The Oxidation of Tungsten Carbonyl in Carbon Tetrachloride

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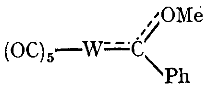
WHILE attempting to generate methoxyphenylcarbene (I) by a thermal or photochemical scission of the tungsten carbonyl derivative (II),[1]† we noticed that carbon tetrachloride solutions of (II) readily decompose yielding phosgene and methyl benzoate. Tungsten hexacarbonyl itself affords phosgene by an even simpler process, which we have studied in some detail.

$Ph—\ddot{C}—OMe$

(I)



$(OC)_5—W\!=\!C(OMe)Ph$

(II)

The transformation occurs most readily under an oxygen atmosphere and is completely inhibited when air is excluded from the reaction system. By-products include the lower oxides of tungsten which are finally converted into WO_3 in the presence of an excess of oxidant.

We believe that phosgene formation is initiated by a reversible reaction between $W(CO)_6$ and O_2 to produce a highly activated oxidizing agent of unknown structure or stoicheiometry. This species then abstracts chlorine from the CCl_4, generating the trichloromethyl radical, which finally reacts with O_2 to yield phosgene.

The following evidence supports the above mechanism.

(1) Light does not accelerate the reaction, therefore the primary intermediacy of $W(CO)_5$, a species whose formation is light-catalyzed and which is involved in most of the chemistry of $W(CO)_6$ derivatives,[2,3] is excluded.

(2) When $W(^{13}CO)_6$ [prepared by the photolysis of $W(CO)_6$ under a ^{13}CO atmosphere;[3] *ca.* 32% ^{13}C labelled‡] is used as the substrate, the phosgene obtained from the reaction is unlabelled ($<1\%$),‡ this means that CCl_4, and not $W(CO)_6$ is the carbon source.

(3) The rate of phosgene production is increased when bromotrichloromethane is used as the solvent, as anticipated, since this is a more efficient precursor to the trichloromethyl radical.[4]

(4) Trichloromethyl radical is known to react with oxygen to afford phosgene.[5]

In conclusion we would emphasize some of the special consequences of this surprising, though simple, discovery. Firstly, the verbal communications between inorganic chemists warning of the nonreproducibility of physical measurements on some metal carbonyls in chlorocarbon solvents are shown to have ample justification; this nonreproducibility is the result of the great susceptibility of these compounds to oxidation. Secondly, a series of reactions requiring initial attack of radical reagents on carbon of $W(CO)_6$ and derivatives is predicted, and the invention of new selective oxidation methods, including our own derived scheme for allylic hydroxylation, is anticipated. Finally, with the aim of determining the importance of trace oxygen as a synergist or inhibitor, a re-investigation of the numerous polymerization systems which use metal carbonyl–halogenocarbon initiators now becomes desirable.

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† This compound is synthesized (60%) by the alkylation of tetramethylammonium benzoylpentacarbonyltungstate(0) (ref. 1) with trimethyloxonium fluoroborate (H. Meerwein, *Org. Synth.*, 1966, **46**, 120). The published diazomethane methylation (ref. 1) affords a poorer product in much lower yield. Trimethyloxonium fluoroborate (m.p. 174—178°) can be prepared conveniently in very high purity by treatment of dimethoxycarbonium fluoroborate (B. G. Ramsey and R. W. Taft, *J. Amer. Chem. Soc.*, 1966, **88**, 3058; H. Meerwein, K. Bodenbenner P. Borner, F. Kunert, and K. Wunderlich, *Annalen*, 1960, **632**, 38) with dimethyl ether in methylene chloride.

‡ Isotopic analyses were carried out with an AEI MS902 mass spectrometer. The phosgene was analyzed as the diphenyl carbonate derivative.

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