Reactions of Some Metal Carbonyls with 1-Methoxycyclohexa-1,4-diene and Related Compounds

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1-METHOXYCYCLOHEXA-1,4-DIENE has been found to react with chromium hexacarbonyl in refluxing nonane to give an 82% yield of the chromium tricarbonyl adduct of benzene. More complex analogues also readily aromatise with loss of methanol: for example 1,4,5,8-tetrahydro-2-methoxynaphthalene gave the adduct, m.p. 97—100°, of 1,4-dihydronaphthalene; 1,4- and 1,5-dimethoxycyclohexa-1,4-dienes gave the adduct of anisole, and the 1,4-dihydro-derivative of œstrone methyl ether 17-ketal gave the adduct of 3-deoxyœstrone 17-ethylene ketal in about 70% yield.

To examine the effects of substitution for selectivity in loss of one of two OMe, 2,4-dimethoxy-1-methylcyclohexa-1,4-diene and 4,5-dimethoxy-1-methylcyclohexa-1,4-diene were treated as described above. The former gave a mixture of about equal parts of the adducts of 2- and 4-methylanisole and the latter a similar mixture of 3- and 4-methylanisole. Substitution of the alkyl group was more successful in enabling removal of a selected oxygen. Competition between OMe and OPrβ resulted in loss of the former: 5-methoxy-1-methyl-4-isopropoxycyclohexa-1,4-diene gave only the adduct of 4-methylisopropoxybenzene. Similarly 1-methoxy-4-isopropoxy- and 1-methoxy-5-isopropoxycyclohexa-1,4-diene both produced the adduct of isopropoxybenzene.

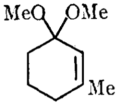
All the complexes are yellow compounds, with two characteristic CO stretching frequencies in their infrared spectra falling in the range 1897—1905, 1965—1978 cm.$^{-1}$, typical of arene–chromium tricarbonyl systems.

The starting materials above were all obtained by metal–ammonia reduction of the corresponding aromatic compounds, but possible extensions are indicated by the conversion of (I) into the toluene adduct under the same conditions.

The carbonyls of molybdenum and tungsten behaved similarly, but the adducts were less stable and not so readily isolated.

Removal of the metal carbonyl was readily accomplished in high yield by photo-oxidation to give the aromatic compounds. The process therefore represents an efficient method of removal of an oxygen from a number of phenols and phenol ethers. Some applications will be described elsewhere.

We are indebted to Professor J. Lewis for helpful advice.



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(*Received, June 29th,* 1965; *Com.* 409.)