The Homogeneous Oxidation of Amines to Aldehydes or Ketones: Formation of Amine–Hydrides of Molybdenum

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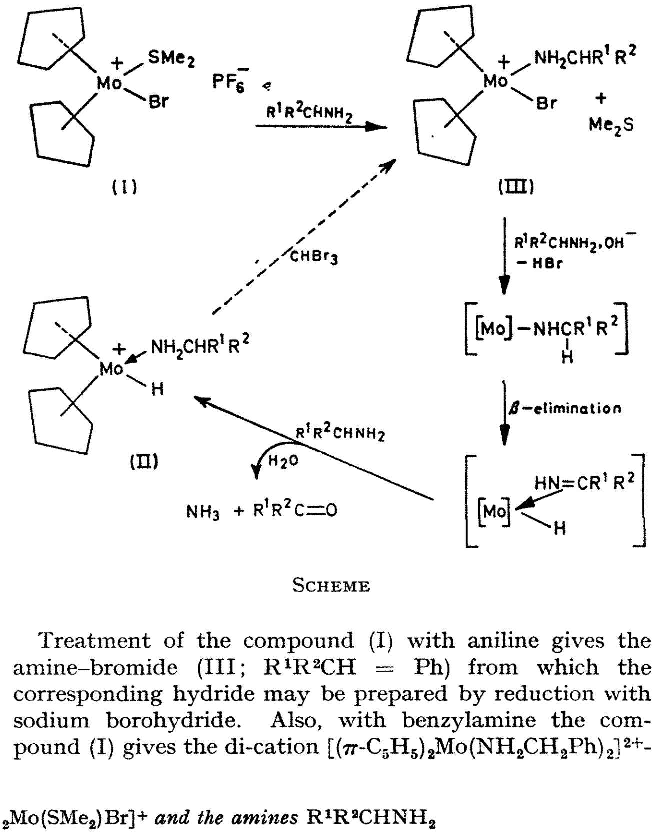
Summary Treatment of the cation $[(\pi\text{-}C_5H_5)_2Mo(SMe_2)Br]^+$ with some amines $R^1R^2CHNH_2$ in water gives the amine-hydrides $[(\pi\text{-}C_5H_5)_2Mo(NH_2CHR^1R^2)H]^+$ together with aldehydes or ketones, $R^1R^2CHO, R^2 = H$ or alkyl.

TREATMENT of the compound $[(\pi\text{-}C_5H_5)_2Mo(SMe_2)Br]^+PF^-$ (I)[1] with an excess of some amines $R^1R^2CHNH_2$ in water at 60° for several hours results in a smooth reaction and orange crystals are precipitated. Analysis, i.r. and ^1H n.m.r. data show the crystals to be the air-sensitive amine-hydride derivatives $[(\pi\text{-}C_5H_5)_2Mo(NH_2CHR^1R^2)H]^+PF_6^-$ (II). The compounds (II) are isolated in high yields, *ca.* 80%.

The distillates obtained from the acidified reaction mixtures give copious precipitates with acidified solutions of 2,4-dinitrophenylhydrazine (dnph). The mass spectra of the recrystallised dnph adducts shows them to be the Schiffs base products $R^1R^2CH{=}N{\cdot}NH[C_6H_3(NO_2)_2]$ formed from the aldehydes or ketones $R^1R^2CHO, R^1{=}H$ or alkyl: the reactions and products are shown in the Table.

We suggest that the amine-hydrides (II) and the aldehydes or ketones are formed by following reaction sequences shown in the Scheme.

Evidence for the above mechanism arises from the following observations: (i) that the amine–bromides (III) can be isolated, either by treatment of the corresponding amine–hydride with bromoform (shown when $R^1R^2CH{=}Me,Et, Bu^n,Pr^i$), or, directly from the compound (I) and the anhydrous amine (shown when $R^1R^2CH = Me,Et$): (ii) that treatment of the amine–bromide (III; $R^1R^2CH = Et$) with aqueous sodium hydroxide gives the aldehyde MeCHO: (iii) that this mechanism is essentially similar to that suggested for the formation of transition-metal hydrides from alcohols in the presence of base.[2]



SCHEME

Treatment of the compound (I) with aniline gives the amine-bromide (III; $R^1R^2CH = Ph$) from which the corresponding hydride may be prepared by reduction with sodium borohydride. Also, with benzylamine the compound (I) gives the di-cation $[(\pi\text{-}C_5H_5)_2Mo(NH_2CH_2Ph)_2]^{2+}$-

Products of the reaction between $[(\pi\text{-}C_5H_5)_2Mo(SMe_2)Br]^+$ *and the amines* $R^1R^2CHNH_2$

Amines	Molybdenum products	ν_{Mo-H} cm^{-1}	τ_{Mo-H}	R^1R^1CHO
$MeNH_2$	$[(\pi\text{-}C_5H_5)_2Mo(NH_2Me)H]^+$	1890	18·9	—
$EtNH_2$	$[(\pi\text{-}C_5H_5)_2Mo(NH_2Et)H]^+$	1830	19·0	MeCHO
Pr^iNH_2	$[(\pi\text{-}C_5H_5)_2Mo(NH_2Pr^i)H]^+$	1830	19·0	Me_2CO
Bu^tNH_2	$[(\pi\text{-}C_5H_5)_2Mo(NH_2Bu^n)H]^+$	1830	19·0	Pr^nCHO
$2\text{-}BuNH_2$	$[(\pi\text{-}C_5H_5)_2Mo(NH_2\text{-}2\text{-}Bu)H]^+$	1830	19·0	MeEtCO
$PhNH_2$	$[(\pi\text{-}C_5H_5)_2Mo(NH_2Ph)Br]^+$	—	—	—
$PhCH_2NH_2$	$[(\pi\text{-}C_5H_5)_2Mo(NH_2CH_2Ph)_2]^{2+}$	—	—	—

$[PF_6^-]_2$ in high yield. These latter reaction show that oxidation of amines does not occur with all amines.

Treatment of the tungsten analogue of the complex (I) with methylamine also gives an amine–hydride, $[(\pi\text{-}C_5H_5)_2W(NH_2Me)H]^+PF_6^-$ but the reaction is slow (100° for 3 days, $\nu_{W-H} = 1940\ cm^{-1}$, $\tau_{W-H} = 17{\cdot}0$).

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[1] R. H. Crabtree, A. R. Dias, M. L. H. Green, and P. J. Knowles, *J. Chem. Soc.* (*A*), **1971**, **1350**.

[2] L. Vaska and J. W. DiLuzio, *J. Amer. Chem. Soc.*, 1962, **84**, 4989.