Preliminary communication

BUTATRIENE-HEXACARBONYLDIIRON COMPLEXES VIA DEHYDROXYLATION OF UNSATURATED DIOLS BY $Fe_3(CO)_{12}$

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Summary

Butatriene—diiron hexacarbonyl complexes have been prepared simply and in good yield from thermal reaction of $Fe_3(CO)_{12}$ with 2-butynediols or 2,3-diiodo-2-butene-1,4-diols. Geometric isomers of these complexes are usually obtained where such isomerisation is possible. Another product of reaction, derived from loss of HOH from the butynediol, is described.

It has been shown that the coordination of cumulenes to iron carbonyl generally leads to their enhanced stabilization [1—3], and that cumulenes which are not isolable under standard conditions may be effectively trapped in such complexes [1,2a,3]. With proper means of removing the metal function, these complexes become potential sources for the generation or regeneration of cumulenes in situ. To date, cumulene—diiron hexacarbonyl complexes have been prepared by direct reaction of isolable cumulene with iron carbonyl or by metal-induced dehalogenation of unsaturated halides when the free cumulene was not stable [1—3]. The yields from the latter reactions vary but are generally low. Often the starting halo compound is itself the product of a multistep synthesis.

Herein is reported a facile synthesis of butatriene—diiron hexacarbonyl (I) by reaction of readily available 2-butyne-1,4-diols (II) with $Fe_3(CO)_{12}$ (eq. 1 and Table 1). This reaction represents a novel dehydroxylation by iron carbonyl, and the yields of I are quite good with the more substituted diols II.

(II)

(see Table 1 for R's)

(I)*

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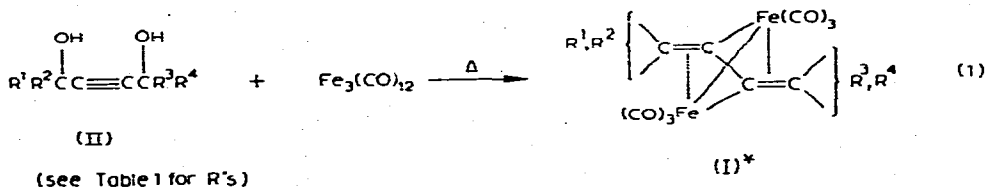
*The structure given has been determined by Bright and Mills for a complex of a butatriene—diiron

TABLE 1

BUTATRIENE–DIIRON HEXACARBONYL COMPLEXES (I)^a FROM $R^1R^2C(OH)C≡CC(OH)R^3R^4$ (II)^b OR $R^1R^2C(OH)Cl=CC(OH)R^3R^4$ (III) AND $Fe_3(CO)_{12}$ IN THF

Substituents	Yield (%) From II	From III	M.p. (°C)	lit. (°C)	PMR (CDCl₃) δ (ppm)	J (Hz)	Infrared ν(CO) (hexane) (cm⁻¹)
(a) $R^1 = R^2 = R^3 = R^4 = H$	<1	14	65–66	66[2a], 69–70[1b]	4.68d(1H), 4.05d(1H)	~1.7	2079, 2040, 2012, 2001, 1983
(b) $R^1 = R^2 = H$; $R^3, R^4 = H, C_6H_5$	8	41	77–78		7.31(br)d(5H), 6.13s(1H), 4.91d(1H), 4.22d(1H)	~1.9	2075, 2035, 2004, 2000, 1982
					[7.25(5H), 6.55s(1H)]	[~1.9]	
(c) $R^1, R^2 = R^3, R^4 = H, CH_3$	0	38	103–104	104[1b]	4.91d(1H), 4.18d(1H)]		2071, 2052, 2000, 1993, 1977
					5.87q(1H), 1.85d(3H),	~6.5	
					[5.14q(1H), 2.01d(3H)]	[~6.6]	
					[5.87q(1H), 5.16q(1H),	[~6.3]	
					2.03d(3H), 1.83d(3H)]		
(d) $R^1 = R^2 = H$; $R^3 = R^4 = CH_3$	14		46–47		4.67d(1H), 4.10d(1H), 2.21s(3H), 1.96s(3H)	~1.1	2076, 2034, 2003, 1997, 1980
(e) $R^1 = R^2 = H$; $R^3 = R^4 = C_6H_5$	38		81–82	oil[3]	7.14–7.66(10H), 4.23d(1H), 4.89d(1H)	~1.4	2071, 2034, 2000, 1996, 1983
(f) $R^1, R^2 = H, CH_3$; $R^3 = R^4 = CH_3$	20		74–76		5.84q(1H), 2.17s(3H), 1.96s(3H), 1.86d(3H)	~6.3	2071, 2033, 2002, 1995, 1977
					[5.19q(1H), 2.13s(3H), 1.99d(3H), 1.96s(3H)]	[~6.3]	
(g) $R^1, R^2 = H, C_6H_5$; $R^3R^4C =$ cyclohexadienyl	41		124–126		7.25m(5H), 6.13s(1H), 1.82–2.47(10H)		2065, 2033, 2000, 1995, 1976
(h) $R^1R^2C = R^3R^4C =$ cyclohexadienyl	76		112–113		1.72–2.35		2061, 2025, 1992, 1981, 1966
(i) $R^1 = R^2 = R^3 = R^4 = CH_3$	66		115–117	108[2a], 118[1b]	2.14s(1H), 1.95s(1H)		2052, 2024, 1997, 1983, 1965

^{a}All new compounds gave M^+ in the mass spectrum, and satisfactory CH analyses. ^{b}Sources of diols: IIa, IIc, III from Fluka; IIb, IId, IIe from Grignard reaction on propargyl alcohol followed by benzaldehyde, acetone, or benzophenone, respectively; IIf from similar reaction with 2-methyl-3-butyn-2-ol, then acetaldehyde; IIg, IIh from similar reaction with 1-ethynylcyclohexanol, then benzaldehyde or cyclohexanone [6], respectively.
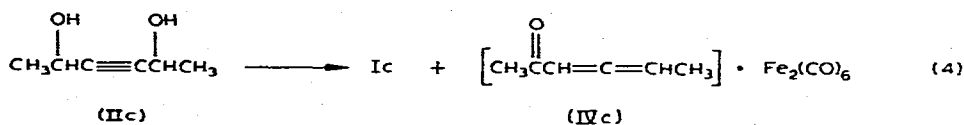
The reaction was effected in a number of solvents, THF giving better yields than methanol or ethanol which in turn were better solvents than benzene. In a typical reaction in THF, II (0.1 mol) and $Fe_3(CO)_{12}$ (0.14 mol) were heated at reflux for 1 h. Workup was carried out by evaporation of the solvent, trituration of the residue by hexane and chromatography on florisilalumina with petroleum ether (40—60°).

The yields of the less-substituted products (e.g. Ia, Ib, Ic) could be increased by modifying II with the addition of a mole of iodine [4] to give the 1,4-dihydroxy-2,3-diiodo-2-butene (III) (eq. 2), and treating this material (0.1 mol) with $Fe_3(CO)_{12}$ (0.25 mol) in THF for 1/2 h (eq. 3 and Table 1).

$$\text{II} \quad + \quad \text{I}_2 \quad \xrightarrow[\text{H}_2\text{O}]{\text{KI}} \quad \begin{array}{c} \text{OH} \\ | \\ \text{R}^1\text{R}^2\text{C} \\ \diagdown \\ \text{C}=\text{C} \diagup ^{\text{I}} \\ \diagup \diagdown \\ \text{I} \text{CR}^3\text{R}^4 \\ | \\ \text{OH} \end{array} \qquad (2)$$

(III)

$$\text{III} \quad + \quad Fe_3(CO)_{12} \quad \xrightarrow{\Delta} \quad \text{I} \qquad (3)$$
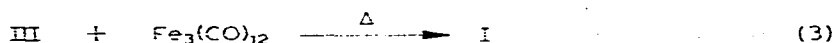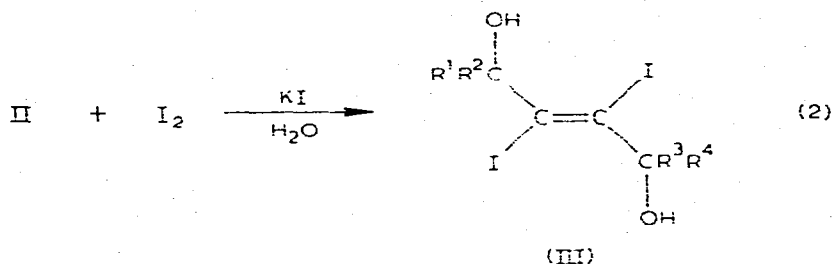
Isomeric mixtures of I were generally obtained when the diol II was substituted with two different groups at one of both of the carbinol carbons; e.g., IIb, IIc, IIf. The predominant isomer which made up more than 70% of the total was removed by fractional recrystallization. NMR data of the less abundant isomer(s) in mixture are given in brackets in Table 1. It is strongly suggested from these data that the preferred conformations of methyl and of phenyl are opposite; i.e., in one, the group is *cis* to iron; in the other, *trans*. The problem of conformation assignment is presently under study by spectroscopic techniques.

Other organometallic complexes could be separated from the reaction mixtures in lower yield. A recurring type IV for cases where at least one R = H is a complex in which the original diol formally loses one molecule of water and adds $Fe_2(CO)_6$. NMR and IR studies point to a ligand derived from a 1,2-hydrogen shift and loss of C—O single bond character, but with metal coordination of a ketonic C=O formed [for example, see eq. 4; IVc, red-brown needles, m.p. 95—96°, ν (cm^{-1}) 2070, 2027, 2003, 1985, 1968 (hexane); 1540s, 1420s, 715s (KBr); δ (ppm) 4.80q (1H, $J \sim$6.5 Hz), 2.76s (1H), 2.05d (3H, $J \sim$6.5 Hz), 2.00s (3H)]. This type of complex and others isolated from the various reactions will be described in a more detailed report.

$$\begin{array}{c} \text{OH} \text{OH} \\ | | \\ \text{CH}_3\text{CHC}\equiv\text{CCHCH}_3 \end{array} \quad \longrightarrow \quad \text{Ic} \quad + \quad \left[\text{CH}_3\overset{\overset{\text{O}}{\|}}{\text{C}}\text{CH}=\text{C}=\text{CHCH}_3 \right] \cdot Fe_2(CO)_6 \qquad (4)$$

(IIc) (IVc)

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References

1 (a) A. Nakamura, P.-J. Kim and N. Hagihara, J. Organometal. Chem., 3 (1965) 7; (b) A. Nakamura, Bull. Chem. Soc. Jap., 38 (1965) 1868.
2 K.K. Joshi, J. Chem. Soc. A, (1966) (a) 594; (b) 598.
3 A. Zimniak and W. Jasiobedzki, Rocz. Chem., 49 (1975) 759.
4 A.W. Johnson, J. Chem. Soc., (1946) 1014.
5 D. Bright and O.S. Mills, J. Chem. Soc. Dalton, (1972) 2465.
6 P.S. Pinkney, G.A. Nesty, R.H. Wiley and C.S. Marvel, J. Amer. Chem. Soc., 58 (1936) 972.