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PREPARATION OF ANTI-1-FORMYL-π-ALLYLIRON TRICARBONYL ANION. AN EXAMPLE OF A COMPLEXED π-ALLYL ANION

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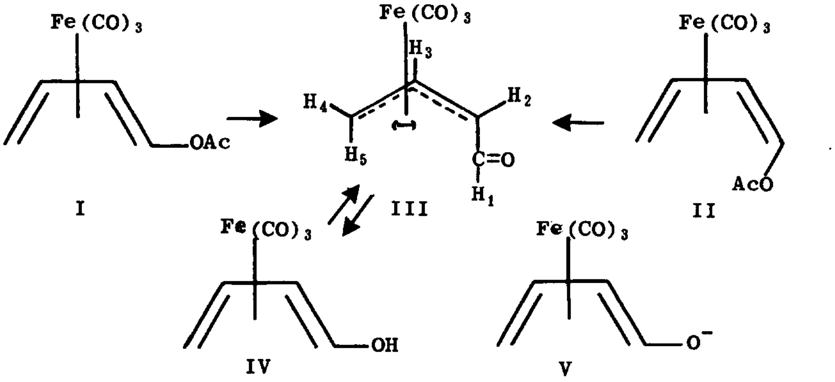
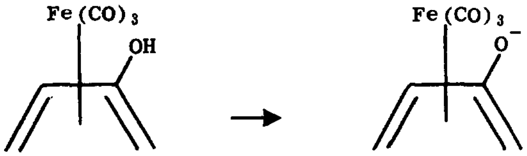
Complexes in which a π-bonded allyl group acts (in other than a formal sense[1]) as a four-electron donor are rare, the only example reported among iron-carbonyl complexes being a perfluoro derivative.[2] We wish to report that such a complex is formed when either *syn*-(I) or *anti*-(II)-1-acetoxybutadieneiron tricarbonyl[3] is hydrolyzed, and that the anion reverts to the enol complex upon protonation or benzoylation.



We were led to suspect the intermediacy of III when we found that the reaction of *anti*-acetate (II) with methyl lithium followed by trapping of the anion with benzoyl bromide leads, even at -60°, to the *syn*-benzoate.[3] We have now found that salts of 1-hydroxybutadieneiron tricarbonyl have the π-allyl anion structure, rather than the alkoxybutadiene structure V. Thus treatment of I in an inert atmosphere with $NaOCH_3/CH_3OH$ followed by removal of solvent, addition of water, filtration and removal of water gives the yellow, air-sensitive sodium salt of III. The salt could be purified by acidification and dissolution in organic solvents followed by re-extraction into aqueous alkali. This procedure gives the sodium salt of III as a pale yellow solid, m.p. (sealed, N_2 filled capillary) 140° (dec.). Reaction of this salt with benzoyl bromide produced, in 65% isolated yield, the known[3] syn-benzoate. Careful acidification of III with boric acid and extraction into benzene gives, after removal of the solvent and sublimation (35-40°/.0005 mm) the beautifully crystalline but extremely air sensitive syn-1-hydroxybutadieneiron tricarbonyl (IV), m.p. 60-63°.

The π-allyl anion structure is assigned to III on the basis of its IR and NMR spectra. In DMSO solution the salt shows carbonyl absorption at 1585 cm^{-1} (the anion of acetylacetone absorbs at ~ 1580 cm^{-1})[4] as well as carbon monoxide absorptions at 1995, 1970, and 1875 cm^{-1}. Its NMR spectrum in DMSO-d_6 is entirely different from that of the acetate or alcohol, showing a low field doublet (6.99 δ), assigned to the aldehyde group (H_1), and multiplets at 5.14 (H_3), 4.33 (H_2), 1.89 (H_4), and 1.30 (H_5). H_4 and H_5 are not coupled to one another, a circumstance which is typical of π-allyl complexes,[5] while butadiene complexes show coupling of about 2.5 Hz for the analogous protons. The syn-isomer of III seems unlikely on chemical grounds, and is also disfavored by the observation of coupling between H_2 and H_4 ($J = 1.5$ Hz). Such coupling could be expected to be absent in the syn-isomer. In addition the observed J_{23} of 5 Hz favors an anti rather than syn structure.

The assignment of the π-allyl anion structure to III is strengthened by the observation that the anion (VII) from 2-hydroxybutadieneiron tricarbonyl[3] (VI), for which such a structure cannot be written, has an IR spectrum which does not show any unusual carbonyl absorption and whose NMR spectrum closely resembles those of the alcohol and acetate, with no absorption below 4.48 δ.



VI VII

Acknowledgment

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