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IRONTRICARBONYL COMPLEXES OF DIARYL- HEPTAFULVENES AND SESQUIFULVALENES. THE REACTION OF TROPONEIRON TRICARBONYL WITH DIARYLKETENES.

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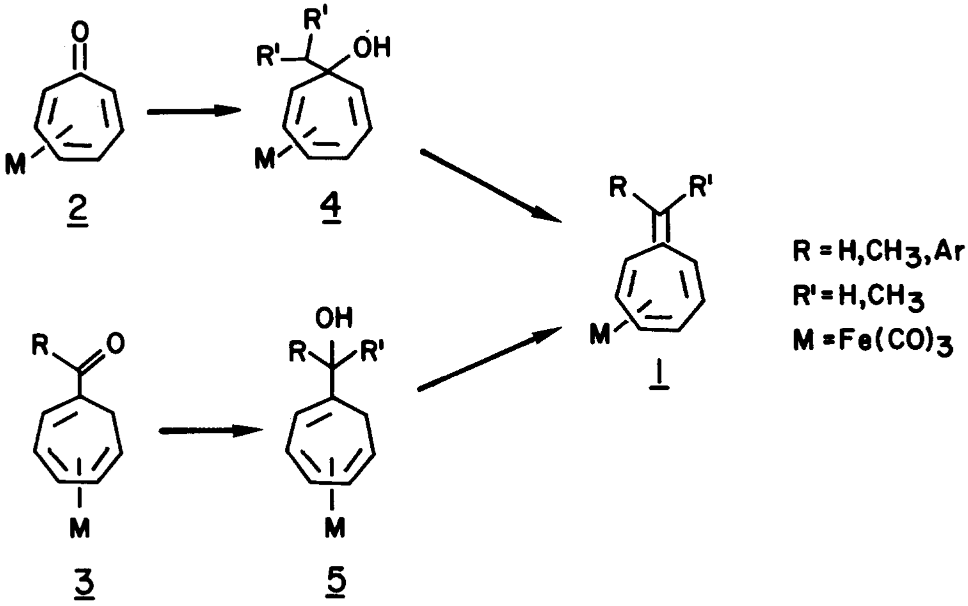
Recently Lewis et al. have shown that heptafulvenes can be stabilized by irontricarbonyl complexation.[1,2] The synthesis of these fulvenes (1) was accomplished via a Grignard or sodium borohydride reduction of tropone (2) and acylcycloheptatriene (3) complexes followed by dehydration of the corresponding alcohols (4 and 5 respectively) over silica gel.



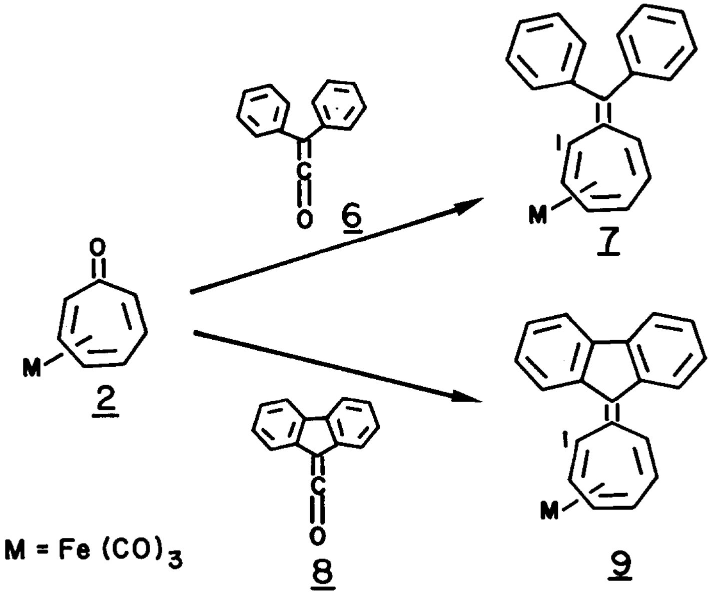
We wish to report a novel one step synthesis of the hitherto unknown irontricarbonyl complexes of two diaryl-fulvenes, 8,8-diphenylheptafulvene (7)[3] and dibenzosesquifulvalene (9),[4] by the reaction of tropone complex 2 with diphenylketene (6) and diphenyleneketene (8) respectively.

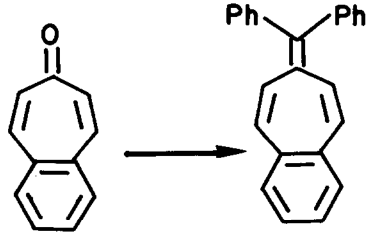
Troponeiron tricarbonyl reacts slowly with excess of freshly prepared diphenylketene,[5] in benzene solution at room temperature, affording after chromatography (alumina, elution with hexane) an orange red crystalline product [mp. 138-140°, 20% yield from CH_2Cl_2 - EtOH] which exhibited in the ir spectrum only iron-coordinated carbonyl absorptions at 2040 and 1940 cm^{-1} with no other carbonyl signals at lower frequencies. The elemental analysis and mass spectrum suggested structure <u>7</u> as the product. This structure was further confirmed from the uv spectrum [λ_{max} (C_6H_{12}) 232 nm (ε 18700), 263 (15900), 333 (12400), 394 (7400)] and the 100MHz pmr spectrum [δ ($CDCl_3$) 3.02 (H_4,bt,J=8); 4.05 (H_1,d,8); 5.34 (H_5,bt,8); 5.6 (H_2,H_3,H_6,m), 7.1(10H aromatic,m)]. This spectrum closely resembles that of the previously prepared heptafulvene complexes.[1]

Similarly, treating <u>2</u> with diphenyleneketene[6] in cyclohexane solution gave deep-red crystals of dibenzosesquifulvalene complex <u>9</u> [mp. 165-166°, from $CHCl_3$ - hexane] whose structure was inferred from the analytical and spectroscopic data [ν_{max} 2045, 1970, 1988 cm^{-1} ; λ_{max} (C_6H_{12}) 253 nm (ε 21400), 275 (15800), 285 (13200), 366 (7600), 454 (14200); pmr: δ ($CDCl_3$) 3.10 (H_4,bt,8); 4.80 (H_1,bd,8) 5.78 (H_2,H_3,m); 5.98 (H_5,dd, 8,11); 6.47 (H_6,d,11) 7.2, 7.7 (8H aromatic,m)].

A plausible mechanism for the formation of the complexed fulvenes (<u>7</u> and <u>9</u>) *involves a [2+2] cycloaddition of ketene and tropone complex to form a spiro β-lactone* intermediate <u>14</u> which decomposes readily under the reaction conditions with loss of CO_2 . The reaction of ketenes with carbonyl compounds to form β-lactons has been previously studied.[7] 3,4-Benzotropone (<u>10</u>) reacts with diphenylketene to give diphenyl-benzoheptafulvene (<u>11</u>).[8] However, tropone reacts analogously only with 8-oxoheptafulvene (<u>12</u>)[9] to form heptafulvalene <u>13</u> but prefers another course with diphenyl-[8] or dichloro-ketene.[10]

Consideration of this regiospecific and periselective cycloaddition by frontier orbital theory is based on the propensity of ketenes to undergo concerted $\pi 2_s + \pi 2_a$ interaction between the ketene HOMO and ketenophile LUMO.[11] Here, the low-lying unoccupied molecular orbital of tropone complex, which is formed by interaction of an e-level of the $Fe(CO)_3$ fragment[12] with tropone π_4 MO,[13] interacts in a favorable $\pi 2_s + \pi 2_a$ manner <u>via</u> its carbonyl group with diphenylketene HOMO. This interaction is qualitatively illustrated by <u>15</u>.





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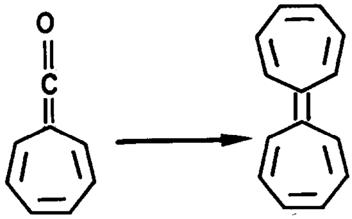

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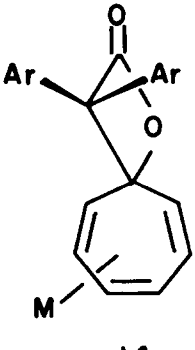

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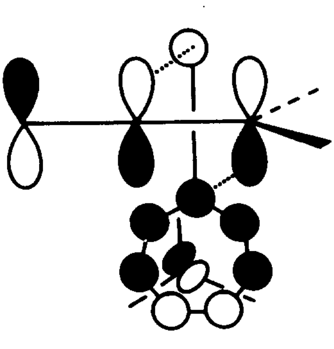

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References and Footnotes

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