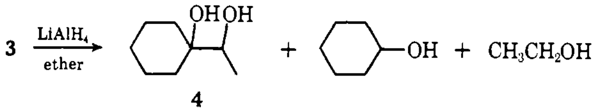
ample, ozonolysis, to completion, of ethylidenecyclohexane (**1**) (0.25 molar) in pinacolone solvent at −45°, using ozone in nitrogen, yielded a colorless, viscous liquid after evaporative removal of most of the pinacolone at low temperature (0–10°). Gpc analysis of this residue indicated the presence of only cyclohexanone and acetaldehyde in approximately equal proportions, along with some remaining pinacolone and a trace of *tert*-butyl acetate. Analysis of the separated pinacolone revealed that it contained 1 equiv (relative to cyclohexanone) of *tert*-butyl acetate.

The neat residue, upon very rapid heating (placed in a hot bath at 170°), emitted a bluish-white light[6] (visible in a darkened room) and erupted violently to discharge acetaldehyde to the atmosphere. Similar heating of a decane solution containing the ozonolysis residue and 9,10-diphenylanthracene, 9,10-dibromoanthracene, or rubrene produced a very bright luminescence with a duration of 1–2 min.[7] Neither ozonides nor ketone diperoxides have been observed to luminesce during thermal decomposition.

The nmr of the crude residue also served to confirm the dioxetane structure. A multiplet centered at δ 5.2 compares well with the methine hydrogen quartet for trimethyl-1,2-dioxetane, reported[8] at δ 5.22. The methyl doublet for **3** at δ 1.22 also compares favorably with the corresponding doublet for trimethyl-1,2-dioxetane found at 1.35.[8] The crude residue was devoid of ozonide and acetaldehyde as determined by nmr, gpc, and infrared analysis. The yield of dioxetane **3** was estimated at 50–75%.

Lithium aluminum hydride reduction of the crude residue further served to confirm the assignment of structure **3** to the residue. Hydride reduction in ether yielded, in the proportions indicated (mole per cent), ethylidenecyclohexane glycol (**4**) (18%), cyclohexanol (40%), and ethanol (31%). For comparison, authentic glycol **4** was prepared by hydrolysis of the epoxide of ethylidenecyclohexane. By contrast, hydride reduction of ozonide[9] or of the presumed 1,2,3-trioxolane[10] does not yield glycols.



We have examined the ozonolysis of a variety of olefins in pinacolone and other Baeyer–Villiger solvents and invariably find that ozonide is not formed and that the dioxetane is detectable. Routinely, the dioxetane is detected by light emission on sudden warming of the ozonolysis residue after removal of the solvent at low temperature. If the dioxetane is lower boiling than the solvent, it is concentrated by low-temperature distillation.[8] Ozonolysis of 2-methylbutene, cyclopentene, or indene in pinacolone results in light emission on warming the reaction residues and glycol formation on hydride reduction.

We have also prepared trimethyl-1,2-dioxetane and **3** by a conventional method[11] and find that hydride reduction yields the corresponding glycol in both cases. The dioxetanes so prepared are identical in all respects with those obtained by ozonolysis.

The observations reported here serve to place our earlier mechanistic proposal[2] on firm ground. It also appears that the technique employed here, *i.e.*, ozonolysis in Baeyer–Villiger solvents, represents a very useful synthetic procedure for the cleavage of double bonds. Rearrangements and abnormal ozonolysis products[12] are minimized and the work-up of peroxidic products is avoided. In addition, it now appears that ozonolysis of olefins in Baeyer–Villiger solvents at low temperature represents a superior method for the synthesis of dioxetanes.

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Diiron Enneacarbonyl Induced Rearrangement of Santonin

Sir:

Santonin (**1**) undergoes several remarkable rearrangements when photolyzed in solution[1] or in the solid state.[2] We now wish to report that treatment of santonin with diiron enneacarbonyl [$Fe_2(CO)_9$] results in a reaction showing the following novel features: (i) nonphotolytic rearrangement of santonin to the iron tricarbonyl complex of a compound believed to be formed on solid-state irradiation; (ii) the first reduction of a carbonyl group by $Fe_2(CO)_9$.

Reaction of santonin (1.17 g) with $Fe_2(CO)_9$ (3.45 g) in rigorously dried benzene at 40° (oil bath temperature) for 4.0–4.5 hr, followed by careful chromatography of the mixture on a Florisil column, gave a pale yellow solid [**2**, eluted with 7:3 petroleum ether (bp 38–52°)–ether] in 10.8–14.1% yield, unreacted santonin (eluted with 7:3 petroleum ether–ether or ether), and a pale yellow solid (**3**, eluted with 9.5:1.0 methylene chloride–ethanol) in 0.22–0.54% yield. The yields are based on the reaction being repeated four times. Both complexes were reasonably air stable.

The minor product, mp 109.0–110.5° (sealed tube), was assigned structure **3** on the basis of elemental analysis (*Anal.* Calcd for $C_{18}H_{18}O_6Fe$: C, 55.98; H, 4.70; Fe, 14.46. Found: C, 56.12; H, 4.69; Fe, 14.18) and spectral results. The ir spectrum (KBr) of **3** showed intense terminal metal carbonyl stretching bands at 2060, 2009, and 1983 cm^{-1} (shoulders at 2022 and 1994 cm^{-1}), lactone carbonyl stretching at 1771

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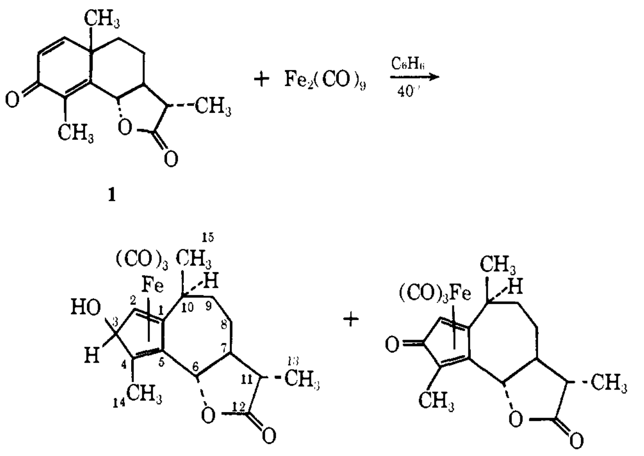

cm^{-1}, and dienone carbonyl stretching at 1607 cm^{-1}. These bands are at different positions from those of the isomeric santonin–iron tricarbonyl complex[3] but very close to those reported for a variety of cyclopentadienone complexes.[4] The mass spectrum of the compound gave a parent peak at *m/e* 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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