The Interaction of Acyl Halides and Organosilicon Hydrides Catalysed by Platinum and Rhodium Complexes. A New Route to Ketones

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Summary Acyl halides react with triethylsilane in presence of certain platinum complexes to give aldehydes, but in the presence of rhodium catalysts (*e.g.* *mer*-[$RhCl_3(PBu^n{}_2Ph)_3$]) formation of ketones can predominate.

THE reaction between acyl halides and silicon hydrides to give aldehydes is known to be catalysed by palladium on charcoal.[1] We have now found that certain platinum complexes are effective homogeneous catalysts for this reaction; thus from the appropriate acyl chloride and triethylsilane (1 : 1·25 molar ratio) in the presence of a 1—2 × 10^{-3} molar proportion of the complex *cis*-[$PtCl_2(PPh_3)_2$] at 120°, *o*-methoxybenzaldehyde is obtained in 78% yield after 2 h and benzaldehyde in 68% yield after 18 h. With this catalyst similar treatment of n-hexoyl chloride gives the aldehyde in only 20% yield, but use of the rhodium catalyst *trans*-[$RhCl(CO)(PEtPh_2)_2$] gives it in 68% yield (see Table).

The reaction between triethylsilane and certain substituted benzoyl chlorides can take a different course in presence of rhodium catalysts, to produce ketones (see Table). Yields of ketone of over 60% have been obtained from *p*-methoxybenzoyl chloride. Electron-releasing substituents in the aryl group appear to favour ketone formation while electron-withdrawing substituents favour aldehyde. The relative yields of ketone and aldehyde seem to be markedly affected by small changes in the catalyst structure.

Reactions between RCOCl *and* Et_3SiH (1 : 1·25 *mole ratio*)

R		10^3 × Molar propn. of catalyst	Reaction Time (h)	Yield R_2CO (%)	Yield RCHO (%)
p-$MeO{\cdot}C_6H_4$	*mer*-[$RhCl_3(PBu^n{}_2Ph)_3$]	1·0	18	40	4
"	"	2·0	18	63	2
"	"	1·8	12	57	3
p-$Me{\cdot}C_6H_4$	"	1·8	48	36	11
Ph	"	1·8	54	40	8
p-$Cl{\cdot}C_6H_4$	"	1·8	17	12	32
p-$NO_2{\cdot}C_6H_4$	"	1·8	12	<2	35
PhCH=CH	"	1·8	19	<2	22
p-$MeO{\cdot}C_6H_4$	*trans*-[$RhCl(CO)(PEtPh_2)_2$]	1·0	18	63	2
"	"	1·0	15	57	5
"	"	1·0	12	53	4
	[$RhCl(CO)(PEt_2Ph)_2$]	1·0	12	35	22
"	"	1·0	12	45	2
"	[$RhCl(CO)(PEt_3)_2$]	1·0	18	27	4
$C_5H_{11}{}^n$	[$Rh(CO)(PEt_2Ph)_2$]	2·0	2	<2	68

Reaction schemes involving stepwise processes of known general types, mainly oxidative-addition reductive-elimination sequences, can readily be written to account for the products; thus, ketones may arise by loss of R_2CO from complexes such as $[Rh(R)(COR)(Cl)(CO)L_2]$. In the formation of aldehydes, the triethylsilane may function by forming a complex such as $[L_2Pt(H)Cl_2(SiEt_3)]$; this could then lose Et_3SiCl to give the complex $[L_2Pt(H)(Cl)]$, which in turn could take up a molecule of acyl chloride to give a complex from which RCHO is subsequently eliminated. Hydride complexes may also behave as reducing agents in the formation of ketones, but another possibility is that the triethylsilane serves (by forming Et_3SiCl and HCl) to take up chlorine liberated in a reaction such as: (ligands)-$Rh^{III}Cl_3 \rightleftharpoons$ (ligands)$Rh^{I}Cl + Cl_2$.

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[1] J. D. Citron, *J. Org. Chem.*, 1969, **34**, 1977.