THE REACTIONS OF CYCLOOCTADIENES WITH THE HEXACARBONYLS OF GROUP VI TRANSITION ELEMENTS

G. J. LEIGH* AND E. O. FISCHER
Inorganic Chemistry Institutes of the Technische Hochschule and the University, Munich (Germany)
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INTRODUCTION

Cyclo-octadienes form complexes with many transition elements in low oxidation states[1]. In many of these, the diene probably acts as a chelating agent, and it is therefore not surprising that 1,5-cyclooctadiene, which has the most favourable configuration for chelation, gives rise to the majority of the complexes. A few complexes of 1,3-cyclooctadiene and 1,4-cyclooctadiene are known, and silver is unusual in forming complexes with all three dienes[2].

It also happens that hydrocarbons may isomerise upon complex formation. For example, 2,5-dimethyl-2,4-hexadiene reacts with iron pentacarbonyl to form *trans*-2,5-dimethyl-1,3-hexadieneiron tricarbonyl[3]. Iron carbonyls in particular seem good catalysts for olefin rearrangement, especially when reaction mixtures are irradiated with UV light[4]. In the cyclooctadiene system, rhodium(III) chloride trihydrate reacts with 1,3-cyclooctadiene to give $(1,5\text{-}C_8H_{12}RhCl)_2$ in 66% yield after 24 hours at 50° (ref. 5).

There is one report of a rearrangement with a cyclooctadiene and a Group VI carbonyl. 1,5-Cyclooctadiene reacts with chromium hexacarbonyl in di-*n*-butyl ether to yield the complex of *o*-xylene, $o\text{-}(CH_3)_2C_6H_4\cdot Cr(CO)_3$[6]. This reaction must proceed with hydrogen evolution. In lower-boiling hydrocarbon solvents, another complex, apparently derived from the 1,5-diene, $C_8H_{12}Cr(CO)_4$, is formed[6,7]. The analogous compounds of molybdenum and tungsten were also prepared in low-boiling hydrocarbon solvents[6-9].

The work reported was undertaken in order to clarify the rearrangements and isomerisations of cyclooctadienes upon reaction with Group VI hexacarbonyls.

DESCRIPTION OF RESEARCH

The results of Fröhlich on the conversion of 1,5-cyclooctadiene to complexed *o*-xylene were confirmed. Yields were generally very low (~ 2%), since decomposition set in soon after the yellow *o*-xylene complex was observed in solution. In all cases where di-*n*-butyl ether was used as a solvent, *o*-xylene was also detected in the reaction mixture solution by gas-liquid chromatography. 1,5-Cyclooctadiene was unaffected by refluxing for 24 hours in di-*n*-butyl ether, either alone or in the presence of chromium(III) chloride. It has already been shown that $(1,5\text{-}C_8H_{12})\cdot Cr(CO)_4$ does not yield any *o*-xylene complex when refluxed in di-*n*-butyl ether[6]. This tends to indicate that the conversion to *o*-xylene occurs during complex formation.

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* Present address: Department of Chemistry, Faculty of Technology, University of Manchester (England).

A variety of solvents, reaction temperatures and reactant ratios were investigated, as was also the effect of ultra-violet radiation. Using heptane, octane, dioxane, tetrahydrofuran, dimethoxyethane, dimethoxyethane–diglyme mixtures or dioxane–diglyme mixtures as solvent, only the known complex 1,5-$C_8H_{12}Cr(CO)_4$ was detected as product.

Neither molybdenum nor tungsten hexacarbonyl brought about rearrangement of 1,5-cyclooctadiene in di-*n*-butyl ether, and in this solvent, and in several others (dioxane, dimethoxyethane, and dioxane–diglyme mixtures) the complexes 1,5-$C_8H_{12}M(CO)_4$ [M = Mo, W] were the only products.

1,3-Cyclooctadiene reacts with molybdenum hexacarbonyl in dioxane to give a small yield (1.8 %) of a yellow sublimable solid, which was identified as 1,5-$C_8H_{12}Mo(CO)_4$, which is already known. This was confirmed by allowing a solution in benzene to oxidise in air and examining the products by gas–liquid chromatography. The 1,5-diene was detected, but no 1,3-diene. The 1,3-diene also reacts with tungsten hexacarbonyl in di-*n*-butyl ether, giving a small (4.2 %) yield of 1,5-$C_8H_{12}W(CO)_4$. In contrast, the reaction in octane produces a product (1 %) which may be 1,3-$C_8H_{12}W(CO)_4$. The two tungsten complexes differ considerably in their physical properties.

The 1,3-cyclooctadiene used in these experiments was found to contain a small amount of 1,5-cyclooctadiene. This was estimated (by gas-liquid chromatography) to be 0.6 %. The proportion was not increased by refluxing in dioxane. If all the 1,5-diene impurity had reacted with the carbonyls and if the resultant complex were to be recovered quantitatively, the yields of diene complex should be 1.7 and 2.2 % for the molybdenum and tungsten reactions, respectively. It seems probable, therefore, that a rearrangement of 1,3-diene to 1,5-diene on both molybdenum and tungsten has been observed.

A yellow, crystalline compound was also obtained from chromium hexacarbonyl and 1,3-cyclooctadiene, but in yields too small to allow identification of the product.

DISCUSSION OF RESULTS

It is premature to discuss in detail the mechanisms of reactions which are evidently complex and of which the isolated products represent only a small fraction of the total products. Certain general observations may be relevant, however. A full explanation of the mechanisms is probably related to that of the general isomerisations of olefins in the presence of transition metal compounds and ions, about which there is still vigorous discussion[10, 11]. It seems possible that these occur via the formation of metal–hydrogen bonds. Davies' objections[10] to this concept do not hold if the systems he was discussing involve rapid hydrogen exchange.

The large amount of decomposition observed in these reactions may be due, in part, to reactions involving the formation of metal–hydrogen bonds. Bonds to hydrogen from transition elements of the First Period are generally less stable than those from Second and Third Period elements[12]. It is therefore possible that hydrogen is lost from the chromium system because of the thermal instability of the metal–hydrogen bond. The aromatisation of linear trienes in the presence of metal hexacarbonyls at high temperatures[13] is another example of this type of reaction. In this connection it would be of interest to investigate in detail the reaction of 1,3,5-cyclooctatriene and chromium hexacarbonyl. In hexane solvent this is known to produce $C_8H_{10}Cr(CO)_3$[14]. Work in this field is continuing.

EXPERIMENTAL

All manipulations were carried out in an atmosphere of pure, dry nitrogen, using standard techniques. Infrared spectra were obtained using a Perkin-Elmer PE 21 spectrometer and NMR spectra using a Varian A60 spectrometer.

Preparation of 1,5-cyclooctadienemolybdenum tetracarbonyl from 1,3-cyclooctadiene

Molybdenum hexacarbonyl (1.5 g) and 1,3-cyclooctadiene (2.0 ml) were heated together in dioxane (20 ml) on a bath maintained at 120° for 17 h. During this time 54 ml of gas (measured at room temperature) were evolved. The reaction mixture was cooled, filtered, the residue washed on the filter with hexane and the volatiles removed from the filtrate by distilling them *in vacuo* into a trap cooled with liquid nitrogen. The residue was sublimed twice *in vacuo* at 50°. The yield was 0.033 g (1.8 %). The yellow-brown solid melted at 125–9° (with decomposition) and was identified by its infrared and NMR spectra. For the latter, products from several experiments were combined, chromatographed on silica gel using hexane and benzene as eluents, resublimed and the benzene solution for the NMR measurements then prepared. (Found: C, 45.9; H, 3.83; Mo, 30.5. $C_{12}H_{12}MoO_4$ calcd.: C, 45.58; H, 3.69; Mo, 30.2 %.)

Preparation of 1,5-cyclooctadienetungsten tetracarbonyl from 1,3-cyclooctadiene

Tungsten hexacarbonyl (1.5 g) and 1,3-cyclooctadiene (2.0 ml) were heated together in refluxing di-*n*-butyl ether for 30 h. The reaction mixture was cooled, decanted, and the residue washed with hexane until the washings were colourless. The volatiles were removed from the solution by distilling them *in vacuo* into a trap cooled with liquid nitrogen. The residue from this operation was sublimed *in vacuo*, and the sublimate resublimed *in vacuo* at 70° and again at 50°. The yield of brown product, m.p. 141–2°, was 0.073 g (4.2 %).

The products from two reactions were combined and chromatographed on silica gel, using hexane and benzene as eluents. The product showed two peaks in the NMR spectrum, as is to be expected of a 1,5-diene complex and its infrared spectrum was very similar to that already reported. (Found: C, 35.7; H, 2.98; W, 45.9. $C_{12}H_{12}O_4W$ calcd.: C, 35.66; H, 2.99; W, 45.5 %.)

1,3-Cyclooctadienetungsten tetracarbonyl

Tungsten hexacarbonyl (2.0 g) and 1,3-cyclooctadiene (2.0 ml) were heated together in refluxing octane (20 ml) for 17 h. The reaction mixture was cooled, decanted and the residue washed with benzene until the washings were colourless. The volatiles were removed from the solution by distilling them *in vacuo* into a trap cooled with liquid nitrogen. The residue from this operation was sublimed, yielding 0.023 g (1.0 %) of a dark brown product, melting point 54°, unreacted hexacarbonyl and an oil.

The products from two reactions were combined and chromatographed on silica gel using hexane and benzene as eluents. The purified product, melting point 56–8°, had an infrared spectrum quite different from that of the 1,5-diene complex, a hexane solution showing carbonyl absorptions at 2028(w), 1980(m), 1959(vs) and 1905(vs) cm⁻¹. (Found: C, 37.6; H, 3.05; W, 47.2 %. $C_{12}H_{12}O_4W$ calcd.: C, 35.66; H, 2.99; W, 45.5 %.)

The physical properties of these compounds are detailed in Table 1.

TABLE 1

PHYSICAL PROPERTIES OF COMPOUNDS $C_8H_{12}M(CO)_4$

w = weak, m = medium, s = strong, vs = very strong.

	Literature values	*This work*	
		Compound derived from 1,5-C_8H_{12}	*Compound derived from 1,3-C_8H_{12}*
1,5-C_8H_{12}Mo(CO)$_4$			
Melting point[a]	119–20° (ref. 8) 103° (ref. 5)	129–31°	125–29°
NMR[b,d]	2.43, 4.59 (in carbon tetrachloride)[5]	2.53, 4.69 (in carbon tetrachloride)	
	(1,5-diene at 2.31, 5.33)	1.70, 4.15 (in benzene) (1,5-diene at 2.48, 5.51)	1.78, 4.18 (in benzene)
Infrared (carbonyl region)[c,d]	2050, 1950, 1895 cm⁻¹ (in carbon tetrachloride)[5]	2045(s), 1953(vs), 1905(s), 1873(w)? cm⁻¹ (in hexane)	2041(m), 1992(w)? 1957(vs), 1912(s) cm⁻¹ (in hexane)
1,5-C_8H_{12}W(CO)$_4$			
Melting point[a]	147° (ref. 7) 110° (decomp.)[9]		141–2°
NMR[b]			1.83, 3.86 (in benzene)
Infrared (carbonyl region)[c]	2037, 1946, 1897 cm⁻¹ (in hexane)[8] 2041, 1946, 1898 cm⁻¹ (carbon disulphide)[8]		2041(m), 1953(vs), 1901(s) cm⁻¹ (in hexane)

[a] Melting always accompanied by decomposition. M.p.s. therefore not very reproducible. [b] ppm, *vs.* $(CH_3)_4Si$, 10. [c] ± 4 cm⁻¹ for this work. [d] Solutions in carbon tetrachloride are unstable.

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SUMMARY

The reactions of 1,3-cyclooctadiene and 1,5-cyclooctadiene with chromium, molybdenum and tungsten hexacarbonyls have been investigated. In the appropriate solvents, 1,5-cyclooctadiene rearranges on chromium, yielding *o*-xylene, and 1,3-cyclooctadiene isomerises on molybdenum and tungsten, yielding complexes of the 1,5-diene.

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