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# HYDROSILYLATION OF AROMATIC AZOMETHINS

## I. INTERCONVERSION OF FINAL AND INTERMEDIATE COMPOUNDS IN THE PROCESS OF CATALYTIC REACTION OF TRIALKYL- OR ARYL-HYDROSILANES WITH BENZYLIDENE ANILINE

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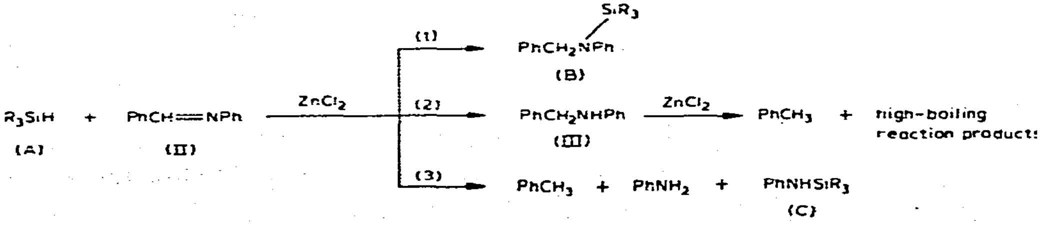
## Summary

Catalytic reaction of trialkyl- or aryl-hydrosilanes with benzylidene aniline is a complex process and can, in the most general case, include the following reactions: hydrosylilation (1) and reduction (2) of benzylidene aniline, reduction-silylation with splitting (3), silylation (4) and hydrogenolysis (5) of *N*-benzylaniline, aniline silylation (6), *N*-benzylaniline hydrogenative silylation (7), *N*-silylaniline hydrogenative desilylation (8), *N*-silyl-*N*-benzylaniline hydrogenative desilylation (9), *N*-silyl-*N*-benzylaniline hydrogenolysis (10) and dehydrogenation of the initial trialkyl- or aryl-hydrosilane (11).

Benzylidene aniline and related compounds are known to be capable of undergoing hydrosylilation if $ZnCl_2$ [1], ZhCl · THF [2], various rhodium [3,4] or palladium [3] compounds are used as catalysts. The interaction of trialkyl- or aryl-hydrosilanes with benzylidene aniline, catalyzed by zinc chloride, was previously shown [5] to be a complex process, which includes hydrosilylation (1), reduction (2), reduction-silylation with splitting (3) and others.



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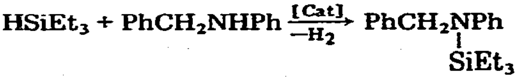
It is to be noted that: (i) aniline does not react with trialkyl- or aryl-hydrosilanes (A) in the presence of $ZnCl_2$; (ii) in the zinc chloride catalyzed reaction of *N*-benzylaniline (III) with the hydrosilylation product B, with or without A, neither aniline nor *N*-(trialkyl- or aryl-silyl)aniline (C) is formed. Similar reaction products were also formed when complex compounds of platinoids were used as catalysts [6]. The reaction of triethylsilane (I) with benzylidene aniline (II), catalyzed by Nb, Ta or W compounds, involved mainly the reduction of II to *N*-benzylaniline (III), no hydrosilylation being observed in this case [7].

The formation of *N*-(triethylsilyl)-*N*-benzylaniline (IV) on reacting triethylsilane (I) with benzylidene aniline (II), catalyzed by zinc chloride, results from hydrosilylation of II but not from silylation of *N*-benzylaniline (III). since IV is not formed from the reaction of I with III in the presence of $ZnCl_2$ (Table 1). Silylation of *N*-benzylaniline (III) with triethylsilane (I) was observed when $WOCl_4$ and $K_2[IrCl_6]$ were used as catalysts (Table 1) (eq. 4). Thus, in some



$$HSiEt_3 + PhCH_2NHPh \xrightarrow[-H_2]{[Cat]} PhCH_2\underset{\substack{|\\ SiEt_3}}{N}Ph \qquad (4)$$

(I) (III) (IV)

cases, *N*-silyl-*N*-benzylaniline can be formed not only as a result of hydrosilylation of II, but also from silylation of the intermediate reduction product, *N*-benzylaniline (III).

In the reaction of triethylsilane (I) with *N*-benzylaniline (III), when tri-n-octylammonium hexachloroiridate $[(C_8H_{17})_3NH]_2 \cdot [IrCl_6]$ or tri-n-octylammonium tetrachloropalladiate $[(C_8H_{17})_3NH]_2 \cdot [PdCl_4]$ were used as catalysts, resulted in the formation of toluene, aniline (V) and *N*-(triethylsilyl)aniline (VI) (Table 1). This points to possible hydrogenolysis of *N*-benzylaniline (III) followed by silylation of the aniline formed (eq. 5 and 6).

$$2\ Et_3SiH + PhCH_2NHPh \xrightarrow{[Cat]} PhCH_3 + PhNH_2 + (Et_3Si)_2 \qquad (5)$$

(I) (III) (V)

$$PhNH_2 + Et_3SiH \xrightarrow[-H_2]{[Cat]} PhNHSiEt_3 \qquad (6)$$

(V) (I) (VI)

This scheme of *N*-(triethylsilyl)aniline (VI) formation is confirmed by the fact that aniline and hydrogen are formed in the reactions studied, although hydrogenative silylation of *N*-benzylaniline (III) cannot be excluded (eq. 7). Aniline

$$Et_3SiH + PhCH_2NHPh \xrightarrow{[Cat]} Et_3SiNHPh + PhCH_3 \qquad (7)$$

(I) (III) (VI)

formation is, in this case, possible as a result of hydrogenative desilylation (eq. 8).

$$Et_3SiNHPh + Et_3SiH \xrightarrow{[Cat]} PhNH_2 + (Et_3Si)_2 \qquad (8)$$

(VI) (I) (V)

TABLE 1

COMPOSITION OF THE PRODUCTS OF THE REACTION BETWEEN TRIETHYLSILANE (I) AND *N*-BENZYLANILINE (III) (MOL RATIO 1 : 1) IN THE PRESENCE OF VARIOUS CATALYSTS

| Catalyst mol. fraction of initial triethylsilane | Reaction products (wt. %) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Triethylsilane (I) | Triethylchlorosilane [a] | Hexaethyldisilane [b] | Toluene | Aniline (V) | *N*-(Triethylsilyl)aniline (VI) | *N*-Benzylaniline (III) | *N*-Benzyl-*N*-(triethylsilyl)aniline (IV) |
| $TaCl_5$ (0.10) | 47.3 | 16.1 | 3.4 | | | | 33.2 | |
| $WOCl_4$ (0.10) | 3.0 | 17.2 | 3.1 | | | | 22.2 | 54.5 |
| $NbOCl_3 \cdot (C_8H_{17})_3N$ (0.04) | 38.8 | | | | | | 61.2 | |
| $NbOCl_2 \cdot C_7H_5O_2$ (0.05) | 38.8 | | | | | | 61.2 | |
| $NbOCl_2 \cdot (CH_3COCHCOCH_3)_2$ (0.05) | 70.4 | | 7.6 | | | | 22.0 | |
| $K_2[PtCl_6]$ (0.06) | 37.2 | 31.3 | 5.4 | | | | 26.1 | |
| $K_2[IrCl_6]$ (0.03) | 11.1 | 26.2 | 11.5 | | | | 38.0 | 13.2 |
| $[(C_8H_{17})_3NH]_2[PtCl_6]$ (0.04) | 46.1 | 28.0 | 8.5 | | | | 17.4 | |
| $[(C_{10}H_{21})_4P]_2[PtCl_6]$ (0.05) | 58.9 | traces | 27.1 | | | | 14.0 | |
| $[(C_8H_{17})_3NH]_2[PtCl_6]$ (0.06) | 15.9 | 18.3 | 19.2 | | | | 46.6 | |
| $[(C_8H_{17})_3NH]_2[IrCl_6]$ (0.04) | 29.1 | 8.5 | 7.9 | ~1 | 3.8 | 3.2 | 46.5 | |
| $[(C_8H_{17})_3NH]_2[PdCl_4]$ (0.06) | traces | 19.5 | 20.2 | 19.4 | 11.1 | 11.2 | 18.6 | |
| $(Ph_3P)_3RhCl$ (0.014) | 44.6 | traces | 6.5 | | | | 48.9 | |
| $ZnCl_2$ (0.05) [c] | 28.1 | 6.0 | 8.0 | 5.0 | | | 42.9 | |

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[a] Small impurity of triethylsilanole is present. [b] Small impurity of hexaethyldisiloxane is present. [c] High-boiling products (10 wt.%) are present.

TABLE 2

COMPOSITION OF THE PRODUCTS OF THE REACTION BETWEEN TRIETHYLSILANE (I) AND *N*-(TRIETHYLSILYL)ANILINE (VI) IN THE PRESENCE OF VARIOUS CATALYSTS (Cat.)

| Catalyst | Mol. ratio I : VI : Cat. | Reaction products (wt. %) | | | | |
|---|---|---|---|---|---|---|
| | | Triethylsilane (I) | Triethylchlorosilane [a] | Aniline (V) | Hexaethyldisilane [b] | *N*-(Triethylsilyl)-aniline (VI) |
| $NbOCl_3 \cdot (C_8H_{17})_3N$ | 1.2 : 1.0 : 0.03 | 66.0 | traces | 5.4 | traces | 28.6 |
| $ZnCl_2$ | 1.0 : 1.0 : 1.0 | 49.7 | 4.2 | | 13.0 | 33.1 |
| $(Ph_3P)_3RhCl$ | 1.0 : 1.0 : 0.01 | 61.5 | | 6.0 | 9.1 | 23.4 |
| $K_2[PtCl_6]$ | 1.0 : 1.0 : 0.05 | 64.6 | 8.3 | | 10.0 | 17.1 |
| $[(C_8H_{17})_3NH]_2[PdCl_4]$ | 1.0 : 1.0 : 0.02 | 45.3 | 3.8 | | 7.1 | 43.8 |
| $[(C_8H_{17})_3NH]_2[IrCl_6]$ | 1.0 : 1.0 : 0.02 | 40.3 | 3.7 | | 14.2 | 41.8 |

[a] Small impurity of triethylsilanole is present. [b] Small impurity of hexaethyldisiloxane is present.

And indeed this reaction is observed, e.g., when $NbOCl_3 \cdot (C_8H_{17})_3N$ and $(Ph_3P)_3RhCl$ are used as catalysts (Table 2). But, and this is very important, reaction 8 does not take place in the presence of such catalysts as tri-n-octylammonium hexachloroidate and tetrachloropalladiate. When these two catalysts are used during the reaction of triethylsilane (I) with *N*-benzylaniline (III), aniline formation is therefore caused by the hydrogenolysis reaction 5, and not by reaction 8. Aniline silylation by triethylsilane (reaction 6) does actually take place under the conditions studied, as is seen from the data in Table 3.

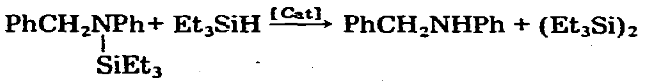
TABLE 3

COMPOSITION OF THE PRODUCTS OF THE REACTION BETWEEN TRIETHYLSILANE AND ANILINE (MOL. RATIO 1 : 1) IN THE PRESENCE OF VARIOUS CATALYSTS

| Catalyst (mol. fraction of initial triethyl silane) | Reaction of products (wt. %) | | | | |
|---|---|---|---|---|---|
| | Triethylsilane (I) | Aniline (V) | Triethylchlorosilane [a] | Hexaethyldisilane [b] | *N*-(Triethylsilyl)aniline (VI) |
| $NbOCl_2 \cdot C_7H_5O_2$ (0.08) | 55.5 | 44.5 | traces | | |
| $NbOCl_2 \cdot (CH_3COCHCOCH_3)_2$ (0.05) | 55.5 | 44.5 | traces | | |
| $K_2[PtCl_6]$ (0.05) | 22.0 | 24.1 | 19.1 | 10.9 | 23.9 |
| $K_2[IrCl_6]$ (0.05) | 18.0 | 13.4 | 11.0 | 12.6 | 45.0 |
| $NbOCl_3 \cdot (C_8H_{17})_3N$ (0.04) | 55.5 | 44.5 | traces | traces | |
| $WOCl_4$ (0.10) | 20.0 | 31.5 | 33.4 | 13.6 | 1.5 |
| $[(C_8H_{17})_3NH]_2[IrCl_6]$ (0.02) | traces | 23.7 | 12.4 | 10.7 | 53.2 |
| $[(C_8H_{17})_3NH]_2[RuCl_6]$ (0.03) | 2.4 | 17.7 | 12.6 | 8.9 | 58.4 |
| $[(C_{10}H_{21})_4P]_2[PtCl_6]$ (0.03) | 21.4 | 38.7 | 17.8 | 8.5 | 13.2 |
| $[(C_8H_{17})_3NH]_2[PtCl_6]$ (0.04) | 25.3 | 35.4 | 24.0 | 7.8 | 7.5 |
| $[(C_8H_{17})_3NH]_2[PdCl_4]$ [c] (0.04) | 5.0 | 34.1 | 15.3 | 37.8 | 7.8 |
| $(Ph_3P)_3RhCl$ (0.006) [d] | 3.6 | 14.0 | 10.3 | 11.1 | 61.0 |

[a] Small impurity of triethylsilanole is present. [b] Small impurity, of hexaethyldisiloxane is present. [c] Reaction conduced at room temperature for 19 h, high boiling compounds present in reactions products. [d] In benzene solution.

If hydrogenative desilylation of *N*-(triethylsilyl)aniline (IV) by triethylsilane (I) (reaction 8) is possible, one can also expect a similar reaction between the latter and the product of hydrosylilation; *N*-(triethylsilyl)-*N*-benzylaniline (IV) (eq. 9). In this case, the reaction of hydrogenative desilylation produces *N*-benzylaniline (III), i.e., the product which always accompanies benzylidene aniline hydrosilylation. Thus, it can be assumed in certain cases (see Table 4) that *N*-benzylaniline (III) formation in the hydrosilylation of benzylidene aniline (II) is caused not only by the reduction of II (reaction 2) but also by the hydrogenative desilylation of the product of hydrosilylation, *N*-(triethyl silyl)-*N*-benzylaniline (IV) (reaction 9). This reaction is not of a general nature but only takes place under certain conditions (see Table 4). For instance, reaction 9 was not observed when tri-n-octylammonium hexachlororuthenate and tris(triphenylphosphine)rhodium chloride were used as catalysts, although using these catalysts in the hydrosylilation of benzylidene aniline (II) by triethylsilane (I) resulted in the formation of both *N*-benzylaniline (III) and *N*-(triethylsilyl)-*N*-benzylaliline (IV). This once again confirms that the reduction of benzylidene aniline by triethylsilane to *N*-benzylaniline (III) does actually take place under the conditions of catalytic hydrosilylation.



$$\underset{\textstyle SiEt_3}{PhCH_2\underset{|}{N}Ph} + Et_3SiH \xrightarrow{[Cat]} PhCH_2NHPh + (Et_3Si)_2 \qquad (9)$$

(IV) (I) (III)

It is noteworthy that *N*-(triethylsilyl)aniline (VI) and toluene were formed in the reaction of hydrogenative desilylation (9) when the catalyst used is potassium hydroplatinate (Table 4). This indicates the possibility of *N*-(triethylsilyl)-

TABLE 4

COMPOSITION OF THE PRODUCTS OF THE REACTION BETWEEN TRIETHYL SILANE (I) AND *N*-(TRIETHYL SILYL)-*N*-BENZYL ANILINE (IV) IN THE PRESENCE OF VARIOUS CATALYSTS (Cat.)

| Catalyst | Mol. ratio I : IV : Cat. | Reaction products (wt. %) | | | | |
|---|---|---|---|---|---|---|
| | | Triethylsilane | Triethylchlorosilane [a] | Hexaethyldisilane [b] | *N*-(Triethylsilyl)-*N*-benzyl aniline (IV) | *N*-Benzylaniline (III) |
| $NbOCl_2 \cdot C_7H_5O_2$ | 1 : 1 : 0.06 | 48.0 | traces | 8.1 | 23.1 | 20.8 |
| $NbOCl_2 \cdot (CH_3COCHCOCH_3)_2$ | 1 : 1 : 0.06 | 48.8 | | 8.9 | 17.8 | 24.5 |
| $K_2[PtCl_6]$ [c] | 1 : 1 : 0.08 | 13.8 | 9.1 | 26.0 | 27.6 | 16.7 |
| $[(C_8H_{17})_3NH]_2[RuCl_6]$ | 1 : 1 : 0.04 | 17.8 | 8.0 | 34.4 | 39.3 | |
| $NbOCl_3$ | 1.5 : 1 : 0.06 | 31.1 | | 11.1 | 45.6 | 12.2 |
| $(Ph_3P)_3RhCl$ | 1 : 1 : 0.01 | 36.4 | | 8.6 | 55.0 | |
| $ZnCl_2$ | 0.9 : 1 : 0.55 | 44.5 | | 16.5 | 10.6 | 28.4 |

[a] Small impurity of triethylsilanole is present. [b] Small impurity of hexaethyldisoloxane is present. [c] Toluene (<1%) and *N*-(triethylsilyl)aniline (VI) (6.8%) are also present in the mixture of reaction products.

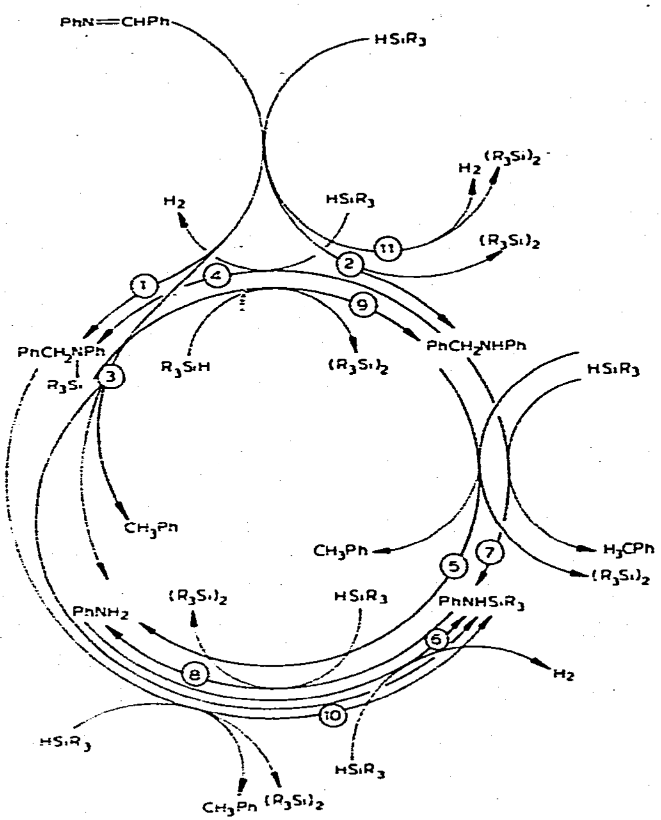
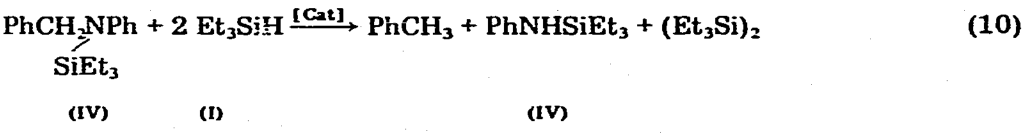


Fig. 1. Scheme of reaction pathways (numbers correspond to those used in text).

*N*-benzylaniline (IV) hydrogenolysis (reaction 10). The possibility of *N*-(triethylsilyl)aniline (VI) being formed due to the conversion of *N*-benzylaniline (III) according to reactions 5—7 can be excluded, since these reactions were not observed in the presence of $K_2[PtCl_6]$ (Table 1).



$$\underset{\text{(IV)}}{\mathrm{PhCH_2\underset{\diagup}{N}Ph}\atop \mathrm{SiEt_3}} + \underset{\text{(I)}}{2\,\mathrm{Et_3SiH}} \xrightarrow{[\mathrm{Cat}]} \mathrm{PhCH_3} + \underset{\text{(IV)}}{\mathrm{PhNHSiEt_3}} + (\mathrm{Et_3Si})_2 \qquad (10)$$

Analysis of the data in Tables 1—4 indicates one more reaction is possible, catalytic dehydrogenation of trialkyl- or aryl-hydrosilanes (reaction 11). Hydrogen evolved in most of the reactions studied, but was not quantified.

$$2\,\mathrm{R_3SiH} \xrightarrow[-\mathrm{H_2}]{[\mathrm{Cat}]} (\mathrm{R_3Si})_2 \qquad (11)$$

The reactions 1—11, discussed above are shown in Fig. 1.

## Experimental

The mixture of starting compound and catalyst was sealed in a glass ampoule. The total weight of the reaction mixture was approximately 0.3 g. The ampoule was then heated for 16 h at 120—130°C. When tris(triphenylphosphine)rhodium chloride was used as catalyst (in benzene solution), the reaction time was 5 days at 60°C. The ampoule was then opened, ether added, the contents of the ampoule separated from sediment (if it was present) and the sediment washed with ether. Combined ether extracts 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 the initial compounds and the composition of reaction products are given in Tables 1—4.

Compounds with tri-n-octylammonium cations, $[(C_8H_{17})_3NH]_2 \cdot [MCl_6]$, where M = Pt, Ru or Ir, were prepared by N.M. Sinitsin and coworkers in accordance with procedure in ref. 8; the platinum complex $[(C_{10}H_{21})_4P]_2 \cdot [PtCl_6]$ was prepared and kindly provided for the study by T.M. Buslayeva. Complexes of Nb, Ta, and W used as catalysts were synthetized by S.M. Sinitsina and coworkers in accordance with previously described procedures [9,10]. $(Ph_3P)_3RhCl$ was prepared in accordance with a conventional procedure [11].

## Acknowledgements

We wish to express gratitude to N.M. Sinitsin, T.M. Buslayeva, S.M. Sinitsina and their coworkers for cooperation and for kindly providing the compounds used as catalysts in the reactions we studied.

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