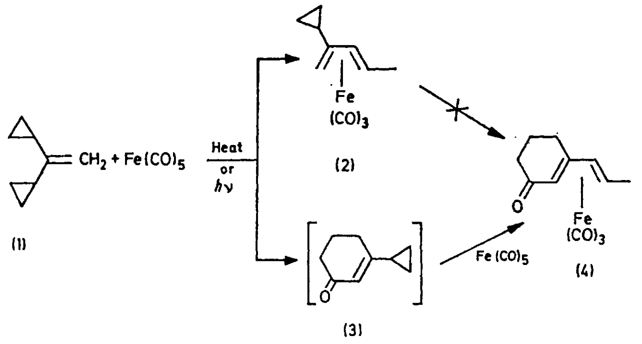
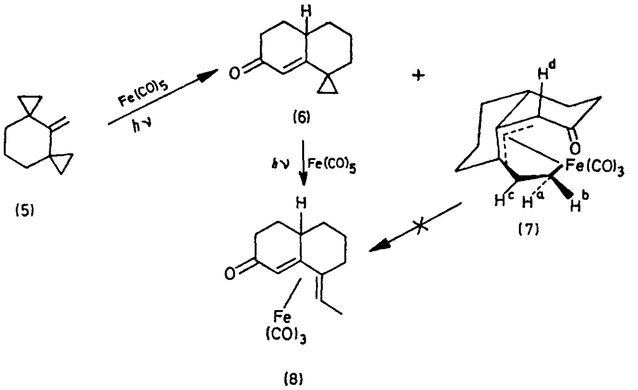
Photoreactions of a Methylene-spirane and Dispirane with $Fe(CO)_5$. σ,π-Complex Formation from a Double Cyclopropane Rearrangement

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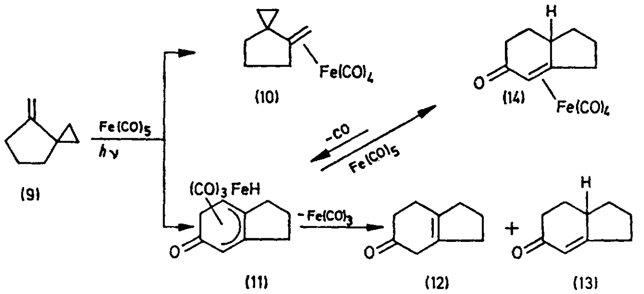
† The ability of vinylcyclopropanes to enter into 1,5-conjugative additions with electrophiles,[4] nucleophiles,[5] and free-radicals[6] and into [2+5] cycloadditions with dienophiles,[7] is well documented.

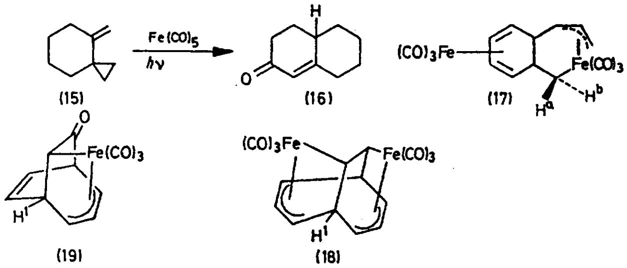
‡ The photoreactions described here were carried out under nitrogen in light petroleum (40—60°) solutions using a 70 W mercury-arc lamp in a water-cooled pyrex immersion vessel.

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]



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.

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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 ^1H 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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