1126. *The Actions of Halogens on Phosphine-substituted Group VI Metal Carbonyls. Part II.*[1] *A Novel Synthesis of Some Phosphine Oxide Complexes*

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The action of excess of halogens on some triphenylphosphine and 1,2-bis-diphenylphosphinoethane (diphos) derivatives formed from hexacarbonyl-molybdenum and -tungsten has been investigated. On treatment with excess bromine the complexes $Mo(CO)_4(PPh_3)_2$ and $Mo(CO)_3(PPh_3)_3$ both yield a mixture of the Mo^V and Mo^{VI} phosphine oxide complexes $MoOBr_3,2Ph_3PO$ and $MoO_2Br_2,2Ph_3PO$ after exposure to moist air. With chlorine, the complex $MoOCl_3,2Ph_3PO$ is isolated. Oxidation of the diphosphine complexes, $Mo(CO)_4(diphos)$ and $Mo(CO)_2(diphos)_2$, gives the corresponding oxido-complexes $MoOBr_3[Ph_2P(O)\cdot CH_2\cdot CH_2\cdot P(O)Ph_2]$, $MoO_2Br_2[Ph_2P(O)\cdot CH_2\cdot CH_2\cdot P(O)Ph_2]$, $MoOCl_3[Ph_2P(O)\cdot CH_2\cdot CH_2\cdot P(O)Ph_2]$, and $MoO_2Cl_2[Ph_2P(O)\cdot CH_2\cdot CH_2\cdot P(O)Ph_2]$. In the case of tungsten, similar reactions occur but the sexivalent state of the metal seems to be preferred. The triphenylphosphine compounds yield the product $WO_2Cl_2,2Ph_3PO$, and from the diphosphine complexes $WO_2Cl_2[Ph_2P(O)\cdot CH_2\cdot CH_2\cdot P(O)Ph_2]$ and $WO_2Br_2[Ph_2P(O)\cdot CH_2\cdot CH_2\cdot P(O)Ph_2]$ are isolated. All the complexes are solid, air-stable, and non-electrolytes; they have been characterised by magnetic-moment measurements, melting points, infrared spectra, and analyses.

In Part I [1] we discussed the action of halogens on the complexes $M(CO)_4(diphos)$ and $M(CO)_2(diphos)_2$, where $M = Mo$ or W and diphos $= Ph_2P\cdot CH_2\cdot CH_2\cdot PPH_2$, under controlled conditions, to yield seven-co-ordinate diamagnetic derivatives of M^{II}, $M(CO)_3(diphos)X_2$, where $X = Br$ or I, and paramagnetic derivatives of M^{I}, $[M(CO)_2(diphos)_2]I_3$, containing the tri-iodide ion. In this Paper we report the complete oxidation of a variety of phosphine substituted Group VI metal carbonyls using an excess of the halogens bromine and chlorine.

A suspension of $Mo(CO)_3(PPh_3)_3$, when shaken with an excess of bromine in chloroform for one hour, yields a dark yellow oil on removal of solvent. This oil fumes in the presence of moist air and on standing yields a yellow crystalline solid which can be separated into two components by Soxhlet extraction with chloroform. A greenish yellow product is obtained from the extract, the analyses corresponding to the formulation $MoOBr_3,2Ph_3PO,(CHCl_3)_2$. On heating under a high vacuum for several hours the chloroform is removed to give the paramagnetic Mo^V complex, $MoOBr_3,2Ph_3PO$ (μ_{eff} 1·73 B.M.). On evaporation of the mother liquor to a smaller quantity, an orange-yellow product crystallises out, and this was shown to be the diamagnetic Mo^V complex $MoO_2Br_2,2Ph_3PO$. The course of the reaction did not appear to depend upon the solvent, as the same mixture of products was obtained when dichloromethane, carbon tetrachloride, benzene, or hexane were used as reaction media instead of chloroform.

The identity of these products has been confirmed by two independent means. First, the complex $Mo(CO)_3(Ph_3PO)_3$ has been prepared, and reaction with excess bromine yields the same mixture of products; secondly, reaction of triphenylphosphine oxide with the salt K_2MoOBr_5 yields $MoOBr_3,2Ph_3PO$. The analyses, melting points, infrared spectra, and magnetic moments are identical with those of the products from the first reaction.

Passage of a stream of chlorine through a suspension of the complex $Mo(CO)_3(PPh_3)_3$ in carbon tetrachloride results in the formation of a green oil which fumes on exposure to moist air and eventually yields a green solid. Extraction of this with chloroform yields a green complex, the analysis corresponding most closely to the formulation $MoOCl_3,2Ph_3PO,(CHCl_3)_{1.5}$. The chloroform can be removed by heating under a high vacuum, to give the known Mo^V compound $MoOCl_3,2Ph_3PO$. This had been prepared

[1] Part I, J. Lewis and R. Whyman, *J.*, 1965, 5486.

previously by the reaction of triphenylphosphine oxide with molybdenum pentachloride in ethanol.[2]

The complexes shown in Table 1 were prepared using experimental conditions essentially similar to those for the halogenation of $Mo(CO)_3(PPh_3)_3$.

TABLE 1

Complex	Colour	M. p.	μ_{eff} (B.M.) at 20°
$MoOBr_3,2Ph_3PO,(CHCl_3)_2$	Green-yellow	280—281°	1·71
$MoOBr_3,2Ph_3PO$	Green-yellow	276—277	1·73
$MoO_2Br_2,2Ph_3PO$	Golden-yellow	267—268	Diamagnetic
$MoOCl_3,2Ph_3PO$	Pale green	276—278	1·72
$MoOBr_3[Ph_2P(O)\cdot CH_2\cdot CH_2\cdot P(O)Ph_2]$	Yellow	337—338 (decomp.)	1·73
$MoO_2Br_2[Ph_2P(O)\cdot CH_2\cdot CH_2\cdot P(O)Ph_2]$	Yellow	345—347 (decomp.)	Diamagnetic
$MoOCl_3[Ph_2P(O)\cdot CH_2\cdot CH_2\cdot P(O)Ph_2]$	Pale green	347—348 (decomp.)	1·65
$MoO_2Cl_2[Ph_2P(O)\cdot CH_2\cdot CH_2\cdot P(O)Ph_2]$	White	337—339 (decomp.)	Diamagnetic
$WO_2Cl_2,2Ph_3PO$	White	276—278	Diamagnetic
$WO_2Cl_2[Ph_2P(O)\cdot CH_2\cdot CH_2\cdot P(O)Ph_2]$	White	355—357 (decomp.)	Diamagnetic
$WO_2Br_2[Ph_2P(O)\cdot CH_2\cdot CH_2\cdot P(O)Ph_2]$	Pale yellow	358—360 (decomp.)	Diamagnetic

The reaction of both *cis-* and *trans-*$Mo(CO)_4(PPh_3)_2$ and $Mo(CO)_3(PPh_3)_3$ with excess halogen gives rise to the same products, identified by infrared spectra, magnetic moments, and analyses. Similarly, the same types of reaction are observed from the halogen oxidation of $Mo(CO)_4$(diphos) and $Mo(CO)_2$(diphos)$_2$ and the corresponding pairs of tungsten compounds.

In the molybdenum reactions the main product is Mo^V and only a small amount of the Mo^{VI} complex is obtained, in contrast to the case of tungsten where derivatives of W^{VI} only are isolated. This variation is in agreement with the fact that the five-valent state is known to be more stable in the case of molybdenum than tungsten. However, in the chlorination of the complexes $W(CO)_4(PPh_3)_2$ and $W(CO)_3(PPh_3)_3$, although $WO_2Cl_2,2Ph_3PO$ was the only product isolated pure, the residue from the reaction was blue and its infrared spectrum corresponded to that expected for the phosphine oxide adduct $WOCl_3,2Ph_3PO$. All attempts at purification of this solid, however, resulted in complete decomposition. In the chlorination reaction of $W(CO)_4$(diphos) and $W(CO)_2$(diphos)$_2$ the only product isolated was the derivative of W^{VI} and no evidence was obtained for the formation of a W^V complex. The reaction of bromine with $W(CO)_4(PPh_3)_2$ and $W(CO)_3(PPh_3)_3$ yields a yellow product, its infrared spectrum indicating the presence of the complex $WO_2Br_2,2Ph_3PO$, but this was not obtained pure and all attempts at purification resulted in decomposition. It appears that the complexes of tungsten are less stable than the corresponding complexes of molybdenum.

Attempts to prepare the molybdenum(VI) derivatives by peroxide oxidation of the molybdenum(V) complexes resulted in complete loss of halogen and the formation of peroxy-derivatives.

In this study chloroform adducts were obtained with some of these complexes. In Part I[1] we mentioned the inclusion of dichloromethane in some of the metal–phosphine–carbonyl–iodide complexes. The formation of these adducts does not fall into any apparent order and must be related to lattice-energy effects. No evidence was obtained for their formation with any of the tungsten complexes or with the diphosphine dioxide derivatives of molybdenum.

It is not immediately apparent how the phosphine oxide complexes are formed. Gas-burette measurements indicate that all the carbon monoxide is lost spontaneously, and it is thought that the first step in the reaction is the removal of carbon monoxide to form a complex of the type $MoCl_4,2Ph_3P$. Complexes of this type have been prepared[3] by the displacement of n-propyl cyanide from $MoCl_4,2Pr^nCN$ by triphenylphosphine. Any excess triphenylphosphine will be chlorinated to form Ph_3PCl_2, and on exposure to moist air this

[2] S. M. Horner and S. Y. Tyree, jun., *Inorg. Chem.*, 1962, **1**, 122.
[3] E. A. Allen, B. J. Brisdon, and G. W. A. Fowles, *J.*, 1964, 4531.

will rapidly hydrolyse to triphenylphosphine oxide with the evolution of hydrogen chloride. Displacement of triphenylphosphine in the complex by triphenylphosphine oxide accompanied by further oxidation would then lead to the formation of the complex $MoOCl_3,2Ph_3PO$. This mechanism could hold for the oxidation of the complexes $Mo(CO)_3(PPh_3)_3$ and $Mo(CO)_2(diphos)_2$, where, in the formation of $MoCl_4,2Ph_3P$ and $MoCl_4,diphos$, phosphine will be liberated, but it is difficult to account for the same sequence of reactions in the cases of the $Mo(CO)_4(PPh_3)_2$ and $Mo(CO)_4diphos$ series.

Infrared Spectra.—Table 2 lists the metal–oxygen and phosphorus–oxygen infrared-active stretching frequencies observed in these complexes. In K_2MoOCl_5 a value of

TABLE 2

Infrared spectra (cm.$^{-1}$) in Nujol

Complex	Mo=O or W=O stretch	P=O stretch
Ph_3PO		1193s
$Ph_3P(O)\cdot CH_2\cdot CH_2\cdot P(O)Ph_2$		1186s, 1175s
$MoOBr_3,2Ph_3PO$	973	1152s
$MoO_2Br_2,2Ph_3PO$	946, 903	1175s, 1147s
$MoOCl_3,2Ph_3PO$	972	1160s
$MoOBr_3[Ph_2P(O)\cdot CH_2\cdot CH_2\cdot P(O)Ph_2]$	965	1193w, 1154s
$MoO_2Br_2[Ph_2P(O)\cdot CH_2\cdot CH_2\cdot P(O)Ph_2]$	940, 897	1188w, 1161s
$MoOCl_3[Ph_2P(O)\cdot CH_2\cdot CH_2\cdot P(O)Ph_2]$	973	1188w, 1164s
$MoO_2Cl_2[Ph_2P(O)\cdot CH_2\cdot CH_2\cdot P(O)Ph_2]$	945, 903	1191m, 1175s, 1168s
$WO_2Cl_2,2Ph_3PO$	960, 913	1170s, 1162s
$WO_2Cl_2[Ph_2P(O)\cdot CH_2\cdot CH_2\cdot P(O)Ph_2]$	956, 909	1194m, 1173s, 1166s
$WO_2Br_2[Ph_2P(O)\cdot CH_2\cdot CH_2\cdot P(O)Ph_2]$	954, 907	1190w, 1159s

967 cm.$^{-1}$ has been assigned to the Mo^V=O stretching frequency,[4] and this peak has also been observed in the molybdenyl trichloro-complexes prepared by Horner and Tyree.[2] The values assignable to Mo^V=O stretching frequencies in the complexes reported here lie in the range 965—973 cm.$^{-1}$, in good agreement with previous work.

For the molybdenum(VI) and tungsten(VI) complexes, two strong bands appear at *ca.* 950 and 910 cm.$^{-1}$. If these are both metal–oxygen vibrations, this could imply a *cis* distribution of the oxygen groups around the metal. However, the corresponding uranyl group [5] often exhibits two infrared-active metal–oxygen vibrations, although the linear oxygen–metal–oxygen system, which has been established in this case, would be expected to give only one metal–oxygen stretching frequency in the infrared spectrum.

As previously observed,[2,6] the stretching frequency of the phosphorus–oxygen bond is lowered on co-ordination, and in several cases there is a splitting of this band. Possible explanations for this splitting have been discussed.[6] However, it must be emphasised that in a molecule of this type, in addition to coupling between the metal–oxygen and the phosphorus–oxygen, of the phosphine oxide–metal group, considerable coupling with the metal–oxygen of the (M=O) grouping will occur. This in general will tend to raise the phosphorus–oxygen frequency and lower the metal–oxygen frequencies.

EXPERIMENTAL

Physical measurements and analyses were carried out as described previously.[1]

Oxotribromobis(triphenylphosphine oxide)molybdenum(v)–Bis-chloroform Adduct.—A suspension of the complex $Mo(CO)_3(PPh_3)_3$ (1·5 g.) in chloroform (25 ml.) was shaken with bromine (0·5 ml.) in chloroform (25 ml.) under nitrogen for 1 hr. The solvent was removed under a vacuum and the resulting yellow-brown oil allowed to stand in the air; it fumed and crystallised as a yellow solid. Extraction with chloroform (100 ml.) (Soxhlet) yielded a yellow extract which in cooling deposited greenish yellow crystals of the *compound* $MoOBr_3,2Ph_3PO,(CHCl_3)_2$

[4] C. G. Barraclough, J. Lewis, and R. S. Nyholm, *J.*, 1959, 3552.
[5] K. Nakamoto, " Infrared Spectra of Inorganic and Coordination Compounds," Wiley, London, 1963.
[6] F. A. Cotton, R. D. Barnes, and E. Bannister, *J.*, 1960, 2199.

(1·1 g.) (Found: C, 40·1; H, 2·8; Br, 20·2; Cl, 18·1; P, 5·2. $C_{38}H_{32}Br_3Cl_6MoO_3P_2$ requires C, 39·8; H, 2·8; Br, 20·9; Cl, 18·6; P, 5·4%). It is air-stable, soluble in acetone, ethanol, chloroform, and dichloromethane but insoluble in carbon tetrachloride.

Oxotribromobis(triphenylphosphine oxide)molybdenum(v).—The foregoing complex $MoOBr_3,2Ph_3PO,(CHCl_3)_2$ was heated at 80°/0·01 mm. for several hours; a loss in weight corresponding to the removal of 2 mol. of chloroform occurred, leaving the *complex* $MoOBr_3,2Ph_3PO$ as greenish yellow crystals (Found: C, 47·5; H, 3·3; Br, 26·0; P, 6·5. $C_{36}H_{30}Br_3MoO_3P_2$ requires C, 47·6; H, 3·3; Br, 26·4; P, 6·8%). It has the same properties as the chloroform adduct.

Dioxodibromobis(triphenylphosphine oxide)molybdenum(VI).—The filtrate from the Soxhlet extraction was evaporated under a vacuum to *ca.* 15 ml., and a quantity of golden-yellow crystals of the *complex* $MoO_2Br_2,2Ph_3PO$ separated out. It was washed with a little chloroform and dried *in vacuo* (0·26 g.) (Found: C, 51·3; H, 3·6; Br, 18·5; P, 7·1. $C_{36}H_{30}Br_2MoO_4P_2$ requires C, 51·2; H, 3·6; Br, 19·0; P, 7·3%). The compound is air-stable and more soluble in common organic solvents than the Mo(v) complex.

Oxotrichlorobis(triphenylphosphine oxide)molybdenum(v).—A slow stream of dry chlorine was bubbled through a suspension of the complex $Mo(CO)_3(PPh_3)_3$ (1·5 g.) in carbon tetrachloride (100 ml.) for 2 hr. The solution was decanted from the greenish yellow oil which crystallised as a dark green solid on exposure to moist air. This solid was extracted with chloroform (100 ml.) (Soxhlet) and on cooling the extract green crystals separated. These were washed with chloroform and dried in a high vacuum at 80° to give pale green crystals of the complex $MoOCl_3,2Ph_3PO$ (0·62 g.) (Found: C, 55·7; H, 3·9; Cl, 13·7; P, 7·9. Calc. for $C_{36}H_{30}Cl_3MoO_3P_2$: C, 55·8; H, 3·9; Cl, 13·8; P, 8·0%).

Oxotribromo - (1,2 - bisdiphenylphosphinoethane dioxide)molybdenum(v). — The complex $Mo(CO)_4(Ph_2P\cdot CH_2\cdot CH_2\cdot PPh_2)$ (1·2 g.) in chloroform (25 ml.) was shaken with bromine (0·4 ml.) in chloroform (20 ml.) for 1 hr. The solvent was removed under a vacuum and the remaining orange-brown oil allowed to stand in the air; it fumed and crystallised as a yellow solid. Extraction with chloroform (150 ml.) gave the *complex* $MoOBr_3,[Ph_2P(O)\cdot CH_2\cdot CH_2\cdot P(O)Ph_2]$ as yellow crystals (0·9 g.) (Found: C, 39·8; H, 3·2; Br, 31·0; P, 7·8. $C_{26}H_{24}Br_3MoO_3P_2$ requires C, 39·9; H, 3·1; Br, 30·7; P, 7·9%). The complex is sparingly soluble in acetone, chloroform, dichloromethane, nitrobenzene, and nitromethane, but insoluble in all other common solvents.

Dioxodibromo-(1,2-bisdiphenylphosphinoethane dioxide)molybdenum(VI).—The filtrate from the extraction was evaporated under a vacuum to *ca.* 20 ml., and yellow crystals of the *complex* $MoO_2Br_2,[Ph_2P(O)\cdot CH_2\cdot CH_2\cdot P(O)Ph_2]$ separated out. This was washed with a little chloroform and dried *in vacuo* (0·2 g.) (Found: C, 43·9; H, 3·4; Br, 22·3; P, 8·2. $C_{26}H_{24}Br_2MoO_4P_2$ requires C, 43·5; H, 3·3; Br, 22·3; P, 8·6%). It has similar properties to the tribromide but is slightly more soluble in organic solvents.

Oxotrichloro-(1,2-bisdiphenylphosphinoethane dioxide)molybdenum(v).—A slow stream of dry chlorine was bubbled through a solution of the complex $Mo(CO)_4(Ph_2P\cdot CH_2\cdot CH_2\cdot PPh_2)$ (1·0 g.) in chloroform (50 ml.) for 5 hr. Bright green crystals separated and were filtered off, washed well with chloroform, and dried under a vacuum. The *molybdenum complex* $MoOCl_3[Ph_2P(O)\cdot CH_2\cdot CH_2\cdot P(O)Ph_2]$ (0·8 g.) was pale green (Found: C, 47·9; H, 3·9; Cl, 16·6; P, 9·5. $C_{26}H_{24}Cl_3MoO_3P_2$ requires C, 48·1; H, 3·7; Cl, 16·4; P, 9·6%). It is very slightly soluble in acetone, chloroform, and dichloromethane, but insoluble in carbon tetrachloride.

Dioxodichloro-(1,2-bisdiphenylphosphinoethane dioxide)molybdenum(VI).—The filtrate from the chlorination reaction was reduced in volume to *ca.* 30 ml., and after standing for several days white crystals of the *compound* $MoO_2Cl_2[Ph_2P(O)\cdot CH_2\cdot CH_2\cdot P(O)Ph_2]$ separated out. It was washed with a little chloroform and dried *in vacuo* (0·15 g.) (Found: C, 49·4; H, 3·6; Cl, 11·4; P, 9·7. $C_{26}H_{24}Cl_2MoO_4P_2$ requires C, 49·6; H, 3·8; Cl, 11·3; P, 9·9%). It has similar physical characteritics to the trichloride.

Dioxodichlorobis(triphenylphosphine oxide)tungsten(VI).—A slow stream of dry chlorine was bubbled through a suspension of the complex $W(CO)_3(PPh_3)_3$ (2·0 g.) in carbon tetrachloride (150 ml.) for 5 hr. After filtration, the pale yellow filtrate was reduced in volume to *ca.* 50 ml. and after several days white crystals of the *compound* $WO_2Cl_2,2Ph_3PO$ separated out. It was washed with carbon tetrachloride and dried *in vacuo* (0·3 g.) (Found: C, 51·2; H, 3·7; Cl, 8·6; P, 7·4. $C_{36}H_{30}Cl_2O_4P_2W$ requires C, 51·3; H, 3·6; Cl, 8·4; P, 7·4%). It is very slightly soluble in chloroform, dichloromethane, carbon tertachloride, and nitrobenzene.

Dioxodichloro-(1,2-bisdiphenylphosphinoethane dioxide)tungsten(VI).—The tungsten complex

$W(CO)_4(Ph_2P\cdot CH_2\cdot CH_2\cdot PPh_2)$ (1·0 g.) in chloroform (75 ml.) was treated with chlorine as above for 3 hr. White crystals of the *complex* $WO_2Cl_2[Ph_2P(O)\cdot CH_2\cdot CH_2\cdot P(O)Ph_2]$ which separated were washed with chloroform and dried *in vacuo* (0·74 g.) (Found: C, 43·5; H, 3·5; Cl, 10·1; P, 8·7. $C_{26}H_{24}Cl_2O_4P_2W$ requires C, 43·5; H, 3·3; Cl, 9·9; P, 8·7%). Its physical properties are similar to those of the triphenylphosphine oxide complex.

Dioxodibromo-(1,2-bisdiphenylphosphinoethane dioxide)tungsten(VI).—The tungsten complex $W(CO)_4(Ph_2P\cdot CH_2\cdot CH_2\cdot PPh_2)$ (1·0 g.) in chloroform (20 ml.) was shaken with bromine (0·5 ml.) in chloroform (25 ml.) for 3 hr. The solvent was removed under a vacuum and the resulting orange-yellow oil allowed to stand in the air; it fumed and crystallised as an orange yellow solid. The *complex* $WO_2Br_2[Ph_2P(O)\cdot CH_2\cdot CH_2\cdot P(O)Ph_2]$ (1·1 g.) was washed with light petroleum and dried at 80°/0·01 mm. for several hours (Found: C, 38·6; H, 3·0; Br, 20·0; P, 7·6. $C_{26}H_{24}Br_2O_4P_2W$ requires C, 38·7; H, 3·0; Br, 19·9; P, 7·7%). It is slightly soluble in acetone, dichloromethane, and nitrobenzene, but insoluble in other common organic solvents.

Alternative Preparations of Oxotribromobis(triphenylphosphine oxide)molybdenum(V).— (a) Triphenylphosphine oxide was prepared by the oxidation of triphenylphosphine with hydrogen peroxide.[7] The product was heated under a high vacuum to remove all traces of the peroxo-adduct.

The complex $Mo(CO)_3(Ph_3PO)_3$ was prepared by refluxing a mixture of triphenylphosphine oxide (2·8 g.) and molybdenum hexacarbonyl (1·3 g.) (*i.e.*, phosphine oxide : carbonyl = 2 : 1) in *p*-xylene (40 ml.) under dry nitrogen for 4 hr. On cooling after filtration, yellow crystals of the *product* separated out. It was washed with a little *p*-xylene and dried *in vacuo* (3·5 g.) (Found: C, 67·1; H, 4·4; P, 9·0. $C_{57}H_{45}MoO_6P_3$ requires C, 67·5; H, 4·4; P, 9·2%).

A suspension of the complex $Mo(CO)_3(Ph_3PO)_3$ (1·0 g.) in carbon tetrachloride (30 ml.) was treated with bromine (0·5 ml.) in carbon tetrachloride (20 ml.) and the mixture shaken for 1 hr. The solvent was decanted from the yellow-brown oil which gave a yellow solid without fuming. This solid, after extraction with chloroform (100 ml.) gave greenish yellow *crystals* of $MoOBr_3,2Ph_3PO$ (0·35 g.) which were washed with chloroform and dried at 80°/0·01 mm. for several hours (Found: C, 47·2; H, 3·2; Br, 26·1; P, 6·6. $C_{36}H_{30}Br_3MoO_3P_2$ requires C, 47·6; H, 3·3; Br, 26·4; P, 6·8%). After removal of solvent from the filtrate further yellow crystals separated out. From the infrared spectrum these were shown to be a mixture of $MoOBr_3,2Ph_3PO$ and $MoO_2Br_2,2Ph_3PO$.

(b) A solution of K_2MoOBr_5 in concentrated hydrobromic acid was prepared by the addition of potassium bromide to a solution of molybdenyl hydroxide in 45% hydrobromic acid.[8] Triphenylphosphine oxide (2·8 g.) in chloroform (50 ml.) was treated with K_2MoOBr_5 (3·0 g.) in hydrobromic acid (40 ml.) (*i.e.*, phosphine oxide : molybdenum = 2 : 1), and the chloroform layer separated. After removal of some solvent under a vacuum, the *product* crystallised as greenish yellow crystals, was washed with chloroform and dried at 80°/0·01 mm. (1·6 g.) (Found: C, 47·6; H, 3·3; Br, 26·0; P, 7·1%).

Alternative Preparation of Oxotribromo-(1,2-bisdiphenylphosphinoethane dioxide)molybdenum(V).—1,2-Bisdiphenylphosphinoethane dioxide was prepared by the oxidation of 1,2-bisdiphenylphosphinoethane with hydrogen peroxide as before.[7] 1,2-Bisdiphenylphosphinoethane dioxide (1·0 g.) in chloroform (40 ml.) was treated with K_2MoOBr_5 (1·4 g.) in hydrobromic acid (15 ml.) (*i.e.*, diphosphine dioxide : molybdenum = 1 : 1), and the *product* isolated from the chloroform layer as above (2·1 g.) (Found: C, 39·9; H, 3·2; Br, 30·8; P, 7·8. $C_{26}H_{24}Br_3MoO_3P_2$ requires C, 39·9; H, 3·1; Br, 30·7; P, 7·9%).

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[7] R. L. Shriner and C. N. Wolf, *Org. Synth.*, 1950, **30**, 97.
[8] E. A. Allen, B. J. Brisdon, D. A. Edwards, G. W. A. Fowles, and R. G. Williams, *J.*, 1963, 4649.