corresponding N-acetylhexosaminic acids, thus differing from previously reported mechanisms for the metabolism of N-acetylhexosamines.[8] The purified enzyme preparation did not catalyze the disappearance of glucosamine, galactosamine or glucose.

[8] L. F. Leloir, C. E. Cardini and J. M. Olsoarria, *Arch. Biochem. Biophys.*, **74**, 84 (1958).

DEPARTMENT OF MEDICAL MICROBIOLOGY, UNIVERSITY OF SOUTHERN CALIFORNIA SCHOOL OF MEDICINE
LOS ANGELES, CALIFORNIA, AND L. I. HOCHSTEIN
SCRIPPS CLINIC AND RESEARCH FOUNDATION J. B. WOLFE
LA JOLLA, CALIFORNIA H. I. NAKADA

RECEIVED JUNE 3, 1959

PREPARATION AND SOME PROPERTIES OF TRICHLOROCYANOSILANE[1]

Sir:

Treatment of mercury(II) cyanide with disilicon hexachloride liquid or vapor at approximately 100° results in a volatile, colorless liquid, melting point −46.2 ± 0.2°, which can be separated from unchanged disilicon hexachloride by distillation *in vacuo* through traps maintained at −63 and −78°. The −63° trap retains unchanged disilicon hexachloride, identified by its −1° melting point. The −78° trap retains the colorless liquid which exhibits these vapor pressures:

t, °C.	−45.2	−30.7	−22.9	00.0	10	20
P_{mm} (obs.)	2.3	6.2	10.0	37.6	62.2	101.6
P_{mm} (calcd.)	2.25	6.24	10.3	37.8	62.1	99.3

The calculated values are obtained from the equation

$$\log P_{mm} = 7.751 - (1687/T)$$

from which a ΔH_{vap} of 7,720 calories per mole and an extrapolated boiling point of 73.2° can be calculated. Thus the Trouton constant for this liquid is 22.2.

The formula $SiCl_3CN$ was established for this compound by analysis corresponding to the formula $Si_{1.00}Cl_{2.98}(CN)_{0.95}$ and by the vapor density measurement at 27.8° corresponding to an apparent molecular weight of 158.8; calculated for $SiCl_3CN$, 160.4.

The new compound is stable indefinitely at −78° *in vacuo* and in the vapor phase at room temperature. In the liquid phase at room temperature the compound undergoes a slow decomposition, producing silicon tetrachloride and nonvolatile brown solids.

Trichlorocyanosilane undergoes rapid hydrolysis. With limited amounts of water vapor hydrogen cyanide and hexachlorosiloxane result. The water solution from complete hydrolysis gives a strong Turnbull's Blue test for CN^-.

The infrared absorption spectrum of the vapor shows a strong sharp peak at 2200 cm.$^{-1}$ characteristic of CN stretching[2,3] and a moderately strong sharp peak at 2080 cm.$^{-1}$, previously assigned as an isocyanide stretching frequency.[3] A strong broad band with maximum absorption at 728 cm.$^{-1}$, considerably displaced from the SiCl band at 800 cm.$^{-1}$ for $SiCl_4$ and at 810 cm.$^{-1}$ for $HSiCl_3$, is undoubtedly the SiCl band since it is the only other major band in the spectrum.

A more detailed study of the spectrum for this compound is indicated before one can draw any well-founded conclusions concerning its structure. However, the features so far observed are compatible with either a very rapid cyanide–isocyanide equilibrium[3] greatly favoring the cyanide form, or a cyanide model with asymmetry introduced by back-bonding involving the 3*d* orbitals of the silicon. This explanation could also account for the shift of the SiCl band to longer wave lengths.

An unsuccessful attempt to prepare $SiCl_3CN$ has been reported[4]; Goubeau and Reyhing examined several metathetic reactions involving various tetravalent silicon halides and different group I cyanides. On the basis of the failure of this previous attempt and the conditions of the present preparation, a mechanism involving addition of cyanyl radical to the silicon-silicon bond is suggested.

Further investigations of the chemical properties of the new compound and its derivatives are in progress.

---

[1] The authors wish gratefully to acknowledge the partial support of this work by the Research Corporation under a Frederick Gardner Cottrell Grant.

[2] H. R. Linton and E. R. Nixon, *Spectrochim. Acta*, **10**, 299 (1958).

[3] T. A. Bither, W. H. Knoth, R. V. Lindsay, Jr., and W. H. Sharkey, THIS JOURNAL, **80**, 4151 (1958).

[4] J. Goubeau and J. Reyhing, *Z. anorg. u. allgem. Chem.*, **294**, 96 (1958).

DEPARTMENT OF CHEMISTRY
PURDUE UNIVERSITY ALEXANDER KACZMARCZYK
LAFAYETTE, INDIANA GRANT URRY

RECEIVED JUNE 10, 1959

SIMPLE SYNTHESES OF PYRIMIDINE-2'-DEOXYRIBONUCLEOSIDES[1]

Sir:

Recent studies with 5-fluoro-2'-deoxyuridine (β-FUDR) and 5-fluoro-2'-deoxycytidine (β-FCDR) have demonstrated their usefulness as anti-tumor agents in several experimental tumors[2,3] and in clinical trials.[4] β-FUDR was prepared[5] by enzymic procedures, while β-FCDR was synthesized[6] from β-FUDR. In view of the need for 5-fluorinated-2'-deoxynucleosides, we report the total syntheses of pyrimidine-2'-deoxyribonucleosides by the mercuri procedure.[7,8] It was found that *crys-*

---

[1] This investigation was supported in part (to the Sloan-Kettering Institute) by funds from the National Cancer Institute and the National Institutes of Health, Public Health Service (Grant No. CY-3190).

[2] C. Heidelberger, L. Griesbach, O. Cruz, R. J. Schnitzer and E. Grunberg, *Proc. Soc. Exp. Biol. Med.*, **97**, 470 (1958).

[3] J. H. Burchenal, E. A. D. Holmberg, J. J. Fox, S. C. Hemphill and J. A. Reppert, *Cancer Research*, **19**, 494 (1959).

[4] A. R. Curreri and F. Ansfield, *Cancer Chemotherapy Reports* (Cancer Chemotherapy National Service Center), **2**, 8 (1959); M. L. Murphy, R. R. Elison, F. S. Aquila, R. Sullivan, M. C. Li and J. H. Burchenal, *ibid.*, **2**, 12 (1959); I. J. Wolman and R. D. Gens, *ibid.*, **2**, 14 (1959). As of this writing, β-FCDR has not been available in sufficient quantities for clinical trial.

[5] R. Duschinsky, E. Pleven, E. Malbica and C. Heidelberger, Abstr. 132nd Meeting, Am. Chem. Soc., 1957, p. 19-C. The β-configuration was confirmed by hydrogenation (Pd-charcoal) to 2'-deoxyuridine.

[6] J. J. Fox, I. Wempen and R. Duschinsky, Abstr. Fourth Intl. Congress of Biochem., Vienna, 1958, p. 6.

[7] J. J. Fox, N. Yung, J. Davoll and G. B. Brown, THIS JOURNAL, **78**, 2117 (1956).

[8] See J. J. Fox, *Record Chem. Progr.* (*Kresge-Hooker Sci. Lib.*), **19**, 173 (1958), for a review of the mercuri reaction.