at 1300° K. and under standard conditions from the elements were found to be: CuCl(g), $\Delta H_{1300°K.} = 18.8 \pm 4$ kcal.; Cu_3Cl_3(g), $\Delta H_{1300°K.} = -63.1 \pm 2$ kcal.; and CuBr(g), $\Delta H_{1300°K.} = 23.3 \pm 0.9$ kcal. The D_0 values calculated from the thermal data were 3.80 ± 0.15 and 3.42 ± 0.15 volts for CuCl(g) and CuBr(g), respectively. Free energy equations are given for both cuprous chloride molecular species.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Preparation and Some Properties of Triphenylsilyl Isocyanate and Triphenylsilyl Isothiocyanate

BY HENRY GILMAN, BURT HOFFERTH AND H. W. MELVIN

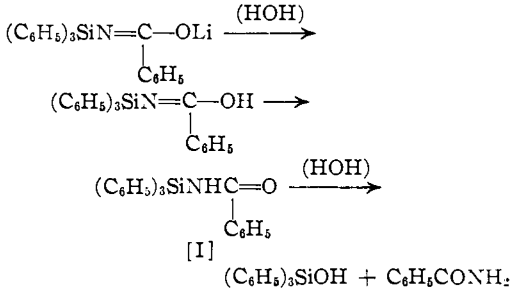
In connection with studies concerning the introduction of functional groups into organosilicon molecules, we have prepared triphenylsilyl isocyanate and triphenylsilyl isothiocyanate. One of the procedures used was described earlier.[1,2] It was found that N-triphenylsilylurethan could not be prepared as a derivative of triphenylsilyl isocyanate directly by reaction with absolute ethanol. An attempt to make it by double decomposition between sodium urethan and triphenylsilyl chloride yielded triphenylsilyl isocyanate and none of the expected product. Efforts to prepare N-triphenylsilylurea by the action of triphenylsilyl chloride upon urea also produced triphenylsilyl isocyanate. When thiourea was substituted for urea, triphenylsilyl isothiocyanate was obtained. The formation of the isocyanate from urea and sodium urethan and the isothiocyanate from thiourea are new methods of synthesis for these triphenylsilyl pseudohalides.

$$(C_6H_5)_3SiCl + (NH_2)_2CO\ [\text{or}\ Na(NHCOOC_2H_5)] \longrightarrow (C_6H_5)_3SiNCO$$

Triphenylsilyl isothiocyanate was also prepared by the reaction of triphenylsilyl chloride with silver isothiocyanate, lead isothiocyanate and ammonium isothiocyanate, respectively.

In studying the chemical properties of these compounds[2] their reactions with phenylmagnesium bromide and phenyllithium were investigated. By analogy with the reported mechanism of the reaction of phenylmagnesium bromide with phenyl isocyanate[3] and isothiocyanate,[4,5] it is highly probable that addition of phenyllithium to triphenylsilyl isocyanate occurred first at the terminal unsaturated linkage, as follows:

$$(C_6H_5)_3SiN{=}C{=}O \xrightarrow{(C_6H_5Li)}$$



$$(C_6H_5)_3SiN{=}\underset{\displaystyle C_6H_5}{\underset{|}{C}}{-}OLi \xrightarrow{(HOH)}$$
$$(C_6H_5)_3SiN{=}\underset{\displaystyle C_6H_5}{\underset{|}{C}}{-}OH \longrightarrow$$
$$(C_6H_5)_3SiNH\underset{\displaystyle C_6H_5}{\underset{|}{C}}{=}O \xrightarrow{(HOH)}$$
$$[I] \qquad (C_6H_5)_3SiOH + C_6H_5CONH_2$$

Compound I, containing a silicon-nitrogen linkage, should undergo ready hydrolysis to give triphenylsilanol and benzamide. Actually, these products were isolated in good yields when triphenylsilyl isocyanate reacted with either phenyllithium or phenylmagnesium bromide. It has been suggested by a reader that the triphenylsilanol may have come from hydrolysis of triphenylsilyllithium, which may have formed intermediately by reaction of triphenylsilyl isocyanate[6] and phenyllithium.

In the case of triphenylsilyl isothiocyanate the above mechanisms involving phenyllithium do not present a complete picture. The formation of tetraphenylsilane in yields up to 74% indicates that the isothiocyanate moiety may have behaved as a pseudo-halogen undergoing reaction like that observed with triphenylsilyl chloride.

After the completion of this study, a report[2b] on the preparation of triphenylsilyl isocyanate by the action of silver isocyanate upon triphenylsilyl chloride appeared. The melting point reported was 95 ± 1°; our best melting point of this compound, prepared by this and two other methods, was 100–101°. Also, the reported melting point of triphenylsilyl isothiocyanate[2c] prepared from triphenylsilyl chloride and silver isothiocyanate, was 76 ± 1°. Our product, prepared by this procedure as well as other methods, melts at 100–101°. This difference may possibly be due to the existence of two different crystalline forms of the same compound. A mixed melting point determination between the isocyanate and the isothiocyanate showed a depression.

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(1) Forbes and Anderson, This Journal, **62**, 761 (1940).

(2) The observed molar refractions for the methyl silicon isothiocyanates agree closely with values calculated for the isothiocyanates: see (a) Anderson, *ibid.*, **69**, 3049 (1947); (b) Forbes and Anderson, *ibid.*, **70**, 1043 (1948); (c) Anderson, *ibid.*, **70**, 1220 (1948).

(3) Gilman, Kirby and Kinney, *ibid.*, **51**, 2252 (1929).

(4) Gilman and Kinney, *ibid.*, **46**, 493 (1924).

(5) Gilman and Breuer, *ibid.*, **55**, 1262 (1933).

(6) There is a possibility that the cyanate may undergo reactions leading to the products isolated.

TABLE I

REACTIONS FOR THE PREPARATION OF TRIPHENYLSILYL ISOCYANATE AND TRIPHENYLSILYL ISOTHIOCYANATE

$(C_6H_5)_3SiCl$[a] and	Product	Method	M. p.,[b] °C.	Yield, %	Analyses, % Calcd. Si	Calcd. N	Calcd. S	Found Si	Found N	Found
Urea	$(C_6H_5)_3SiNCO$	A	100–101[c]	67[c]	9.3	4.6		9.4 9.3	4.2 4.2	
Thiourea	$(C_6H_5)_3SiNCS$	A	99–100.5[d]	68	8.8	4.4	10.1	8.8	4.4	9.9
Sodium urethan[e]	$(C_6H_5)_3SiNCO$[f]	B[g]	98–100	48	9.3	4.6		9.2	4.4 4.3	
Silver isocyanate	$(C_6H_5)_3SiNCO$	B[h]	100–102	85	9.3	4.6		9.2	4.2 4.2	
Silver isothiocyanate	$(C_6H_5)_3SiNCS$	B[i]	100–101	73						
Lead isothiocyanate[j]	$(C_6H_5)_3SiNCS$[k]	B	97–99	97						
Ammonium isothiocyanate	$(C_6H_5)_3SiNCS$[k]	B[l]	97–98	56						

[a] Triphenylsilyl chloride was prepared by the method of Kraus and Rosen, THIS JOURNAL, **47**, 2739 (1925). [b] All melting points are uncorrected. [c] When first isolated, the m. p. was 98–99°. With 0.4 g. of copper powder catalyst, the yield was 78%. [d] The m. p. was 96–97° when rapidly crystallized from petroleum ether (b. p. 77–115°). Slow recrystallization raised the m. p. [e] Prepared by the method of Tompkins and Degering, THIS JOURNAL, **69**, 2616 (1947). [f] Also identified by the method of mixed melting points. [g] Sodium urethan (0.022 mole) was prepared in 30 ml. of dry xylene. Triphenylsilyl chloride (0.017 mole) was added to the cooled suspension and the mixture refluxed for fifteen hours. [h] Here, 0.034 mole of each reactant was refluxed in 200 ml. of pure benzene for one hour. After filtering the suspension and removing the benzene by distillation, the residue was distilled. The distillate melted at 89–90°. Slow recrystallization from petroleum ether (b. p. 60–70°) raised the m. p. Subsequent runs afforded yields of 82 and 83.5%. [i] Five g. (0.017 mole) of triphenylsilyl chloride and 3.1 g. (0.018 mole) of silver isothiocyanate were suspended in 40 ml. of pure benzene and the mixture refluxed for three hours. After the product was crystallized from petroleum ether (b. p., 77–115°), it melted at 98–99°. It was identified by the method of mixed melting points. [j] Lead isothiocyanate was prepared by the method described in "Inorganic Syntheses," Vol. I, McGraw-Hill Book Co., Inc., New York and London, 1939, p. 85. [k] Identified by the method of mixed melting points. [l] Ammonium isothiocyanate (0.02 mole) and triphenylsilyl chloride (0.017 mole) were refluxed in 50 ml. of pure benzene for one week.

TABLE II

REACTIONS OF TRIPHENYLSILYL ISOCYANATE AND TRIPHENYLSILYL ISOTHIOCYANATE

Compound	C_6H_5Li	C_6H_5MgBr	C_2H_5OH	HOH
$(C_6H_5)_3SiNCO$	97% $(C_6H_5)_3SiOH$[a] 80% $C_6H_5CONH_2$[b]	83% $(C_6H_5)_3SiOH$[c] 77% $C_6H_5CONH_2$	$(C_6H_5)_3SiNCO$[d]	$(C_6H_5)_3SiOH$[e]
$(C_6H_5)_3SiNCS$	56% $(C_6H_5)_3SiOH$[f] 17% $(C_6H_5)_4Si$[f] 57% $C_6H_5CSNH_2$[f,g]	70% $(C_6H_5)_3SiOH$ 4.5% H_2S 0.0% $(C_6H_5)_2CO$[h]		$(C_6H_5)_3SiOH$[e]

[a] In this run, 0.017 mole of triphenylsilyl isocyanate in 50 ml. of dry ether was treated with 0.027 mole of phenyllithium in 38 ml. of ether. During the reaction, a white precipitate formed, and this addition product was subsequently hydrolyzed. In another experiment, the intermediate was treated with anhydrous hydrogen chloride. Triphenylsilyl chloride and benzamide were isolated and identified. [b] Recrystallized from hot water and identified by the method of mixed melting points. [c] To triphenylsilyl isocyanate (0.017 mole) in 60 ml. of dry ether was added phenylmagnesium bromide in 18 ml. of ether, which volume was just sufficient to give a positive Color Test I [Gilman and Schulze, THIS JOURNAL, **47,** 2002 (1925)]. [d] Five ml. of absolute ethanol and 5 g. (0.017 mole) of the isocyanate were refluxed for one and one-half hours in 70 ml. of pure benzene. Then 5 ml. more of ethanol was added and the whole refluxed four hours longer. The isocyanate was recovered unchanged. [e] The solvent was wet acetone, prepared by adding 3 drops of water to 10 ml. of pure acetone. One-half gram of triphenylsilyl isocyanate was dissolved in this solvent and the solution allowed to stand at room temperature for five hours. The acetone was removed under vacuum and the triphenylsilanol crystallized from petroleum ether (b. p. 60–70°). Identification was effected by the method of mixed melting points. However, triphenylsilyl isocyanate underwent no change after being in water for eight days. When triphenylsilyl isothiocyanate was placed in wet acetone for five hours, triphenylsilanol formed. Unlike triphenylsilyl isocyanate, triphenylsilyl isothiocyanate was completely hydrolyzed after six days in water. [f] These products were obtained in these proportions when 0.0157 mole of triphenylsilyl isothiocyanate in 60 ml. of dry ether was treated with 18.3 ml. of an ethereal solution containing 0.015 mole of phenyllithium. A white precipitate settled. This precipitate was collected and after crystallizing from benzene, was identified as tetraphenylsilane by the method of mixed melting points. Triphenylsilanol and thiobenzamide were found in the ether layer after hydrolysis. These were separated by extracting the mixture with hot water, in which thiobenzamide is soluble. When 0.047 mole of triphenylsilyl isothiocyanate in 100 ml. of dry ether was treated with 0.163 mole of phenyllithium in 175 ml. of dry ether, stirred overnight and worked up in the usual way, 74.2% of tetraphenylsilane, 3.5% of benzophenone and some hexaphenyldisiloxane were obtained. By trapping gases evolved during hydrolysis with lead acetate solution, 44% of the sulfur was accounted for. [g] Identified by the mixed m. p. method with a sample prepared according to the directions of Gabriel and Heymann, *Ber.*, **23**, 158 (1890). [h] Triphenylsilyl isothiocyanate (0.047 mole) in 70 ml. of dry ether was treated with 0.142 mole of phenylmagnesium bromide in 138 ml. of dry ether and refluxed with stirring for twenty hours. In a subsequent experiment, the reactants were refluxed over a hot plate for twenty hours, but during the latter part of this heating the ether was lost because of condenser difficulty. This amounted to a "forced" reaction. Under these conditions, 70% of triphenylsilanol and 17% of benzophenone were isolated. Two other runs in which the mole ratio of triphenylsilyl isothiocyanate and phenylmagnesium bromide was 1:1 gave 70% of triphenylsilanol and as yet unidentified products.

Triphenylsilyl isocyanate is relatively resistant to hydrolysis,[2b] since after eight days in water at room temperature, no change in melting point was observed. Under similar conditions, triphenylsilyl isothiocyanate was converted to triphenylsilanol. However, this silicon isothiocyanate does appear to be stable[2c] for long periods when exposed to the atmosphere. On the other hand, if the compounds are dissolved in wet acetone, hydrolysis to triphenylsilanol proceeds fairly rapidly.

Experimental

Two general methods were used in these preparations. In Method A, 0.017 mole of triphenylsilyl chloride was fused for four hours with 0.017 mole of urea and thiourea, respectively, in a 22 × 175 mm. test-tube fitted with a calcium chloride tube. The fused mass was removed, crushed and extracted with three 25-ml. portions of petroleum ether (b. p. 77–115°). The insoluble material proved to be ammonium chloride.

In Method B, double decomposition between triphenylsilyl chloride and sodium urethan, silver isocyanate, silver isothiocyanate, lead isothiocyanate, and ammonium isothiocyanate, respectively, was effected. In this method, the reactions were carried out in a round bottom flask provided with a condenser and a mechanical stirrer. The inert gas used was dry nitrogen. See Table I and accompanying footnotes for the results obtained by these two methods.

The results of the treatment of triphenylsilyl isocyanate and triphenylsilyl isothiocyanate with phenyllithium and phenylmagnesium bromide are given in Table II. In these reactions with the organometallic compounds, a three-necked flask provided with a condenser and a mechanical stirrer was used. The inert gas was dry nitrogen.

The melting point of a mixture of triphenylsilyl isocyanate (m. p., 100–101°) and triphenylsilyl isothiocyanate (m. p., 99–100.5°) was 80–85°.

Summary

Triphenylsilyl chloride was treated with urea and with sodium urethan to form triphenylsilyl isocyanate. When thiourea, lead isothiocyanate, and ammonium isothiocyanate, respectively, were used, triphenylsilyl isothiocyanate resulted. The products were shown to be identical with those obtained from the corresponding silver salts.

The reactions of triphenylsilyl isocyanate and triphenylsilyl isothiocyanate with phenylmagnesium bromide and phenyllithium were studied.

AMES, IOWA RECEIVED SEPTEMBER 6, 1949

[CONTRIBUTION FROM NICHOLS LABORATORY, NEW YORK UNIVERSITY]

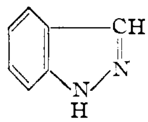
Structure and Ultraviolet Absorption Spectra of Indazole, 3-Substituted Indazole and Some of Their Derivatives[1]

BY V. ROUSSEAU[2] AND H. G. LINDWALL

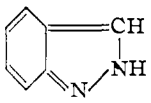
The application of ultraviolet absorption spectra to the problem of the structure of indazole and 3-substituted indazole has been found to give results that are in agreement with those of von Auwers[3] based on the spectrochemical property of optical exaltation exhibited by indazoles.

von Auwers was enabled to report on the structure of indazole and 3-substituted indazole by comparing their specific exaltations, the surplus of the specific refraction over the theoretical, with those of their two isomeric series of N-alkyl and N-acyl derivatives. The specific exaltation of indazole, its 1-alkyl and 1-acyl derivatives were found to be of the same degree of magnitude but lower than those of the corresponding 2-alkyl and 2-acyl derivatives. The same observations were made when the specific exaltations of 3-substituted indazoles and 1,3-disubstituted indazoles were compared with those of the corresponding 2,3-disubstituted indazoles. Since the structure of the pairs of N-alkyl and N-acyl derivatives of indazole and 3-substituted indazoles employed had been established, it was reasonable to conclude that indazole and 3-substituted indazoles are built according to the pattern of their 1-alkyl derivatives, the benzenoid structure I. The desmotropic quinoid form II, whose existence had earlier been postulated, cannot be present in any appreciable amount.

I



II



A simpler and perhaps more convincing way of arriving at the ultimate structure lies in comparing the ultraviolet absorption spectrum of indazole with the spectra of 1-methyl- and 2-methylindazole. Of these three curves (Fig. 1) the one for indazole and the one for 1-methylindazole are very similar, but both differ markedly from the one for 2-methylindazole. Indazole then must be assigned the benzenoid structure, I, with the virtual exclusion of the quinoid structure, II. Comparison of the ultraviolet absorption spectra of 3-cyanoindazole and indazole-3-acid with those of their corresponding 1-methyl and 2-methyl derivatives (Fig. 2 and 3) also forces the assignment of the benzenoid structure to 3-substituted indazoles.

The preparation of 3-cyanoindazole by the diazotization of *o*-aminobenzyl cyanide at room temperature has previously been reported.[4] However, the synthesis of the intermediate *o*-aminobenzyl cyanide described here differs in some respects from earlier methods.[4,5] *o*-Nitrophenylpyruvic acid oxime was prepared from the condensation of *o*-nitrotoluene and diethyl oxalate followed by hydrolysis of the *o*-nitrophenylpyruvate formed before steam distillation of the unreacted *o*-nitrotoluene, since the pyruvate is also steam distillable.[6] The acid oxime was then isolated directly from the reaction mixture in 56% yield. The action of hot acetic anhydride on *o*-nitrophenylpyruvic acid oxime resulted in the

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[1] Presented in part before the Organic Division of the American Chemical Society, Atlantic City, September, 1949.

[2] College of Mount St. Vincent, New York 63, N. Y.

[3] v. Auwers, Hugel and Ungemach, *Ann.*, **527**, 291 (1937).

[4] Pschorr and Hoppe, *Ber.*, **43**, 2543 (1910).

[5] Reissert, *ibid.*, **41**, 3810 (1908).

[6] Di Carlo, THIS JOURNAL, **66**, 1420 (1944).