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HYDROSILYLATION OF AROMATIC AZOMETHINS

II *. REACTION OF TRIETHYLSILANE WITH BENZYLIDENE ANILINE IN THE PRESENCE OF TRIS(TRIPHENYLPHOSPHINE)RHODIUM CHLORIDE *

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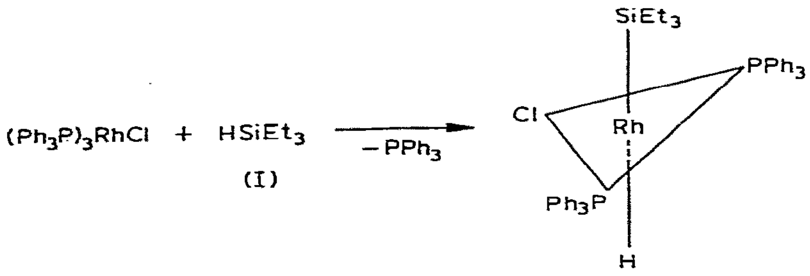
Summary

The reaction of triethylsilane (I) with benzylidene aniline (II), catalyzed by tris(triphenylphosphine)rhodium chloride involves the following: hydrosilylation and reduction of II and hydronegative desilylation of *N*-(triethylsilyl)-*N*-benzylaniline (III). The role of the silyl—rhodium complex $(Ph_3P)_2(Et_3Si)Rh(H)Cl$ in the above reactions is demonstrated and the mechanism of the observed transformations discussed.

In the preceding paper [1], catalytic interaction of trialkyl- or aryl-hydrosilanes with aromatic azomethins was shown to be a complex process. Tris(triphenylphosphine)rhodium chloride was the most selective catalyst used. The main final products of the reaction between triethylsilane (I) and benzylideneaniline (II)



(A)

(1)

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* For part 1 see ref. 1.

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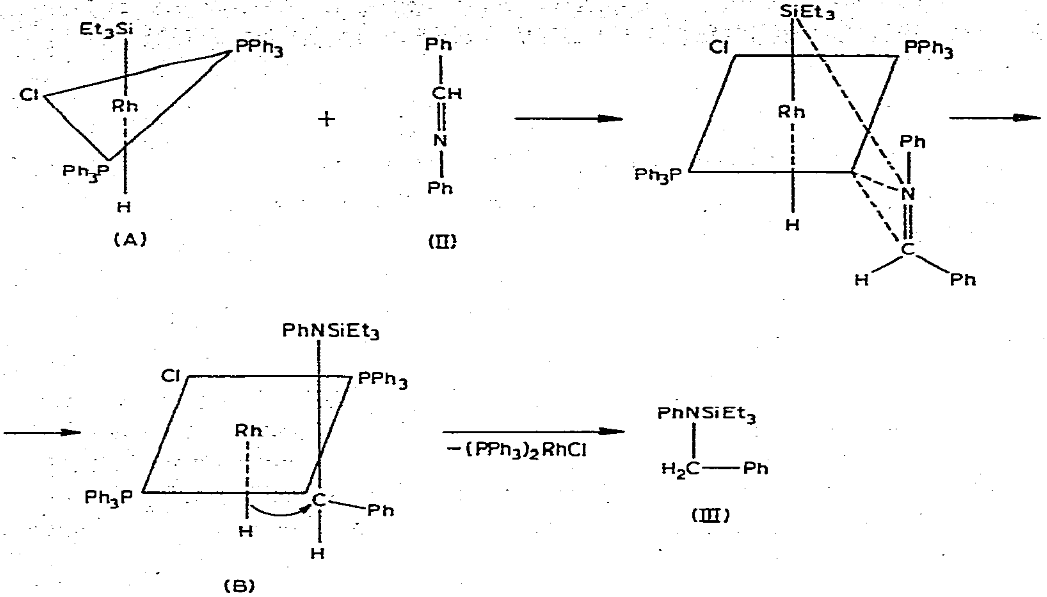
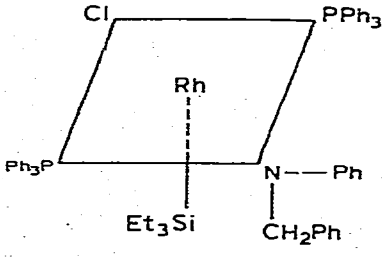
were *N*-(triethylsilyl)-*N*-benzylaniline (III), *N*-benzylaniline (IV) and hexaethyldisilane (V).

The reaction mechanism of the hydrosilylation of benzylidene aniline (II) is expected to be similar to that for carbonyl-containing compounds [2—6]. The first stage is oxidative addition of triethylsilane to the cationic rhodium complex (eq. 1) [7—10]. The azomethin is then coordinated to the silyl—rhodium complex A after which insertion activated by this coordination of the C=N bond in the rhodium—silicon bond takes place and the intermediate product B is formed; reductive elimination gives the final reaction products (eq. 2).



(2)

It is also possible that after coordination the hydrogen of the Ph—H bond attacks the carbon atom (or the C=N bond, activated by coordination, inserts itself into the rhodium—hydrogen bond) to give the intermediate compound C; reductive elimination leads to the final reaction products [3].



(C)

The reaction of bis(triphenylphosphine)rhodium chloride with triphenylphosphine (from reaction 1) results in regeneration of the catalyst (eq. 3). A silyl-

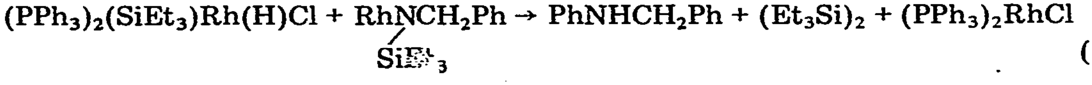
$$(PPh_3)_2RhCl + PPh_3 \rightarrow (PPh_3)_3RhCl \qquad (3)$$

rhodium complex may also be formed by reaction 4. However, the reaction of

$$(PPh_3)_2RhCl + HSiEt_3 \rightarrow \underset{(A)}{(PPh_3)_2(SiEt_3)Rh(H)Cl} \qquad (4)$$

benzylidene aniline with complex A prepared by the method in ref. 8 gives only the product of benzylidene aniline reduction, *N*-benzyl aniline (IV) (Table 1). This was quite unexpected since, firstly, we obtained the silyl—rhodium complex A (with hexane added) from the reaction between triethylsilane (I) and benzylidene aniline (II) catalyzed by tris(triphenylphosphine)rhodium chloride; and secondly, if complex A is used in catalytic quantities the products of reaction between I and II should, in addition to *N*-benzylaniline (IV), contain the product of hydrosilylation, *N*-(triethylsilyl)-*N*-benzylaniline (III) (Table 1).

This led to the assumption that there is a possibility that hydrogenative desilylation of *N*-(triethylsilyl)-*N*-benzylaniline (III) by silyl—rhodium complex A is taking place. Indeed, an almost quantitative conversion of hydrosilylation product (III) into the reduced form (IV) was observed in the above mentioned reaction (at 1 : 1 mol. ratio) (Table 2) (reaction 5). It is quite probable that the



$$\underset{(A)}{(PPh_3)_2(SiEt_3)Rh(H)Cl} + \underset{(III)}{Rh\underset{SiEt_3}{N}CH_2Ph} \rightarrow \underset{(IV)}{PhNHCH_2Ph} + \underset{(V)}{(Et_3Si)_2} + (PPh_3)_2RhCl \qquad (5)$$

reaction mechanism 5 involves stages of *N*-(triethylsilyl)-*N*-benzylaniline (III) coordination with silyl—rhodium complex (A), insertion of the amino group into the rhodium—silicon bond with simultaneous splitting-off of the triethylsilyl group, and reductive elimination which leads to the final reaction products.

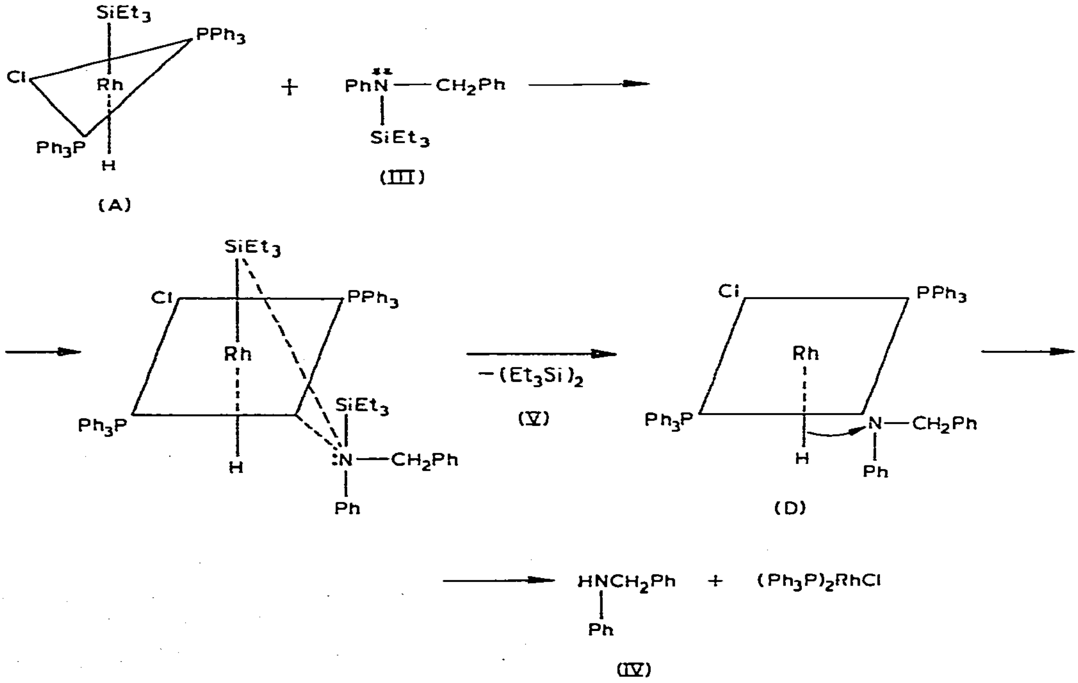


TABLE 1

REACTIONS BETWEEN TRIETHYLSILANE (I) AND BENZYLIDENE ANILINE (II) CATALYZED BY SILYL—RHODIUM COMPLEX A

Initial compounds (mol)			Reaction products (wt. %)			
Benzylidene aniline (II)	Triethylsilane (I)	Complex A	Hexaethyldislane (V) [a]	Benzylidene aniline (II)	*N*-Benzyl aniline (IV)	*N*-(Triethylsilyl)-*N*-benzylaniline (III)
1.0	1.0	0.04	18.8	20.3	48.0	12.9
1.0	1.5	0.04	11.5	3.1	18.7	66.7
1.0	5.1	0.033	25.6	13.4	36.8	24.2
1.0	—	1.08	14.1 [b]	28.9	28.3	—

[a] A small impurity of hexaethyidisiloxane is present. [b] Reaction products also contain 28.7 wt.% of triethylchlorosilane, in other cases the precise quantity of triethyl chlorosilane could not be measured (chromatographs together with benzene).

We can obviously not disregard the possibility of *N*-benzylaniline (IV) being formed from the reaction of triethylsilane (I) with benzylidene aniline (II), excluding the hydrosilylation stage (reaction 6 or 6a).

$$2\,\underset{(A)}{(PPh_3)_2(SiEt_3)Rh(H)Cl} + PhN{=}CHPh \rightarrow \underset{(IV)}{PhNHCH_2Ph} + \underset{(V)}{(SiEt_3)_2} + 2(Ph_3P)RhCl \qquad (6)$$

$$\underset{(A)}{(PPh_3)_2(SiEt_3)Rh(H)Cl} + PhN{=}CHPh \xrightarrow{HSiEt_3} \underset{(IV)}{PhNHCH_2Ph} + \underset{(V)}{(Et_3Si)_2} + (Ph_3P)_2RhCl \qquad (6a)$$

The formation of *N*-benzylaniline (IV) by catalytic hydrogenation of benzylidene aniline (II) by hydrogen (hydrogen is evolved during the catalytic dehydrogenation of organohydrosilane [1]) (eq. 7) does not seem to take place, since

$$\underset{(II)}{PhCH{=}NPh} + H_2 \overset{(Ph_3P)_3RhCl}{\not\longrightarrow} \underset{(IV)}{PhCH_2NHPh} \qquad (7)$$

attempts to hydrogenate benzylidene aniline with molecular hydrogen in the presence of tris(triphenylphosphine)rhodium chloride failed.

Hydrogenolysis of *N*-benzyl aniline (IV) proceeds to a slight extent (not more than 5% after 5 days heating at 60°C) (Table 2) (eq. 8).

$$\underset{(IV)}{PhCH_2NHPh} + (PPh_3)_2(Et_3Si)Rh(H)Cl \xrightarrow{HSiEt_3} PhCH_3 + \underset{(V)}{(Et_3Si)_2} + (Ph_3P)_2RhCl + PhNH_2 \qquad (8)$$

As can be seen from Table 1, the ratio between the hydrosilylation and reaction products is dependent on the quantity of triethylsilane used. That the yield of *N*-(triethylsilyl)-*N*-benzylaniline (III) is a maximum at hydrosilane/azomethin mol. ratio >1, and a large excess of triethylsilane results in a reduction in

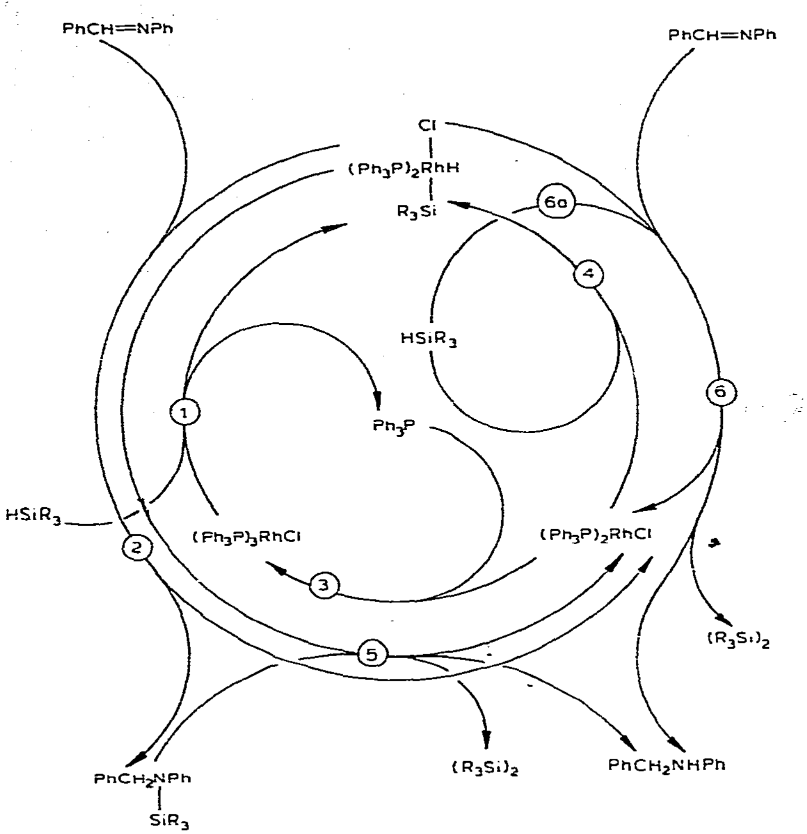


Fig. 1. Scheme of reaction pathways (number correspond to those used in the text.

the yield of III is, most probably associated with the reactions of hydrosilylation and reduction proceedingat different rates.

The reactions 1—6, discussed above, are shown in Fig. 1.

TABLE 2

REACTIONS BETWEEN TRIETHYL SILANE (I), *N*-(TRIETHYLSILYL)BENZYLANILINE (III) AND *N*-BENZYLANILINE (IV) CATALYZED BY SILYL—RHODIUM COMPLEX (A)

Initial compounds (mol)				Reaction products (wt. %) [d]			
N-(Triethylsilyl)-*N*-benzylaniline (III)	*N*-Benzylanaline (IV)	Triethylsilane (I)	Complex A	Hexaethyldisilane [a] (V)	*N*-Benzylaniline (IV)	*N*-(Triethylsilyl)-*N*-benzylaniline (III)	Note
—	1.0	1.3	0.04	23.3	76.7	—	*b*
1.0	—	—	1.0	23.0	77.0	—	*c*
1.0	—	1.1	0.013	15.5	33.0	51.5	*c*

[a] A small impurity of hexaethyldisiloxane is present. [b] Reaction products also contain triethylchlorosilane, aniline, and toluene. [c] Reaction products also contain triethylchlorosilane. [d] In all cases it is impossible to determine chromatographically precise quantities of low-boiling substances because of the presence of benzene.

Experimental

All the reactions were conducted in benzene solution in sealed glass ampoules. The total quantity of initial compounds <0.3 g. The ampoules were heated for 5 days at 60°C. Reaction products were analysed by GLC (column length 2 m; carrier gas, helium, 10 wt.% of SE-30 or SKTFT-50 on chromosorb W).

Molar ratios of initial compounds and the composition of reaction products are given in Tables 1 and 2.

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