

REACTIONS OF GROUP IV ORGANOMETALLIC COMPOUNDS XX*. ADDITION REACTIONS OF ARYLSULFONYL ISOCYANATES WITH ORGANOSILYLAMINES AND PYROLYSIS OF THE ADDUCTS

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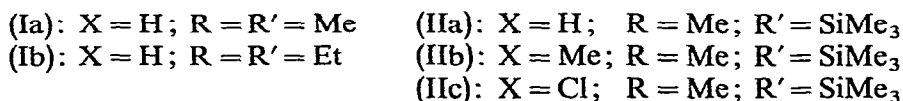
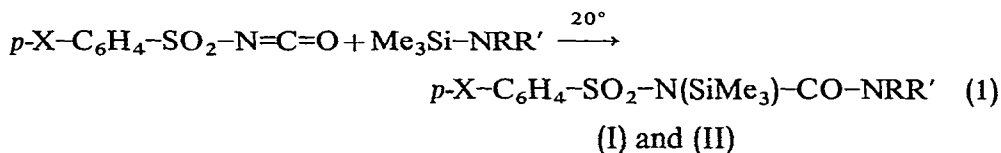
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SUMMARY

The reactions between (trimethylsilyl)amines or heptamethyldisilazane and *p*-substituted benzenesulfonyl isocyanates occurred exothermically at room temperature, giving 1/1 adducts quantitatively. Pyrolysis of the adducts of heptamethyldisilazane with arenesulfonyl isocyanates afforded *N,N*-bis(trimethylsilyl)arenesulfonamides and methyl isocyanate. This result was quite different from that found in our former pyrolyses of isocyanate adducts.

It is known that organosilylamines react with various types of acceptor molecules to give insertion products¹. In this note, insertion reactions of (trimethylsilyl)amines and heptamethyldisilazane to arenesulfonyl isocyanates, a new class of powerful acceptors, are reported. An unexpected isocyanate expulsion reaction was found to occur in the pyrolysis of the adducts from heptamethyldisilazane.

The reactions between (trimethylsilyl)dimethylamine or -diethylamine and benzenesulfonyl isocyanate proceeded exothermically and quantitatively at room temperature and 1/1 adducts, (Ia), (Ib), were obtained. An equimolar mixture of heptamethyldisilazane and *p*-X-substituted benzenesulfonyl isocyanates reacted exothermically at room temperature, giving 1/1 adducts, (IIa), (IIb) and (IIc), where X = H, Me and Cl, respectively.



* For Part XIX see ref. 7.

The adducts, (I) and (II), were characterized by means of elementary analysis, NMR and IR spectrometry, and by derivation of the adducts into (arenesulfonyl)urea derivatives on hydrolysis.

TABLE I

N-(BENZENESULFONYL)-*N*-(TRIMETHYLSILYL)-*N'*,*N'*-DIALKYLUREAS, (Ia), (Ib), AND *N*-(*p*-SUBSTITUTED-BENZENESULFONYL)-*N*,*N'*-BIS(TRIMETHYLSILYL)-*N'*-METHYLUREAS, (IIa), (IIb) AND (IIc)

Adduct	X	R	R'	Time ^a (h)	B.p. (°C/mm)	Anal. found (calcd.) (%)	
						C	H
(Ia)	H	Me	Me	1	134–135/0.15	48.22 (47.97)	6.27 (6.72)
(Ib)	H	Et	Et	1	[43–46] ^b	51.50 (51.19)	7.64 (7.38)
(IIa)	H	Me	Me ₃ Si	24	142–143/0.08	47.23 (46.89)	7.39 (7.22)
(IIb)	Me	Me	Me ₃ Si	24	160–161/0.50	47.95 (48.34)	7.31 (7.59)
(IIc)	Cl	Me	Me ₃ Si	24	152–153/0.25	46.56 (47.01)	7.08 (7.06)

^a Temp. 20°. ^b M.p.

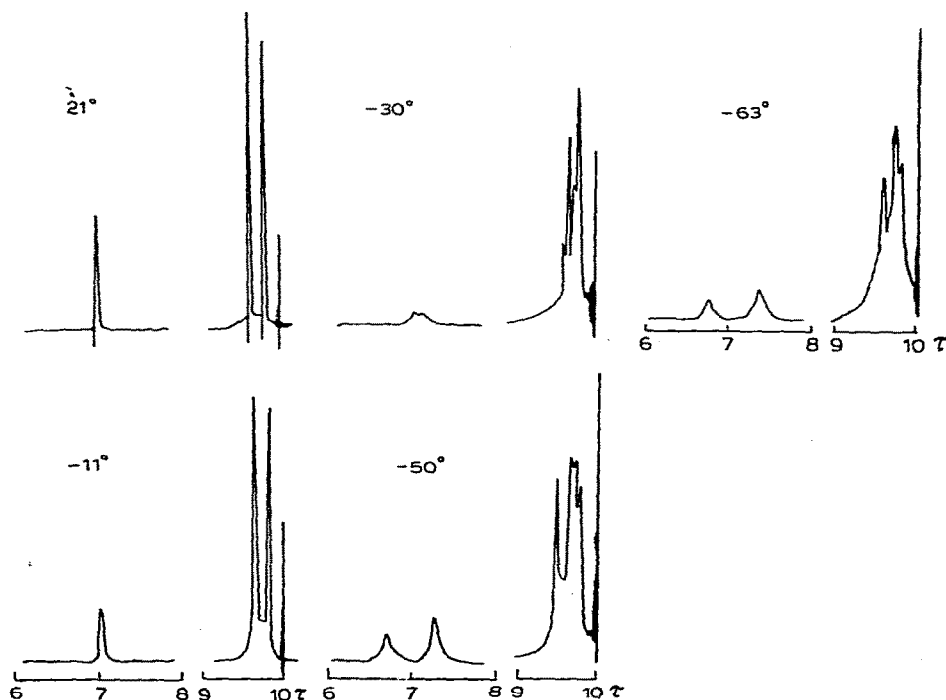
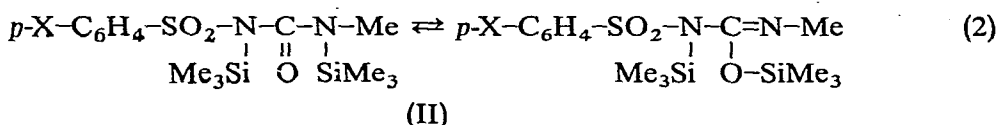


Fig. 1. NMR spectra of (IIc) at various temperatures.

Table 1 shows the reaction conditions, and b.p.'s and analytical data for the adducts, (I) and (II).

Infrared and nuclear magnetic resonance spectral data are given in the Experimental. The absorptions attributed to carbonyl groups of (IIa), (IIb) and (IIc) (1605, 1610 and 1620 cm^{-1} , respectively) seem to be extremely low, but Pump and Wannagat² assigned 1615 cm^{-1} as $\nu(\text{C}=\text{O})$ of $(\text{Me}_3\text{SiNH})_2\text{CO}$. The NMR spectra of (IIc) at variable temperature (21 $\sim$ -63°) are shown in Fig. 1. In spite of the coalescence of *N*-methyl protons at -11° , four trimethylsilyl proton signals at low temperature did not coalesce, showing the predominant existence of carbonyl form at higher temperature than -30° . The NMR spectra of (IIa) and (IIb) at variable temperature are quite similar to those of (IIc), from which the following equilibrium (2) might be presumed at lower temperature, along with the carbonyl form predominating at room temperature.



These results are reflected in the pyrolysis reactions of (II). When the adducts (IIa), (IIb) and (IIc) were pyrolyzed at 150° for 72 h in a sealed tube, *N,N*-bis(trimethylsilyl)arenesulfonamides (III) and trimethyl isocyanurate (IV), the cyclic trimer of methyl isocyanate, were obtained, as is shown in Table 2.

These results are quite different from those found in our former pyrolyses of isocyanate adducts^{3,4}: (1) the adduct between heptamethyldisilazane and phenyl isocyanate as in eqn. (3), (2) the adduct⁴ between heptamethyldisilazane and benzoyl isocyanate as in eqn. (4).

In these two cases, the pyrolysis products contained hexamethyldisiloxane, which would arise from the *O*-silylated form of the adducts. However, no disiloxane could be detected in the pyrolysis of (IIa), (IIb) or (IIc).

When the adduct of *N*-ethylhexamethyldisilazane with benzenesulfonyl iso-

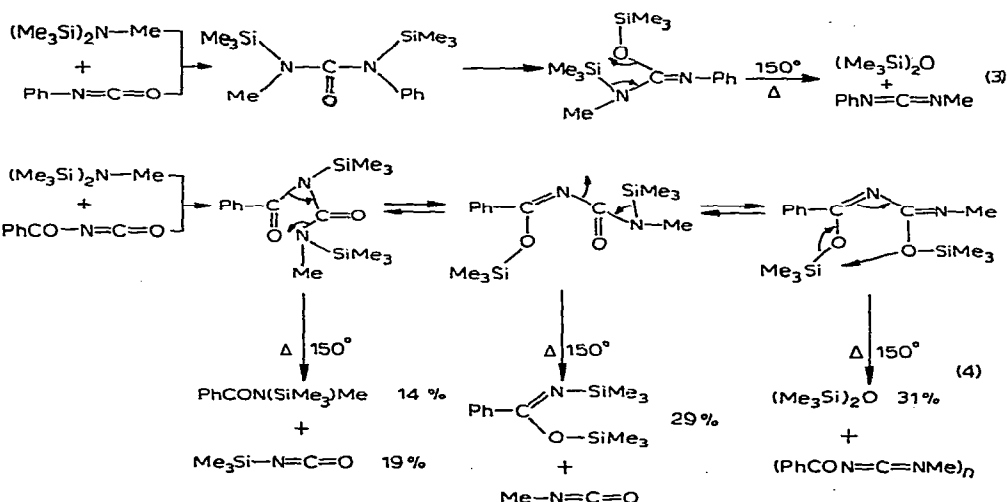
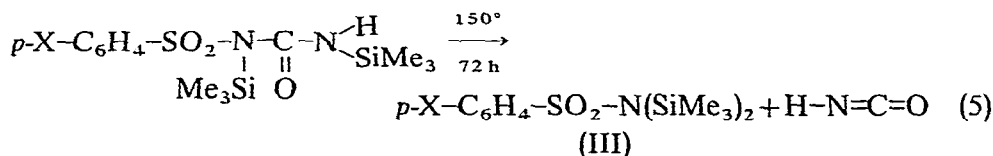


TABLE 2

N,N-bis(trimethylsilyl)arylsulfonamides (III) and trimethyl isocyanurate (IV)

Adduct	(III)	Yield (%)	B.p. (C/mm)	Analysis, found (calcd.) (%)		Yield of (IV) (%)
				C	H	
(IIa)	(IIIa)	58	142-145/0.48	47.48 (47.80)	7.82 (7.70)	41
(IIb)	(IIIb)	40	123-125/0.45	49.17 (49.47)	7.73 (8.00)	30
(IIc)	(IIIc)	60	129-130/0.90	43.29 (42.91)	6.36 (6.62)	65

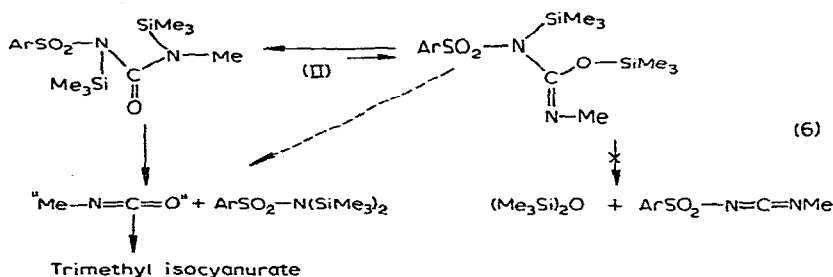
cyanate was pyrolyzed under the same conditions, ethyl isocyanate was obtained in 46% yield, along with (IIIa) (65%). The pyrolysis of the adduct between hexamethyldisilazane and arylsulfonyl isocyanate gave hydrogen isocyanate in a cold trap, as shown in eqn. (5).



	yield	yield
X = H,	46%	35%
X = Me,	35%	48%
X = Cl,	48%	53%

Therefore, it appears that the formation of trimethyl isocyanurate may occur through cyclic trimerization of methyl isocyanate intermediately formed in the pyrolysis of (II).

In conclusion, pyrolysis of the adducts between heptamethyldisilazane and arenesulfonyl isocyanates occurs solely through the carbonyl form of (II), and not via the imine form (eqn. 6). This course of reaction may, perhaps, be accounted for by the strong electron-withdrawing effect of the sulfonyl group depressing the *O*-silylated form (II) at the higher temperatures needed for reaction.



EXPERIMENTAL

The three arenesulfonyl isocyanates were prepared by the method of Field and Settlage⁶: X = H, b.p. 64.5-66.0°/0.12 mm (yield 25%); X = Me, b.p. 88-90°/0.60

mm (31%); $X = \text{Cl}$, b.p. $79\text{--}80^\circ/0.10$ mm (17%). Infrared and nuclear magnetic resonance spectra were measured using Nippon-Bunko IR-S and JEOL Minimar, respectively. All NMR spectra were recorded in trichloroethylene solution.

Reaction of (trimethylsilyl)dimethylamine with benzenesulfonyl isocyanate

Equimolar amounts (2.7 mmoles) of (trimethylsilyl)dimethylamine and benzenesulfonyl isocyanate were reacted in a sealed tube filled with argon at 20° for 1 h. The resulting colorless viscous liquid was distilled, giving quantitatively *N*-(benzenesulfonyl)-*N*-(trimethylsilyl)-*N',N'*-dimethylurea (Ia), b.p. $134\text{--}135^\circ/0.15$ mm. IR: $\nu(\text{CO})$ 1680, $\nu_{\text{as}}(\text{SO}_2)$ 1350, $\nu_{\text{s}}(\text{SO}_2)$ 1180 cm^{-1} . NMR: $\tau(\text{Me}_3\text{Si})$ 9.68(9), $\tau(\text{MeN})$ 7.08(5.7), $\tau(\text{C}_6\text{H}_5)$ 2.0–2.8(5) ppm.

Reaction of (trimethylsilyl)diethylamine with benzenesulfonyl isocyanate

The reaction was carried out in the same manner as above. *N*-(benzenesulfonyl)-*N*-(trimethylsilyl)-*N',N'*-diethylurea (Ib), m.p. $43\text{--}46^\circ$, was obtained in 98% yield. NMR: $\tau(\text{Me}_3\text{Si})$ 9.57, $\tau(\text{CH}_3\text{C})$ 8.89, $\tau(\text{CH}_2\text{N})$ 6.10 ppm.

Reactions of heptamethyldisilazane with arenesulfonyl isocyanates

Equimolar amounts (2.0 mmoles) of heptamethyldisilazane and 3 arenesulfonyl isocyanates ($X = \text{C}_6\text{H}_5$, *p*- MeC_6H_4 , *p*- ClC_6H_4) were reacted in a sealed tube under argon at 20° for 24 h (less reactive than the above cases); 1/1 adducts were obtained by vacuum distillation (Table 1).

N-(benzenesulfonyl)-*N,N'*-bis(trimethylsilyl)-*N'*-methylurea (IIa). IR: $\nu(\text{C}=\text{O})$ 1605, $\nu_{\text{as}}(\text{SO}_2)$ 1355, $\nu_{\text{s}}(\text{SO}_2)$ 1160 cm^{-1} . NMR (-60°): $\tau(\text{Me}_3\text{Si})$ 9.76, 9.72 and 9.54, $\tau(\text{MeN})$ 7.33 and 6.75; NMR (22°C): $\tau(\text{Me}_3\text{Si})$ 9.82 and 9.68, $\tau(\text{MeN})$ 7.15 ppm.

N-(*p*-Toluenesulfonyl)-*N,N'*-bis(trimethylsilyl)-*N'*-methylurea (IIb). IR: $\nu(\text{C}=\text{O})$ 1610, $\nu_{\text{as}}(\text{SO}_2)$ 1360, $\nu_{\text{s}}(\text{SO}_2)$ 1150 cm^{-1} . NMR (-63°): $\tau(\text{Me}_3\text{Si})$ 9.78, 9.73, 9.70 and 9.56, $\tau(p\text{-Me})$ 7.65, $\tau(\text{MeN})$ 7.33 and 6.77; NMR (0°): $\tau(\text{Me}_3\text{Si})$ 9.79 and 9.73, $\tau(p\text{-Me})$ 7.65, $\tau(\text{NMe})$ 7.13 ppm.

N-(*p*-Chlorobenzenesulfonyl)-*N,N'*-bis(trimethylsilyl)-*N'*-methylurea (IIc). IR: $\nu(\text{C}=\text{O})$ 1620, $\nu_{\text{as}}(\text{SO}_2)$ 1360, $\nu_{\text{s}}(\text{SO}_2)$ 1150 cm^{-1} . NMR (-50°): $\tau(\text{Me}_3\text{Si})$ 9.78, 9.70, 9.68 and 9.53, $\tau(\text{MeN})$ 7.28 and 6.72; NMR (21°): $\tau(\text{Me}_3\text{Si})$ 9.78 and 9.65, $\tau(\text{MeN})$ 7.09 ppm.

Pyrolysis of the adducts (IIa), (IIb) and (IIc).

The adducts (IIa)–(IIc) were thermally decomposed in sealed tubes at 150° for 72 h. In all three cases, a white crystalline solid appeared on the upper part of the sealed tube, and were recrystallized from ethyl alcohol. This compound was identified as trimethyl isocyanurate (IV), m.p. $174.0\text{--}174.5^\circ$ (Lit.⁵ 174°), from m.p., infrared spectrum and analysis. (Found: C, 42.10; H, 5.31; N, 24.54. $\text{C}_6\text{H}_9\text{N}_3\text{O}_3$ calcd.: C, 41.94; H, 5.15; N, 24.82%.)

Vacuum distillation of the residual products gave *N,N*-bis(trimethylsilyl)-arenesulfonamides (IIIa)–(IIIc), for which yields, b.p.'s and analytical data were shown in Table 2.

(IIIa) ($X = \text{H}$). IR: $\nu(\text{Me}_3\text{Si})$ 1240, $\nu_{\text{as}}(\text{SO}_2)$ 1345, $\nu_{\text{s}}(\text{SO}_2)$ 1155 cm^{-1} . NMR: $\tau(\text{Me}_3\text{Si})$ 9.68 ppm.

(IIIb) (X = Me). IR : $\nu(\text{Me}_3\text{Si})$ 1240, $\nu_{\text{as}}(\text{SO}_2)$ 1345, $\nu_{\text{s}}(\text{SO}_2)$ 1150 cm^{-1} . NMR : $\tau(\text{Me}_3\text{Si})$ 9.67, $\tau(p\text{-Me})$ 7.58.

(IIIc) (X = Cl). IR : $\nu(\text{Me}_3\text{Si})$ 1240, $\nu_{\text{as}}(\text{SO}_2)$ 1350, $\nu_{\text{s}}(\text{SO}_2)$ 1168 cm^{-1} . NMR : $\tau(\text{Me}_3\text{Si})$ 9.65 ppm.

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