Interaction of Acyl Chlorides and Triethylsilane Catalysed by Rhodium Complexes

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The aroyl chlorides XC_6H_4COCl react with triethylsilane in the presence of *mer*-[$RhCl_3(PBu_2Ph)_3$], (A), or better, *trans*-[$RhCl(CO)(PEtPh_2)_2$], (B), at 120 °C to give ketones, $(XC_6H_4)_2CO$, and aldehydes, XC_6H_4CHO, in a ratio which varies with the nature of X, *e.g.*, with catalyst (B), for X = *p*-OMe the yields of aldehyde and ketone are 2 and 63% respectively while for X = *p*-NO_2 the yields are 66 and 0%. For X = *p*-MeO, the aldehyde : ketone ratio varies as *x* in the catalyst *trans*-[$RhCl(CO)(PEt_xPh_{3-x})_2$] is varied progressively from 0 to 3. With catalyst (B), the chlorides RCOCl (R = $PhCH{=}CH_2$, Pr^i, and n-C_5H_{11}) also give fair yields of aldehydes, while for R = Et comparable amounts of aldehyde and ketone are produced. The expected dialdehydes are obtained in good yield from *m*- and *p*-phthaloyl chloride, but products of a different type are formed from *o*-phthaloyl and succinyl chloride. For *p*-nitrobenzoyl chloride with catalyst (B) in toluene, studies have been made of the effect of varying the reaction temperature and the nature of the silicon hydride in the series $SiHEt_3$, $SiHPh_3$, SiH_2Ph_2, and $SiH(OEt)_3$; in all cases some nitrobenzene is formed together with *p*-nitrobenzaldehyde, the proportion varying with the nature of the silane and being especially high for triphenylsilane. A catalytic cycle is suggested involving known types of oxidative additions and reductive eliminations, reduction of Rh^{III} to Rh^{I} species by the silicon hydride, and rearrangement of Rh(COR) to Rh(CO)R systems.

ACYL HALIDES have been known for some years to react with organosilicon hydrides at elevated temperatures to give organosilicon chlorides and aldehydes according to equation (1), but while good yields of silicon chlorides are obtained yields of aldehydes are low, presumably because of secondary reactions at the high temperatures involved.[1] (The reaction was at one time thought to

$$RCOCl + SiHR'_3 \longrightarrow RCHO + SiClR'_3 \quad (1)$$

take place in diethyl ether [2] but this was later shown to be incorrect.[1]) Aluminium trichloride catalyses the reaction. Nickel(II) and zinc(II) chlorides also catalyse the interaction of acyl and aroyl halides with triethylsilane but the reactions are complex and do not yield aldehydes, though these appear to form and then react further.[3] Palladium on charcoal was later found to be an effective catalyst for the acyl chloride–silicon hydride interaction. In many cases the reaction proceeds at room temperature, and 40—70% yields of aliphatic and aromatic aldehydes can be obtained.[4] Triethylsilane is more effective than the hydrides $SiHMePh_2$ and SiHClMePh, while $SiHCl_2Me$, $SiHClMe_2$, $SiHMe_2Ph$, and SiH_2Ph_2 are unreactive. In the light of this demonstration of effective heterogeneous catalysis by a transition metal, we decided to seek homogeneous catalysts, and initially studied the action of rhodium complexes.

RESULTS

We first used *mer*-[$RhCl_3(PBu^n_2Ph)_3$] as catalyst for the interactions of aroyl chlorides and $SiHEt_3$. A slow reaction occurred even at 80 °C, but 120 °C was used to give more acceptable reaction rates. (Separate experiments confirmed that no appreciable reaction occurs at this temperature in the absence of a catalyst.) The reaction between the halides XC_6H_4COCl and $SiHEt_3$ in 1 : 1.25 mol ratio, in the presence of *mer*-[$RhCl_3(PBu^n_2Ph)_3$] (1—2 mmol), gave both the aldehydes XC_6H_4CHO and, unexpectedly, the ketones $(XC_6H_4)_2CO$. In general, as Table 1 shows, the proportion of aldehyde increased markedly with increase in the electron-withdrawing ability of X, so that with X = *p*-MeO only 3% of aldehyde was formed, together with 57% ketone, while with X = *p*-O_2N no ketone was detected and the aldehyde was produced in 35% yield. Cinnamoyl chloride gave no ketone, but a 22% yield of the aldehyde. In all cases the quoted yields refer to the isolated amounts of the ketone or the 2,4-dinitrophenyl hydrazone of the aldehyde. The reaction times quoted are those for disappearance of the ν(SiH) band from the i.r. spectrum of the mixture; the disappearance of the ν(CO) band of the acid chloride and the appearance of the corresponding bands of the aldehyde and ketone were also usually monitored, and

TABLE 1

Interaction of aroyl chlorides, RCOCl (1 mol), and triethylsilane (1.25 mol) in the presence of either *mer*-[$RhCl_3(PBu_2Ph)_3$] (A) or *trans*-[$RhCl(CO)(PEtPh_2)_2$] (B) at 120° C[a] (Yields are of ketone or of aldehyde 2,4-dinitrophenylhydrazone isolated.)

R	Catalyst	Amount of catalyst/mmol	t^b/h	Yield/%	
				R_2CO	RCHO
p-$MeOC_6H_4$	A	1.8	12	57	3
p-MeC_6H_4	A	1.8	48	36	11
Ph	A	1.8	54	40	8
p-ClC_6H_4	A	1.8	17	12	32
p-$O_2NC_6H_4$	A	1.8	12	0	35
PhCH=CH	A	1.8	19	0	22
p-$MeOC_6H_4$	B	2.0	18	63	2
p-$O_2NC_6H_4$	B	2.0	2	0	66
PhCH=CH	B	2.0	6	0	53
Et	B	2.0	5	25	27
Pr^i	B	2.0	5	0	59
Bu^t	B	2.0	90	0	9
n-C_5H_{11}	B	2.0	2	0	68

[a] Bath temperature (see Experimental section). [b] Approximate time for disappearance of ν(SiH).

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[1] J. E. Baines, Ph.D. Thesis, University of Leicester, 1957; see C. Eaborn, 'Organosilicon Compounds,' Butterworths, London, 1960, p. 212.

[2] J. W. Jenkins and H. W. Post, *J. Org. Chem.*, 1950, **12**, 556.

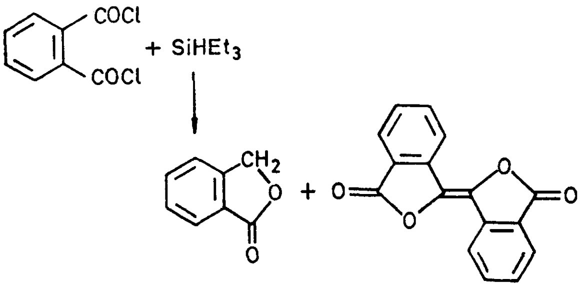
[3] E. Frainnet and J. Causse, *Compt. rend.*, 1967, **C265**, 49; Z. I. Sergeeva, D. D. Tsitovich, and M. G. Voronkov, *Doklady Akad. Nauk S.S.S.R.*, 1960, **134**, 1371; I. I. Lapkin, T. N. Povarnitsyna, and L. A. Kostaveva, *Zhur. obshchei Khim.*, 1969, **39**, 1460.

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

the relative intensities of the aldehyde and ketone bands were consistent with the relative yields of isolated products.

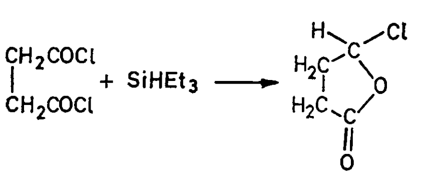
Consideration of the probable reaction mechanism suggested that when the Rh^{III} complex *mer*-$[RhCl_3(PBu^n_2Ph)_3]$ was used the effective catalyst was actually a Rh^I complex formed in a reduction by the silicon hydride, and so the effectiveness of the Rh^I complex *trans*-$[RhCl(CO)(PEt_2Ph)_2]$ was next examined. The results in Table 1 show that it is, indeed, a more effective catalyst, reaction times being shorter and yields of aldehydes and ketones higher; the ketone was obtained from *p*-methoxybenzoyl chloride in 63% yield (together with 2% of the aldehdye), and the aldehyde from *p*-nitrobenzoyl chloride in 66% yield. A 53% yield of the aldehyde was obtained from cinnamoyl chloride. The aliphatic acyl chlorides RCOCl with R = Pr^i and n-C_5H_{11} also gave fair yields of the aldehyde, while for R = Et aldehyde and ketone were produced in comparable amounts in a total yield of over 50%. For R = Bu^t reaction was very slow and only a small amount of aldehyde was obtained.

The highest yields in the reactions examined were the 77 and 74%, respectively, of the dialdehydes *m*- and *p*-$(OHC)_2C_6H_4$ obtained from *m*- and *p*-phthaloyl chloride and $SiHEt_3$ (in 1 : 2.25 mol ratio); the absence of ketone products in these cases is consistent with the strongly electron-withdrawing nature of the COCl and CHO groups. *o*-Phthaloyl chloride gives products of a different type [equation (2)]. Correspondingly, succinyl chloride reacted with $SiHEt_3$ (1 mol) to give γ-chloro-γ-butyrolactone, (III), in 87% yield [equation (3)], but when 2 mol of $SiHEt_3$ were used in an attempt to remove the second chlorine atom and so produce the analogue of (I) the catalyst decomposed after 1 equivalent of the hydride had been used up and the product was again (III).



(2)

(I) (46%) (II) (10%)



(3)

(III) (87%)

The effect of varying the phosphine in the catalyst *trans*-$[RhCl(CO)L_2]$ was briefly examined for L = $PEt_{3-x}Ph_x$ (x = 0—3) with *p*-methoxybenzoyl chloride (Table 1). The nature of the phosphine markedly influenced both the overall yield and the ketone : aldehyde ratio (and possibly also the rate of reaction), but not in any systematic way, and it seems likely that both steric and electronic factors are involved.

A more detailed study was made of the conversion of *p*-nitrobenzoyl chloride into *p*-nitrobenzaldehyde by $SiHEt_3$ (1.25 mol) (or in a few cases other silicon hydrides) in the presence of *trans*-$[Rh(CO)(PEt_2Ph)_2]$ (2 mmol) in toluene. The progress of the reaction was again monitored by recording i.r. spectra of samples taken at appropriate intervals, and the disappearance of the ν(SiH) band was regarded as the end of the reaction, although in some cases a small amount of the acid chloride still remained at this point. G.l.c. was then used to determine the yields of *p*-nitrobenzaldehyde and some other products. The results are in Table 1, and the main features are indicated in (*a*)—(*d*) below. (Unless otherwise indicated, $SiHEt_3$ was the reducing agent.) (*a*) The rate of reaction, as judged by the time taken for disappearance of $SiHEt_3$, decreased markedly when the temperature was lowered from 120 to 90 to 70 °C and the yield of aldehyde also decreased. However, when a small sample of the reaction mixture at 120 °C, taken when a little $SiHEt_3$ still remained, was added to a reaction mixture at 90 or 70 °C the rates of reaction at these lower temperatures were considerably increased, to become comparable with that at 120 °C, but the yields of aldehyde were lower than at 120 °C. (*b*) Addition of a further small amount of $SiHEt_3$ to the mixture at 120 °C after the disappearance of the ν(SiH) band removed the small amount of residual acid chloride but did not significantly improve the yield of aldehyde. However, use of an initial excess of the silane in a reaction at 70 °C did increase the yield of aldehyde from *ca.* 36 to *ca.* 56%, but without causing any apparent increase in the rate of disappearance of the acid chloride. (*c*) In all cases some nitrobenzene was formed. With $SiHEt_3$ the aldehyde : nitrobenzene ratio remained fairly constant at 9 : 1 as the temperature was varied from 120 to 70 °C. Use of $SiHPh_3$ as reducing agent at 120 °C resulted in a slower reaction, but a marked increase in nitrobenzene (*ca.* 30% yield) at the expense of aldehyde. The presence of even a little $SiHEt_3$ (0.25 mmol) together with $SiHPh_3$ (10 mmol) led to substantial restoration of the yield of aldehyde, probably at the expense of nitrobenzene (*ca.* 18% yield). (*d*) Use of $SiH(OEt)_3$ also led to a marked increase in the yield of nitrobenzene (up to 19%) at the expense of *p*-nitrobenzaldehyde.

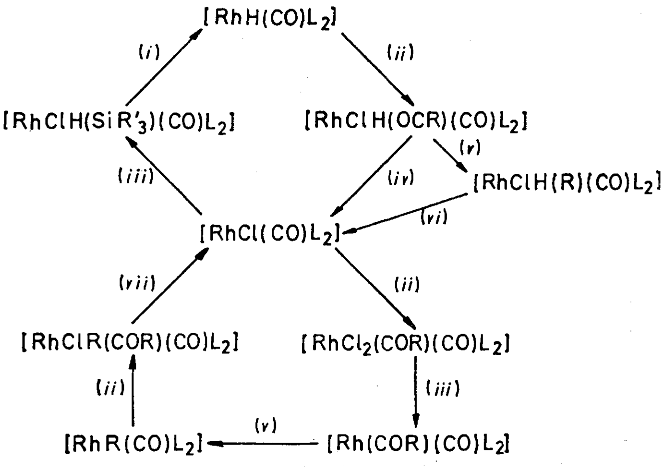
The following additional observations are relevant to the subsequent discussion of mechanism. (*i*) When *p*-nitrobenzaldehyde was treated with $SiHEt_3$ in toluene in the presence of *trans*-$[RhCl(CO)(PEtPh_2)_2]$ at 120 °C for 1 h, *ca.* 65% of the aldehyde reacted and triethyl(*p*-nitrobenzyloxy)silane, $SiEt_3(OCH_2C_6H_4NO_2$-*p*), was formed in *ca.* 50% yield based on unrecovered aldehyde; a small amount of nitrobenzene was also formed. When $SiHPh_3$ was used, 5% of nitrobenzene was formed, together with products of higher molecular weight which were not investigated. (*ii*) When a solution of $SiHEt_3$ (2.0 mmol), triethylamine (2.5 mmol), and *mer*-$[RhCl_3(PBu_2Ph)_3]$ (2.0 mmol) was kept at 50 °C for 15 min, triethylamine hydrochloride was obtained in the theoretical yield based on the overall process (4). (We cannot say whether 2 mol of $Et_3N{\cdot}HCl$ are

$$mer\text{-}[RhCl_3(PBu_2Ph)_3] + 2Et_3N \xrightarrow{SiHEt_3} [RhCl(PBu_2Ph)_3] + 2Et_3N{\cdot}HCl \quad (4)$$

directly formed, together with, say, $Et_3SiSiEt_3$, or whether, as seems more likely, 1 mol of chlorotriethylsilane and 1 mol of hydrochloride are produced with the former then undergoing hydrolysis during the work up.) The rhodium complex produced could not be characterised, but was a dark red oil apparently similar to the oils obtained on treatment of $[RhCl_3(PR_3)_3]$ complexes with sodium tetrahydridoborate or lithium tetrahydridoaluminate.[5] (*iii*) Treatment of the complexes *mer*-$[RhCl_3(PBu_2Ph)_3]$ and $[RhCl(CO)(PEtPh_2)_2]$ with an excess of $SiHEt_3$ at 120 °C led to decomposition and deposition of rhodium metal. When acyl chlorides were initially present such decomposition occurred only after all the acyl chloride had reacted.

DISCUSSION

Plausible catalytic cycles can readily be devised to account for the formation of the aldehydes, ketones, and fully decarbonylated RH compounds using sequences of oxidative additions and reductive eliminations involving Rh^I and Rh^{III} complexes, rearrangements of RCORh to RRh(CO) systems, and reductions of $[RhCl_2(X)(CO)L_2]$ to $[RhX(CO)L_2]$ complexes by the silicon hydride. The Scheme presents perhaps the simplest cycles which can be written. All the steps are of well known types, except for loss of R_2CO from Rh(R)(COR) systems, and in this case the corresponding reaction is well established for Pt(R)(COR) systems.[6] It will be appreciated, however, that other more complex sequences can be derived by reasonable permutations of oxidative additions of $SiHR'_3$, HCl, and RCOCl with reductive eliminations of $SiHR'_3$, $SiClR'_3$, HCl, RH, RCHO, R_2CO, H_2, and HCl. Indeed, the substantial acceleration caused by addition to the reaction mixture at 70 °C of a small sample of the mixture produced by incomplete reaction at 120 °C suggests that the effective catalyst is not the initially taken $[RhCl(CO)(PEtPh_2)_2]$, and that this complex does not take part in the cycles, as we have assumed for simplicity, but that a more reactive catalyst is generated from it. Possibilities include three-coordinate rhodium(I) species or the hydride $[RhH(CO)(PEtPh_2)_2]$, with the cycles being adjusted to avoid re-formation at any stage of $[RhCl(CO)(PEtPh_2)_2]$; cycles avoiding $[RhCl(CO)(PEtPh_2)_2]$ can be written by assuming that the silicon hydride readily converts all Rh–Cl into Rh–H bonds. When *mer*-$[RhCl_3(PBu_2Ph)_3]$ is used as catalyst it seems highly probable that it is rapidly converted by $SiHEt_3$ into $[RhCl(PBu_2Ph)_3]$. It is not known whether the overall reaction (4) involves interaction of the silane with the complex itself or with chlorine produced by its (normally reversible) dissociation.



SCHEME (*i*), $-SiClR'_3$; (*ii*), RCOCl; (*iii*), $SiHR'_3$; (*iv*), $-RCHO$; (*v*), $-CO$; (*vi*), $-RH$; (*vii*), $-R_2CO$

The increase in the aldehyde : ketone product ratio with increasing electron withdrawal by X in the reactant XC_6H_4COCl is consistent with the suggestion that the rearrangement $Rh(COC_6H_4X) \longrightarrow Rh(CO)(C_6H_4X)$ is facilitated by electron withdrawal by X,[7] since the more readily the rearrangement occurs the greater the likelihood of producing the ketone rather than the aldehyde. Again, the rearrangement is known to occur more readily for aryl than alkyl RCORh systems,[7] and, consistently, aldehyde greatly predominates for most of the aliphatic acyl halides examined.

The formation of nitrobenzene from *p*-nitrobenzyl chloride is readily accounted for, since it is known that an aryl and a hydrido-ligand can leave together from rhodium.[8,9] Decarbonylations of the type $RCOCl \longrightarrow RCl$ are catalysed by Rh^I complexes,[7,8] and, since in the presence of silicon hydrides Rh–Cl bonds are likely to be converted into Rh–H bonds, formation of RH compounds would be expected to take over from RCl in the presence of such hydrides. In terms of the Scheme, formation of the XC_6H_5 species, as of the ketones, would be expected to increase, at the expense of the aldehydes, with decreasing electron withdrawal by X, but we sought such a product only from *p*-nitrobenzoyl chloride, the one case for which g.l.c. analysis was used. Since decarbonylation of aldehydes is known to be catalysed by Rh complexes,[8,9] and since we observed the formation of some nitrobenzene from *p*-nitrobenzaldehyde under our conditions, it is possible that some of the nitrobenzene formed in the *p*-nitrobenzoyl chloride reaction came from initially produced aldehyde, but it seems unlikely that much did since the presence of acyl chloride would probably prevent effective oxidative addition of the aldehyde to the rhodium. The enhancement of the nitrobenzene yield when $SiHPh_3$ is used in place of $SiHEt_3$ may be associated with the greater stability of $RhH(SiPh_3)$ than of $RhH(SiEt_3)$ systems, which allows more time for the decarbonylation to occur.

Brief consideration must be given to the fact that good yields of aldehydes and ketones can be obtained from acid chlorides, even though it is known that aldehydes and ketones react very readily, often at room temper-

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[5] J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.*, 1964, 2508.

[6] J. D. Ruddick and B. L. Shaw, *J. Chem. Soc. (A)*, 1969, 2801.

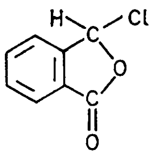
[7] M. C. Baird, J. T. Mague, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc. (A)*, 1967, 1347.

[8] K. Ohno and J. Tsuji, *J. Amer. Chem. Soc.*, 1968, **90**, 99.

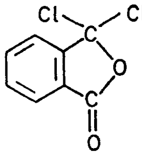
[9] M. C. Baird, C. J. Nyman, and G. Wilkinson, *J. Chem. Soc. (A)*, 1968, 348.

ature, with silicon hydrides in the presence of Rh^{I} complexes to give hydrosilylation derivatives of primary or secondary alcohols, RR'CHOSiR''_3,[10] and we confirmed that *p*-nitrobenzaldehyde reacts in this way under the conditions used for the *p*-nitrobenzoyl chloride reactions. Presumably oxidative addition of the acyl halides occurs so readily that the aldehydes are excluded from effective interaction with the rhodium centres while significant amounts of the chlorides are present.

The formation of γ-chloro-γ-butyrolactone, (III), from succinyl chloride can be understood in terms of initial formation of the monoaldehyde $\text{HCO}{\cdot}\text{CH}_2\text{CH}_2{\cdot}\text{COCl}$, which then cyclizes, as proposed by Kuivila for formation of the same product on treatment of succinyl chloride with organotin hydrides.[11] Formation of compound (I) from *o*-phthaloyl chloride can be interpreted in a similar fashion provided that rapid reduction of the intermediate species (IV) is assumed, which is reasonable since the chlorine to be removed is at a reactive benzylic position. However, 3,3-dichlorophthalide, (V), can be formed fairly readily from *o*-phthaloyl chloride,[12] and direct catalysed reduction of this species by the hydride is also possible, though less likely. The formation of *trans*-3,3'-biphthalide, (II), may involve intermediate carbene species, possibly formed from compound (V); compound (II) is known to be formed from *o*-phthaloyl chloride on treatment with silver powder at 150 °C [13] or from the chloride or its isomer (IV) on treatment with certain phosphines.[14]



(IV)



(V)

Reactions of Arenesulphonyl Chlorides.—The complex *trans*-$[\text{RhCl(CO)(PEtPh}_2)_2]$ catalysed a reaction between arenesulphonyl halides, RSO_2Cl, and SiHEt_3 at 120 °C. The products expected by analogy with the reactions of acyl halides are the sulphinic acids RSO_2H, and such a product, $p\text{-MeOC}_6\text{H}_4\text{SO}_2\text{H}$, was obtained in 25% yield from *p*-methoxybenzenesulphonyl chloride. However, when *p*-chlorobenzenesulphonyl chloride was used a more complex reaction occurred [equation (5)]. The

$$p\text{-ClC}_6\text{H}_4\text{SO}_2\text{Cl} + \text{SiHEt}_3 \longrightarrow (p\text{-ClC}_6\text{H}_4)_2\text{SO}_2 + \underset{(46\%)}{(p\text{-ClC}_6\text{H}_4\text{SO})_2} + \text{SiClEt}_3 \quad (5)$$

primary initial product is probably the sulphinic acid $p\text{-ClC}_6\text{H}_4\text{SO}_2\text{H}$, since this compound reacted with SiHEt_3 in the presence of the catalyst (and, less readily, even in its absence) to give the disulphoxide $(p\text{-ClC}_6\text{H}_4\text{SO})_2$. The formation of the sulphone in reaction (5) is directly analogous to the formation of ketones from acyl chlorides, and catalytic cycles analogous to those in the Scheme can be written for the formation of the sulphinic acids and sulphones.

EXPERIMENTAL

General.—All reactions were carried out under dry nitrogen in a flask fitted with a reflux condenser and a side-arm for sampling by means of a syringe. The reaction temperatures noted below and in Table 1 are actually those of the bath used to heat the mixtures. In all cases the silicon hydride was added to the mixture of the catalyst and acyl chloride, since addition of the hydride directly to the complex caused decomposition. The identities of the organic products mentioned below were confirmed where appropriate by use of i.r., n.m.r., and mass spectrometry, comparison with authentic samples being made when necessary. The 2,4-dinitrophenylhydrazine reagent was prepared immediately before use by adding concentrated sulphuric acid (2 cm³) dropwise to a solution of the hydrazine (1 g) in methanol (40 cm³).

Preparation of Catalysts.—The complexes *mer*-$[\text{RhCl}_3(\text{PBu}^{\text{n}}{}_2\text{Ph})_3]$, m.p. 156—157 °C, *trans*-$[\text{RhCl(CO)(PEtPh}_2)_2]$, m.p. 161—164 °C (decomp.), *trans*-$[\text{RhCl(CO)(PEt}_2\text{Ph})_2]$, m.p. 116—118 °C, *trans*-$[\text{RhCl(CO)(PEt}_3)_2]$, m.p. 74—76 °C, and *trans*-$[\text{RhCl(CO)(PPh}_3)_2]$, m.p. 195—197 °C, were made by established methods.

Reactions of Triethylsilane with Acid Chlorides.—p-*Methoxybenzoyl Chloride.* (i) Triethylsilane (1.45 g, 0.0125 mol) was added to a solution of *mer*-trichlorotris(di-n-butylphenylphosphine)rhodium(III) (0.016 g, 0.018 mmol) in *p*-methoxybenzoyl chloride (1.70 g, 0.010 mol). When the mixture was warmed its colour changed from orange to yellow. It was heated in an oil-bath at 120 °C for 12 h, the progress of the reaction being monitored by recording the i.r. spectra of small samples. The solid which separated on cooling was filtered off, recrystallised from light petroleum (b.p. 80—100 °C), and dried *in vacuo* to give 4,4'-dimethoxybenzophenone (0.69 g, 57%), m.p. 143—144 °C (lit.,[15] 144 °C). The filtrate was treated with a solution of 2,4-dinitrophenylhydrazine to give an orange-red precipitate, which was recrystallised twice from glacial acetic acid to give *p*-methoxybenzaldehyde 2,4-dinitrophenylhydrazone (0.11 g, 3%), m.p. 253—254 °C (lit.,[16] 254 °C).

(ii) Similar procedures with other catalysts (0.01 mmol) and with the reaction times noted in Table 1 gave the results shown.

p-Chlorobenzoyl chloride in the presence of mer-$[\text{RhCl}_3(\text{PBu}_2\text{Ph})_3]$. The reaction was carried out as described for $p\text{-MeOC}_6\text{H}_4\text{COCl}$, but with 17 h of heating. The mixture was subsequently kept at 0 °C overnight, and the precipitate was filtered off and recrystallised from ethanol to give 4,4'-dichlorobenzophenone (0.15 g, 12%), m.p. 146—147 °C (lit.,[15] 147—148 °C). From the filtrate, *p*-chlorobenzaldehyde 2,4-dinitrophenylhydrazone (1.02 g, 32%), was obtained, m.p. 264—265 °C (from MeCO_2H) (lit.,[16] 266 °C).

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[10] I. Ojima, M. Nihonyagi, and Y. Nagai, *J.C.S. Chem. Comm.*, 1972, 938; R. J. P. Corriu and J. E. Moreau, *ibid.*, 1973, 38; C. Eaborn, K. Odell, and A. Pidcock, *J. Organometallic Chem.*, 1973, **63**, 93.

[11] H. G. Kuivila, *J. Org. Chem.*, 1960, **25**, 284.

[12] F. B. Garner and S. Sugden, *J. Chem. Soc.*, 1927, 2877.

[13] A. Ador, *Annalen*, 1872, **164**, 230.

[14] H. Kunzeck and K. Rühlmann, *J. Organometallic Chem.*, 1972, **42**, 391.

[15] Beilstein's Handbuch der Organischen Chemie.

[16] ' Dictionary of Organic Compounds,' 4th edn., eds. J. R. A. Pollock and R. Stevens, Eyre and Spottiswoode, London, 1965.

p-*Toluoyl chloride in the presence of* mer-[RhCl$_3$(PBu$_2$Ph)$_3$]. The reaction was carried out as described for p-MeOC$_6$H$_4$COCl but with heating for 36 h. The chlorotriethylsilane and residual SiHEt$_3$ were removed under reduced pressure, and the solid which separated was filtered off and recrystallised from ethanol to give di-p-tolyl ketone (36%), m.p. 94—95 °C (lit.,[15] 95 °C). The filtrate was treated with 2,4-dinitrophenylhydrazine to give, after two recrystallisations from glacial acetic acid, p-methylbenzaldehyde 2,4-dinitrophenylhydrazone (0.34 g, 11%), m.p. 240—242 °C (lit.,[16] 232—234 °C).

Benzoyl chloride in the presence of mer-[RhCl$_3$(PBu$_2$Ph)$_3$]. Triethylsilane (7.25 g, 0.0625 mol) was added to PhCOCl (7.02 g, 0.05 mol) and *mer*-[RhCl$_3$(PBu$_2$Ph)$_3$] (0.080 g, 0.09 mmol) and the mixture was kept in a bath at 120 °C for 54 h with the usual i.r. monitoring. It was then distilled and the fraction of b.p. 40—75 °C at 10 mmHg * was washed with methanol into a solution of 2,4-dinitrophenylhydrazine. The precipitate was recrystallised from glacial acetic acid to give benzaldehyde 2,4-dinitrophenylhydrazone (1.16 g, 8%), m.p. 237—238 °C (lit.,[16] 237 °C). The residue from the distillation was washed with methanol into a solution of 2,4-dinitrophenylhydrazine to give, after recrystallisation from glacial acetic acid, benzophenone 2,4-dinitrophenylhydrazone (3.62 g, 40%), m.p. 237—238 °C (lit.,[16] 238 °C).

p-*Nitrobenzoyl chloride.* (i) Triethylsilane (1.45 g, 0.0125 mol) was added to a mixture of p-O$_2$NC$_6$H$_4$COCl (1.85 g, 0.010 mol) and *mer*-[RhCl$_3$(PBu$_2$Ph)$_3$] (0.016 g, 0.018 mmol). When the mixture was warmed the aroyl halide dissolved to give an orange solution which then turned yellow. After 12 h at 120 °C the mixture had become dark orange, and cooling gave a solid which was filtered off and recrystallised from water to give pale yellow crystals. The filtrate was extracted with boiling water and the aqueous extracts deposited pale yellow crystals on cooling. The combined pale yellow crystals (0.53 g, 35%), m.p. 104—106 °C (lit.,[16] 106 °C) were shown to be p-nitrobenzaldehyde. After the extractions the residual oil gave no precipitate with 2,4-dinitrophenylhydrazine.

(ii) A similar procedure but involving *trans*-[RhCl(CO)(PEtPh$_2$)$_2$] (0.020 mmol) and a reaction time of only 2 h gave p-nitrobenzaldehyde in 66% yield.

3-*Phenylpropenoyl chloride.* (i) Triethylsilane (1.45 g, 0.0125 mol) was added to a mixture of 3-phenylpropenoyl chloride (1.65 g, 0.010 mol) and *trans*-[RhCl(CO)(PEtPh$_2$)$_2$] (0.012 g, 0.020 mmol). The mixture was kept at 120 °C for 6 h then cooled and washed with methanol into 2,4-dinitrophenylhydrazine solution to give 3-phenylpropenal 2,4-dinitrophenylhydrazone (1.65 g, 53%), m.p. 254—255 °C (decomp.) (from MeCO$_2$H) [lit.,[16] 255 °C (decomp.)].

(ii) With *mer*-[RhCl$_3$(PBu$_2$Ph)$_3$] (0.018 mmol) as catalyst, and with 19 h reaction, the same product was obtained in 22% yield.

Propionyl chloride. Triethylsilane (1.45 g, 0.125 mol) was added to propionyl chloride (9.2 g, 0.10 mol) and *trans*-[RhCl(CO)(PEtPh$_2$)$_2$] (0.12 g, 0.020 mmol), and the mixture was heated under reflux by partial immersion in a bath at 120 °C. Fractionation gave propionaldehyde (1.58 g, 27%), b.p. 47—50 °C (lit.,[16] 49 °C), then a fraction of b.p. 95—110 °C, which was treated with 2,4-dinitrophenylhydrazine to give diethyl ketone 2,4-dinitrophenylhydrazone (3.35 g, 25%), m.p. 155—156° (from EtOH) (lit.,[16] 156 °C).

Isobutyryl chloride. There action was carried out, but for 6 h, as described for propionyl chloride. Working up as described for the 3-phenylpropenoyl analogue gave isobutyraldehyde 2,4-dinitrophenylhydrazone (1.48 g, 59%), m.p. 181—182 °C (from EtOH) (lit.,[16] 182 °C).

Pivaloyl chloride. The procedure used for 3-phenylpropenoyl chloride, but with 90 h reaction, gave pivaldehyde 2,4-dinitrophenylhydrazone (0.23 g, 9%), m.p. 208—210 °C (from MeCO$_2$H) (lit.,[16] 210 °C).

n-*Hexanoyl chloride.* A procedure similar to that described for butyryl chloride, but with reaction under reflux for only 2 h, gave hexanal 2,4-dinitrophenylhydrazone (1.91 g, 68%), m.p. 104—105 °C (lit.,[16] 104 °C).

Succinyl chloride. A mixture of SiHEt$_3$ (11.6 g, 0.10 mol), succinyl chloride (7.75 g, 0.05 mol), and *trans*-[RhCl(CO)(PEtPh$_2$)$_2$] was heated in a bath at 120 °C for 0.5 h. Residual SiHEt$_3$ and SiClEt$_3$ were distilled off, and the residue fractionated to give γ-chloro-γ-butyrolactone (5.2 g, 87%), b.p. 66—68 °C at 2 mmHg (lit.,[11] 45 °C at 0.4 mmHg).

1,2-*Phthaloyl chloride.* When a mixture of SiHEt$_3$ (2.61 g, 0.0225 mol), 1,2-phthaloyl chloride (2.03 g, 0.020 mol), and *trans*-[RhCl(CO)(PEtPh$_2$)$_2$] (0.012 g, 0.020 mol) was heated in a bath at 120 °C the initially yellow-green solution turned orange and after *ca.* 5 min a solid separated. After 2 h the mixture, which had darkened, was allowed to cool and the solid was filtered off and recrystallised from ethanol to give pale yellow *trans*-3,3′-biphthalide, (II) (0.13 g, 10%), m.p. 331-332 °C (lit.,[16] 331 °C) (Found: C, 72.7; H, 3.1. Calc. for C$_{16}$H$_8$O$_4$: C, 72.7; H, 3.3%). The filtrate from the reaction mixture was evaporated under reduced pressure until a solid began to separate, and n-hexane (25 cm^3) was added and the mixture cooled to 0 °C. The precipitate was filtered off, and recrystallised from water to give phthalide, (I) (0.62 g, 46%), m.p. 74—75 °C (lit.,[16] 75 °C). The residual oil gave no precipitate when treated with 2,4-dinitrophenylhydrazine.

1,3- *and* 1,4-*Phthaloyl chloride.* (i) A mixture of SiHEt$_3$ (2.61 g, 0.0225 mol), 1,3-phthaloyl chloride (2.03 g, 0.010 mol), and *trans*-[RhCl(CO)(PEtPh$_2$)$_2$] (0.012 g, 0.020 mmol) was kept in a bath at 120 °C for 3.5 h, then allowed to cool. Treatment with 2,4-dinitrophenylhydrazine gave isophthalaldehyde 2,4-dinitrophenylhydrazone (2.4 g, 77%), m.p. 240—241 °C (lit.,[16] 242 °C).

(ii) A similar procedure, but with 6 h reaction, and precipitation with 4-nitrophenylhydrazine (some 2N-acetic acid was added to induce crystallisation) gave terephthalaldehyde 4-nitrophenylhydrazone (2.82 g, 74%), m.p. 275—278 °C (lit.,[16] 281 °C).

Reaction of Triethylsilane with mer-[RhCl$_3$(PBu$_2$Ph)$_3$].—Triethylsilane (0.232 g, 2.0 mmol) and triethylamine (0.25 g, 2.49 mmol) were added to an orange solution of *mer*-[RhCl$_3$(PBu$_2$Ph)$_3$] (0.875 g, 1.0 mmol) in benzene (5 cm^3). When the mixture was warmed at 50 °C for 15 min the orange solution turned dark red and a solid separated. This was filtered off, washed with benzene, and dried to give triethylamine hydrochloride [0.267 g, 97% based on equation (4)], the i.r. spectrum of which was identical with that of an authentic sample.

Influence of Conditions on the Reaction between p-*Nitrobenzoyl Chloride and Silicon Hydrides.*—The reactions involved p-nitrobenzoyl chloride (10 mmol), silicon hydride (12.5 mmol), and *trans*-[RhCl(CO)(PEtPh$_2$)$_2$] (20 μmol) dissolved in a solvent (10 cm^3), which was toluene unless otherwise stated. (The toluene was purified by passage through a column of activated alumina.) An atmosphere

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* 1 mmHg ≈ 13.6 × 9.8 Pa.

of dry nitrogen was maintained in the reaction vessel, which was fitted with a Subaseal cap through which samples were taken for i.r. spectroscopy. The temperature noted in Table 2 is that of the bath in which the flask was immersed.

TABLE 2

Effect of varying the phosphine ligand, L, of *trans*-[RhCl(CO)L_2] (1 mmol) in the reaction between *p*-methoxybenzoylchloride, RCOCl (1 mol), and triethylsilane (1.25 mol) (Yields are of the ketone or of the aldehyde 2,4-dinitrophenylhydrazone isolated)

L	t */h	Yield/%	
		R_2CO	RCHO
PPh_3	12	45	2
$PEtPh_2$	18	63	2
PEt_2Ph	12	35	22
PEt_3	18	27	4

* The bath temperature was 120 °C and the time is that for disappearance of ν(SiH).

Reaction was normally taken to be complete when the ν(Si–H) band had disappeared. A known amount of n-eicosane was added as a standard, and g.l.c. analysis carried out with a 1.5 m column of free fatty acid polymer (ffap) on Chromosorb G (100—120 mesh) at 200 °C with nitrogen as carrier gas.

Interaction of p-*Nitrobenzaldehyde and Silicon hydride*.—(i) When *p*-nitrobenzaldehyde was used in place of *p*-nitrobenzoyl chloride in the reaction with triphenylsilane at 120 °C for 44 h, g.l.c. analysis revealed that nitrobenzene was formed in 5% yield. The products of higher molecular weight were not investigated. (ii) (Experiment conducted by D. A. Norfolk.) A mixture of *p*-$O_2NC_6H_4CHO$ (0.75 g), $SiHEt_3$ (1.45 g), *trans*-[RhCl(CO)($PEtPh_2$)$_2$] (6 mg), and eicosane (0.51 g) in toluene (5 cm^3) was kept at 120 °C for 1 h. G.l.c. analysis indicated that *ca.* 0.4 g of triethyl(4-nitrobenzyloxy)silane (46% based on aldehyde converted) had been formed, together with a small amount of $PhNO_2$. (Calibration was carried out with an authentic sample of the product prepared from *p*-nitrobenzyl alcohol and $SiClEt_3$ in the presence of Et_3N.)

Reaction of p-*Methoxybenzenesulphonyl Chloride*.—Triethylsilane (2.03 g, 0.0175 mol) was added to *p*-methoxybenzenesulphonyl chloride (2.07 g, 0.01 mol) and *trans*-[RhCl(CO)($PEtPh_2$)$_2$] (0.012 g, 0.02 mmol) in toluene (5 cm^3). The yellow solution was heated under reflux for 2 h, and toluene was removed under reduced pressure from the resulting dark red solution. Addition of light petroleum (b.p. 40—60 °C) gave a dark solid, which was recrystallised from water and shown to be *p*-methoxybenzenesulphinic acid (0.43 g, 25%), m.p. 94—96° (lit.,[15] 97—98 °C), *m/e* 172 (M^+). Removal of the light petroleum from the mother liquor left an intractable red oil.

Reaction of p-*Chlorobenzenesulphonyl Chloride*.—Triethylsilane (2.03 g, 0.0175 mol) was added to *p*-chlorobenzenesulphonyl chloride (2.11 g, 0.01 mol) and *trans*-[RhCl(CO)($PEtPh_2$)$_2$] (0.012 g, 0.02 mmol) and the mixture was heated under reflux for 1 h. The resulting dark red solution was transferred to an alumina column (Laporte Spence, grade 'H'), and elution with chloroform–hexane (1 : 4) gave di(*p*-chlorophenyl) sulphone (0.13 g, 9%), m.p. (from EtOH) 146–147 °C (lit.,[15] 147 °C), *m/e* 286 (M^+). Further elution with methanol gave di(*p*-chlorophenyl) disulphoxide (0.73 g, 46%), m.p. (from EtOH), 136—137° (lit.,[15] 137—138 °C), *m/e* 318 (M^+).

TABLE 3

Yields of *p*-nitrobenzaldehyde and nitrobenzene formed in the reaction between *p*-nitrobenzoyl chloride (10 mmol) and organosilicon hydrides (12.5 mmol) in the presence of *trans*-[RhCl(CO)($PEtPh_2$)$_2$] (20 μmol) in benzene (10 cm^3) (Yields were determined by g.l.c. analysis)

Silane	θ_c [a]/°C	t [b]/h	Yield/%	
			p-$O_2NC_6H_4CHO$	$PhNO_2$
$SiHEt_3$	120	1	55	5
	120	1	51	5
	90	19	28	3
	90	20	30	5
	90	22	35	5
	90 [c]	1.25 [d]	39	6.5
	70	35 [d]	29	2.5
	70	43 [d]	36	4.5
	70	1.5 [d]	30	2
$SiHPh_3$	120	8.5	13.5	32
	120	8 [d]	9.5	28
SiH_2Ph_2 [e]	120	1.5 [f]	3	5.5
	120	3.5	1	10
$SiH(OEt)_3$	120	8	22 [g]	19
		10	26 [g]	14

[a] Bath temperature. [b] Approximate time for disappearance of ν(SiH). [c] A small quantity of reaction mixture taken at 120 °C almost to disappearance of the ν(SiH) band was added. [d] A small amount of aroyl chloride still remained, as revealed by the presence of the relevant ν(C=O) bond. [e] A gas, assumed to be hydrogen, was evolved on mixing the reactants. [f] A small ν(SiH) band still remained. [g] Significant quantities of *m*-nitrobenzaldehyde were also detected. The reality of this apparent isomerisation will be investigated.

Reaction of p-*Chlorobenzenesulphinic Acid*.—Triethylsilane (2.32 g, 0.02 mol) was added to *p*-chlorobenzenesulphinic acid (1.72 g, 0.01 mol) and *trans*-[RhCl(CO)($PEtPh_2$)$_2$] (0.012 g, 0.02 mmol) and the temperature of the mixture was raised with an oil-bath. Gas evolution began at a bath temperature of 70 °C and the solid sulphinic acid began to dissolve. The mixture was heated at 100 °C for 2 h, then allowed to cool. Addition of n-hexane and cooling gave a solid, which was filtered off and recrystallised from ethanol to give di(*p*-chlorophenyl) disulphoxide (0.98 g, 64%), m.p. 136—137 °C.

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