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NITRO- AND AMINO-ARYLALKYLSILANES AND -SILOXANES

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SUMMARY

A method of preparation of nitrophenylethyl-silanes and -siloxanes by the addition reaction of compounds containing a Si–H bond, with nitrostyrene, has been suggested.

It has been found that the hydrogen atom of the Si–H bond goes to the β-atom of the carbon of the C=C bond of nitrostyrene.

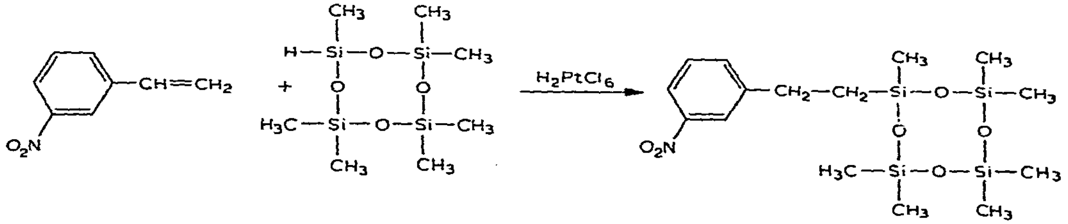
The possibility of using aminophenylethylsiloxanes obtained from the corresponding nitro derivatives, for the synthesis of azo dyes has been suggested.

INTRODUCTION

Aminoarylalkylsilanes are usually obtained by the nitration of the corresponding arylalkylsilanes, followed by reduction[1-8]. The nitration reaction leads to the mixtures of isomers and cannot always be used for the synthesis of compounds containing the functional groups at a silicon atom, or for the synthesis of siloxanes.

The present paper describes another preparative method based upon the hydride addition of compounds containing a Si–H bond, to nitrostyrene.

Our work has shown that this reaction enables various organosilicon compounds of definite composition and structure to be obtained, *e.g.*, the reaction follows the scheme of the reaction of heptamethylcyclosiloxanes with *m*-nitrostyrene:

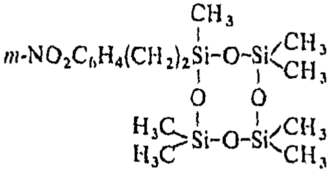
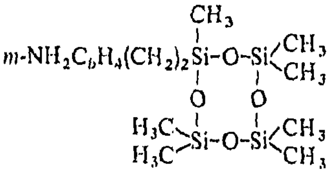


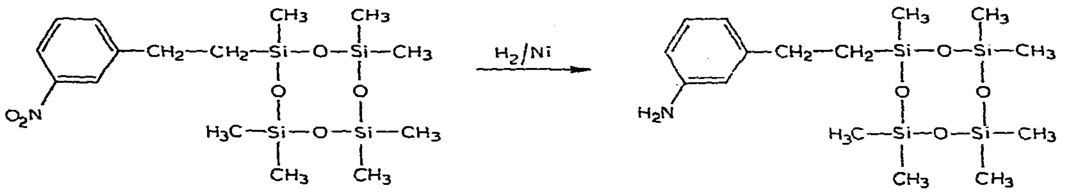
This reaction has been studied as an example of the addition of $H(CH_3)_2SiOSi(CH_3)_2H$, $(CH_3)_3SiOSi(CH_3)_2H$, $\underline{[(CH_3)_2SiO]_3[(CH_3)HSiO]}$ and $R_nSi(H)Cl_{3-n}$, where R is CH_3, C_2H_5 and $n = 1$ or 2.

The properties of the compounds prepared are listed in Table 1; compound (VI) has been obtained by the hydrolysis of (I) and the further addition of $H(CH_3)_2SiOSi(CH_3)_2H$ to *m*-nitrostyrene. All the compounds prepared are either colourless or slightly coloured liquids readily soluble in common organic solvents.

TABLE I

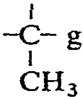
PROPERTIES OF THE SYNTHESIZED COMPOUNDS

No.	Compound	Formula	B.p. °C (mm Hg)	n_D^{20}	d_4^{20}	MR_D Found (calcd.)
I	β-(*m*-Nitrophenyl)ethyldimethylchlorosilane	*m*-$NO_2C_6H_4(CH_2)_2Si(CH_3)_2Cl$	144–145 (2)	1,5294	1,1518	65,26 (64.45)
II	β-(*m*-Nitrophenyl)ethylmethyldichlorosilane	*m*-$NO_2C_6H_4(CH_2)_2Si(CH_3)Cl_2$	167 (4)	1.5414	1.2742	65.15 (64.08)
III	β-(*m*-Nitrophenyl)ethylethyldichlorosilane	*m*-$NO_2C_6H_4(CH_2)_2Si(C_2H_5)Cl_2$	175–176 (3)	1.5350	1.2518	69.15 (68.59)
IV	β-(*m*-Nitrophenyl)ethylpentamethyldisiloxane	*m*-$NO_2C_6H_4(CH_2)_2Si(CH_3)_2OSi(CH_3)_3$	143 (3)	1.4910	1.0188	84.77 (83.56)
V	β-(*m*-Nitrophenyl)ethylheptamethylcyclotetrasiloxane		171–174 (3–4)	1.4718	1.0963	110.13 (109.5)
VI	1,3-Bis[β-(*m*-nitrophenyl)ethyl]tetramethyldisiloxane	[*m*-$NO_2C_6H_4(CH_2)_2Si(CH_3)_2]_2O$	261–263 (1)	1.5350	1.1287	119.36 (118.1)
VII	β-(*m*-Aminophenyl)ethylpentamethyldisiloxane	*m*-$NH_2C_6H_4(CH_2)_2Si(CH_3)_2OSi(CH_3)_3$	132–135 (4)	1.4940	0.9403	82.74 (81.30)
VIII	β-(*m*-Aminophenyl)ethylheptamethylcyclotetrasiloxane		142–144 (1)	1.4754	1.0445	108.24 (107.24)



Compounds (IV) and (V) have been reduced by hydrogen using activated Ni as a catalyst.

The aminoarylalkylsiloxanes are light yellow liquids, that darken on keeping; they are easily soluble in common organic solvents.

The structures of nitro- and amino-arylalkylsilanes and -siloxanes have been supported by their IR spectra. Intensive absorption bands at 1545 cm^{-1} and 1362 cm^{-1} confirm the presence of the nitro-group, but the absorption bands in the region of 3380 cm^{-1} and 3462 cm^{-1} are characteristic for the valency vibrations of the amino-group. The absence of the absorption band in the region of 1380 cm^{-1} (which is characteristic of the  $-\overset{|}{\underset{\underset{CH_3}{|}}{C}}-$ group) in the IR spectra of aminoarylalkylsiloxanes supports the idea that the hydrogen atom of the Si–H bond goes to the β-atom of the C=C bond of nitrostyrene.

The above aminoarylalkylsiloxanes are readily diazotised in water–acetone media, and the products enter into a further coupling reaction both in acidic and basic conditions. The azo-coupling reactions have been carried out with ethyloxyethylaniline, phenylmethylpyrazolone, β-naphthol and 3-oxytetrahydronaphthoquinoline. The dyes obtained are either oils or powders (see for example, the coupling of the diazo-salt of (VIII) with 3-oxytetrahydronaphthoquinoline).

EXPERIMENTAL

m-Nitrocinnamic acid and *m*-nitrostyrene have been prepared by established methods[9].

General method for the addition reaction

m-Nitrostyrene and 3–5 drops of the catalyst (0.1 *N* solution of H_2PtCl_6 in isopropanol) was placed in a four-necked flask with a stirrer, reflux condenser, dropping-funnel, and a thermometer; the mixture was then heated and 0.5 g of the organic hydrosilane or siloxane added to it. When a rise in temperature was observed, the rest of the silane or siloxane was added and the heating and stirring of the mixture continued for some time. The products of the reaction were separated by distillation.

β-(m-Nitrophenyl)ethyldimethylchlorosilane (I)

6 g (0.065 g-mole) of dimethylchlorosilane was added dropwise to 6 g (0.04 g-mole) of *m*-nitrostyrene at 50°; the mixture was then stirred for 2.5 h at 120°. 5.1 g of product (50% theory) was obtained. (Found: C, 48.64; H, 5.20; N, 6.18; Cl, 14.79; Si, 11.55. Calcd.: C, 49.26; H, 5.75; N, 5.75; Cl, 14.57; Si, 11.53%.)

β-(m-Nitrophenyl)ethyldichlorosilane (II)

8.7 g (53 % theory) of (II) was prepared by an analogous method from 6 g (0.04 g-mole) of *m*-nitrostyrene and 4.6 g (0.04 g-mole) of methyldichlorisilane. (Found: C, 40.81; H, 4.32; N, 6.10; Cl, 27.06; Si, 10.25. Calcd.: C, 40.90; H, 4.17; N, 5.30; Cl, 26.88; Si, 10.64 %.)

β-(m-Nitrophenyl)ethylethyldichlorosilane (III)

7.7 g (51 % theory) of (III) was prepared by an analogous method (the initial temperature of reaction was 60°) from 7.5 g (0.05 g-mole) of *m*-nitrostyrene and 1.0 g (0.05 g-mole) of ethyldichlorosilane. (Found: C, 42.74; H, 4.83; N, 5.26; Cl, 24.61; Si, 9.43. Calcd.: C, 43.15; H, 4.67; N, 5.03; Cl, 25.53; Si, 10.10 %.)

β-(m-Nitrophenyl)ethylpentamethyldisiloxane (IV)

10 g (0.067 g-mole) of pentamethyldisiloxane was added dropwise to 10 g (0.067 g-mole) of *m*-nitrostyrene at 80° and the mixture stirred at 150° for 3 h. 13.75 g (68.7 % theory) of (IV) was obtained. (Found: C, 51.83; H, 8.07; N, 5.02; Si, 18.43. Calcd.: C, 52.49; H, 7.74; N, 4.71; Si, 18.90 %.)

β-(m-Nitrophenyl)ethylheptamethylcyclotetrasiloxane (V)

4.5 g (0.03 g-mole) of nitrostyrene was added dropwise to 8.25 g (0.03 g-mole) of heptamethylcyclotetrasiloxane at 80° and the mixture was then stirred for 12 h at 120°. 8.9 g of (V) (69.8 % theory) was recovered. (Found: C, 41.18; H, 6.84; N, 3.37; Si, 26.27. Calcd.: C, 41.73; H, 6.72; N, 3.21; Si, 26.05 %.)

1,3-*Bis[β-(m-nitrophenyl)ethyl]tetramethyldisiloxane (VI)*

9.19 g (0.061 g-mole) of *m*-nitrostyrene was added dropwise to 9.08 g (0.076 g-mole) of tetramethyldisiloxane at 70° and the mixture was then stirred for 3 h at 120°. 3.2 g of (VI) (24 % theory) were recovered.

Hydrolysis of β-(m-nitrophenyl)ethyldimethylchlorosilane

40 ml of water was placed into the four-necked flask with a stirrer, reflux condenser, dropping-funnel, and a thermometer and then 10 g of (I) (0.041 g-mole) was added dropwise during 30 min. The mixture was heated to 80° and kept at that temperature for 1 h. The products were extracted with ether, washed to neutrality and dried over calcium chloride. After the solvent had been distilled, the product was vacuum distilled. 5.2 g of (VI) (30 % theory) were obtained. (Found: C, 54.56; H, 6.38; N, 6.84; Si, 12.73. Calcd.: C, 55.53; H, 6.48; N, 6.48; Si, 13.00 %.)

General method of reduction

The reduction was carried out with hydrogen in the presence of activated Ni in ethanol solution for 25 h at room temperature with shaking, in a closed vessel. The catalyst was removed by filtration and the products separated by distillation.

β-(m-Aminophenyl)ethylpentamethyldisiloxane (VII)

1.6 g of (VII) (51 % theory) were obtained from 3.45 g (0.012 g-mole) of (IV). (Found: C, 57.98; H, 9.15; N, 5.54; Si, 20.78. Calcd.: C, 58.39; H, 9.36; N, 5.24; Si, 21.03 %.)

β-(m-Aminophenyl)ethylheptamethylcyclotetrasiloxane (VIII).

2.1 g of (VIII) (64% theory) was obtained from 3.4 g (0.0079 g-mole) of (V). (Found: C, 44.83; H, 7.83; N, 3.87; Si, 27.87. Calcd.: C, 44.85; H, 7.72; N, 3.49; Si, 27.99%.)

Diazotisation reaction

A solution of 0.7 g (0.0026 g-mole) of (VII) in 10 ml of acetone and 0.81 ml (0.0078 g-mole) of 35.2% HCl were placed in a 100-ml porcelain beaker and the mixture cooled to 0°. At that temperature, a solution of 0.18 g (0.0026 g-mole) of sodium nitrite in 3 ml of water was added dropwise with continuous stirring.
Diazotisation of (VIII) was carried out in the same way.

Coupling reaction

The coupling reactions of diazonium salts of (VII) with ethyloxyethylaniline and of (VIII) with phenylmethylpyrazolone, β-naphthol, and 3-oxytetrahydronaphthoquinoline have been carried out by standard methods[10].

Separation of dyes

After the coupling reaction had been carried out, the lower oily layer of a dye was separated (in some cases the oily layer appeared only after removal of acetone), washed with water, and any water and acetone remaining removed in vacuum.

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