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Preliminary communication

ALUMINIUM HALIDE PROMOTED CARBONYLATION REACTIONS: FACILE SYNTHESIS OF BICYCLO[3.2.1]OCT-2-ENE-4,8-DIONE FROM CYCLOHEXADIENE (TRICARBONYL)IRON

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Summary

Under one atmosphere of CO, aluminium halides promote the carbonylation of cyclohexadiene(tricarbonyl)iron to give 2—4-η-7-σ-cycloheptenediyl-1-one-(tricarbonyl)iron, which can be converted in good yield into the title compound.

Previous studies have shown [1, 2] that aluminium halides (AlX_3) react with cyclooctatetraene(tricarbonyl)iron (I) to give the ketonic organometallic complex (II), which affords the previously rather inaccessible tricyclic ketone, barbaralone. The reaction has been found to be general and other polyolefin-(tricarbonyl)iron compounds also react with AlX_3 to give polycyclic ketones [2]. Here we report the reaction of cyclohexadiene(tricarbonyl)iron (III) with aluminium halides, resulting in a ring expansion by the formal insertion of carbon monoxide to give 2—4-η-7-σ-cycloheptenediyl-1-one(tricarbonyl)iron (IV), which in turn, yields the new unsaturated bicyclic diketone (V). We find that the transformation III—IV is greatly enhanced by the presence of free CO, and thus represents an efficient method of functionalization (carbonylation) of the unsaturated hydrocarbon coordinated to a tricarbonyliron unit.

Complex III has been shown [3] to interact reversibly with AlX_3 (X = Cl or Br) over a period of several hours to give the adduct $(CO)_3C_6H_8Fe\rightarrow AlX_3$. However, when a solution of III containing two equivalents of AlX_3 is stirred under nitrogen in CH_2Cl_2 at room temperature for two days, complex IV is obtained in low yield (~9%) the same reaction is carried out under one atmosphere CO, the yield increases markedly to ~55%. The only other compound isolated is unreacted starting material III.

Compound IV is a pale yellow crystalline solid (subl. 40°C, 0.001 Torr) whose structural assignment** is based on IR and NMR studies including double irradia-

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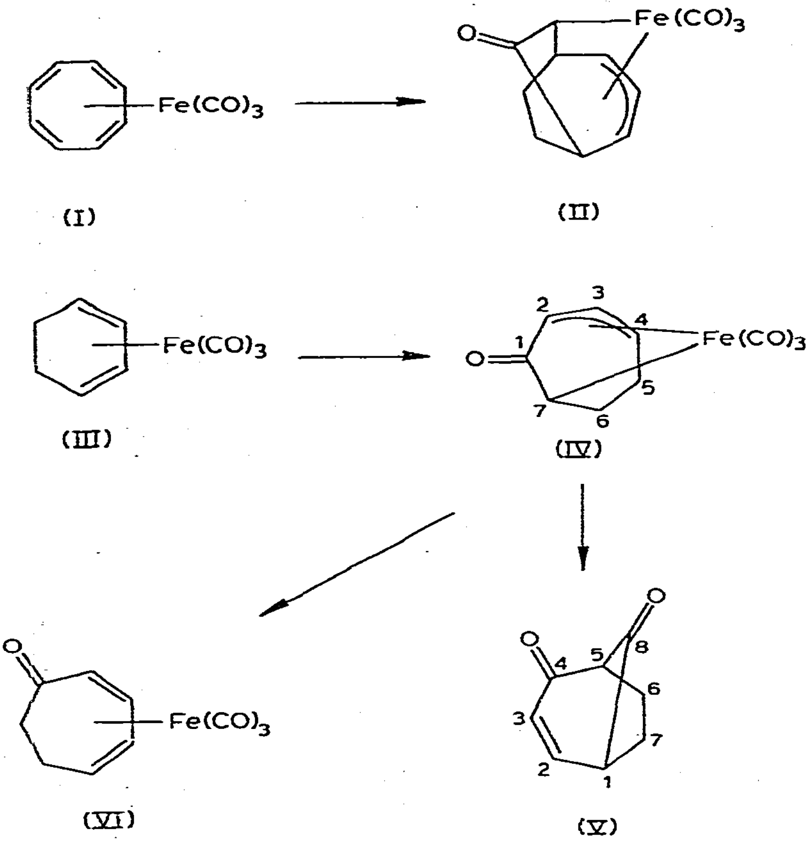
[**] Preliminary results of an X-ray crystallographic study also confirm the structure of compound IV [4].

tion and lanthanide shift experiments: ν_{max} (C_8H_{12}); 2067vs, 2010vs, 1999vs, 1650m cm^{-1}; ^{1}H NMR: δ(C_6D_6-TMS) 1.6m (H55 66), 2.82s(br) (H7), 3.59t(br) (H4, $J_{3,4}$ 8Hz), 4.45t (H3), 5.15d ppm (H2, $J_{2,3}$ 8Hz); ^{13}C NMR δ($CDCl_3$-TMS) 26.3, 34.5 (C5—C6), 56.6 (C7), 78.4, 89.0, 100.2 (C2—C4), 182.4 (C1), 201.5, 206.5 212.1 ppm (Fe—CO). Heating IV in benzene at near reflux temperatures under N_2 gives 25—30% yields of cyclohepta-2,4-dione(tricarbonyl)iron (VI), identified by mass, infrared and NMR spectroscopy [5].

Liberation of the organic fragment from IV is accomplished by heating at 110°C in the presence of CO (100 atm). By this method a 70% yield of V is obtained (distills room temperature, 0.01 Torr) ν_{max} (CCl_4) 1685, 1771 cm^{-1}; ^{1}H NMR δ($CDCl_3$-TMS), 1.7—2.5 mult(br) (H66 77), 3.21t(br) (H1, $J_{1,2}$ 8Hz), 3.41d(br) (H5), 6.27d (H3), 7.46dd ppm (H2, $J_{2,3}$ 9Hz).



A closer examination of the reaction I→II reveals that this conversion is also dependent upon carbon monoxide. In our hands, the yields can be increased from ca. 35% to at least 65% by carrying out the reactions under one atmosphere of CO.

The aluminium halide promoted carbonylation of III provides a convenient route to the bicyclic compound V, and suggests that related reactions may provide an entry into other polycyclic ketones. The enhancement of the reactions by CO suggests that the carbonyl insertion via a σ-bonded organometallic intermediate takes place [6, 7]. Investigation of the mechanism of the reaction and studies of analogous reactions of Lewis acids with other organometallic substrates are currently in progress.

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