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Reactivity of Cumulene Complexes. Two Competing Pathways in Oxidative Solvolysis of Tetramethylbutatriene(hexacarbonyl)diiron

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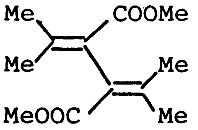
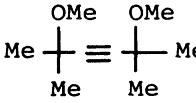
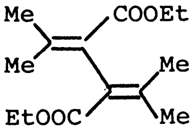
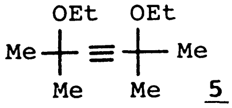
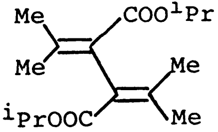
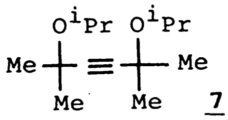
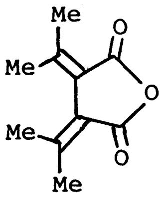
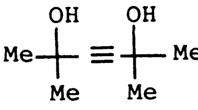
The oxidation of tetramethylbutatriene(hexacarbonyl)diiron in alcohols by ceric ammonium nitrite regioselectively gives diene-diesters and acetylene-diethers in moderate yields. The reaction is the first example showing that both the carbonylation and etherification of cumulene ligand with solvent alcohols take place concurrently on cationic 17-electron species.

Although the liberation of reactive cumulene from cumulene complex seems to provide an effective methodology for organic synthesis, to our knowledge the methodology has been only used for the preparation of 2-acylbutadienes from butatriene(hexacarbonyl)diiron complexes1) by a Friedel-Crafts acylation.2) In the course of the studies of reactivity of cumulene complex by using tetramethylbutatriene(hexacarbonyl)diiron 1, this complex has turned out to be quite inert toward heating and irradiation of light.3) Attempts to liberate a reactive cumulene ligand from the complex 1 have been started by using redox reactions because the complex 1 has an irreversible oxidation wave at E_{pa} = 1.325 V vs. SCE (GC disk, AN/$TBABF_4$) in its cyclic voltammogram. In this communication, we report that the oxidation of the cumulene complex 1 in alcohols by ceric ammonium nitrite (CAN) (Ce(IV) - Ce(III)/AN, 1.299 V)4) regioselectively gives diene-diesters 2, 4, 6 and acetylene-diethers 3, 5, 7 via a cationic intermediate.

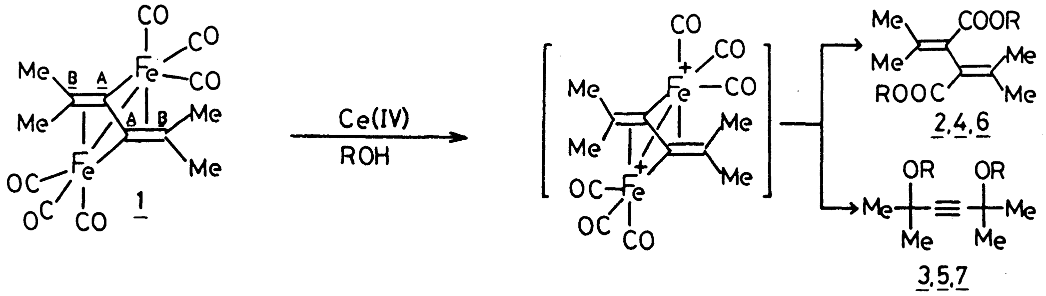
In a typical experiment, CAN (12.1 mmol) was added to a solution of cumulene complex 1 (2.4 mmol) in alcohol (50 cm^3) and benzene (5 cm^3) over 15 min under bubbling of carbon monoxide (CO). The reaction mixture was stirred for an additional 4 h at room temperature. The solution was worked up by dilution with water, ether extraction and chromatography on silica-gel to give diene-diester and acetylene-diether.

Table 1. Oxidative Solvolysis of Tetramethylbutatriene(hexacarbonyl)diiron **1**[a] in the Presence of CAN[b]

Entry	Solvent	Diene,[a] Yield/%[c]	Acetylene,[a] Yield/%[c]
		 **2**	 **3**
1	MeOH/CO	19	66
2	$MeOH/N_2$[d]	22	57
3	MeOH-MeONa[e]/CO	10	—
		 **4**	 **5**
4	EtOH/CO	24	43
		 **6**	 **7**
5	^{i}PrOH/CO	30	18
		 **8**	 **9**
6	$MeCN-H_2O$[f]/CO	47	18
7	MeCN[g]/CO	53	—

a) Satisfactory spectral and analytical data were obtained. b) Reaction conditions (see text): Up to 6 mol equiv. of Ce(IV) were needed; the reaction with 2 mol equiv. of Ce(IV) almost gave recovered material. c) Isolated materials after chromatography. Large amounts of starting complex and small amounts of unknown compounds were found in low-yield reactions. d) N_2 was used instead of CO. e) MeONa (3 mol equiv.) was used. f) MeCN (25 cm^3) - H_2O (25 cm^3). g) After 3 h, the reaction was quenched with water.

The results of the oxidation in alcohols are summarized in Table 1. No attempt has been made to optimize yields, but the yields of acetylene-diethers evidently decline with increasing the bulkiness of alcohols, which means that steric effect of alcohols is more important in the formation of acetylene-diethers than nucleophilicities of them.5,6) The reaction under N_2 shows that the formation of the diene-diester does not require free CO. In the presence of MeONa the diene-diester was selectively obtained in low yield. Acetonitrile (AN) - water system gave anhydride 8 7) as a main product and acetylene-dialcohol 9 as a minor one. The reaction using only AN as a solvent gave selectively anhydride 8 in a moderate yield.



There are two different kinds of reaction sites (A and B) on the cumulene ligand in the complex. Diene-diesters are apparently obtained by the carbonylation containing the migratory insertion of CO 8) at A, while acetylene-diethers by the direct external attack9) of solvent alcohols on the π bond at B. The oxidation of the starting complex with CAN may produce cationic 17-electron species10) having a weakened σ Fe-C bond and a reduced π electron-density in the C=C bond; solvent nucleophilic participation6,11) to this cationic 17-electron species presumably plays a significant role. In the reactions using AN as a solvent (entries 6 and 7) the CO migration proceeds in preference to the direct solvent attack. In addition, entry 7 shows that the yield and selectivity for the CO migration product become higher when AN is used as a neat solvent. These observations indicate that AN assists strongly the CO migration.6)

Further extensions and applications of these reactions are now under investigation.

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3) Cumulene complex 1 was stable in benzene with refluxing for several h and slightly degradated in p-cymene at 150-160 °C. Complex 1 was quite stable in benzene on irradiation by using a high-pressure Hanover mercury lamp; the irradiation in the presence of two mol equivalents of PPh_3 merely gave new two complexes in which one and two carbon monoxide ligands are replaced by PPh_3.

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