled quartz immersion vessel. Reaction solutions of (a) comparable concentrations of I and $Fe(CO)_5$ were comprised of 0.50 g (0.005 mol) of I and 1.5 ml (~0.011 mol) of $Fe(CO)_5$ in 115 ml of solution. Reactions of (b) I in low concentration employed 0.2 g (~0.002 mol) of I and 1.5 ml $Fe(CO)_5$ in ~200 ml of solution.

The product mixture was filtered through Celite and the solution evaporated on a rotary evaporator. The residue was taken up in a minimal amount of pet. ether 40—60 and chromatographed on a column of florisil with a layer of neutral alumina above. The first fractions were eluted with pet. ether 40—60 alone and the latter fractions with increasing concentrations of diethyl ether. Fractions were concentrated and the products recrystallized from pentane or hexane. From (a) the products were eluted in the following order: III, VIII, II, VI, IV, VII, V and IX.

Tetracyclopropylferrole—tricarbonyliron (III), yellow-orange plates (pentane), m.p. 106—107°C, (hexane) 2061, 2020, 1997, 1992, 1979 cm^{-1} (metal CO); *m/e* 492 (M^+), δ (^1H, ppm): 1.34—2.12 (1H), 0.54—1.22 (4H).

$(C_8H_{10})_2Fe_3(CO)_8$ (VIII), green-black solid (hexane), m.p. 197° C dec., (hexane) 2056, 2016, 2011, 1998, 1991, 1971, 1888, 1877 cm^{-1} (metal CO); *m/e* 604 (M^+); δ (^1H, ppm): ~0.1 unresolved (2H), ~0.65 unresolved (3H), 1.0—1.6 (7H), 2.2—2.85 (3H), 1.47 dd (CH_3, J ~1.2, 6 Hz), 4.65 dq ($CH_3C\underline{H}=CH$), 5.20(br) d ($CH_3CH=C\underline{H}$, J ~15 Hz).

$(C_8H_{10})_2COFe_2(CO)_6$ (II), red-orange prisms (pentane), m.p. 132°C dec, (hexane) 2071, 2040, 2007, 2001 cm^{-1} (metal CO), KBr 1668 (ketone CO), *m/e* 520 (M^+), δ (^1H, ppm): 0.53—1.67 (9H), 2.53 m (1H).

Dicyclopropylmaleoyltetracarbonyliron (VI), pale orange needles (pentane), m.p. 119°C dec., (hexane), 2108, 2054, 2049, 2028 cm^{-1} (metal CO), (KBr) 1656, 1634 cm^{-1} (maleoyl CO), *m/e* 302 ($(M - CO)^+$), δ (^1H, ppm): 0.78—1.32 (4H), 1.05 m (1H); δ (^{13}C in C_6D_6, ppm): 8.35, 11.97 (cyclopropyl), 173.03, 199.48, 203.24, 239.77.

$(C_8H_{10})_3COFe_2(CO)_5$ (IV), dark purple prisms (hexane), m.p. 127°C dec., (hexane) 2066, 2020, 2011, 2001, 1962 cm^{-1} (metal CO), (KBr) 1646 cm^{-1} (ketone CO), *m/e* 598 (M^+), δ (^1H, ppm): 0.25—3.05 unresolved.

Tetracyclopropyl-*p*-benzoquinone (VII), pale yellow solid (pentane), m.p. 58°C, (KBr) 1646 cm^{-1} (ketone CO), *m/e* 268 (M^+), δ (^1H, ppm): 0.85—1.00 (4H), 1.75 m (1H).

$(C_8H_{10})_2COFe_2(CO)_6$ (V), orange-red plates (hexane), m.p. 155°C dec., (hexane) 2060, 2019, 1992, 1979, 1965, 1957 cm^{-1} (metal CO), (KBr) 1721 cm^{-1} (ketone CO), *m/e* 520 (M^+), δ (^1H, ppm): 0.34—1.35 (8H), 1.40 d (CH_3, J ~6 Hz), 1.96—2.90 (7H), 4.09 d (1H, J ~9 Hz), 7.85 dd (1H); δ (^{13}C in C_6D_6, ppm): 5.58, 7.92, 8.59, 10.44 ($\underline{C}H_2$ of cyclopropyl), 12.91, 24.25 ($\underline{C}H$ of cyclopropyl), 17.75 ($\underline{C}H_3$), 26.63, 35.39 ($\underline{C}H_2$'s of cyclopentenone), 63.30 ($CH_3\underline{C}H=CH$), 82.88 ($CH_3CH=\underline{C}H$), 162.50 ($\underline{C}H$ of cyclopentenone), 69.12, 106.01, 147.94, 179.73 (quaternary carbons), 205.28 (ketone CO), 211.01 (metal CO's).

$C_8H_{10}COFe_2(CO)_6$ (IX), dark red solid (pentane), m.p. 130°C dec., (hexane) 2064, 2036, 2005, 1993, 1985 cm^{-1}, (KBr) 1693 cm^{-1} (ketone CO), no absorption at 3080 characteristic of cyclopropane, *m/e* 520 (M^+). Insufficient amount of material for NMR.

From (b) the elution proceeded in the order: a brown fraction, a grey fraction, VI, XI, X and a very polar yellow fraction (OH apparent at ~3200 cm^{-1} in the IR spectrum).

$C_8H_{10}COFe_2(CO)_6$ (XI), red needles (pentane), m.p. > 140°C dec., (hexane) 2061, 2015, 1991, 1975, 1957, 1948 cm^{-1} (metal CO), (KBr) 1656 cm^{-1} (ketone CO) and no absorption for cyclopropyl, *m/e* 414 (M^+), δ (^1H, ppm): 1.52 d (CH_3, J ~5.8 Hz), 2.48(br) (4H), 4.38 q (1H, J ~5.8 Hz), 4.44 s (1H), 7.68 dd (1H), δ (^{13}C in $CDCl_3$, ppm): 19.30 (CH_3), 28.54, 34.96 ($\underline{C}H_2$'s of cyclopentenone), 61.02, 81.94 ($\underline{C}H—C—\underline{C}H—CH_3$), 160.83 ($\underline{C}H$ of cyclopentenone), 147.54, 182.58 (quaternary carbons), 212.61 (ketone CO), 209.56, 214.05 (metal CO's).

$C_8H_{10}Fe_2(CO)_7$ (X), violet-black crystals (pentane), m.p. > 120°C dec., (hexane) 2060, 2015, 1992, 1974, 1954 cm^{-1} (metal CO), (KBr) 1631 cm^{-1} (ketone CO), *m/e* 414 (M^+), δ (^{1}H, ppm): 1.84 ($C\underline{H}_3$, $J \sim 6.4$ Hz), 2.43—2.63 (2H), 2.86—3.23 (2H), 5.84 split d (CH_3—CH—$C\underline{H}$—C, $J \sim 9.4$ Hz), 7.53 narrow m (1H).

If the pet. ether-insoluble fractions from (a) and (b) above are taken into 90% EtOH and treated with $Ce(NH_4)_2(NO_3)_6$ in excess, it is possible to isolate XIII by workup as described for the degradative oxidation of VI with ceric ion in this section.

Thermal reactions of I with $Fe_2(CO)_9$

The reactions of I with $Fe_2(CO)_9$ were carried out for 1 h under nitrogen in refluxing pentane. Workup of the product mixtures was as described above for the photochemical reactions. From reactions carried out with 0.5 g I (~0.005 mol) and 2.5 g $Fe_2(CO)_9$ (~0.007 mol) in 50 ml of pentane, the following products were obtained: III, II, IV, V, and IX.

From reactions of I in low concentration (0.1 g, ~0.001 mol) and 2.5 g $Fe_2(CO)_9$ (~0.007 mol) in 100 ml pentane, column chromatography gave separation of a brown fraction, XI, X, and a polar yellow fraction.

Thermal reactions of I with $Fe_3(CO)_{12}$

Solutions of I and $Fe_3(CO)_{12}$ were heated at reflux in benzene for 5 h under nitrogen. Workup was carried out as described above.

The products obtained both from reaction of I (0.5 g, ~0.005 mol) with $Fe_3(CO)_{12}$ (3.0 g, ~0.006 mol) in 50 ml of benzene and from that of I (0.1 g, ~0.001 mol) with $Fe_3(CO)_{12}$ (3.0 g, ~0.006 mol) in 150 ml of benzene were (by order of elution from florisil column) III; a red-brown fraction; VIII; II; IV; V; dark red polar fractions.

Irradiation of X with and without I

The $C_8H_{10}Fe_2(CO)_7$ violet complex X (0.1 g) was irradiated with I (0.3 g) for 5 min in ~80 ml pentane. Workup by evaporation and chromatography gave detectable amounts of II and III (by IR and TLC), and trace quantities of other materials.

Similar treatment but in the absence of I led to almost complete recovery of X.

Irradiation of XI with I

A solution of the red complex $C_8H_{10}COFe_2(CO)_6$ (XI) (0.20 g) and I (0.3 g) was irradiated in ~80 ml of pentane for 1 h. Both materials were largely recovered, with no significant product detected.

Irradiation of II with and without I

The red-orange $(C_8H_{10})_2COFe_2(CO)_6$ complex (II) (1.0 g) was irradiated with I (1.0 g) for ~5 h in ~100 ml hexane. After evaporation and chromatography on florisil the following materials were isolated: III in mixture with excess I, recovered II (0.05 g), IV (0.68 g, ~54%) and small amounts of more polar products.

No significant products were observed after similar treatment of II without the addition of I after 2 h irradiation.

Reaction of II in refluxing toluene

A solution of II (0.5 g) was heated in toluene at reflux for 8 h under nitrogen. Chromatography of the product mixture after evaporation yielded complex III (trace), unreacted II (0.15 g) and tetracyclopropylcyclopentadienone $Fe(CO)_3$ XII (0.12 g), m.p. 87—89 and identical by IR to a sample obtained from the reaction of I with $Fe_3(CO)_{12}$ at high temp. [7].

Photochemical and thermal reactions of III with iron carbonyls

The ferrole III (0.5 g) was irradiated with $Fe(CO)_5$ (1.0 g) in ~100 ml pentane for 1 h and was recovered virtually unchanged.

A solution of III (0.5 g) and $Fe_3(CO)_{12}$ (1.0 g) in 50 ml benzene was refluxed for 2 h. Usual workup of the green solution afforded only unreacted starting material.

Degradative oxidation of VI with cerium(IV) ion

The dicyclopropylmaleoyltetracarbonyliron complex VI (~0.1 g) in ~25 ml 80% ethanol was treated with $Ce(NH_4)_2(NO_3)_6$ (~1.5 g) for 2 h with magnetic stirring. The product mixture was diluted with ~200 ml of water and the organic product taken into ether (~50 ml). After evaporation the residue was eluted on a short column of silica gel with petroleum ether/ether from which a moderately polar fraction of dicyclopropylmaleoyl anhydride (XIII) was obtained, white needles or plates (pentane), m.p. 66—67°C, (KBr) 1835 ms, 1761vs (C=O), 1631m, 1611w (C=C), ~1290s(br) (C—O) cm^{-1}, *m/e* 178 (M^+), 135 (base peak), PMR: $\delta < 2.0$ ppm, unresolved spectrum.

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