BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 3309—3310 (1970)

# Reactions of Group IV Organometallic Compounds. XXI.[1] Addition and Decomposition Reactions of Arenesulfonyl Iso(thio)-cyanates with Trimethylsilyl Ethyl Sulfide and Bis(trimethylsilyl) Sulfide

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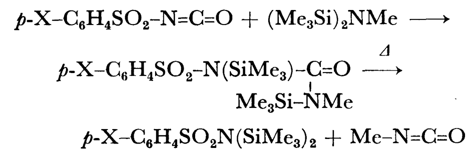
(Received June 16, 1970)

In our previous report,[1] the addition reactions of arenesulfonyl isocyanates with trimethylsilylamines or *N*-methyldisilazane were found to occur exothermically at room temperature, giving the 1 : 1 adducts quantitatively, along with the pyrolysis results (150°C, 72 hr) of these adducts, as is shown in Eq. (1).



$$p\text{-X-C}_6\text{H}_4\text{SO}_2\text{-N=C=O} + (\text{Me}_3\text{Si})_2\text{NMe} \longrightarrow p\text{-X-C}_6\text{H}_4\text{SO}_2\text{-N(SiMe}_3\text{)-}\underset{\text{Me}_3\text{Si-NMe}}{\text{C=O}} \xrightarrow{\Delta} p\text{-X-C}_6\text{H}_4\text{SO}_2\text{N(SiMe}_3)_2 + \text{Me-N=C=O} \quad (1)$$

In continuation of the paper,[1] this note deals with new reactions between arenesulfonyl isocyanates or isothiocyanates and trimethylsilyl ethyl sulfide or bis(trimethylsilyl) sulfide. Formerly, we found that in the case of the reaction between phenyl isocyanate and bis(trimethylsilyl) sulfide,[2] it was necessary to heat the mixture at 80°C for 24 hr to give the 1 : 1 aduct in 80% yield, due to relatively low reactivity of bis(trimethylsilyl) sulfide.

## Results and Discussion

The equimolar mixtures of *p*-X-substituted benzenesulfonyl isocyanate (X = H, Me and Cl) and trimethylsilyl ethyl sulfide were allowed to react at 30—40°C in glass ampoules, and the characteristic absorption at 2240 cm$^{-1}$ ($\nu_{SO_2N=C=O}$) in their IR spectra disappeared completely after ten days. The adducts were thermally unstable and were readily decomposed into starting compounds when heated above 80°C on vacuum distillation (Eq. (2)).

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[1] Part XX of this series: K. Itoh, N. Kato and Y. Ishii, *J. Organometal. Chem.*, **22**, 49 (1970).

[2] K. Itoh, K. Matsuzaki and Y. Ishii, *J. Chem. Soc., C*, **1968**, 2709.

$$p\text{-X-C}_6\text{H}_4\text{SO}_2\text{-N=C=O} + \text{Me}_3\text{Si-SEt} \xrightarrow[80^\circ\text{C}]{30\text{—}40^\circ\text{C, 10 days}}$$

Ia—c

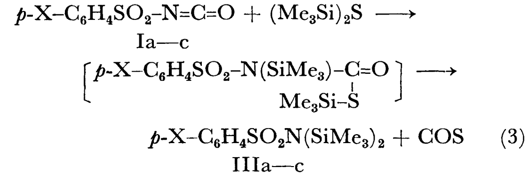
(Ia X=H, b X=Me, c X=Cl)

$$p\text{-X-C}_6\text{H}_4\text{SO}_2\text{-N(SiMe}_3\text{)-CO-SEt} \qquad (2)$$

IIa—c

These adducts (IIa—c) could be obtained solely as residues by distilling off the unreacted starting compounds under 0.03 mmHg, and their IR and NMR spectral data are shown in Experimental. In the case of the reaction with phenyl isocyanate,[2] rather drastic conditions (80°C, 80 hr) was necessary and the 1 : 1 adduct could be isolated on vacuum distillation. The reaction of $\text{Me}_3\text{SiNEt}_2$ with benzoyl isocyanate took place at 80°C for 24 hr, giving the 1 : 1 adduct, bp 72—79°C/0.002 mmHg.[3]

On the other hand, the reactions of arenesulfonyl isocyates (Ia—c) with bis(trimethylsilyl) sulfide did not occur at 30—40°C. These reactions did take place when the equimolar mixtures were heated at 110—120°C for 16 hr in glass ampoules filled with dry argon gas. However, the obtained were *N,N*-bis(trimethylsilyl) arenesulfonamides (IIIa—c) and carbonyl sulfide, which are the decomposition products of the 1 : 1 adducts (Eq. (3)).



$$p\text{-X-C}_6\text{H}_4\text{SO}_2\text{-N=C=O} + (\text{Me}_3\text{Si})_2\text{S} \longrightarrow$$

Ia—c

$$\left[p\text{-X-C}_6\text{H}_4\text{SO}_2\text{-N(SiMe}_3\text{)-}\underset{\text{Me}_3\text{Si-S}}{\underset{|}{\text{C}}}\text{=O}\right] \longrightarrow$$

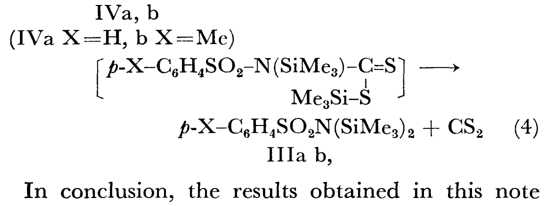
$$p\text{-X-C}_6\text{H}_4\text{SO}_2\text{N(SiMe}_3)_2 + \text{COS} \qquad (3)$$

IIIa—c

We tried to isolate the 1 : 1 adducts under various conditions, but in vain. Bp and yields of IIIa—c are shown in Experimental.

On the other hand, the reaction of phenyl isocyanate with bis(trimethylsilyl) sulfide occurred at 80°C for 24 hr to give a colorless needle-like crystalline 1 : 1 adduct (mp 54°C) in 79% yield.

The reactions between benzenesulfonyl or *p*-toluenesulfonyl isothiocyanate (IVa, b) and bis(trimethylsilyl) sulfide were quite similar to those reactions as are formulated in Eq. (3). The products obtained were *N,N*-bis(trimethylsilyl)arenesulfonamides (IIIa, b) and carbon disulfide (Eq. (4)).



$$p\text{-X-C}_6\text{H}_4\text{SO}_2\text{-N=C=S} + (\text{Me}_3\text{Si})_2\text{S} \longrightarrow$$

IVa, b

(IVa X=H, b X=Me)

$$\left[p\text{-X-C}_6\text{H}_4\text{SO}_2\text{-N(SiMe}_3\text{)-}\underset{\text{Me}_3\text{Si-S}}{\underset{|}{\text{C}}}\text{=S}\right] \longrightarrow$$

$$p\text{-X-C}_6\text{H}_4\text{SO}_2\text{N(SiMe}_3)_2 + \text{CS}_2 \qquad (4)$$

IIIa b,

In conclusion, the results obtained in this note and in the previous paper[1] confirmed the enhanced acceptor power of arenesulfonyl isocyanate, due to the electron-withdrawing property of sulfonyl group, compared with phenyl of benzyl isocyanate.

## Experimental

Three arenesulfonyl isocyanates and two isothiocyanates were prepared as described in the previous paper.[1] IR and NMR spectra were measured using Nippon-Bunko IR-S and JEOL Minimar MH-60, respectively. Microanalyses were carried out with Yanagimoto apparatus.

**Ethylthiol Ester of *N*-(Benzenesulfonyl)-*N*-trimethylsilyl Carbamate (IIa).** The mixture of 10 mmol of benzenesulfonyl isocyanate and 10.5 mmol of trimethylsilyl ethyl sulfide was heated at 30—40°C for ten days. Then, the reaction product showed no $\nu_{\text{SO}_2\text{NCO}}$ absorption at 2240 $\text{cm}^{-1}$ in IR spectrum, and was evacuated under 0.03 mmHg to remove unreacted starting compounds. The adduct IIa had IR ($\text{CCl}_4$) $\text{cm}^{-1}$: 1710 (CO), 1360 ($\text{SO}_2$, as), 1185 ($\text{SO}_2$, s) and 1253 ($\text{SiMe}_3$) and NMR ($\text{CCl}_4$) $\tau$: 9.70 (s, $\text{Me}_3\text{Si}$), 8.72 (t, $\text{CH}_3$), 7.12 (q, $\text{CH}_2$) and 2.25—2.88 ($\text{C}_6\text{H}_5$).

**Ethylthiol Ester of *N*-(*p*-Toluenesulfonyl)-*N*-trimethylsilyl Carbamate (IIb).** The reaction was carried out analogously as was described above. The adduct IIb had IR ($\text{CCl}_4$) $\text{cm}^{-1}$: 1710 (CO), 1360 ($\text{SO}_2$, as), 1177 ($\text{SO}_2$, s) and 1250 ($\text{SiMe}_3$) and NMR ($\text{CCl}_4$) $\tau$: 9.70 (s, $\text{Me}_3\text{Si}$), 8.72 (t, $\text{CH}_3$), 7.60 (s, *p*-$\text{CH}_3$), 7.12 (q, $\text{CH}_2$) and 2.25—2.89 ($\text{C}_6\text{H}_4$).

**Ethylthiol Ester of *N*-(*p*-Chlorobenzenesulfonyl)-*N*-trimethylsilyl Carbamate (IIc).** IIc had IR ($\text{CCl}_4$) $\text{cm}^{-1}$: 1710 (CO), 1360 ($\text{SO}_2$, as), 1180 ($\text{SO}_2$, s) and 1252 ($\text{SiMe}_3$) and NMR ($\text{CCl}_4$) $\tau$: 9.70 (s, $\text{Me}_3\text{Si}$), 8.72 (t, $\text{CH}_3$), 7.12 (q, $\text{CH}_2$) and 2.25—2.88 ($\text{C}_6\text{H}_4$).

**Reactions of Bis(trimethylsilyl) Sulfide with Three *p*-X-Benzenesulfonyl Isocyanates (Ia—c).** The equimolar amounts of $(\text{Me}_3\text{Si})_2\text{S}$ (0.50—0.52 g) and *p*-X-substituted benzenesulfonyl isocyanate (0.50—0.52 g) were allowed to react at 110—120°C for 1 hr in glass ampoules filled with argon. The products obtained were the pyrolysis products of the 1 : 1 adducts, *i.e.*, *N,N*-bis(trimethylsilyl)arenesulfonamides (IIIa—c) and COS. The bp and yields of IIIa—c were as follows: IIIa (X=H) 106—110°C/0.35 mmHg, 79%; IIIb (X=Me) 121—122°C/0.4 mmHg, 72%; IIIc (X=Cl) 120—122°C/0.5 mmHg, 61%. The other product, COS, was confirmed by its characteristic IR absorption at 2030 $\text{cm}^{-1}$ ($\text{CCl}_4$). IIIa—c were identified by their IR and NMR spectral data (which were reported in our previous paper[1]), together with the confirmation of mixed mp and IR spectra of their hydrolysis products.

**Reactions of Bis(trimethylsilyl) Sulfide with Benzenesulfonyl Isothiocyanate (IVa) or *p*-Toluenesulfonyl Isothiocyanate (IVb).** The equimolar amount of benzenesulfonyl isothiocyanate (IVa) 0.52 g and bis(trimethylsilyl) sulfide 0.46 g were heated in a glass ampoule filled with argon gas at 110—120°C for 16 hr. The products obtained were *N,N*-bis(trimethylsilyl)benzenesulfonamide (IIIa) and $\text{CS}_2$ in 60% and 55% yields, respectively.

The reaction of *p*-toluenesulfonyl isothiocyanate (IVb) with bis(trimethylsilyl) sulfide at 110—120°C for 16 hr gave *N,N*-bis(trimethylsilyl)-*p*-toluenesulfonamide (IIIb) and $\text{CS}_2$ in 55% and 61% yield, respectively.

These products IIIa and IIIb coincided completely with those products obtained in the reactions between $(\text{Me}_3\text{Si})_2\text{S}$ and Ia or Ib.

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[3] I. Matsuda, K. Jinda, K. Itoh and Y. Ishii, unpublished results.