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Reactions of Trimethylsilyldiphenylphosphine with Isocyanates

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Abstract Reactions of trimethylsilyldiphenylphosphine with phenylisocyanate and ethylisocyanate were studied at various temperatures for 3 days. Trimethylsilyldiphenylphosphine gave cyclic dimer, cyclic trimer and diphenylcarbodiimide from phenylisocyanate, but gave cyclic trimer, triethylisocyanurate, only from ethylisocyanate.

In these reactions, it is suggested that trimethylsilyldiphenylphosphine was used to be an effective catalyst for cyclization of isocyanates.

Introduction

Many studies have been reported [1,2] on the structures of organosilicon compounds and its reactions with unsaturated compounds, and its mechanisms have been disclosed.

Recently, Schmidbauer[3] reported the stability of the Si-O bond by p_x-d_x overlap, and Wannagat[4] illustrated that the following resonance structures are possible in the Si-N bond:
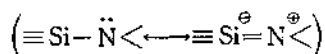
$$\left(\equiv Si - \ddot{N} < \longleftrightarrow \equiv Si \overset{\ominus}{=} N \overset{\oplus}{<} \right)$$

And also Abel [5] explained that there is a π bond character in the metal-hetero (X) bonds such as Si-C, Si-N, Si-O bonds, etc. So, it is suggested that the silicon-hetero atom bonds have the polarization like $Si^{+\delta} - X^{\delta-}$ and reacts as a dipolarophile because the silicon atom has comparatively a small electronegativity, and sometimes the silicon atom makes 5-6 coodination complex compounds or builds up the so-called d_x-p_x overlap by the existence of its vacant d orbital situation.

In general, the reactivity of organometallic compounds are decided by the acceptibility of the metal (M) in the M-X bond or the Lewis acidity and the nucleophilicity of the hetero atom. In the case of silicon atom, the reactivity is mainly governed by the nucleophilicity of the hetero atom, for its acceptibility is remarkably low[6,7]. And the nucleophilicity of the hetero atom is determined by the sum [8] of the two effects of the electronegativity and the $(p-d)_x$ interaction with the silicon atom. Depending on these facts, it is suggested that P (in Si-P) also has a similar bond because of its lone elec-

tron pair of p character. We can estimate that the behavior of Si–P compounds should be more complex because the nucleophilic attack to P (III) is actually to be occurred together with the nucleophilicity of the atom and the convertibility of P (III) into P (V) is to be expected.

Many reports recently have been made on the addition-elimination reactions of polar unsaturated compounds (acceptor) to organosilicon compounds. The studies employing phenylisocyanate as an acceptor are summarized in the following *Table* (1).

Table 1. Reactions of Si-X with PhNCO

Si-X		Product	
Si-N	1 : 1 Adduct [9,10]	$(PhNCO)_3$[11,12]	$(PhN=C=NPh)_3$ [13]
Si-S	1 : 1 Adduct [14]	$(PhNCO)_3$[14]	
Si-O	$PhN=C=NPh$ [15]	$(PhNCO)_3$[15] Decarboxylation product [15] of $(PhNCO)_4$
Si-P		$(PhNCO)_3$[16]	

As we understand in the above *Table* (1), most of Si-X compounds act as a catalyst for the cyclization (dimer-tetramer) of phenylisocyanate, and the formation diphenylcarbodiimide indicates that the 1, 3-transfer [17] of trimethylsilyl group takes place in the process of the reaction.

In the reaction of Si-P compound with phenylisocyanate, the formation of cyclic dimer of phenylisocyanate was only reported by Abel and his co-workers [16] up-to-date as shown *Table* (1).

In this paper we report some interesting facts that in the reaction of trimethylsilyldiphenylphosphine with phenylisocyanate, the reaction products and its ratio were different as the reaction temperatures, and a sole product in the reaction between trimethylsilyldiphenylphosphine and ethylisocyanate was given differently from the reaction of phenylisocyanate.

Experimental

A) Preparation of Trimethylsilyldiphenylphosphine

Trimethylsilyldiphenylphosphine was prepared from triphenylphosphine (50g.) and trimethylchlorosilane (42. 2g.) by the procedure proposed

by Kuchen [18] and Chatt, [19] and purified by distillation, b. p. 126-127°/1 mm.

B) Reactions of Trimethylsilyldiphenylphosphine with Phenylisocyanate

All reactions were carried out in the mole ratio of 1:10 and in the sealed ampoules filled with nitrogen gas. The quantity of the reaction mixture used was 3g. and the reactions were performed for 3 days at room temperature, 60° and 100° respectively. The relative yields of the products (I), (II) and (III) were determined by the *i. r.* spectroscopy, by use of calibration curve (I), 1780 (II), ; 1710; and (III), 2150 cm^{-1} obtained with solution in spectrograde chloroform of authentic materials (I)-(III).

(1) **Reaction at room temperature (15·20°)** Trimethylsilyldiphenylphosphine and phenylisocyantae reacted exothermically and were converted into the solid state a little later. Extraction of the solid with the mixed solvent (3:1 v/v) consisting of hexane and chloroform was resulted in separation into two products. The soluble fraction in this mixed solvent was isolated by evaporation of the solvent and recrystallized from hexane. This compound was identified as NN-diphenyluretidine-2, 4-dione I

(1.77g; 72%) by comparison of its *i. r.* spectrum (ν_{c-o} 1780 cm⁻¹) and mixed melting point(175-176°) with that of authentic material. [Lit., ν_{c-o} 1780 cm⁻¹, m. p., 175°, 179-181°)[16,20]

The insoluble solid in the above mixed solvent was dissolved with acetone and recrystallized from ethanol. This compound was identified as triphenylisocyanurate II (0.69g; 28%) by comparison of its *i. r.* spectrum (ν_{c-o} 1710 cm⁻¹) and melting point (283-284°) with an authentic sample. [Lit., ν_{c-o} 1710 cm⁻¹, m. p., 283-285。][20]

(2) **Reaction at 60°** When the ampoule was opened after 3 days, carbon dioxide was evolved and some of viscous fluid and solid obtained. The mixture was devided in the two parts of solid and liquid by treating with hexane. The former was separated into two products by the same way of reaction (1) and identified as I (0.25g; 10%) and II (0.98g; 40%). And diphenylcarbodiimide III (1.23g; 50%) from the latter was obtained by vacuum distillation at b. p. 115°/0.5mm. This was conformed by comparison of its *i. r.* spectrum ($\nu_{-N-C-N-}$ 2150 cm⁻¹) and boiling point (115°/0.5mm.) with that of authentic sample. [Lit., $\nu_{-N-C=N-}$ 2150 cm⁻¹, b. p., 115°/0.5 mm.][15,21]

(3) **Reaction at 100°** When the ampoule was opened after 3 days, carbon dioxide was evolved more vigorously than the case of reaction (2) and a part of viscous black fluid was transformed into crystal. The reaction products were separated in the same method of reaction (2) and identified as II (0.52g; 21%) and III (1.72g; 70%) respectively. But the small part of the insoluble fraction in acetone (appeared at 1675 cm⁻¹) was not identified. And the original sample, trimethylsilyldiphenylphosphine, was recovered in the reaction of (1), (2) and (3).

C) **Reactions of Trimethylsilyldiphenylphosphine with Ethylisocyanate**

All reactions were carried out in the mole ratio of 1:1 and 1:10, and in the sealed ampoules filled with nitrogen gas. The quantity of the reaction mixture was 3g. and these reactions were carried out for 3 days at room temperature, 60°, 100° and 150°. The reaction rate and the relative yields of products at various temperatures were measured by the *i. r.* spectroscopy by use of calibration curve (IIEt), 1680 cm⁻¹ obtained with solution in spectrograde chloroform of authentic material.

(1) **Reaction at room temperature (15-20°)** The reaction mixture of 1:1 mole ratio was characterised by a very strong infrared absorption of isocyanate at 2260 cm⁻¹, but after 3 days, a new absorption at 1680 cm⁻¹ began to be visible. After 20 days the characteristic absorption of isocyanate was decreased, on the other hand, the new absorption was increased. And after 50 days, the *i. r.* spectrum showed that all isocyanate had reacted. Volatile compounds in the mixture were removed by the vacuum distillation leaving white wax-like material, which is crystallized from benzene and recrystallized from chloroform-hexane (3:1 v/v). This crystal was identified as triethyisocylanurate (IIEt) by comparison of its *i. r.* spectrum (ν_{c-o} 1680 cm⁻¹) and melting point (92-94°) with that of authentic sample. [Lit., ν_{c-o} 1680 cm⁻¹, m. p., 92-93.5°][12] The yields (IIEt) were 0.03g(5%), 0.18g. (35%) and 0.51g. (100%) after 3, 20 and 50 days, respectively. In the mole ratio of 1:10, the same product (IIEt) was also obtained and the yields were 0.04g. (2%), 0.22g. (10%) and 1.56g. (70%) after 3, 20 and 50 days, respectively.

When the reaction mixture was exposed to air for 3 days at room temperature, a colorless crystal was given and recrystallized from chloroform-hexane. This crystal was presumed as the hydrolysis product of the 1:1 adduct [IVa], ethylcarbamyldiphenylphosphine (EtN

H-CO-PPh$_2$, m. p., 168-170°), by the *i. r.* spectrum (ν_{NH} 3378 cm^{-1}, $\nu_{c=o}$ 1642 cm^{-1}, ν_{CH} 2975 cm^{-1} (aliphatic), ν_{CH} 3060 cm^{-1} (aromatic) and PPh$_2$ 1439 cm^{-1})[21] and the qualitative detection of phosphorus.

(2) **Reaction at 60°, 100° and 150°** Triethylisocyanurate (IIEt) was only produced from these reactions. In the case of 1 : 1 mole ratio, ethylisocyanate was converted into *II*Et as follow after 3 days: 0.23g. (45%) at 60°, 0.36g. (73 %) at 100° and 0.51g. (100%) at 150°. And in 1 : 10 mole ratio, it was 0.67-1.11g. (30-50%) at 60°, 0.99-1.98g. (45-90%) at 100° and 1.11 -2.22g. (50-100%) at 150° after 3-7 days respectively. And in the reaction (C) the original sample, trimethylsilyldiphenylphosphine, was also recovered.

Results and Discussion

In 1968, Abel and his co-worker [16] have reported that the cyclic dimer of phenylisocyanate was formed in the reaction between trimethylsilyldiphenylphosphine and phenylisocyanate.

We disclosed that, in the reaction between trimethylsilyldiphenylphosphine and phenylisocyanate, the products and its ratio were different as the reaction temperatures (*Table* 2), and in the reaction of trimethylsilyldiphenylphosphine with ethylisocyanate, the reaction rate was changed as the reaction temperatures, but a single product, triethylisocyanurate, was only given (*Table* 3).

Table 2. Distribution (%) of I, II and III at various temperatures

Temp., °C	I	II	III	Other
Room temp.	72	28	-	-
60	10	40	50	-
100	-	21	70	9

[Me$_3$Si-PPh$_2$]:[PhNCO] =1 : 10 mole ratio (Reaction for 3 days)

Table 3. Yields (%) of (EtNCO)$_3$ at various temperatures

Mole ratio	Room temp.	60°	100°	150°
1 : 1	5	45	73	100
1 : 10	2	30	45	50

[Me$_3$Si-PPh$_2$] : [EtNCO] =1 : 1 and 1 : 10 mole ratio (Reaction for 3 days)

In the reaction of trimethylsilyldiphenylphosphine with phenylisocyanate at room temperature, the main product was the cyclic dimer of phenylisocyanate, NN-diphenyluretidine-2, 4-dion (I), and a little cyclic trimer, triphenylisocyanurate (II), was also produced. The formation of I and II are explained by the subsequent insertion of phenylisocyanate to N-silyl bond in 1 : 1 adduct [IVa], for the reactivity of the Si-N bond in the adduct is much greater than that of the Si-P bond in the original sample.

While the formation of I in the reaction at 60° was decreased extremely, a considerable amount of a new compound(III)was produced with an increase of II. At the same time, a considerable amount of carbon dioxide was released. From these facts, the formation of III is presumed as follows: [IVb] is afforded by the 1, 3-transfer of trimethylsilyl group on the nitrogen atom in the 1 : 1 adduct [IVa], and then [V] is induced by the addition of phenylisocyanate to [IVb] and III is produced passing through [VI] formed by the decarboxylation of [V].

In fact, Rochow et al. [17] have reported that the mutual convertibility of the trimethylsilyl group takes place by the 1, 3-transfer in some N-trimethylsilylamides as the following:
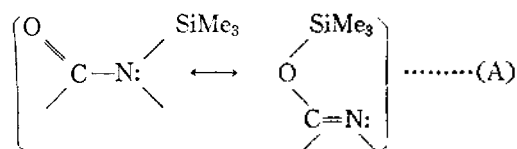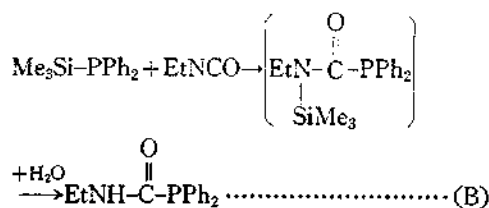
And they predicted this conversion is proceeded for the great affinity of the silicon atom to the oxygen which makes the driving force.

At 100°, I was not formed entirely, but II and III were obtained, at the same time a new absorption appeared at 1675 cm^{-1}. The formation of II was decreased more than in the reaction at 60° and, on the other hand, III was increased and a considerable amount of carbon dioxide was evolved. The fact that III was formed only at high temperature (above 100°) means that the stability of the Si-O bond in the intermediate [IVb] was greater than the Si-N bond in [IVa]. We are considered that the addition of phenylisocyanate unit to the intermediate [IVb] is preferred, for the equilibrium of equation (A) is partial to the right in this case. Besides, we obtained a small amount of the product that was observed at 1675 cm^{-1}, but it was not identified. From the above results and discussion, the following scheme is presumed:

The reaction between trimethylsilyldiphenyl-

phosphine and ethylisocyanate was extremely slower than that in phenylisocyanate, and the reaction rate was increased as rising of the temperature as shown in the above *Table* (3). But the single product in spite of variety of temperatures and the reactant ratio, triethylisocyanurate (IIEt), was only obtained. It seems to be produced by the cyclic trimerization of ethylisocyanate passing through the same route with that of phenylisocyanate. The trimerization of ethylisocyanate by the subsequent insertion is supported by the formation of the hydrolysis product, ethylcarbamyldiphenylphosphine (Et NH-CO-PPh$_2$), of the 1 : 1 adduct [IVa].

$$Me_3Si-PPh_2+EtNCO\rightarrow\left(\begin{array}{c} O \\ \| \\ EtN-C-PPh_2 \\ | \\ SiMe_3 \end{array}\right)$$

$$+H_2O \\ \longrightarrow EtNH-\overset{O}{\overset{\|}{C}}-PPh_2 \cdots\cdots\cdots\cdots\cdots\cdots(B)$$

From the fact that the insertion of ethylisocyanate to the Si–P bond was extremely slow, it is considered that the polarization of C=N bond in ethylisocyanate was due to be weaken by the electron donation of ethyl radical. And in phenylisocyante, the opposite phenomenon occurred by the electron attraction of phenyl radical.

Carbodiimide was not formed even at high temperature in the reaction of ethylisocyanate. It may be thought because of the control of a 1, 3-transfer as shown in the previous equation (A). And the restraint of such a transfer is explained that the Si–N bond is more stabilized by the increase of electron density in the nitrogen atom for the electron repelling of ethyl radical.

Also it is suggested that the restraint of formation of the dimer from ethylisocyanate is made by the fact that the elimination of trimethylsilyl group is not occurred, since the 1 : 2 adduct
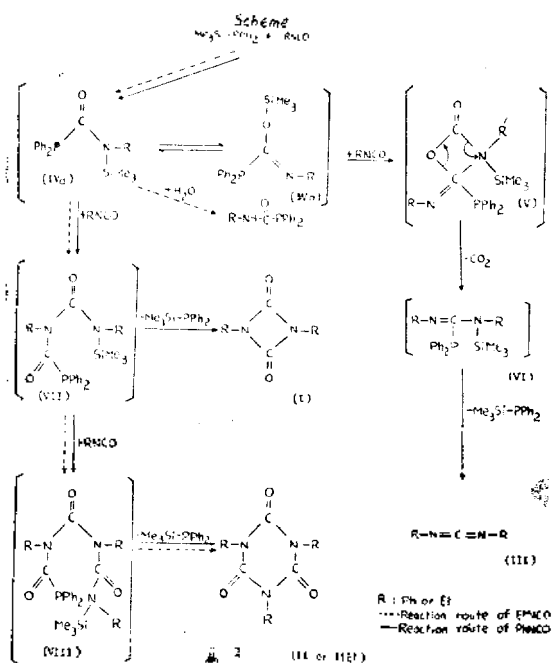
[VII] was more stable in ethylisocyanate than in phenylisocyanate. And so the trimer (IIEt) is produced by the addition of the other molecule of ethylisocyanate to the intermediate [VII].

In conclusion, when the Si-P bond reacted with phenylisocyanate and ethylisocyanate, the reactivity of the former was greater than the latter, and formed NN-diphenyluretidine-2, 4-dione (I), triphenylisocyanurate (II) and diphenylcarbodiimide (III). And the products and its ratio were different according to the reaction temperatures. Namely, at higher reaction temperatures, the products were increased from I to III. In the latter, the reactivity was extremely slow and a sole product of the trimer, triethylisocyanurate (IIEt), was given regardless of the reaction temperatures and reactant ratio. Trimethylsilyldiphenylphosphine in these reactions is acted as the catalyst of the cyclic dimerization and the cyclic trimerization of isocyanates.

Acknowledgement

References

1. M. F. Lappert and B. Prokai, "Advances in Organometallic Chemistry", Academic Press Inc., Vol. 5, P. 225 (1967).
2. E. Y. Lukevits and M. G. Voronkov, "Organic Insertion Reactions of Group IV Elements", Consultants Bureau, New York (1966).
3. H. Schmidbauer, *Angew. Chem.*, **77**, 206 (1965).
4. U. Wannagat, "Advances in Inorganic and Radiochemistry", Vol. 6, 225 (1964).
5. E. W. Abel, R. P. Bush, C. R. Jenkins and T. Zobei, *Trans. Faraday Soc.*, **60**, 1214 (1962).
6. K. Itoh, S. Sakai and Y. Ishii *Chem. Commun.*, 36 (1967).
7. K. Itoh, S. Sakai and Y. Ishii, *Nippon Gogyokagakukaisi*, **70**, 935 (1967).
8. E. W. Abel, D. A. Armitage and D. B. Brady, *Trans. Faraday Soc.*, **62**, 3459(1966).
9. G. Oertel, H. Malz and H. Holtschmidt, *Chem. Ber.*, **97**, 891 (1964).
10. W. Fink, *ibid.*, **97**, 1433 (1964).
11. A. G. Davies and Y. Ishii, At the 18th, meeting of Chem. Soc. of Japan, Preprint, P. 436 No. 2 3213 (1965).
12. A. J. Bloodworth and A. G. Davies, *J. Chem. Soc.*, 6858 (1965).
13. K. Itoh, S. Sakai and Y. Ishii, At the meeting of Chem. Soc. of Japan, 22nd, Preprint, No. 17124 (1969).
14. K. Itoh, K. Matsuzaki and Y. Ishii, *J. Chem. Soc.*, (C), 2709 (1968).
15. K. Itoh, Il Kyu Lee, S. Sakai and Y. Ishii, *ibid.*, (C), 2007 (1969).
16. E. W. Abel and L. H. Saubherwal, *ibid.*, (A), 1105 (1968).
17. J. Pump and E. G. Rochow, *Chem. Ber.*, **97**, 627 (1964).
18. W. Kuchen and H. Buchwald, *ibid.*, **92**, 227 (1959).
19. Chatt and Hart, *J. Chem. Soc.*, 1385 (1960).
20. H. E. Buckles and L. A. Mcgrew, *J. Amer. Chem. Soc.*, **88**, 3582 (1966).
21. L. J. Bellamy. "The infrared spectra of complex molecules", Methuen & Co. Ltd., London, P. 320 (1964).