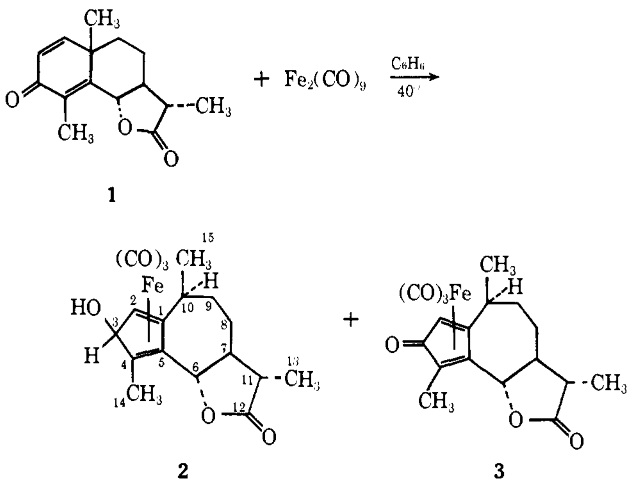

cm^{-1}, and dienone carbonyl stretching at 1607 cm^{-1}. These bands are at different positions from those of the isomeric santonin–iron tricarbonyl complex[3] but very close to those reported for a variety of cyclopentadienone complexes.[4] The mass spectrum of the compound gave a parent peak at *m/e* 386, followed by loss of *four* carbon monoxide units, a process characteristic of cyclopentadienone complexes.[5] The nuclear magnetic resonance (nmr) spectrum of **3** [Varian HA-100, $(CD_3)_2CO$–$CDCl_3$ with tetramethylsilane (TMS) as internal standard] displayed doublet absorption at 1.04 (H-15) and 1.32 ppm (H-13), a singlet at 2.18 ppm (H-14), broad absorption at 3.25 ppm (H-2), and a broad doublet at 4.56 ppm (H-6). These results are expected in light of the reported nmr results for isophotosantonic lactone[6] and some cyclohexadiene and 2,4-cyclohexadienone complexes.[7]

Complex **2**, mp 197.5–199.0° (sealed tube), gave a satisfactory elemental analysis for $C_{18}H_{20}O_6Fe$. *Anal.* Calcd: C, 55.69; H, 5.19; Fe, 14.38. Found: C, 56.02; H, 4.90; Fe, 14.59. The ir spectrum (KBr) was significantly different from **3** in that it showed no carbonyl absorption in the region of 1600–1750 cm^{-1} but a sharp band assigned to -OH stretching appeared at 3310 cm^{-1}. Lactone carbonyl stretching occurred at 1760 cm^{-1} and terminal metal carbonyl stretching bands characteristic of a diene–iron tricarbonyl complex[7–9] were present at 2038 (s), 1972 (s), 1966 (s), 1949 cm^{-1} (sh-m) (under low resolution bands were observed at 2038 and 1963 cm^{-1}). The mass spectrum gave a parent peak at *m/e* 388, followed by loss of three carbonyls. Doublets were observed in the nmr spectrum [$(CD_3)_2CO$–DMSO-d_6] at 1.06 (H-15) and 1.27 ppm (H-13). The vinylic methyl and hydrogen absorbed at 2.07 and 3.06 ppm, respectively. Broad hydroxyl absorption centered at 6.7 ppm disappeared upon addition of D_2O. The protons attached to carbons 3 and 6 gave multiplets at 4.47 and 4.55 ppm. The absorption maximum [223 nm, dioxane] in the ultraviolet spectrum occurred in the region generally observed for diene–iron tricarbonyl complexes.[7,8]

The organic ligand of **3** is the product (isolated as a dimer) of solid-state irradiation of santonin.[2] Thus, $Fe_2(CO)_9$ can effect a rearrangement previously observed only under photolytic conditions. Remarkably, the major product **2** is formed by reduction of the dienone carbonyl by more $Fe_2(CO)_9$. To our knowledge, there is no precedent for such a process although Trost and Bright[10] observed reduction of a carbon–carbon double bond (after dehalogenation) in the reaction of $Fe_2(CO)_9$ with 1,2,5,6-tetrabromopyracene in diethyl ether. We are currently investigating the reactions of **2** and **3** with oxidizing agents.

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Relation between Methylenecyclopropane Cycloadditions and Biradical Fluoroalkene Cycloadditions

Sir:

Dichloromethylenecyclopropane and bicyclopropylidene undergo (2 + 2) thermal dimerizations forming cyclobutanes.[1,2] These dimerizations are remarkably similar to thermal dimerizations of those fluoroalkenes, 1,1-dichloro-2,2-difluoroethylene and tetrafluoroethylene,[3] formally derived by replacing the cyclopropane rings of dichloromethylenecyclopropane and bicyclopropylidene by geminal $=CF_2$ groups. If, as this suggests, methylenecyclopropanes are reactive in the formation of biradicals, then methylenecyclopropanes should also cycloadd in the (2 + 2) manner to conjugated dienes.

Dichloromethylenecyclopropane (**1**) was heated with a large excess of butadiene in a sealed tube for 60 hr at 80°. Bulb-to-bulb distillation followed by vpc separation of the cross-adduct from the butadiene dimer on a 1 m × $^1/_4$ in., 20% Carbowax 20M column gave 84% of **2** (*Anal.* Calcd: C, 54.26; H, 5.69. Found: C, 54.00; H, 5.58). The mass spectrum gave fragments at *m/e* 141 ($C_6H_{10}Cl^+$), 122 ($C_4H_4Cl_2^+$), 54 ($C_4H_6^+$), 51 ($C_4H_3^+$), and 39 ($C_3H_3^+$). The ir spectrum showed absorptions for cyclopropyl at 3010 and 1030 cm^{-1} and for $-CH{=}CH_2$ at 3080, 1860, 1650, 990, and 930 cm^{-1}. The ^1H nmr spectrum integrated for three

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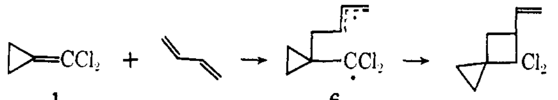
vinyl protons from δ 4.8 to 6.4, one methine proton from 3.4 to 3.9, two methylene protons from 2.1 to 2.4, and four cyclopropyl protons from 0.5 to 1.5. The product is assigned orientation **2** (consistent with the expected most stable biradical intermediate **6** rather than the opposite orientation **3**) on the basis of chemical shifts: the shift of the methine proton, H_m, in **2** (δ 3.4–3.9) compares well to that in **5** (δ 3.1–3.8) but not to that in **4** (δ 2.5–3.2)[4,5] and no particular anisotropy effects are expected from the cyclopropyl ring.[6]



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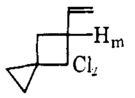

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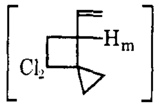

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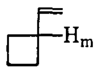

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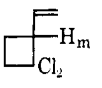

5

A comparison of the properties that fluoroalkenes and methylenecyclopropanes have in common proves interesting. The double bond in tetrafluoroethylene is estimated to be weaker than that in ethylene by 16 kcal/mol on the basis of heats of hydrobromination and chlorination,[7] and about 20 kcal/mol by a thermochemical cycle involving the biradical $\cdot CF_2\text{–}CF_2\cdot$ with a single bond only.[8] Similarly, heats of combustion suggest that the saturation of a double bond in methylenecyclopropanes must be roughly 13 kcal/mol more exothermic than for normal alkenes.[9] A study of bond angles (for example, the F–C–F bond angle in 1,1-difluoroethylene is 109.1°) has led to the conclusion that the carbon orbitals of geminal $=CF_2$ groups in fluoroalkenes are rehybridized to sp^3.[10]

Bond angle deformation appears as a rehybridizing factor in all cyclopropanes. It results in preempting extra p character for the ring bonds, and leaving extra s character, which shows itself in the acidity of the C–H bonds.[11,12]

In ring-fluorinated cyclopropanes the demands of the C–F bonds and of the bent ring bonds for carbon p character cannot be simultaneously met, and large strain energies are observed relative to the unfluorinated compounds.[8]

The most obvious source of rehybridization in the *gem*-difluoroalkenes is the extreme electronegativity of fluorine, which similarly induces a maximum of p character in the orbital used by carbon in bonding to the fluorine. Extra p character in the carbon orbitals of the C–F bonds, as in the cyclopropane ring bonds, must destabilize the double bond by the interplay of two mechanisms. If there is to be a full p orbital available for π overlap in the double bond, then the σ part of the double bond is weakened by being deficient in s character.[13] On the other hand, if the orbitals of the olefinic carbon atom are really rehybridized to sp^3, then there is not a normal p orbital left and the π part of the double bond is severely impaired.

As far as pure electronegativity is concerned, the substitution of CF_3 groups into an alkene should produce an effect equaling or exceeding that of fluorine. 1,1-Bis(trifluoromethyl)-2,2-dichloroethylene (**7**) was

$$(C_6H_5)_3P + (CF_3)_2C{=}O + CBrCl_3 \xrightarrow{\text{under } N_2} \underset{\mathbf{7}}{(CF_3)_2C{=}CCl_2}$$

prepared in 30% yield by heating a bromotrichloromethane solution of triphenylphosphine with an excess of hexafluoroacetone in a sealed tube for 6 hr at 70°. The volatile product isolated by distillation and preparative vpc (20% Carbowax 20M) had a sharp singlet in the ^{19}F nmr at $\phi 60$. The mass spectrum had a parent peak with exact mass 231.9275 (calcd, 231.9281), $(P + 4):(P + 2):P = 0.1:0.64:1.0$ (calcd, 0.1:0.65:1.0), base peak at mass 69 (CF_3^+), and additional peaks corresponding to loss of F, Cl, CF_3, and CCl_2. The gas-phase ir spectrum showed C=C at 1600 cm^{-1} and C—F at 1200–1400 cm^{-1}. 1,1-Bis(trifluoromethyl)-2,2-dichloroethylene (**7**) failed to dimerize or cycloadd butadiene at temperatures as high as 250°.

Evidently a geminal pair of highly electronegative substituents is neither a necessary nor a sufficient condition for reactivity in the biradical mechanism of cycloaddition. From previous observations on the sensitivity of this reaction to structure,[14] three important factors are discernible: (1) exothermicity of double bond opening, (2) accommodation of the odd electrons on the potential biradical, and (3) ease of approach of reactants in formation of the initial new bond. The importance of the third factor is apparent in the field of free-radical polymerization, by the formation of high hydrocarbon polymers only from monomers with terminal methylene groups, and by the low ceiling temperature for isobutylene polymerization. According to these analogies, the difference in hindrance at the site of the initial new bond is a sufficiently important factor to account for the reactivity difference between **1** and **7**.

The behavior of perfluoropropylene[15,16] on dimerization shows that a $=CF(CF_3)$ group is not quite so unfavorable to biradical formation as $=C(CF_3)_2$, and that it may serve as the unattacked or (less favorably) the attacked end of the double bond in biradical formation. The kinetically unfavored head-to-tail dimer accumulates at very high temperatures for thermodynamic reasons.

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