Dimerization and Condensation of Pentane-2,4-dione by $MOCl_4$ [M=Mo or W]

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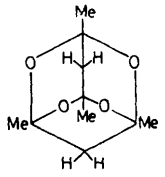
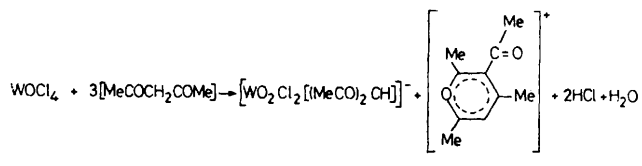
Summary Tungsten(VI) oxide tetrachloride reacts with pentane-2,4-dione to form a salt whose single crystal *X*-ray structure shows a dichloro-dioxopentane-2,4-dionato-tungsten(VI) anion and a 2,4,6-trimethyl-3-acetyl-pyrylium cation; the analogous reaction with molybdenum(VI) oxide tetrachloride yields 1,3,5,7-tetramethyl-2,4,6,8-tetraoxa-adamantane.

WITH dilute solutions of pentane-2,4-dione, $WOCl_4$ yields $WOCl_3$ $(MeCO)_2CH$[1] *via* a solvolysis reaction and $MoOCl_4$ is reduced to give $MoOCl_3(MeCO)_2CH_2$.[2] In studies of solvolysis reactions involving $MoOCl_4$ and $WXCl_4$ (X = O,S,Se) we have now treated these species with undiluted pentane-2,4-dione.



(I)

A white crystalline product (m.p. 124—125°) is formed in the reaction with $MoOCl_4$. Elemental analysis, mass and n.m.r. spectroscopy show the product to be 1,3,5,7-tetramethyl-2,4,6,8-tetraoxa-adamantane (I) formed by the dimerization of two molecules of pentane-2,4-dione. The mass spectrum has a parent ion of mass number 200 and a breakdown pattern consistent with the formulation. The n.m.r. spectrum ($CDCl_3$) has two singlet resonances in the ratio 3:1 at τ 8·63 and 8·30 (Me_4Si standard) which we assign to methyl and methylene resonances respectively. The i.r. spectrum of (I) unlike that of pentane-2,4-dione does not exhibit bands attributable to $\nu_{C=O}$, $\nu_{C=C}$, or ν_{OH}. Previous attempts to dimerize pentane-2,4-dione have been unsuccessful.[3]



SCHEME

From the analogous reaction with $WOCl_4$, a yellow crystalline product was obtained in good yield, of formula $C_{15}H_{20}Cl_2WO_6$. The crystals are monoclinic, space group $P2_1/n$, a = 9·431(8), b = 26·052(20), c = 7·700(8) Å, β = 91·20(10)°, U = 1891·5 Å^3, M = 550·06, D_c = 1·93, D_m = 1·91, Z = 4.

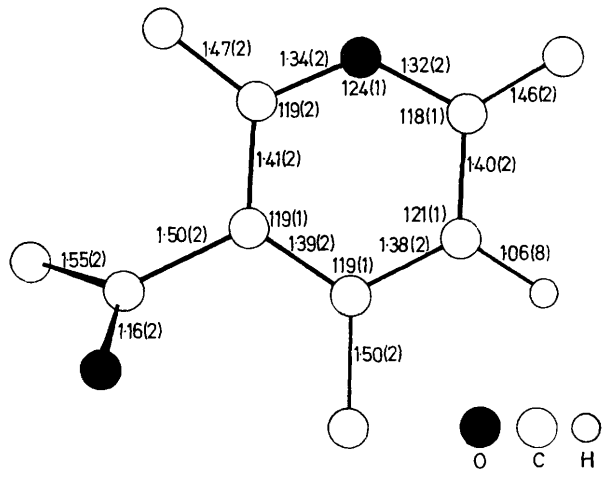


FIGURE 1

Intensities of 2268 independent reflections above the background were measured with $2\theta < 50°$ using Zr filtered Mo-K_α radiation on a G.E.XRD5 Manual Diffractometer by the stationary crystal-stationary counter method. The structure was solved by Patterson and Fourier methods, and refined by full-matrix least squares methods, (W,Cl,O,C anisotropic, the two trigonal H isotropic) to obtain a conventional R factor of 0·045. The methyl hydrogens were not included. An absorption correction (μ = 66·75 cm^{-1}) was made.

The structure [Figures (1) and (2)] consists of $[C_{10}H_{13}O_2]^+$ and $[C_5H_7Cl_2WO_4]^-$. In the anion the tungsten is in a six-co-ordinate distorted octahedral environment. The bond lengths are of comparable length to those in WO_2Cl_2 (2·31 Å)[4] while the terminal tungsten–oxygen bonds are of similar length to that measured by electron diffraction for

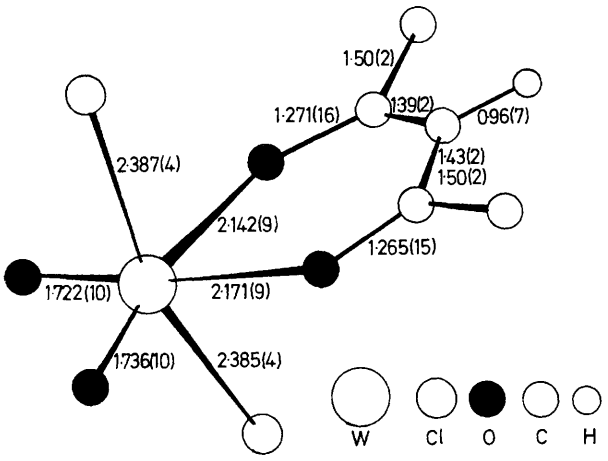


FIGURE 2

$WOCl_4$ (1·684 Å)[5] and by *X*-ray diffraction of a $WOSCl_2$ adduct (1·71 Å).[6] The bond lengths and angles of the chelate ring are similar to those of related species.

The cation is a substituted pyrylium species, 2,4,6-trimethyl -3-acetyl pyrylium. Pyrylium rings are isoelectronic with benzene and thus show aromatic character.[7] Thus the carbon–carbon and carbon–oxygen bond lengths are intermediate between values found for single and double bonds, and the ring approximately planar (the maximum deviation of a contributing atom from the ring plane being 0·04 Å).

The overall condensation and solvolysis reaction can be represented as in the Scheme.

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