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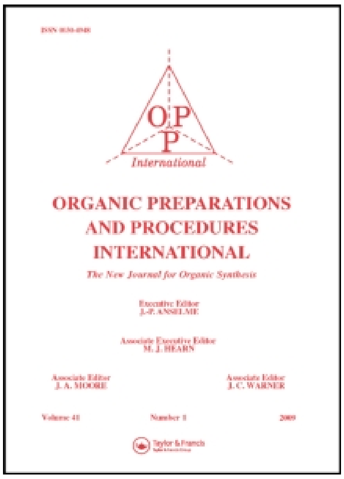

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THE SYNTHESIS OF ARYLAZOTRIPHENYLSILANES

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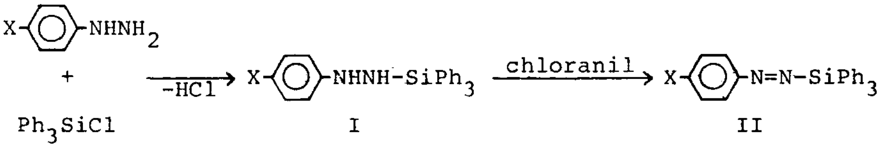
There is considerable interest in the synthesis of arylazotriphenylsilane, since they might be expected to serve as a thermal source of silyl radicals in solution. The liquid silyl azo compounds previously isolated[1-4] are usually more or less contaminated with impurities which can be removed by fractional distillation only with difficulty. We have prepared for the first time novel organosilicon azo systems, arylazotriphenylsilanes (IIa-c) by oxidation of N-triphenylsilyl-N'-arylhydrazines (Ia-c) with chloranil. The procedure is a convenient route for this class of solid compounds, since the products are more soluble than the starting silylhydrazines in hexane and thus easily separable from the blue solutions.



a; X=H, b; X=Cl, c; X=CH$_3$

Compounds IIa-c thus isolated were of high purity and shown to be stable under nitrogen and in dry air; solutions in cyclohexane remained unchanged for several months. The thermal decomposition of IIa in carbon tetrachloride afforded triphenylchlorosilane as the main product. The result suggests that the compounds IIa-c are promising as thermal sources of silyl radicals, although they decompose at higher temperatures compared with PAT.[5,6] A detailed investigation of the mode of decomposition is currently underway.

EXPERIMENTAL

N-Triphenylsilyl-N'-arylhydrazines (I).- A mixture of phenylhydrazine (22 g, 0.2 mole) and triphenylchlorosilane (29 g, 0.1 mole) in anhydrous ether (400 ml) was refluxed for 24 hr and filtered. On evaporation the filtrate gave the crude product, which was recrystallized from triethylamine to yield N-triphenylsilyl-N'-phenylhydrazine (Ia), 25 g (68 %), mp. 129-132°. The structure was assigned by the analytical and spectral data (Table 1 and 2).

Similarly, triphenylchlorosilane was condensed with p-chlorophenylhydrazine to give Ib, (41 %), mp. 117.5-120°.

Likewise, the reaction was carried out with p-methylphenylhydrazine (11.3 g, 0.09 mole), triphenylchlorosilane (26.2 g, 0.09 mole), triethylamine (13.5 g, 0.09 mole) and ether (500 ml) to obtain Ic, 13.4 g (39 %), mp. 115.5-118°.

Arylazotriphenylsilanes.- Treatment of N-triphenylsilyl-N'-phenylhydrazine (Ia) (6.0 g, 16 mmole) with chloranil (3.5 g) in hexane (1.0 l) furnished a deep blue solution. After concentration of the solution (reduced pressure), the unreacted Ia crystallized was removed by filtration. On evaporation the filtrate gave a blue solid, which was readily recrystallized

Table 1.- Analytical Data for I and II

Compound	Mp.[a] (°C)	Yield (%)	Mw[b]	Elemental Analysis Calculated(%) (Found) C	H	N
Ia	129-132[c]	68	366	78.63 (78.85)	6.06 (6.04)	7.64 (7.61)
Ib	117.5-120[c]	41	400	71.89 (72.10)	5.28 (5.12)	6.99 (7.09)
Ic	115.5-118[c]	39	380	78.90 (78.72)	6.36 (6.07)	7.36 (7.13)
IIa	112-113.5[d]	33	364	79.08 (78.99)	5.53 (5.50)	7.69 (7.61)
IIb	95.5-97[e]	12	398	72.25 (71.76)	4.80 (4.30)	7.02 (6.83)
IIc	87.5-89[e]	45	378	79.33 (78.79)	5.86 (5.57)	7.04 (6.66)

[a] Sealed capillary [b] By mass spectrum [c] From triethylamine [d] From benzene-t-butanol (2:1 w/w) [e] From n-hexane

from a mixture of benzene-t-butanol to afford fine deep-blue crystals of phenylazotriphenylsilane (IIa) (2.0 g, 33 %), mp. 112-113.5°.

Similarly, p-chloro- and p-methylphenylhydrazine derivatives, Ib and Ic, were treated with chloranil and the corresponding arylazotriphenylsilanes, IIb and IIc, were isolated in moderate yields (Table 2).

Thermal decomposition of IIa in carbon tetrachloride.- IIa (1 mmole) in carbon tetrachloride (13.6 mmole) was heated for 18 hr at 110° in an evacuated ampoule. Product analyses by

Table 2.- Spectral Data of I and II

Compound	λ_{max} mμ(ε)[a]	IR(cm^{-1}), KBr			NMR(δ, ppm)[b], C_6D_6			
	n → π*	νN-H	νN=N	νSi-Ph	Ar$\underline{H}$	Ar-N$\underline{H}$	Si-N$\underline{H}$	C$\underline{H}_3$
Ia	--	3300	--	1430 1120	7.85-6.63 (m,20)	5.13 (s,1)	3.62 (s,1)	--
Ib	--	3300	--	1430 1120	7.57-6.15 (m,19)	4.63 (s,1)	3.11 (s,1)	--
Ic	--	3300	--	1430 1115	7.93-6.60 (m,19)	4.75 (s,1)	3.25 (s,1)	2.15 (s,3)
IIa	588(70)	--	1450	1430 1120	8.00-7.11 (m)	--	--	--
IIb	590(71)	--	1450	1430 1120	7.65-6.45 (m)	--	--	--
IIc	585(71)	--	1450	1430 1115	8.05-6.67 (m,19)	--	--	2.03 (s,3)

[a] Cyclohexane solution [b] TMS internal standard; Ia and IIa were determined in CCl_4 solution

glpc (silicone columns) showed the presence of triphenylchlorosilane (0.88 mmole), chlorobenzene (0.21 mmole) and benzene (trace). Identification of the isolated products was accomplished by comparison of the IR spectrum with these of authentic samples.

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