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 $-46.2 \pm 0.2°$, 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 backbonding 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.

talline 3,5-di-O-*p*-chloro(or *p*-methyl)benzoyl-2-deoxy-D-ribosyl chlorides coupled readily with the relatively more reactive monomercurypyrimidines[9] to afford (after deacylation) *alpha* and *beta* anomers[11] of 2′-deoxynucleosides.

Methyl-2-deoxy-D-ribofuranoside[12] was converted to the 3,5-di-*O*-*p*-toluyl derivative (75%), m.p. 76.5°, $[\alpha]_D$ −6.2° ($CHCl_3$), found for $C_{22}H_{24}O_6$: C, 68.73; H, 6.21, which with HOAc–HCl gave (70%) 3,5-di-*O*-*p*-toluyl-2-deoxy-D-ribosyl chloride (I), m.p. 109°,[13] $[\alpha]_D$ +108° (dimethylformamide) found for $C_{21}H_{21}O_5Cl$: C, 64.94; H, 5.71; Cl, 9.03. Similarly, the 3,5-di-*O*-*p*-chloro analog (II) of I was prepared (65% over-all yield from 2-deoxy-D-ribose), m.p. 118–120°, found for $C_{19}H_{15}O_5Cl_3$: C, 52.56; H, 3.77; Cl, 25.01. Monomercurithymine (III, $C_5H_4O_2N_2Hg$, found: N, 8.48) was obtained by refluxing 1-acetylthymine[14] with mercuric acetate in methanol. Monomercuri-5-fluorouracil (IV, $C_4HO_2N_2FHg$, found: N, 8.02) was synthesized from 5-fluorouracil[15] and mercuric acetate in refluxing aqueous methanol. Crude monomercuri-5-fluorocytosine (V) was prepared similarly from 5-fluorocytosine[15] (found: N, 12.17). Condensation of halogenose (I) with III in hot toluene followed by the usual processing[7,10] afforded 3′,5′-di-*O*-*p*-toluylthymidine (VI, 50%), m.p. 197°, $[\alpha]_D$ −50° (pyridine), (found for $C_{26}H_{26}O_7N_2$: C, 65.57; H, 5.78; N, 5.94). Deacylation of VI gave thymidine. The α-isomer (VII) of VI obtained (4%) from the mother liquors, m.p. 138° (from MeOH), $[\alpha]_D$ −14.5° (pyridine), found: C, 65.20; H, 5.73; N, 5.92. Deacylation of VII afforded "α-thymidine," m.p. 187°, $[\alpha]_D$ +7.2° (water), found: C, 49.61; H, 5.60; N, 11.35. Similarly, reaction of I with IV yielded anomers of 1-(3′,5′-di-*O*-*p*-toluyl-2-deoxy-D-ribosyl)-5-fluorouracil (VIII); *beta* isomer (41% top fraction from pyridine), m.p. 229°, $[\alpha]_D$ −17° (pyridine), found for $C_{25}H_{23}O_2N_2F$: C, 62.77; H, 4.81; N, 5.80; *alpha* isomer (27% from mother liquors), m.p. 214–215°, $[\alpha]_D$ −72.5° (pyridine), found: C, 62.61; H, 4.68; N, 5.54. Deacylation of VIII yielded the corresponding nucleosides: β-FUDR,[5] m.p. 150–151°, $[\alpha]_D$ +37.5 (water); α-FUDR, m.p. 150–151°,[13] $[\alpha]_D$ −21° (water), found: C, 44.18; H, 4.30; N, 11.59; F, 8.11. Condensation of V with either halogenoses I or II and deacylation afforded a crystalline mixture of FCDR anomers: m.p. 167–170°, $[\alpha]_D$ −0.7°, found for $C_9H_{12}O_4N_3F$: C, 44.54; H, 5.15; N, 16.86, which exhibited about 50% of the antimicrobial activity[16] observed with authentic β-FCDR[6] ($[\alpha]_D$ +65.6°). Condensation of N-acetylcytosinemercury[10] with II in hot xylene gave anomers of 1-(3′,5′-di-*O*-*p*-chlorobenzoyl-2-deoxy-D-ribosyl)-4-acetamido-2(1H)-pyrimidinone: α-isomer (22% from ethyl acetate), m.p. 204.5–205°, $[\alpha]_D$ −66° ($CHCl_3$), found for $C_{25}H_{21}O_7N_3Cl_2$: C, 54.23; H, 4.10; N, 7.65: *beta* isomer (32% from ethanol), m.p. 128–130°, $[\alpha]_D$ −19°, found: C, 55.17; H, 4.09; N, 7.60. Deacylation of each anomer afforded high yields of *alpha* and *beta* cytosine-2′-deoxynucleosides: α-isomer (from ethanol), m.p. 192–193°, $[\alpha]_D$ −44° (1 *N* NaOH), found for $C_9H_{13}N_3O_4$: C, 47.76; H, 5.80; N, 18.53: β-anomer, m.p. 200–201°, $[\alpha]_D$ +78° (1 *N* NaOH), mixed m.p. with 2′-deoxycytidine undepressed.

We are indebted to Mr. T. Gabriel and Mr. V. Gruenman for technical assistance and to Dr. Al Steyermark for microanalyses.

(9) As in the case of N-acetylcytosinemercury,[10] the mercuripyrimidines employed in this report contain mercury and pyrimidine in a 1:1 ratio.

(10) J. J. Fox, N. Yung, I. Wempen and I. L. Doerr, THIS JOURNAL, **79**, 5060 (1957).

(11) The formation of both anomers is to be expected from this condensation reaction due to the absence of the 2-acyloxy function in the halogenose. See B. R. Baker in "The Chemistry and Biology of Purines," Ciba Foundation Symposium, Little, Brown and Co., Boston, Mass., 1957, p. 120.

(12) R. E. Deriaz, W. G. Overend, M. Stacey and L. F. Wiggens, *J. Chem. Soc.*, 2836 (1949).

(13) All melting points are uncorrected. Mixed-melting points of *alpha* and *beta* nucleoside anomers gave depressions.

(14) L. B. Spector and E. B. Keller, *J. Biol. Chem.*, **232**, 185 (1958).

(15) R. Duschinsky, E. Pleven and C. Heidelberger, THIS JOURNAL, **79**, 4559 (1957).

(16) Personal communication from Dr. J. Berger, Hoffman-LaRoche, Inc.

HOFFMANN LAROCHE, INC., NUTLEY, N. J. AND SLOAN-KETTERING DIVISION OF CORNELL UNIVERSITY MEDICAL COLLEGE NEW YORK 21, N. Y.
MAX HOFFER
ROBERT DUSCHINSKY
JACK J. FOX
NAISHUN YUNG

RECEIVED JUNE 3, 1959

A NEW AND SELECTIVE METHOD OF OXIDATION. THE CONVERSION OF ALKYL HALIDES AND ALKYL TOSYLATES TO ALDEHYDES

Sir:

Recently a procedure for oxidizing α-bromoketones to glyoxals, noteworthy for its exceptional simplicity and mildness, was described.[1] In our initial report it was emphasized that this procedure, which employs dimethyl sulfoxide as the oxidizing agent, is not satisfactory for benzyl bromides. Subsequent work has shown that with halides still less reactive than benzyl bromides aldehydes cannot be obtained by the original procedure.

TABLE I

THE OXIDATION OF HALIDES AND TOSYLATES TO ALDEHYDES

Starting compound	Product	Yield, %[a]
$CH_3(CH_2)_7$-Cl	$CH_3(CH_2)_6CHO$	71
$CH_3(CH_2)_7$-Br	$CH_3(CH_2)_6CHO$	74
$CH_3(CH_2)_6$-I	$CH_3(CH_2)_5CHO$	70
p-Br-C_6H_4-CH_2Br	*p*-Br-C_6H_4-CHO	76
p-CH_3-C_6H_4-CH_2Br	*p*-CH_3-C_6H_4-CHO	65
p-NO_2-C_6H_4-CH_2Br	*p*-NO_2-C_6H_4-CHO	76
$CH_3(CH_2)_7OTos$	$CH_3(CH_2)_6CHO$	78
$(CH_3)_3CCH_2OTos$	$(CH_3)_3CCHO$	0[b]
p-Br-C_6H_4-CH_2OTos	*p*-Br-C_6H_4-CHO	65
p-CH_3-C_6H_4-CH_2OTos	*p*-CH_3-C_6H_4-CHO	74
p-NO_2-C_6H_4-CH_2OTos	*p*-NO_2-C_6H_4-CHO	84

[a] The yields are those of the pure 2,4-dinitrophenylhydrazones. In a number of instances the pure aldehydes themselves were isolated in 5 to 10% lower yields. [b] Neopentyl tosylate quantitatively recovered.

We now describe a modification of the original method which enables one smoothly to oxidize, not only benzylic halides, but even strictly ali-

(1) N. Kornblum, J. W. Powers, G. J. Anderson, W. J. Jones, H. O. Larson, O. Levand and W. M. Weaver, THIS JOURNAL, **79**, 6562 (1957).