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PHOTOCHEMICALLY INDUCED 1,5-INSERTION OF CARBON MONOXIDE INTO VINYLCYCLOPROPANE SYSTEMS. A NOVEL SYNTHESIS OF CYCLOHEXENONES MEDIATED BY IRON CARBONYL

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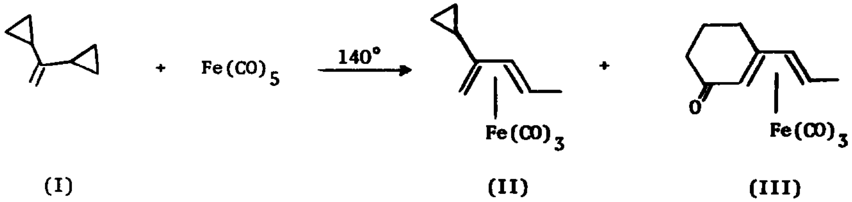
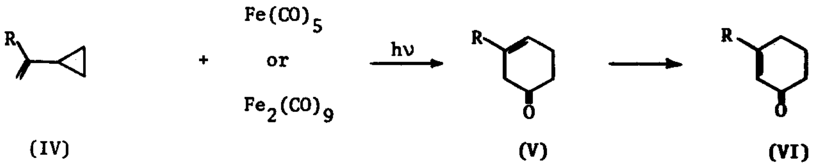
The reactions of some vinylcyclopropanes (IVb, IVc and IVd) with $Fe(CO)_5$ in refluxing solvent have been shown to involve cyclopropane ring-opening with iron complexing to give diene π-complexes as major products[1]. When 1,1-dicyclopropylethylene (I) was similarly exposed to prolonged action of $Fe(CO)_5$, one of the complexes produced was 3-(1'-propenyl)-cyclohex-2-enonetricarbonyl iron (III), evolved from 1,5-carbonyl insertion on opening of the second cyclopropane ring[2].



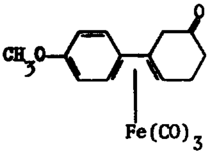
We have found that carbonyl insertion (IV → V → VI) becomes the major reaction pathway when α-substituted cyclopropylethylenes of structure IVa-IVe are irradiated at room temperature in the presence of $Fe(CO)_5$ or $Fe_2(CO)_9$[3].



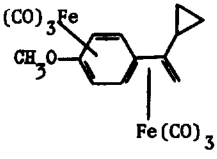
IVa, VIa, R = Me; IVb, VIb, R = phenyl; IVc, VIc, R = p-chlorophenyl;
IVd, Vd, VId, R = p-anisyl; IVe, VIe, R = 2-thienyl

Mps of VIa-VId were in accord with literature values; the hitherto unknown Vd (mp 81-82°; ir: 1715 cm^{-1}) and VIe (mp 60-61°; ir: 1650 cm^{-1}) gave the correct analyses and their ir and nmr spectra were in agreement with assigned structures.

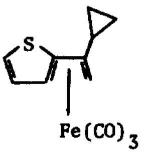
Photolyses were carried out in hexane and benzene solutions of equimolar quantities of organic substrate and iron carbonyl. In all reactions, low yields of organoiron complexes derived from pathways other than carbonyl insertion were detected, with the exception of (IVe), which resulted in fair yields of (IX).



(VII)



(VIII)



(IX)

During the reaction both the direct insertion product (V) and the rearranged product (VI) were detected by ir analysis, but only in the case of IVd was the unconjugated enone (Vd) actually isolated. In the other cases, only the conjugated enones (VI) could be isolated after workup on column chromatography[4].

For R=$\underline{p}$-$CH_3OC_6H_4$ (IVd), an intermediate red complex (60° dec.) of carbonyl insertion is precipitated (in hexane solution). Because of its instability to air and heating and in solution, it was not possible to perform its nmr analysis even at low temperatures. This compound is assigned the formulation 3-(4'-methoxyphenyl)-cyclohex-3-enonetricarbonyl iron (VII)[5] on the basis of its mass spectrum, showing the molecular-ion peak at m/e 342, and its ir analysis (KBr), giving absorptions at (cm^{-1}) 2035, 1967, 1941, 1925 (shoulder) (metal-CO) and at 1710 (ketonic carbonyl). Furthermore, there are no aromatic absorptions, but absorptions for C-C unsaturation (1620, 831 cm^{-1}). Oxidative degradation with Fe^{3+} or Ag^{+} gives Vd, which on acid catalysis rapidly rearranges to VId.

It is assumed that the cyclohexenones VIa-e are formed via a common pathway. The inability to detect intermediates such as VII in all reactions may be attributed to their instability or simply, as in the case of IVa, to the unavailability of electrons[8].

Iron tetracarbonyl complexes appear as minor products in the photoreactions of compounds IVa-e. Their appearance is monitored early in the reaction by ir analysis, and within a short time a more or less steady concentration is reached[9].

For reactions of IVa-d a minute quantity of air-stable yellow complex [ir (hexane) : 2040, 1980, 1965 cm^{-1}] is obtained on chromatography. A sample of this complex derived from IVa gave the parent ion at m/e 222 in mass spectral analysis, equivalent to $Ia{\cdot}Fe(CO)_3$.

Another minor product was detected for reactions of IVb-d[10]. Infrared spectra in hexane solution exhibit five carbonyl absorptions for products from IVb and IVd [ir: 2050, 2040, 1990, 1983, 1965 cm^{-1}] and six absorptions for the product from IVc [ir: 2059, 2043, 2000, 1988, 1982, 1973 cm^{-1}]. Combined fractions of this material from several reactions of IVd were subjected to further analysis. This complex, an air-stable red solid, 102° dec., is assigned the 1-cyclopropyl-1-(4'-methoxyphenyl)ethylene bis-(irontricarbonyl) formulation (VIII) from the following evidence. It shows no C-C unsaturation in the ir(KBr) and gives the parent ion at m/e 454 in mass spectral analysis equivalent to $IVd{\cdot}Fe_2(CO)_6$. Nmr analysis indicates that the cyclopropyl ring is still intact and that the resonances of aromatic protons are no longer present[11].

For R = 2 thienyl (IVe), a second major reaction leads to the formation of an air-sensitive red complex, tentatively assigned as 1-cyclopropyl-1-(2'-thienyl)-ethylene irontricarbonyl (IX) showing molecular-ion peak at m/e = 290 in the mass spectrum and carbonyl absorptions at 2024, 1980 and 1970 cm^{-1}.

Of the two competitive reactions, IV → V → VI and IV → VIII, the latter, though subdued, leads to products of special interest in themselves and is treated separately in the following paper. The efficiency of the photochemical carbonyl insertion reaction (IV → VI) is of general significance and perhaps of synthetic interest. More detailed discussion of these aspects will be given in the full paper.

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REFERENCES

1. S. Sarel, R. Ben-Shoshan and B. Kirson, *J.Am.Chem.Soc.*, **87**, 2517 (1965).
2. R. Ben-Shoshan and S. Sarel, *Chem.Comm.*, 883 (1969).
3. A low yield (~5%) of VId was isolated when IVd was allowed to react with $Fe_2(CO)_9$ without irradiation at room temperature for three hours.
4. For one hour irradiations overall yields of cyclohexenone derivatives relative to initial starting material range from 10% (for IVe) to 30% (for IVa-d) in hexane solution and 55% (for IVd) in benzene solution, with both organic reactant and iron carbonyl unconsumed at quenching in all cases. 1,1-Dicyclopropylethylene under similar reaction conditions gives the cyclohexenone complex (III) in 25% yield.
5. Styrene systems were shown[6] to give rise to diene irontricarbonyl type complexes, involving the π-electrons of both the exocyclic and an adjacent aromatic double bond, in analogy with divinylbenzene[7a] and vinylnaphthalene systems[7b].
6. R. Victor, R. Ben-Shoshan and S. Sarel, following paper.
7. (a) T.A. Manuel, S.L. Stafford and F.G.A. Stone, *J.Am.Chem.Soc.*, **83**, 3597 (1961).
   (b) T.A. Manuel, *Inorg.Chem.*, **3**, 1794 (1964).
8. The insertion is most easily viewed as a donation of carbonyl to an opening cyclopropane ring from an iron tetracarbonyl group complexed at the vinylic position. Under similar reaction conditions cyclopropane rings of compounds such as dicyclopropyl ketone and cyclopropylbenzene are unaffected; therefore, attachment of iron at an α-vinylic position is apparently a prerequisite to cyclopropane ring opening.
9. These complexes (ir C_6H_{12}) : 2080, 2015, 2005 and 1985 cm^{-1} are unstable on work-up and not easily separated from starting material. The only organic substance isolated from its decomposition in solution is the starting material.
10. This minor product appears to be a photoproduct[6]. For the reaction of IVd with $Fe_2(CO)_9$, without irradiation, not even traces of it were produced.
11. Nmr in $CDCl_3$ (τ) : 3.75 (1H, double d), 6.22 (3H, s), 6.44 (1H, m), 6.49 (1H, m), 8.20 (1H, double d), 8.23 (1H, m), 8.60 (1H, d), 8.93-9.51 (4H, m), 10.24 (1H, d). The assignments of resonances for complexes of this type are delineated in the following paper[6].