

Disproportionation Reactions of π -Allyliron Carbonyl Halides. A New Route to Trimethylenemethaneiron Tricarbonyl Complexes

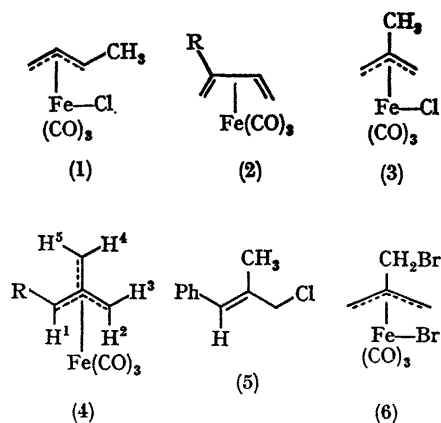
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In their investigation of 1-methallyliron tricarbonyl chloride (1) prepared by the reaction of butadieneiron tricarbonyl (2; R = H) with anhydrous hydrogen chloride, Impastato and Ihrman noted a decomposition reaction leading back to the diene complex.¹ This reaction is not a simple reversal of the addition reaction, but a type of disproportionation, as judged by the formation of butadieneiron tricarbonyl, ferrous chloride, and a mixture of *cis*- and *trans*-but-2-enes. We have now found a similar disproportionation of 2-methallyliron tricarbonyl chloride (3),² which produces trimethylenemethane iron tricarbonyl (4; R = H)³ as well as isobutene, ferrous chloride, and carbon monoxide. This reaction occurs slowly at room temperature in hydrocarbon solvents, or rapidly on heating the dry solid or solution to 100°. A new one-step synthesis of (4; R = H) from commercially available materials was found in the reaction of an excess of 2-methallyl chloride with di-iron nonacarbonyl [$\text{Fe}_2(\text{CO})_9$], followed by fractional distillation without isolation of the intermediate (3). The yield ranged from 14 to 20% of the theoretical based on $\text{Fe}_2(\text{CO})_9$.

A similar method to that used in the one-step synthesis of (4; R = H) was used for the convenient preparation of several substituted trimethylenemethane-iron complexes. The phenyl-substituted allyl halide (5), prepared by sodium borohydride reduction of α -methylcinnamaldehyde followed by treatment with thionyl chloride and pyridine, was treated with an excess of $\text{Fe}_2(\text{CO})_9$ in hexane at 40° until the intermediate allyl complex formed. The solution was then heated under reflux until no more carbon monoxide was evolved. Fractional distillation of the reaction mixture gave a 33% yield of a mixture of $\beta\beta$ -dimethylstyrene (19%)

and 2-methyl-3-phenylpropene (14%) and a 32% yield of phenyltrimethylenemethaneiron tricarbonyl (4; R = Ph), m.p. 63–64°, b.p. 110–114° (0.5 mm.), i.r.: (CCl_4) carbonyl peaks at 2000, 2074 cm^{-1} , n.m.r.: (CCl_4 , Me_4Si) τ 2.89 (s, 5H, ArH), 5.72 (d, 1H, J 3.3 Hz., N-1), 7.13 (d, 1H, J 5.4 Hz., H-5), 7.70 (d, 1H, J 3.3 Hz., H-4), 8.16 (d, 1H,



J 5.4 Hz., H-2), 8.16 (s, 1H, H-3).⁴ A crystallographic analysis of (4; R = H) has been completed by Churchill and Gold.⁵ By the same procedure, a 1:3 mixture (36%) of methyltrimethylenemethaneiron tricarbonyl (4; R = Me) and isopreneiron tricarbonyl (2; R = Me) was obtained by reaction of an excess of $\text{Fe}_2(\text{CO})_9$ with a mixture of 1- and 3-chloro-2,3-dimethylpropene [prepared similarly to (5)]. A possible interpretation of the fact that isopreneiron

tricarbonyl occurs in greater yield (as indicated by n.m.r.) in this reaction is that, in general, diene-iron complexes have greater stability than trimethylenemethaneiron complexes.

The decomposition of the complex (6), obtained by addition of bromine to (4; R = H), might be expected to yield bromotrimethylenemethaneiron tricarbonyl (4; R = Br) by a disproportionation similar to the type already discussed in which one of the C-H bonds of the methyl group

is broken. Instead, a disproportionation involving cleavage of the C-Br bond occurs, so that (4; R = H) is recovered along with 3-bromo-2-bromomethylpropene.

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