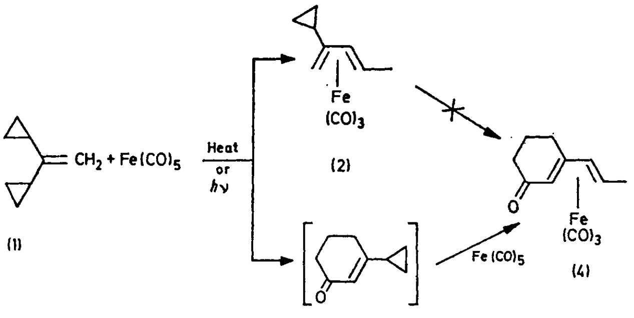
Photoreactions of a Methylene-spirane and Dispirane with $Fe(CO)_5$. σ,π-Complex Formation from a Double Cyclopropane Rearrangement

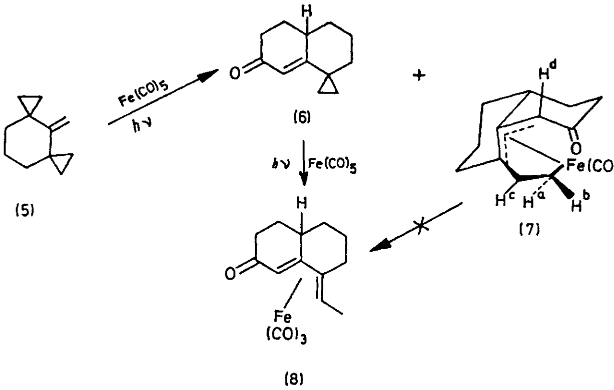
By Shalom Sarel, Avraham Felzenstein, Rae Victor, and Joseph Yovell

(*Department of Pharmaceutical Chemistry, The Hebrew University School of Pharmacy, Jerusalem, Israel*)

Summary The major product from the photoreaction of 4-methylenedispiro[2,1,2,3]decane (**5**) with $Fe(CO)_5$ is shown to be a tricarbonyliron σ,π-complex of structure (**7**), whereas the products from 4-methylenespiro[2,4]-heptane (**9**) and 4-methylenespiro[2,5]octane (**15**) are the respective bi-cyclic enones (**12**)—(**13**) and (**16**).

Our study of the thermolysis[1] and photolysis[3] of vinylcyclopropenes in the presence of $Fe(CO)_5$ has indicated that the small ring may be cleaved *via* two distinctly different reactions; (a) the $Fe(CO)_5$-induced metal insertion into a strained σ-bond coupled with hydrogen migration to provide diene-$Fe(CO)_3$ π-complexes [(**1**) → (**2**)]; (b) the photo-induced cycloinsertion of carbon monoxide across the 'homodienic system' to yield cyclohexenones.† The only example in which these two reactions take place concurrently is that of 1,1-dicyclopropylethylene (**1**), which on on thermolysis with $Fe(CO)_5$ gives rise to a 1 : 1-mixture of (**2**) and (**4**)[1b,4] and on photolysis yields predominantly the cyclohexenone (**4**) product. Since the π-complex (**2**) is inert towards carbon monoxide insertion reactions, the cyclohexenone (**4**)[3] must originate from an alternative independent path, most probably *via* (**3**).





We have now investigated the photoreaction of two olefinic monospiranes, (**9**) and (**15**), and one dispiro-olefin (**5**), with $Fe(CO)_5$.‡ These systems incorporate the energetically most favourable bisected conformation of the vinylcyclopropane system, and (**5**) represents a bridged form of (**1**).

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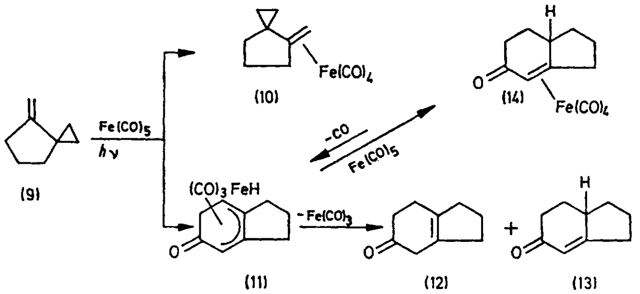
† The ability of vinylcyclopropanes to enter into 1,5-conjugative additions with electrophiles,[4] nucleophiles,[5] and free-radicals[6] and into [2+5] cycloadditions with dienophiles,[7] is well documented.

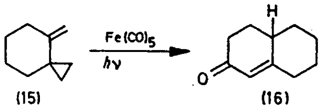
‡ The photoreactions described here were carried out under nitrogen in light petroleum (40—60°) solutions using a 70 W mercury-arc lamp in a water-cooled pyrex immersion vessel.

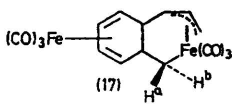
The major product from (**5**) was a yellow tricarbonyliron σ,π-complex (**7**). Its structure was deduced from spectral data [ν (light petroleum) 2056, 1998, 1975 (Fe–CO), 1678 (C=C–CO) cm^{-1}; τ (CCl_4), 10·26 (dd, H^a J 8 Hz), 9·64 (dd, H^b J 8 Hz), § 8·64 (2H, m, H^c) and 6·42 (1H, s, H^d); ^{13}C-H^a J 120 Hz substantiating the sp^3 character of the carbon atom σ-bonded to the metal; m/e 316·0391¶ (calcd. for $C_{15}H_{16}O_4Fe$ 316·0397) and peaks at m/e 288, 260, 232, 176 and 148, corresponding to successive loss of three CO ligands, one Fe atom and one additional CO group].



The minor product from (**5**), m.p. 93°, was assigned the 1,1-ethano-7-keto-$\Delta^{8,9}$-octalin structure (**6**) on the basis of its i.r., u.v., n.m.r. and high-resolution mass spectra.

The photoreaction of (**9**)[10] yielded two major (**13**) and (**14**) and two minor (**10**) and (**12**) products. One of the major products (**14**), a yellow semi-solid material, $\nu_{C=O}$ (neat) 2045, 2035, 1980, 1965 (Fe–CO) and 1675 (C=C–CO) cm^{-1}, decomposed on dissolving in an organic solvent, providing a 1 : 3 mixture of isomeric enones,[11] (**12**) and (**13**), respectively, possibly *via* [(**14**) → (**11**) → (**12**) + (**13**)]. A high yield (75%) of the conjugated enone (**16**) was obtained on photolysing 4-methylenespiro[2,5]octane (**15**) with $Fe(CO)_5$. The physical and spectroscopic properties of (**13**), (**12**) and (**16**) were in accord with literature values.[11]





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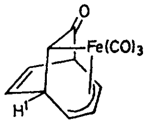

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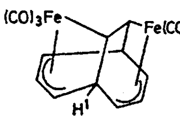

(18)

The difference in structure between the two related substrates, (**1**) and (**5**), has its effect on the chemical stability of intermediates in the $Fe(CO)_5$-induced process. This is reflected in the formation of the dienone-$Fe(CO)_3$ π-complex (**4**) from the former and the nonoccurrence of the (**7**) → (**8**) conversion in the latter case††. Of particular interest is the isolation of the σ,π-complex (**7**) derived from (**5**), the counterpart of which in the (**1**) → (**4**) conversion could not be isolated. Unlike the σ,π-complexes (**18**)[13] and (**19**),[9] the stability of which is attributed to inability of the bridgehead hydrogens H^1 to migrate to form the diene π-complexes,[14] the unexpected stability of (**7**) cannot easily be rationalized.

(*Received*, 10*th September* 1974; *Com.* 1152.)

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§ Cotton and Deganello[8] have noted that the two protons attached to the carbon σ-bonded to the metal in (**17**) are magnetically non-equivalent, both being highly shielded, appearing as dd in ^{1}H n.m.r. (CS_2) τ 8·99 (1H, H^a) and 9·95 (1H, H^b). More examples of high-field shifts of methyl-protons σ-bonded to iron, τ 9·9—10·7, are cited and discussed by Eisenstaadt.[9]

¶ The high-resolution mass spectrum of (**7**) was carried out in the department of Medical Biochemistry, University of Goteborg, Sweden, by the late Professor Einar Stenhagen.

†† *Added in proof:* In a separate experiment in which (**6**) was irradiated with $Fe(CO)_5$ under similar conditions (**7**) could not be detected in the reaction product. Instead (**8**) was isolated in a small quantity; yellow crystals, m.p. 118°, ν(hexane) 2050, 1990, 1970 (Fe–CO) and 1660 cm^{-1} (C=C–C=O); δ(100 MHz, $CDCl_3$) 1·40(1H,s), 1.44(3H,s, Me), 1·50(1H,s), and 1·66—2·87 (11H,m); m/e 316 (M^+; 9%) and 194, ($M-3CO-C_3H_2$) (100%). It is clear that (**6**) is not the precursor of (**7**) and that the formation of (**7**) and (**8**) occurs by different photochemical pathways.

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