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Catalytic Trimerization of Isocyanates by Neutral Pentacoordinated Silicon Hydrides

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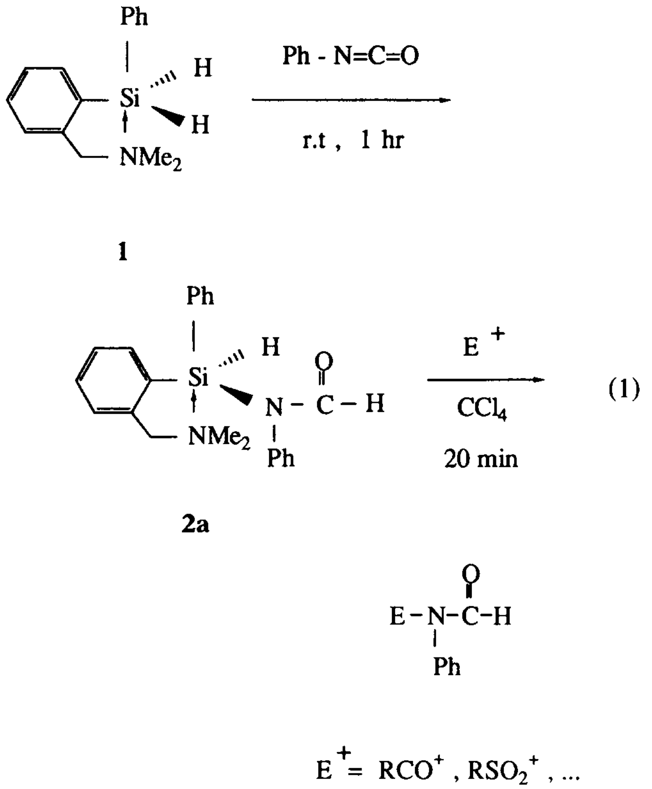
ABSTRACT

Pentacoordinated hydrosilanes react with excess of aryl isocyanates to give isocyanurates under mild and neutral conditions. The catalytic species are the initially formed N-*silylformamides, which incorporate three equivalents of isocyanate, and then rearrange to* N-*silylformamide and isocyanurates.*

INTRODUCTION

It has been known for a long time that aromatic isocyanates undergo dimerizations and trimerizations in the presence of certain specific catalysts [1]. Richter and Ulrich [2] reported that the otherwise stable benzyl isocyanate can be dimerized to a 1,3-diazetidine or trimerized to an isocyanurate under the influence of 1,2-dimethylimidazole. Also, there have been some reports concerning the trimerization of isocyanates by tin alkoxides and ditin oxides [3]. We report here the trimerization of aryl isocyanates initiated by hypervalent silicon hydrides.

Recently, we demonstrated the reactivity of hypervalent silicon hydride **1** toward phenyl isocyanate under mild conditions and the synthetic utility of the formamidosilane **2a** by further cleavage of the Si–N bond with electrophiles [4] (Equation 1).



(1)

Coupling reactions of **1** with various H acidic materials showed the two hydrogen atoms to be exchangeable [5, 6]. We were therefore interested to bring about further reactions of synthetic interest of the amidosilane **2a**. Our attempts to make insertion of Ph–N═C═O into the second Si–H bond failed, and instead resulted in the formation of **3a**, the trimer of phenyl isocyanate [7]. As exemplified,

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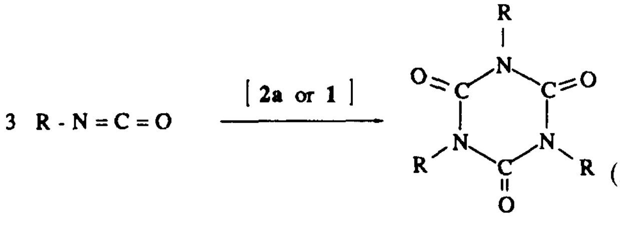
1 is mixed with Ph–N=C=O (1 equiv) for 1 h, and then 3 equiv of Ph–N=C=O are added to the reaction mixture. After 3–4 h at room temperature, there is a separation of white solid compound. After filtration, the solid compound is characterized as only **3a**, as depicted in Equation 2.



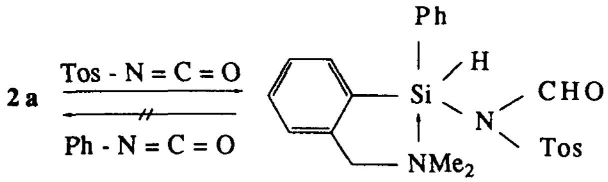
(2)

3a, R = C_6H_5

3b, R = 4-MeC_6H_4

To test the catalytic efficiency of **1**, the reaction has been performed with 30 equiv of Ph–N=C=O and the trimer **3a** has been isolated in 85% yield. The yield is better when the reaction is performed directly with excess of Ph–N=C=O relative to **1** (in situ reaction) instead of first preparing the *N*-silylamide **2a** and then adding excess of Ph–N=C=O. *N,N*-Dimethylbenzylamine and/or diphenylsilane have no effect on Ph–N=C=O under similar conditions.

To gain an insight into the reaction mechanism for formation of the trimer, the reactivity of the intermediate *N*-silylamide **2a** has been studied toward various other electrophilic isocyanates (Equation 3).



(3)

N-silylamide **2a** does not react with the less electrophilic cyclohexyl isocyanate C_6H_{11}–N=C=O. Fast exchange takes place with the more electrophilic *p*-tolylsulfonyl isocyanate to give **2c**, which has also been prepared by reaction of **1** with *p*-tolylsulfonylisocyanate. **2c** is less reactive and does not get cleaved with weak electrophiles. We have not observed any reaction of **2c** with Ph–N=C=O (even in excess). *p*-Tolyl isocyanate (3 equiv) on reaction with **2a** gives mainly the formation of symmetrical trimer **3b**, which was authentically prepared by trimerization of *p*-tolyl isocyanate [3].

In view of the above results, and according to previous data [3b], the most probable mechanism for trimerization is repeated insertion of Ar–N=C=O into the Si–N bond of the Si–NR (C=O)– group, and, after three insertions, elimination of trimer with reformation of the intermediate silylamide **2a** (Equation 4). We believe that the efficient catalyst for trimerization is the *N*-silylamide **2a**, rather than the pentacoordinated hydrosilane **1**, which is only the precursor of **2a**.

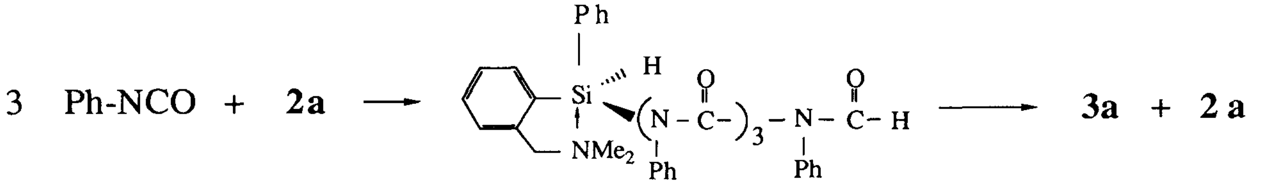
The present reaction represents a unique catalytic behavior of hypervalent silicon hydrides for trimerization of aryl isocyanates in good yields, under very mild and neutral conditions.

EXPERIMENTAL

NMR spectra were measured on a Bruker AW 60 (60 MHz) for ^1H and on Bruker WP 200 SY or AC 250 instruments for ^{29}Si and $^{13}C(CDCl_3, TMS)$; 70 eV mass spectra were recorded with a Jeol JMS-D100. Microanalyses were performed by the Laboratoire de Microanalyse du CNRS at Lyon-Vernaison, France. The isocyanates were purchased from Aldrich Chemical Co. and used as received. Compound **1** was prepared by a published procedure [6]. CCl_4 and $CDCl_3$ were distilled prior to use and degassed. All reactions with isocyanates were conducted under a dry argon atmosphere.

Reaction of **1** *with Isocyanates: General Procedure*

This is exemplified by the reaction of **1** with phenyl isocyanate. To a stirred solution of **1** (1.8 g, 7.47 mmol) in carbon tetrachloride (6 mL) was added 0.89 g (7.47 mmol) of phenyl isocyanate. After 1 h, the ^1H NMR spectrum of the crude product showed the total disappearance of **1** (no signal for SiH_2 at δ 4.84) and the formation of **2a**: ^1H NMR (CCl_4): δ 1.75 (s, 6H, $N(CH_3)_2$), 3.39 (s, 2H, CH_2), 5.29 (s, 1H, SiH), 7.95 (s, 1H, CHO), 6.8–8.3 (m, 14H, ArH), ^{13}C NMR ($CDCl_3$): δ 45.5 (q, $N(CH_3)_2$), 63.2 (t, CH_2N), 120–150 (Ar), 167.9 (d, J = 196 Hz, CHO). ^{29}Si NMR ($CDCl_3$): δ −47.4 (d, J = 263 Hz). Compound **2a** was used further without purification as it decomposes upon concentration. Phenyl isocyanate (2.45 mL, 22.5 mmol) was added, and the reaction mixture stirred for 3 h. A white solid separated from the solution. Recrystallization of the solid from $CHCl_3$ yielded **3a** as a colorless, crystalline solid [3b]: (1.37,



(4)

3.83 mmol) (yield 38%): mp 284–285°C; IR 1712 cm^{-1} (C=O) ^{1}H NMR (CDCl$_3$): δ 7.35 (m, Ar–H); ^{13}C NMR (CDCl$_3$): δ 127–134 (m, C–Ar), 149.1 (s, C=O). MS: m/e 357. In another experiment, **1** (1.8 g, 7.47 mmol) was mixed with an excess of phenyl isocyanate (26.7 g, 225 mmol) in CCl$_4$ (50 mL). After 10 minutes, a solid started to deposit. The mixture was stirred for 5 h. Filtration separated **3a** as a white solid mp 281–284°C (22.7 g, 63.7 mmol). Yield 85%.

N-*2(dimethylaminomethyl)phenylphenylsilyl* N-p-*Toluenesulfonamide*, **2c**

Addition of *p*-toluenesulfonyl isocyanate (2 g, 10 mmol) to 2.4 g (10 mmol) of **1** in CCl$_4$ resulted in an exothermic reaction. After stirring for 15 minutes, the insertion compound **2c** was identified on the basis of NMR data: ^{1}H δ 1.91 (br s, 6H, N(CH$_3$)$_2$), 2.29 (s, 3H, CH$_3$), 3.52 (s, 2H, CH$_2$N), 5.11 (s, 1H, Si–H), 6.45–8.0 (m, 13H, Ar–H), 8.43 (s, 1H, C(O)H). ^{13}C: δ 21.91 (q, CH$_3$Ar), 45.98 (q, N(CH$_3$)$_2$), 63.06 (t, CH$_2$N), 125.6–144.5 (C, Ar), 166.6 (d, J = 194.9 Hz, C(O)H). ^{29}Si (CDCl$_3$): δ −56.14 (d, J = 277.0 Hz, Si–H). The product was not isomerized in solution after two weeks (only one signal by ^{29}Si NMR, DEPT technique).

p-*Tolyl Isocyanurate*, **3b**

p-Tolyl isocyanate (6 mmol) was added to **1** (1 mmol) at room temperature and stirred overnight. There was a separation of solid compound, which was collected by filtration and identified as trimeric *p*-tolyl isocyanurate, **3b**. (5.85 g), yield 73%, mp 221–222°C, IR (CHCl$_3$) 1714 cm^{-1} (C=O). ^{1}H NMR (CDCl$_3$): δ 2.32 (s, 9H, Ar–CH$_3$), 7.60 (m, 12H, Ar–H). ^{13}C (CDCl$_3$): δ 21.63 (s, Ar–CH$_3$), 127–134 (m, C–Ar), 149.09 (s, C=O). MS: m/e 399(22)M^{+}, 266 (8), 133 (100), 107 (20), 104 (30), 91 (15), 77 (17).

Trimerization of Isocyanates with **2**

p-Tolyl isocyanate (0.4 g, 3 mmol) was added to **2a** (1 mmol) in CCl$_4$ (5 mL). The mixture was stirred overnight. After filtration, the solid mixture was analyzed by mass spectroscopy (EI, 70 eV): 399 (12), 385 (4), 371 (2), 357 (1), 266 (4), 133 (100), 118 (8), 104 (15), 91 (8), 77 (6), 64 (4). The mass peak at 399 was attributed to trimeric *p*-tolyl isocyanurate, **3b**. The peaks at 385 (4) and 371 (2) were respectively attributed to di-*p*-tolyl phenyl isocyanurate and *p*-tolyl diphenyl isocyanurate.

Cyclohexyl isocyanate (3.75 g, 3 mmol) was added to **2** in the same conditions as above. No reaction occurred after one night and starting compounds were recovered, with partial isomerization of **2** (N to O silyl migration) [8].

The reaction of **2a** (0.41 g, 1 mmol) with *p*-toluenesulfonyl isocyanate (0.2 g, 1 mmol) in CCl$_4$ at 25°C for 2 h resulted in the formation of phenyl isocyanate and **2c**, as shown by ^{29}Si NMR: disappearance of the signal at −47.4 ppm and a new peak at −56.1 ppm. Addition of an excess of phenyl isocyanate (0.36 g, 3 mmol) did not cause any change of the silicon moiety; precipitation of **3a** was not observed, even after 72 h.

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[7] Preliminary experiments have been performed by Myriam Perrot-Petta.

[8] Unpublished data from this laboratory.