

A Benzyne–Triosmium Compound as an Intermediate in the Formation of Benzene from Benzyl Alcohol†

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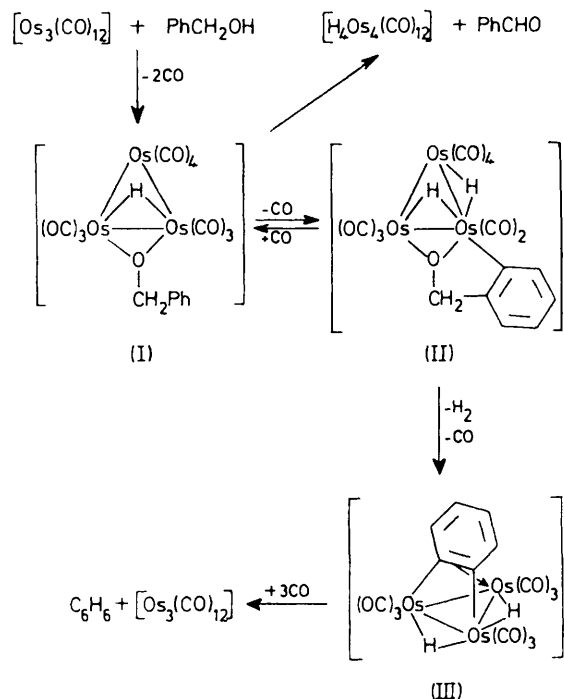
Summary The bridged alkoxo-compound $[\text{HOs}_3(\text{CO})_{10}(\text{OCH}_2\text{Ph})]$, formed from $[\text{Os}_3(\text{CO})_{12}]$ and benzyl alcohol, gives benzene, benzaldehyde, $[\text{Os}_3(\text{CO})_{12}]$, and $[\text{H}_4\text{Os}_4(\text{CO})_{12}]$ at 146 °C in a sealed tube, benzene being formed *via* the *ortho*-metallated intermediate $[\text{H}_2\text{Os}_3(\text{CO})_9(\text{OCH}_2\text{C}_6\text{H}_4)]$ and the benzyne compound $[\text{H}_2\text{Os}_3(\text{CO})_9(\text{C}_6\text{H}_4)]$.

phenol give, among other products, triosmium clusters containing vinylidene (C:CH₂),¹ benzyne (*o*-phenylene),¹ and OC₆H₄² respectively as triply-bridged ligands. We now report that benzyl alcohol gives triosmium co-ordinated fragments which may be displaced as benzene or benzaldehyde. Compound (I) $[\text{HOs}_3(\text{CO})_{10}(\text{OCH}_2\text{Ph})]$ derived from the alcohol and $[\text{Os}_3(\text{CO})_{12}]$ in refluxing xylene,³ decomposes in nonane (146 °C, sealed n.m.r. tube, 23 days) to give benzene, benzaldehyde (mol ratio, 2·4:1), $[\text{Os}_3(\text{CO})_{12}]$ (major organometallic product), $[\text{H}_4\text{Os}_4(\text{CO})_{12}]$, and

MANY types of organic molecule react with $[\text{Os}_3(\text{CO})_{12}]$ to give co-ordinated fragments. Thus ethylene, benzene, and

† No reprints available.

only traces of other compounds. Similarly, $[\text{HOs}_3(\text{CO})_{10}(\text{OCH}_2\text{C}_6\text{H}_4\text{Me-}p)]$ (146 °C, 60 days) gives the same osmium compounds, toluene (57%), and *p*-tolualdehyde (17%), while $[\text{HOs}_3(\text{CO})_{10}(\text{OCHMePh})]$ (146 °C, 45 days) gives MeCOPh as the main organic product.

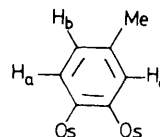


SCHEME

While not firmly establishing reaction pathways to these products, we have obtained other derivatives of (I) showing that one route to benzene is *via* the *ortho*-metallated compound (II) and the benzyne compound (III) (see Scheme). Thus by monitoring the $\nu(\text{CO})$ bands in the i.r. spectrum of a refluxing octane solution of (I) flushed with N_2 to remove displaced CO (unlike the sealed tube experiments above) we observed the presence of $[\text{H}_2\text{Os}_3(\text{CO})_9(\text{OCH}_2\text{-C}_6\text{H}_4)]$ (II) and of $[\text{H}_2\text{Os}_3(\text{CO})_9(\text{C}_6\text{H}_4)]$ (III), both of which could be isolated by t.l.c. in *ca.* 10% yield. The $\nu(\text{CO})$ bands in the i.r. spectrum of (II) are indistinguishable from those of $[\text{H}_2\text{Os}_3(\text{CO})_9(\text{OCMe}_2\text{C}_6\text{H}_4)]$ obtained from $[\text{HOs}_3-$

$(\text{CO})_{10}(\text{OCMe}_2\text{Ph})]^\ddagger$ which has a structure, we argued, like that shown for (II).² The formation of (II) from (I) is reversible. By a separate experiment we have shown that (III) is formed from (II), together with $[\text{H}_4\text{Os}_4(\text{CO})_{12}]$, in refluxing xylene, while its formation from $[\text{Os}_3(\text{CO})_{12}]$ and benzene in these reactions is not possible since much higher temperatures are required for this. Treatment of (III) with an atmosphere of CO in a sealed tube at 146 °C gives benzene and $[\text{Os}_3(\text{CO})_{12}]$ exclusively, so we have been able to observe separately each step in the Scheme leading to benzene. Thus, while hydrogen atom transfer from the *ortho*-position of the ring in (I) leads eventually to benzene, we believe that there is a competitive hydrogen atom transfer from the CH_2 group of (I) resulting in benzaldehyde and $[\text{H}_2\text{Os}_3(\text{CO})_{10}]$ which gives $[\text{H}_4\text{Os}_4(\text{CO})_{12}]$ under the reaction conditions.³ The latter is a β -elimination and a normal mode of decomposition of alkoxo-transition metal compounds. The conversion of (II) into (III) probably involves loss of CO and H_2 rather than CH_2O since $[\text{HOs}_3(\text{CO})_{10}(\text{OCHMePh})]$ gives MeCOPh and not benzene which would require the loss of acetaldehyde.

Interestingly, both $[\text{HOs}_3(\text{CO})_{10}(\text{OCH}_2\text{C}_6\text{H}_4\text{Me-}p)]$ and its *ortho*-isomer give the same isomer of $[\text{H}_2\text{Os}_3(\text{CO})_9(\text{C}_6\text{H}_3\text{Me})]$ (A) with the methyl substituent *para* to osmium [¹H n.m.r., CDCl_3 , 27 °C: τ 2.22 (d, H_a), 2.35 (d, H_c), 3.34 (dd, H_b), 7.70 (s, *Me*), 28.93 (s, OsH_2); J_{ortho} 8.0 and J_{meta} 2.0 Hz].



(A)

Different isomers were expected on the basis of the reaction scheme shown, but we now believe that ready hydrogen shifts between the ligand and the metal have led to the more stable isomer in each case. Presumably a methyl group *ortho* to osmium gives a less stable isomer than when it is further removed from the metal.

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[†] This evidence and the observation of the molecular ion in the mass spectrum adequately characterise (II), even though too little material was obtained to isolate it analytically pure. Compound (III) is spectroscopically identical (i.r., ¹H n.m.r., and mass) with that obtained directly from C_6H_6 and $[\text{Os}_3(\text{CO})_{12}]$. (ref. 1).

¹ A. J. Deeming and M. Underhill, *J. C. S. Dalton*, 1974, 1415.

² K. A. Azam, A. J. Deeming, R. E. Kimber, and P. R. Shukla, *J. C. S. Dalton*, in the press.

³ S. A. R. Knox, J. W. Koepke, M. A. Andrews, and H. D. Kaesz, *J. Amer. Chem. Soc.*, 1975, **97**, 3942.