Studies of Transition-metal Oxo- and Nitrido-complexes. Part 4.[1] Reactions of Osmium Tetraoxide with Alkynes and Dienes in the Presence of Tertiary Amines

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Osmium tetraoxide (OsO_4) reacts with alkynes R (R = C_2H_2, C_2Ph_2, PhC_2H, or MeC_2Ph) in the presence of tertiary amines L (L = pyridine or isoquinoline) to give *trans*-dioxo-osmium(VI) complexes $[Os_2O_4(O_4R)L_4]$. Reaction with dienes R (R = cyclo-octa-1,5-diene, 2,3-dimethylbuta-1,3-diene, or 4-vinylcyclohexene) in the presence of the same tertiary amines gives products $[Os_2O_4(O_4R)L_4]$ and $[OsO_2(O_2R)L_2]$. The structures of these complexes are discussed on the basis of their vibrational and ^1H n.m.r. spectra. Hydrolysis of some of the complexes has been carried out and the organic products identified.

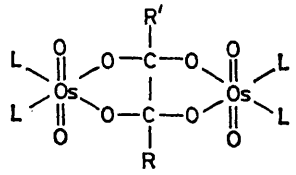
THE reaction between osmium tetraoxide (OsO_4) and monoalkenes has been extensively studied,[1-6] as have the hydrolyses of the resulting oxo-osmium(VI) esters to give *cis* diols.[3,7] As part of our continuing study on the interaction of OsO_4 with unsaturated substrates, we have characterised the oxo-osmium complexes formed with alkynes and dienes, and have isolated the organic hydrolysis products of these species. The catalytic oxidation of diphenylacetylene by OsO_4 with potassium chlorate has also been noted.

RESULTS AND DISCUSSION

Aminedioxotetrolato-osmium(VI) *Esters*.—The reduction of OsO_4 by acetylene has been used for the quantitative determination of osmium metal.[8] Later studies showed that in the presence of excess of tertiary amine acetylene reacts with OsO_4 to give products of stoicheiometry $2OsO_4{\cdot}4L{\cdot}C_2H_2$ (L = pyridine [3] or isoquinoline [4]). We have confirmed this latter work and extended it by treating OsO_4 with a series of alkynes. For these studies we used OsO_4 in the presence of excess of amine, and also the adducts $OsO_4{\cdot}L$ which we have recently reported,[1] since in these latter species the initial Os : L reacting ratio is fixed as 1 : 1. We find, however, that whether OsO_4 and excess of amine or the $OsO_4{\cdot}L$ adducts are used the same amine ester products are formed.

The adducts $OsO_4{\cdot}L$ (L = pyridine or isoquinoline) were treated with a range of alkynes R [R = acetylene (C_2H_2), diphenylacetylene ($C_{14}H_{10}$), phenylacetylene (C_8H_6), or methylphenylacetylene (C_9H_8)] in a reacting mol ratio of 2 : 1 in diethyl ether or tetrahydrofuran. The crystalline brown products have the stoicheiometry $2OsO_4{\cdot}4L{\cdot}R$. Despite the low solubilities of the products in organic solvents, we were able to measure their molecular weights in dichloromethane and the results are in close agreement with the above formula. The complexes are diamagnetic in the solid state and in solution, as expected [9] for oxo-osmium(VI) complexes.

We propose structure (1) for the pyridine and isoquinoline complexes, as we have previously suggested for $[Os_2O_4(O_4C_2H_2)(NC_5H_5)_4]$.[4] This structure, which involves octahedral Os^{VI} with *trans*-oxo-ligands, is consistent with the observed stoicheiometry, molecular weights, and diamagnetism of the complexes, and also with vibrational and ^1H n.m.r. spectroscopic studies (Table 1). In addition to bands due to co-ordinated ligands, the i.r. spectra of the solids show strong bands near 840 cm^{-1} and weaker bands near 300 cm^{-1} as observed for other complexes containing the *trans* O=Os=O 'osmyl' unit; as before,[1,4,5] we assign these to asymmetric stretches $\nu_{asym}(OsO_2)$ and deformations $\delta(OsO_2)$ of the osmyl unit respectively. Raman spectra in the 800—1 000 cm^{-1} range show strong bands near 880 cm^{-1} assigned to the symmetric stretch $\nu_{sym}(OsO_2)$ again as found in osmyl complexes.[10] These latter bands are somewhat broader for the aminetetrolato-esters than for the analogous monomeric diolato-complexes {*e.g.* $[OsO_2(O_2R)(NC_5H_5)_2]$} presumably because, for structure (1), two $\nu_{asym}(OsO_2)$ and two $\nu_{sym}(OsO_2)$ modes are predicted but are expected to be close in frequency. We tentatively assign i.r. bands near 950 and 650 cm^{-1} as predominantly due to C–O and Os–O stretching vibrations respectively since they are present in the corresponding $[OsO_2(O_2R)(NC_5H_5)_2]$ (R = alkene) complexes [4] but are not observed for the parent alkynes or amines. The i.r. spectrum of $[Os_2O(O_4C_2H_2)(NC_5H_5)_4]$ has a band at 2 820 cm^{-1} as expected for ν(C–H) in alkanes, while the ^1H n.m.r. spectrum of the complex in $CDCl_3$ solution shows a resonance due to protons adjacent to the donor



(1) L = pyridine or isoquinoline

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oxygen atoms at δ 6.02 (2 H) p.p.m., supporting the proposed structure. Integration of the ¹H n.m.r. spectra of the protons adjacent to the donor oxygen atoms against the α-pyridine protons confirms the stoicheiometries of the complexes.

TABLE 1

Analytical and spectroscopic data for oxo-osmium(VI) esters

	Analysis (%) [a]				¹H N.m.r. spectra	Vibrational spectra: selected bands (cm⁻¹) [d]			
Complex	C	H	N	*M* [a,b]	(δ/p.p.m.) [c]	ν(C–O)	ν(OsO)	ν(OsO_2)	δ(OsO_2)
(*a*) Aminedioxotetrolato-osmium(VI) esters									
$[Os_2O_4(O_4C_2H_2)(NC_5H_5)_4]$	31.7 (31.1)	2.8 (2.6)	6.3 (6.6)		6.02 (2 H)	1 004s	590m	838, 830vs, *883*vs	292, 282w
$[Os_2O_4(O_4C_{14}H_{10})(NC_5H_5)_4]$	40.7 (40.7)	3.1 (3.0)	5.6 (5.6)	977 (1 003)		985s		835, 825vw, *881*vs	307w
$[Os_2O_4(O_4C_8H_6)(NC_5H_5)_4]$	36.5 (36.3)	3.1 (2.8)	6.0 (6.0)	905 (927)	6.22 (1 H)	990s	565m	838, 833vs, *880*vs	299, 282w
$[Os_2O_4(O_4C_9H_8)(NC_5H_5)_4]$	37.3 (37.0)	3.0 (3.0)	5.8 (6.0)			965s	582m	829vs, *880*vs	303w
$[Os_2O_4(O_4C_2H_2)(NC_9H_7)_4]$	43.2 (43.4)	2.9 (2.9)	5.2 (5.3)	1 082 (1 051)	6.18 (2 H)	995s		834, 823vs, *882*vs	325w
$[Os_2O_4(O_4C_{14}H_{10})(NC_9H_7)_4]$	49.6 (49.9)	3.1 (3.2)	4.6 (4.7)			985s		830, 817vs	310w
$[Os_2O_4(O_4C_9H_8)(NC_9H_7)_4]$	47.1 (47.4)	3.1 (3.2)	4.9 (4.9)			970s		832, 820vs *878*vs	306, 300w
(*b*) Aminediolatodioxo-osmium(VI) esters									
(*i*) $[Os_2O_4(O_4R)L_4]$									
$[Os_2O_4(O_4C_6H_{10})(NC_5H_5)_4]$	34.2 (34.4)	3.4 (3.3)	5.9 (6.2)	840 (907)		998s		825vs, *877*vs	301w
$[Os_2O_4(O_4C_8H_{12})(NC_5H_5)_4]$ [e]	36.1 (36.0)	3.5 (3.5)	5.5 (6.0)	969 (933)	3.95 (3 H), 4.81 (2 H)	990s	592m	835, 830vs, *879*vs	290w
$[Os_2O_4(O_4C_8H_{12})(NC_5H_5)_4]$ [f]	36.0 (36.0)	3.5 (3.5)	5.6 (6.0)	934 (933)	4.75 (4 H)	970s		830vs, *880*vs	333w
$[Os_2O_4(O_4C_8H_{12})(NC_9H_7)_4]$ [f]	46.5 (46.6)	3.7 (3.6)	4.6 (4.9)	1 177 (1 133)	4.80 (4 H)	1 007s		832, 820vs, *878*vs	332w
(*ii*) $[OsO_2(O_2R)L_2]$									
$[OsO_2(O_2C_8H_{12})(NC_5H_5)_2]$ [f]	41.3 (41.5)	4.3 (4.3)	5.3 (5.4)	536 (521)	4.67 (2 H)	970s	593m	840, 835vs, *876*vs	288w
$[OsO_2(O_2C_8H_{12})(NC_9H_7)_2]$ [f]	50.1 (50.3)	4.2 (4.2)	4.3 (4.5)	611 (621)	4.70 (2 H)	972s	600m	840, 828vs, *880*vs	282w

[a] Calculated values are given in parentheses. [b] Determined osmometrically in dichloromethane. [c] For protons adjacent to donor oxygen atoms (relative to $SiMe_4$, recorded in $CDCl_3$). [d] For solids. Raman bands are italicised. [e] Complex derived from 4-vinylcyclohexene. [f] Complex derived from cyclo-octa-1,5-diene.

Hydrolysis. Since hydrolysis of the osmium(VI) esters formed by reaction of OsO_4 with monoalkenes is known to give good yields of the corresponding glycols,[2,3] it is of interest to investigate the hydrolysis of the complexes obtained with alkynes. The only hitherto reported hydroxylation of alkynes using OsO_4 appears in the patent literature [11] but no osmium-containing intermediates were isolated.

The hydrolyses were carried out using the procedure adopted by Criegee *et al.*[3] for the hydrolysis of monoalkene esters, modified by using sodium sulphite solution neutralised to prevent possible rearrangement of the expected diketo-product. Thus hydrolysis of $[Os_2O_4(O_4C_{14}H_{10})(NC_5H_5)_4]$ gave benzil and benzoic acid while $[Os_2O_4(O_4C_8H_6)(NC_5H_5)_4]$ gave benzoic acid, with very little phenylglyoxal being detected. Hydrolysis of $[Os_2O_4(O_4C_9H_8)(NC_5H_5)_4]$ yielded 1-phenylpropane-1,2-dione (Table 2). Benzil and benzoic acid respectively are obtained from the oxidation of diphenylacetylene and phenylacetylene with ruthenium tetraoxide (RuO_4),[12] no α-diketo-product being produced from oxidation of terminal alkynes.

Catalytic oxidation of alkynes by OsO_4. Osmium tetraoxide has been used together with oxidising agents such as hydrogen peroxide,[13,14] t-butyl hydroperoxide,[15] and potassium chlorate [13,16] for the catalytic *cis* hydroxylation of alkenes. We find that a similar catalytic procedure may be used for the oxidation of alkynes: thus diphenylacetylene may be oxidised to benzil in 79% yield by the use of a catalytic amount of OsO_4 with potassium chlorate in a t-butyl alcohol–acetone–water

TABLE 2

Hydrolysis of oxo-osmium(VI) esters

Alkyne	Oxo-osmium(VI) ester	Hydrolysis product
Diphenylacetylene	$[Os_2O_4(O_4C_{14}H_{10})(NC_5H_5)_4]$	Benzil (65%)
Phenylacetylene	$[Os_2O_4(O_4C_8H_6)(NC_5H_5)_4]$	Benzoic acid (57%)
Methylphenylacetylene	$[Os_2O_4(O_4C_9H_8)(NC_5H_5)_4]$	1-phenylpropane-1,2-dione (54%)

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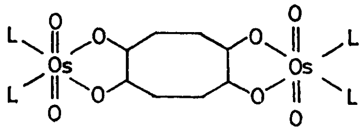
[16] K. A. Hofmann, *Chem. Ber.*, 1912, **45**, 3329.

solvent system. Catalytic hydroxylation of alkynes using OsO_4 and H_2O_2 however yields no α-diketo-product but the corresponding hydroxyaldehydes and hydroxyacids.[11] Further investigation on this aspect of the work is in progress.

Aminediolatodioxo-osmium(VI) *Esters from Dienes*.—The hydroxylation of some dienes using OsO_4 has been reported,[14,17-20] but little work was carried out on the reactions of OsO_4 with dienes in the presence of amines.[3,21] Products of stoicheiometries $20O_4$·4py·R and OsO_4·2py·R have been isolated depending on the initial OsO_4 : diene ratio used, but no structures were suggested, the products being characterised only by osmium analyses.[3]

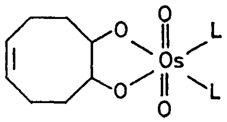
$[Os_2O_4(O_4R)L_4]$. Treatment of OsO_4 in a 2 : 1 mol ratio with a range of dienes R [R = cyclo-octa-1,5-diene (C_8H_{12}), 4-vinylcyclohexene (C_8H_{12}), or 2,3-dimethylbuta-1,3-diene (C_6H_{10})] in the presence of excess of pyridine or isoquinoline gave brown diamagnetic products of stoicheiometry $2OsO_4$·4L·R. On the basis of molecular-weight measurements in dichloromethane and spectroscopic evidence, we formulate these products as $[Os_2O_4(O_4R)L_4]$ containing *trans*-dioxo-ligands. Thus, for the product formed from cyclo-octa-1,5-diene, structure (2) is proposed.



(2) L = pyridine or isoquinoline

The i.r. spectra of the solid complexes, as before, show bands characteristic of *trans*-dioxo-' osmyl ' complexes, $\nu_{asym}(OsO_2)$ and $\delta(OsO_2)$ appearing near 840 and 300 cm^{-1} respectively; Raman spectra show bands near 880 cm^{-1}, polarised in solution, assigned to $\nu_{sym}(OsO_2)$. Infrared bands tentatively assigned to ν(C–O) and ν(Os–O) are listed in Table 1. Proton n.m.r. spectra of the complexes show a resonance for the protons adjacent to the donor oxygen atoms near δ 4.7 p.p.m. as expected. Integration of the ^1H n.m.r. spectra of the protons adjacent to the donor oxygen atoms against the α-pyridine protons confirms the pyridine : diene ratio of 4 : 1.

$[OsO_2(O_2R)L_2]$. Reaction of OsO_4 with excess of cyclo-octa-1,5-diene in the presence of excess of tertiary amine L (L = pyridine or isoquinoline) gave products of stoicheiometry OsO_4·2L·R. The i.r. and Raman spectra are very similar to those of the $[Os_2O_4(O_4R)L_4]$ species above, but the ^1H n.m.r. spectra show alkenyl protons at δ 5.58 (2 H) p.p.m. and protons adjacent to the donor oxygen atoms at δ 4.67 (2 H) p.p.m., indicating that only one of the double bonds has reacted. We therefore formulate these products as $[OsO_2(O_2C_8H_{12})L_2]$, structure (3).



(3) L = pyridine or isoquinoline

Hydrolysis. The hydroxylation of dienes using OsO_4 as oxidising agent to give tetrols[14,18,20] or unsaturated diols[17-19] has been reported. However, there has been no systematic investigation of the hydrolysis of the amineosmium(VI) esters formed from dienes, although it is known that *cis* hydroxylation of monoalkenes by OsO_4 is greatly accelerated by tertiary amines, and that aminediolatodioxo-osmium(VI) esters are involved.[3] It has been reported that treatment of OsO_4, pyridine, and cyclo-octa-1,5-diene with hydrogen sulphide gives *cis*-cyclo-octene-5,6-diol in 14% yield.[22] We have repeated this work and, by isolating the intermediate $[OsO_2(O_2C_8H_{12})(NC_5H_5)_2]$ and hydrolysing this with sodium sulphite solution, have isolated the diol in 76% yield, appreciably higher than that (3%) reported for the similar oxidation using potassium permanganate.[23]

EXPERIMENTAL

Osmium tetraoxide–amine adducts, OsO_4·L, were prepared as previously reported.[1]

Osmium(VI) *Esters from Alkynes*, $[Os_2O_4(O_4R)L_4]$.—*Pyridine complexes*. The preparation of $[Os_2O_4(O_4C_{14}H_{10})(NC_5H_5)_4]$ is typical. To a solution of $OsO_4 \cdot C_5H_5N$ (0.5 g) in diethyl ether or tetrahydrofuran (thf) (5 cm^3) was added dropwise with stirring a solution of diphenylacetylene (0.13 g) in diethyl ether or thf (5 cm^3). After 5 min the brown product was filtered off, copiously washed with diethyl ether, and dried *in vacuo* (45% yield).

Isoquinoline complexes. The preparation of $[Os_2O_4(O_4C_9H_8)(NC_9H_7)_4]$ is typical. To a solution of $OsO_4 \cdot C_9H_7N$ (0.6 g) in diethyl ether was added dropwise with stirring a solution of methylphenylacetylene (0.09 g) in diethyl ether (4 cm^3). After 5 min the brown precipitate was filtered off, copiously washed with diethyl ether, and dried *in vacuo* (40% yield).

Alternatively, the products can be prepared by treating OsO_4 with alkyne in the presence of excess of pyridine or isoquinoline.

Hydrolyses. *Of* $[Os_2O_4(O_4C_{14}H_{10})(NC_5H_5)_4]$. To a solution of $Na_2[SO_3]$ (1 g) acidified with HCl to pH 7.3 was added ethanol (5 cm^3) and the complex $[Os_2O_4(O_4C_{14}H_{10})(NC_5H_5)_4]$ (0.6 g). The solution was heated under reflux for 3 h and allowed to cool. The precipitated osmium complex was filtered off and the filtrate continuously extracted with diethyl ether. The ether extract was dried over $Mg[SO_4]$ and evaporated *in vacuo*. Purification of the crude product using preparative thin-layer chromatography (silica, chloroform solvent) yielded benzil in 65% yield, m.p. 95 °C

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[21] R. Criegee, W. Hörauf, and W. Schellenberg, *Chem. Ber.*, 1953, **86**, 126.

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(lit.,[24] 95 °C); the product was characterised by its mass (M 210) and i.r. spectra.

The aqueous layer was acidified with HCl to pH 2 and continuously extracted with diethyl ether. The extract was dried over Mg[SO_4] and evaporated *in vacuo*. Purification of the crude product using preparative t.l.c. yielded benzoic acid in 19.2% yield, m.p. 120 °C (lit.,[24] 122 °C); the product was characterised by its mass (M 122) and i.r. spectra.

Of trans-[$Os_2O_4(O_4C_8H_6)(NC_5H_5)_4$]. The hydrolysis followed the same procedure as above. No product was obtained by extraction of the alkaline solution with diethyl ether. On extraction of the acidified aqueous solution, however, benzoic acid was obtained in 57% yield, m.p. 117 °C. The product was characterised by its mass (M 122) and i.r. spectra.

Of [$Os_2O_4(O_4C_9H_8)(NC_5H_5)_4$]. The hydrolysis followed the same procedure as above. The reaction mixture was continuously extracted with diethyl ether and the ether extract dried over Mg[SO_4] and evaporated *in vacuo*. The crude product was purified by preparative t.l.c. (silica, benzene solvent) to give 1-phenylpropane-1,2-dione (54%) as a yellow oil. The product was characterised by its mass (M 148), i.r., and ^{1}H n.m.r. spectra [δ in $CDCl_3$ 7.93—8.08 (2 H), 7.59 (5 H) (Ph), and 2.51 p.p.m. (3 H, Me)].

Catalytic oxidation of diphenylacetylene. To a solution of diphenylacetylene (0.678 g) in t-butyl alcohol (10 cm^3), acetone (10 cm^3), and water (3 cm^3) were added with stirring OsO_4 (0.05 g) and K[ClO_3] (1.5 g). The reaction mixture was heated under reflux at 56 °C for 24 h, allowed to cool, and extracted with diethyl ether (3 × 20 cm^3). The ether extract was dried over Mg[SO_4] and evaporated *in vacuo*. The crude product was purified by preparative t.l.c. (silica, chloroform solvent) to give benzil (79%), m.p. 93 °C. The product was characterised by its mass (M 210) and i.r. spectra.

Osmium(VI) *Esters from Dienes*.—The preparation of these species followed similar procedures and were carried out under dry nitrogen since the products were hygroscopic.

(*i*) [$Os_2O_4(O_4R)L_4$]. *Pyridine complexes*. The preparation of [$Os_2O_4(O_4C_6H_{10})(NC_5H_5)_4$] is typical. To a solution of OsO_4 (0.3 g) in diethyl ether (10 cm^3) containing pyridine (0.25 g) was added dropwise with stirring 2,3-dimethylbuta-1,3-diene (0.05 g). After 5 min the brown precipitate was filtered off and copiously washed with diethyl ether. The product was recrystallised from dichloromethane and diethyl ether and dried *in vacuo* (60% yield).

Isoquinoline complexes. The preparation of [$Os_2O_4(O_4C_8H_{12})(NC_9H_7)_4$] is typical. To a solution of OsO_4 (0.4 g) in diethyl ether (10 cm^3) containing isoquinoline (0.5 g) was added dropwise with stirring a solution of cyclo-octa-1,5-diene (0.08 g) in diethyl ether (5 cm^3). After 5 min the brown precipitate was filtered off and copiously washed with diethyl ether. The product was recrystallised from CH_2Cl_2 and diethyl ether and dried *in vacuo* (65% yield).

(*ii*) [$OsO_2(O_2R)L_2$]. *Pyridine and isoquinoline complexes*. These were prepared in the same way as [$Os_2O_4(O_4R)L_4$] but a five-fold excess of diene was used. The products were recrystallised from dichloromethane and diethyl ether and dried *in vacuo*.

Hydrolysis of trans-[$OsO_2(O_2C_8H_{12})(NC_5H_5)_2$]. To a solution of K_2[SO_3] (2 g) in water (40 cm^3) and ethanol (5 cm^3) was added [$OsO_2(O_2C_8H_{12})(NC_5H_5)_2$] (1.9 g). The solution was heated under reflux for 2 h and allowed to cool. The precipitated osmium complex was filtered off and the filtrate continuously extracted with diethyl ether. The ether extract was dried over Mg[SO_4] and evaporated *in vacuo* to give *cis*-cyclo-octene-5,6-diol in 76% yield. Purification of the product was not necessary, m.p. 104 °C (lit.,[22,23] 104 °C). The product was characterised by its mass (M 142) and ^{1}H n.m.r. spectra [δ in $CDCl_3$ 5.73 (2 H, alkene) and 4.04 p.p.m. (2 H, protons adjacent to OH)].

Elemental analyses were obtained by the Microanalytical Department, Imperial College, oxygen analyses by F. Pascher (Bonn). Molecular weights were determined osmometrically on a Perkin-Elmer–Hitachi 115 instrument. Infrared spectra were recorded from 200 to 4 000 cm^{-1} on a Perkin-Elmer 457 instrument as Nujol mulls between caesium iodide plates. Raman spectra were obtained on a Spex Ramalog 5 instrument with a DPC-2 detector using a CRL-52 krypton-ion laser. Solids were scanned as 10% samples in 90% KBr spinning discs. Proton n.m.r. spectra were recorded on a 60-MHz Perkin-Elmer R-12 spectrometer. Mass spectra were obtained on a VG 7070 instrument. Magnetic-susceptibility measurements were made on solids by the Gouy method and on solutions by the Evans method.[25]

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[8/414 *Received*, 6*th March*, 1978]

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