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

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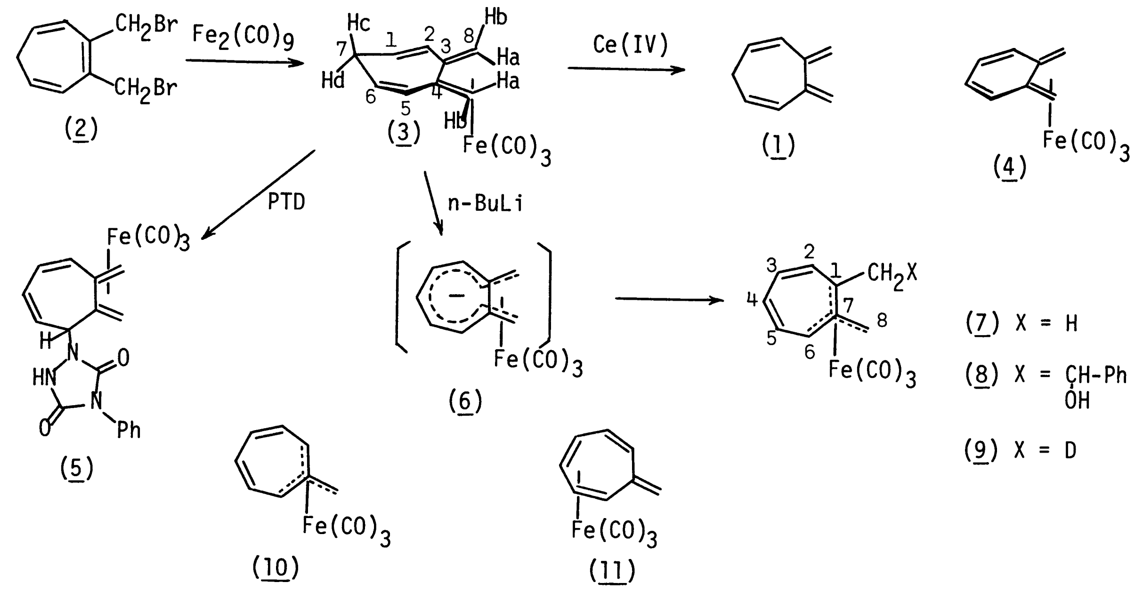
Title compound was obtained by the reaction of 3,4-bisbromomethyl-1,3,5-cycloheptatriene with enneacarbonyldiiron, and quenching of an anion formed from the complex and n-butyl lithium with electrophiles afforded 1,6,7,8-tetrahapto (heptafulvene)tricarbonyliron derivatives.

We have reported the synthesis and the cycloadditions of 3,4-dimethylene-1,5-cycloheptadiene (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 (2)[1] with large excess of enneacarbonyldiiron in ether afforded a stable (3,4-dimethylene-1,5-cycloheptadiene)tricarbonyliron (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}; ^{1}H-nmr (CDCl$_3$) 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] ^{13}C-nmr (CDCl$_3$) 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 (3) can be elucidated by a complete similarity of nmr pattern of exo-methylene part to those of (o-xylylene)tricarbonyliron (4)[3] as well as elemental and mass spectral analyses. Oxidative decomposition of 3 with ceric ammonium nitrate in acetone afforded 1 in quantitative yield.

Reaction of 3 with 4-phenyl-1,2,4-triazoline-3,5-dione did not give a Diels-Alder adduct but yielded an ene-adduct (5) as colorless crystals, mp 112~115° (d) in 81% yield; ir (KBr) 2045, 2030, 1985, 1970, 1775, 1705 cm^{-1}; ^{1}H-nmr (CDCl$_3$) 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 lithium in hexane to a solution of 3 in THF at -35° under argon atmosphere formed an anion (6) 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 (7) (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}; ^{1}H-nmr ($CDCl_3$) 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}; ^{1}H-nmr ($CDCl_3$) δ 1.20 (s, 1H), 1.47 (s, 1H), 1.84 (d,d, J=13.5, 6.5 Hz, 1H), 2.12 (bs, OH), 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 ^{1}H-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 1 was unsuccessful. It is interesting that the acidity of hydrocarbon (1) is remarkably increased by complex formation with irontricarbonyl.

References and Notes

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