(3,4-DIMETHYLENE-1,5-CYCLOHEPTADIENE)TRICARBONYLIRON

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Title compound was obtained by the reaction of 3,4-bisbromomethyl-1,3,5cycloheptatriene with enneacarbonyldiiron, and quenching of an anion formed from the complex and n-butyl lithium with electrophiles afforded 1,6,7,8-tetrahapto (heptafulvene)tricarbonyliron derivatives.

We have reported the synthesis and the cycloadditions of 3,4-dimethylene-1,5-cycloheptadiene $(\underline{1})$.¹⁾ Here we describe the syntheses of (3,4-dimethylene-1,5-cycloheptadiene)tricarbonyliron and 1,6,7,8-tetrahapto (heptafulvene)tricarbonylirons.

Reaction of 3,4-bisbromomethyl-1,3,5-cycloheptatriene $(\underline{2})^{1}$ with large excess of enneacarbonyldiiron in ether afforded a stable (3,4-dimethylene-1,5-cycloheptadiene)tricarbonyliron ($\underline{3}$) in 74% yield as pale yellow liquid; λ_{max}^{EtOH} 220^{Sh} nm (log ε 4.38), 310^{Sh} (3.30); ir (neat) 2040, 1930 cm⁻¹; ¹H-nmr (CDCl₃) δ 0.22 (d, J=2.8 Hz, Ha), 1.83 (d, J=2.8 Hz, Hb), 2.64 (d,t, J=14.9, 5.9 Hz, Hc), 2.99 (d,t, J=14.9, 3.8 Hz, Hd), 5.77 (m, 4H);²) ¹³C-nmr (CDCl₃) δ 26.3 (C-7), 40.7 (C-8), 101.3 (C-3), 129.8 (C-1), 130.8 (C-2), 205.7 (CO); Mass 258 (M⁺), 230, 202, 174. The structure of the complex ($\underline{3}$) can be elucidated by a complete similarity of nmr pattern of exo-methylene part to those of (o-xylylene)tricarbonyliron ($\underline{4}$)³ as well as elemental and mass spectral analyses. Oxidative decomposition of $\underline{3}$ with ceric ammonium nitrate in acetone afforded $\underline{1}$ in quantitative yield.

Reaction of <u>3</u> with 4-phenyl-1,2,4-triazoline-3,5-dione did not give a Diels-Alder adduct but yielded an ene-adduct (<u>5</u>) as colorless crystals, mp 112~115° (d) in 81% yield; ir (KBr) 2045, 2030, 1985, 1970, 1775, 1705 cm⁻¹; ¹H-nmr (CDCl₃) δ -0.09 (d, J=3 Hz, 1H), 0.11 (d, J=3 Hz, 1H), 1.81 (d, J=3 Hz, 1H), 2.11 (d, J=3 Hz, 1H), 5.30 (d, J=4 Hz, 1H), 6.03 (d,d, J=10, 5 Hz, 1H), 6.37 (m, 1H), 6.56 (m, 2H), 7.4 (m, 5H); Mass 405 (M-CO), 377, 349. Addition of a molar equivalent of n-butyl 1ithium in hexane to a solution of <u>3</u> in THF at -35° under argon atmosphere formed an anion (<u>6</u>) as deep reddish solution. However, we could not measure spectroscopic data of the anion because of its instability. Quenching of the anion with water and benzaldehyde afforded (1-methylheptafulvene)tricarbonyliron (<u>7</u>) (28%, reddish liquid) and [1-(2-hydroxy-2-phenylethyl)heptafulvene]tricarbonyliron (8) (5%, reddish viscous liquid), respectively. Quenching of the anion with deuterium oxide instead



of water gave monodeuterio-methyl derivative (9). (7); λ_{max}^{EtOH} 268 nm (log ε 4.34), 342^{sh} (3.31), 468^{sh} (2.18); ir (neat) 2030, 1970 cm⁻¹; ¹H-nmr (CDCl₃) δ 1.46 (s, 1H), 1.66 (Me), 1.89 (s, 1H), 3.31 (d, J=7.6 Hz, H-6), 5.8~6.2 (m, 4H), Mass 258 (M⁺), 230, 202, 174. (8); λ_{max}^{EtOH} 269 nm (log ε 4.28), 344^{sh} (3.32), 474^{sh} (2.29); ir (neat) 3300, 2030, 1960 cm⁻¹; ¹H-nmr (CDCl₃) δ 1.20 (s, 1H), 1.47 (s, 1H), 1.84 (d,d, J=13.5, 6.5 Hz, 1H), 2.12 (bs, 0H), 2.65 (d,d, J=13.5, 6.5 Hz, 1H), 3.24 (d, J=7.5 Hz, H-6), 4.86 (t, J=6.5 Hz, -CHOH), 5.8~6.4 (m, 4H), 7.25 (bs, 5H), Mass 336 (M-CO), 308, 280.

The ¹H-nmr patterns of 7^{-9} agree well with that of 1,6,7,8-tetrahapto (heptafulvene)tricarbonyliron (trimethylenemethane type complex) (10)^{4,5)} but not with 1,2,3,4-tetrahapto complex (11).^{5,6)}

Attempted generation of an anion, which corresponds to iso- π -electronic species of 7,8-dimethylene-1,3,5-cyclooctatriene,⁷⁾ from <u>1</u> was unsuccessful. It is interesting that the acidity of hydrocarbon (<u>1</u>) is remarkably increased by complex formation with irontricarbonyl.

References and Notes

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