cyano and triisothiocyano compounds is associated with the electrical configuration (acidity) of the other group attached to the central atom rather than with either the molar volume of the group or the boiling point of the compound itself.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Methyl Silicon Isocyanates and *n*-Butyl Silicon Triisocyanate

BY GEORGE S. FORBES AND HERBERT H. ANDERSON

This paper on the methyl silicon isocyanates describes the first isolation of organosilicon pseudo halides; the introduction of methyl groups into silicon tetraisocyanate was first attempted, unsuccessfully, using methylmagnesium iodide, and also dimethylmercury. All three methyl silicon isocyanates and also *n*-butyl silicon triisocyanate were then prepared through reaction of silver isocyanate with the appropriate alkylchlorosilanes, with yields of at least eighty per cent.

Preparation of Alkyl Silicon Isocyanates.—The homogeneity of their reaction products indicated that the methylchlorosilanes, obtained from the Dow Corning Corporation of Midland, Michigan, had been carefully purified. A thirty-gram sample of each methylchlorosilane was treated with a 25% excess of silver isocyanate, added in three portions; benzene was the solvent used in preparation of the monomethyl and dimethyl compounds, while isopropylbenzene proved more suitable for the trimethyl derivative. After the usual half-hour at 90°,[1] the suspension of silver salts was filtered and washed. After distilling off the benzene, the triisocyanate and diisocyanate were recovered; the monoisocyanate was distilled directly from the higher-boiling isopropylbenzene. Each individual compound was distilled at least twice in a plain column, 4 mm. i. d. and 500 mm. long, and final fractions were taken at the following (uncorrected) temperatures: $(CH_3)Si(NCO)_3$, 169.2–169.6° at 755 mm.; $(CH_3)_2Si(NCO)_2$, 138.3–138.5° at 760 mm.; $(CH_3)_3Si(NCO)$, 90.5–90.8° at 760 mm.

TABLE I

DATA ON ALKYL SILICON ISOCYANATES

Compound		$(CH_3)_4Si$[2]	$(CH_3)_3Si(NCO)$	$(CH_3)_2Si(NCO)_2$	$(CH_3)Si(NCO)_3$	$Si(NCO)_4$[1]	$(n C_4H_9)Si(NCO)_3$
B. p., °C.		26.5	91.0 ± 0.3	139.2 ± 0.3	170.8 ± 0.3	185.6 ± 0.5	215.5 ± 0.5
M. p., °C.		....	−49.0 ± 3	−31.2 ± 3	2.7 ± 0.5	26	−37 ± 3[b]
Refractive index at 20° (Abbe) ± 0.0010		1.3591	1.3960	1.4221	1.4430	1.4610	1.4479
d^{20}_4, found		0.6464	0.867	1.076	1.267	1.442[a]	1.141
Molar refraction, ml.	Found	30.02	31.92	33.60	35.39	37.29	48.53
	Calcd.	(30.02)	31.84	33.66	35.47	(37.29)	49.34
Log P = $A - B/T$	A	....	7.8446	8.1540	8.4150	9.0198	8.4830
	B		1807	2174	2457	2816	2737
ΔH vap. (calcd.), kcal.		....	8.3	10.0	11.2	12.9	12.5
Trouton constant		....	22.7	24.1	25.3	26.5	25.6
Molecular wt. (Dumas)	Found	....	117.5	146.5	176	204	225
	Calcd.	....	115.2	142.2	169.1	196	211.2
Carbon, %[3]	Found	....	41.6	33.7	28.1	..	..
	Calcd.	....	41.7	33.8	28.4	..	..
Hydrogen, %[3]	Found	....	8.1	4.4	1.6	..	4.0
	Calcd.	....	7.9	4.3	1.8		4.3
Nitrogen, % (Dumas)	Found	....	12.0	19.5	25.0	..	20.3
	Calcd.		12.2	19.7	24.8		20.0

[a] Calculated from D^{25}_4 of 1.434. [b] Forms glass persistently; difficult to convert glass to crystalline solid.

n-Butyltrichlorosilane, prepared from tetrachlorosilane and the alkylmagnesium bromide and boiling at 148.7–149.3°, was gradually added to an excess of silver isocyanate suspended in benzene, in a reaction of moderate vigor. The middle fraction, boiling at 134.6–135.4° under 59 mm., was used for all measurements.

Chemical Properties.—The monoisocyanate floats on water and hydrolyzes slowly at the interface; the diisocyanate hydrolyzes slowly at first and finally at a moderate rate. *n*-Butyl silicon triisocyanate hydrolyzes at a moderately fast rate; when shaken with an equal volume of water, the temperature rise is only about 20°—much less than in the vigorous hydrolysis of silicon tetraisocyanate.

These four new liquids are easily soluble in petroleum ether (30–60°), carbon disulfide, carbon tetrachloride, benzene and isopropylbenzene.

Physical Properties (See Table I).—All four compounds were colorless liquids. The vapor of trimethyl silicon isocyanate was nauseating and also very easily inflammable. Dynamic

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(1) Forbes and Anderson, THIS JOURNAL, **62**, 761 (1940).

(2) Bygden, *Z. physik. Chem.*, **90**, 243 (1915). Index and density at 18.7°.

(3) Combustions in oxygen with lead chromate and silver wire in tube. See Elving and McElroy, *Ind. Eng. Chem., Anal. Ed.*, **13**, 660 (1941).

vapor pressure measurements, following a standard method,[4] always made on the day of final purification, employed mercury thermometers which had been calibrated in the same apparatus with boiling water, bromobenzene or aniline; the apparatus was of Pyrex glass, and included stopcocks and ground joints in non-critical positions. Errors in temperatures could not have exceeded 0.3°; the four vapor pressure equations predicted the observed points with an average error of approximately three mm. All three methyl silicon isocyanates showed sharp melting points, and freezing points without perceptible supercooling; on the other hand, *n*-butyl silicon tended to supercool and form a glass to such an extent that the use of liquid nitrogen and vigorous stirring were necessary to obtain a crystalline solid of fairly sharp melting point. Due to incomplete drainage and other uncertainties, the readings of the toluene thermometer used in obtaining some of the melting points appeared subject to errors possibly as great as three degrees. Densities were obtained using a special 2-ml. micropycnometer.

Discussion

Swarts' rule of linear progression in boiling points[5] does not fit the new methyl compounds satisfactorily. Calculations based on the "increment method," by adding 32.0° to the boiling point of the corresponding chloride[6] for each replacement of one chlorine by isocyanate, predicted the following boiling points: monoisocyanate, 89.7° (57.7 + 32.0); diisocyanate, 134.0° (70.0 + 64.0); triisocyanate, 161.7° (65.7 + 96.0).

After this isolation of the complete series of methyl silicon isocyanates, and of *n*-butyl silicon triisocyanate, the stable existence of at least a part of the ethyl and *n*-propyl series can be inferred.

Summary

1. Certain alkylchlorosilanes yielded the corresponding (new) isocyanates upon treatment with silver isocyanate.

The complete methyl series consisted of trimethyl silicon isocyanate, $(CH_3)_3Si(NCO)$, boiling at 91.0°, dimethyl silicon diisocyanate, $(CH_3)_2Si(NCO)_2$, boiling at 139.2°, and methyl silicon triisocyanate, $(CH_3)Si(NCO)_3$, boiling at 170.8°.

n-Butyl silicon triisocyanate, $(n\text{-}C_4H_9)Si(NCO)_3$, boiling at 215.5°, showed a marked tendency to supercool.

2. Physical data included vapor pressure equations, melting points, refractive indices, densities and molar refractions. The heat of hydrolysis seems to decrease as the number of alkyl groups increases.

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(4) See for instance: Mack and France, "Laboratory Manual of Physical Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1934, p. 47.

(5) Swarts, *Bull. soc. chim.*, **35**, 1557 (1924).

(6) Anderson, THIS JOURNAL, **64**, 1757 (1942).

[CONTRIBUTION FROM RESEARCH LABORATORIES, THE UPJOHN COMPANY]

Actidione, an Antibiotic from Streptomyces Griseus[1]

BY JARED H. FORD AND BYRON E. LEACH

It has been found in this Laboratory that the beers from streptomycin-producing strains of *Streptomyces griseus* contain another antibiotic which we have named actidione. In contrast to streptomycin, actidione is very effective against many yeasts but has little or no activity against bacteria.

Simultaneous bio-assays for actidione and streptomycin on a series of production beers demonstrated a wide variation in the ratio of concentrations of the two antibiotics. In a few cases the actidione content was as high as 200-250 mg. per l. but the average was about 80–100 mg. per l. A number of strains of *S. griseus* which produce actidione but little or no streptomycin and vice versa have been obtained by irradiating the conidia with X-rays.[2]

The crude product was isolated from the filtered beer by extracting with chloroform either directly or after a preliminary concentration step which involved adsorption on activated carbon, elution with 80% acetone and removal of acetone from the eluates by distillation. The chloroform extracts were orange-brown or an intense green, depending on the culture medium employed, but most of the color was removed by treatment with carbon. After removing the chloroform by distillation *in vacuo*, the resulting crude products were orange-brown sticky oils having a moldy odor. Bio-assays indicated a purity of 30–60% based on crystalline actidione as the standard.[3]

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(1) An outline of this work was reported in a preliminary communication: Leach, Ford and Whiffen, THIS JOURNAL, **69**, 474 (1947).

(4) Observations of Drs. George M. Savage and Alma J. Whiffen of these Laboratories.

(3) The assay method was developed by Dr. Alma J. Whiffen. It is a modification of the paper-disc plate method for streptomycin[4] and employs *Saccharomyces pastorianus* ATCC 2366 as the test organism. The medium consists of 10 g. of glucose, 2.5 g. of Difco yeast extract, 1.0 g. of potassium dihydrogen phosphate and 20 g. of agar made up to 1.0 l. with distilled water and adjusted to *p*H 6.0. The inoculation was at the rate of 1.8 × 10⁶ yeast cells per ml. of medium. The *p*H of the aqueous test solutions is not critical and the samples may also be assayed in methanol, ethanol or acetone.

(4) Loo, Skell, Thornberry, Ehrlich, McGuire, Savage and Sylvester, *J. Bact.*, **52**, 610 (1945).