

The generality of this method for preparing other β -arabinosides for biological evaluation is currently under investigation.¹²

(12) The synthesis of 1- β -D-arabinofuranosyl-5-fluorouracil (Vc) by another route was announced by J. J. Fox, N. Yung, I. Wempfen, R. Duschinsky and L. Kaplan, Abstr. Intl. Union Pure and Applied Chemistry (Symposium on Natural Products), Australia, August 1960, p. 66. Their synthesis begins with 5-fluorouridine (prepared from 5-fluorouracil) which is converted *via* a 2,2'-anhydronucleoside intermediate to Vc in 26% yield based upon 5-fluorouracil (personal communication from Fox and Yung).

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SYNTHESIS OF PHENYLCHLOROTRISPHOSPHONITRILE

Sir:

We wish to report the direct preparation and positive identification of phenylchlorotrisphosphonitrile, $[\text{Ph}(\text{Cl})\text{PN}]_3$. Although previous workers have studied the synthesis of the $[\text{Ph}(\text{Cl})\text{PN}]_n$ system, none has reported isolation of the trimer. Thus Bode and Bach¹ treated PhPCl_4 with ammonium chloride and could isolate only a partially hydrolyzed derivative for which analysis indicated the formula $\text{N}_3\text{P}_3\text{Ph}_3\text{Cl}(\text{OH})_2$. Shaw and Stratton² repeated the reaction and isolated $[\text{Ph}(\text{Cl})\text{PN}]_4$ in two isomeric forms. Herring,³ using the novel procedure of treating NaN_3 with PhPCl_2 , isolated a mixture of phenylchlorophosphonitriles with an average molecular weight of 5000. Recently, Tesi⁴ reported synthesis of $[\text{Me}(\text{Cl})\text{PN}]_3$ by treatment of $\text{N}_3\text{P}_3\text{Cl}_3(\text{NMe}_2)_3$ with MeMgBr to give $\text{N}_3\text{P}_3\text{Me}_3(\text{NMe}_2)_3$ which was converted to $[\text{Me}(\text{Cl})\text{PN}]_3$ by treatment with HCl . Although this procedure gives an $[\text{R}(\text{Cl})\text{PN}]_3$ compound, it is not a direct synthesis.

In our preparation PhPCl_4 was made by chlorination of PhPCl_2 (Victor Chemical Works) in carbon tetrachloride then recrystallization from the same solvent under dry nitrogen. A solution of 121 g. (0.484 mole) of PhPCl_4 in 250 ml. of dried and redistilled *s*-tetrachloroethane was added over a period of 28 hr. to a slurry of 197 g. (3.71 moles) of NH_4Cl in 50 ml. of dry xylene. Reflux was then maintained for an additional 24 hours; unreacted ammonium chloride was filtered off, washed with dry benzene, and the washes were combined with the filtrate. Concentration of the solution gave a gummy solid (I) and solution (II) which could not be separated effectively by filtration. However, addition of petroleum ether converted (I) to a solid which was filtered off and recrystallized from acetonitrile to give 8 g. of crude trimer, m.p. 135–150° (A). Solution (II) was distilled to dryness to give a hard gum which was crystallized fractionally from acetonitrile to give an additional 12 g. of crude trimer, m.p. 130–150° (B). The infrared curves of A and B were similar, showing strong absorptions in the 1200 cm^{-1} region, typical of the trimeric phosphonitrile ring. A was frac-

- (1) H. Bode and H. Bach, *Ber.*, **75**, 215 (1942).
- (2) R. A. Shaw and C. Stratton, *Chem. & Ind.*, **52** (1959).
- (3) D. L. Herring, *Chem. & Ind.*, 717 (1960).
- (4) G. Tesi, *Proc. Chem. Soc.*, **404** (1960).

tionally recrystallized three times from acetonitrile to give 3 g. of material, the analytical sample, m.p. 161–163° (Fisher-Johns block, uncorrected). *Anal.*⁵ Calcd. for $\text{C}_6\text{H}_5\text{ClPN}$: P, 19.66; N, 8.90; C, 45.74; H, 3.20; Cl, 22.51; mol. wt. calcd. for $(\text{C}_6\text{H}_5(\text{Cl})\text{PN})_3$, 473. Found: P, 19.63; N, 9.01; C, 45.67; H, 3.44; Cl, 22.38; mol. wt.,⁶ 445, 448. The principal P–N ring infrared absorptions are at 1180 cm^{-1} (s) and 1210 cm^{-1} (s), with no discernible absorptions at the reported values² for the tetramer. Infrared analysis indicated that the remainder of the reaction product contained additional trimer and also tetramer. Although recovery of trimer from this residue is difficult, procedures for its accomplishment are being investigated.

Using a different procedure, the tetramer recently has been prepared in this laboratory in better than 60% yield and this work will be reported shortly. Both trimer and tetramer now are being studied with respect to alkylation, arylation, and other substitution reactions.

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(5) Schwartzkopf Microchemical Laboratories.

(6) Ebulliometric measurement in benzene. We are indebted to Dr. Ralph Griffith, Sinclair Research Laboratories, for this measurement.

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STEREOCHEMISTRY OF SUBSTITUTION TO ASYMMETRIC SILICON

Sir:

Since the removal of the barrier to synthesis of optically active organosilicon compounds having reactive groups bonded to asymmetric silicon, and the discovery of many stereospecific reactions at silicon,^{1,2,3} one of the major remaining tasks has been stereochemical correlation of configuration for a few key compounds containing the α -naphthylphenylmethylsilyl group (α -NpPhMeSi-, designated R_3Si^* -below), in order that the stereochemistry of many reactions of these compounds might become known.

One of the most widely used methods for correlating configurations of optically active compounds having *similar* structures is the Fredga method based on *differences* in phase behavior.⁴ This method as applied by K. Mislow has provided many fruitful results in recent years, and the pertinent case observed in the present work is his "case 2"⁵ in which pure optical isomers of two dif-

- (1) L. H. Sommer and C. L. Frye, *J. Am. Chem. Soc.*, **81**, 1013 (1959).
- (2) L. H. Sommer and C. L. Frye, *ibid.*, **82**, 3796 (1960).
- (3) L. H. Sommer and C. L. Frye, *ibid.*, **82**, 4118 (1960).
- (4) See A. Fredga in "The Svedberg," Almquist and Wikesells, Uppsala, 1944, p. 261, and J. Timmermans, *J. chim. phys.*, **49**, 162 (1952). Conclusions drawn on the basis of a *difference* in phase behavior without exception have proved accurate.
- (5) K. Mislow and M. Heffler, *J. Am. Chem. Soc.*, **74**, 3668 (1952). For a recent application of "case 2" for determination of the configurational relationships between the pure enantiomers of 3-thiooctanedioic acid and 3-methyloctanedioic acid see K. Mislow and W. C. Meluch, *ibid.*, **78**, 5920 (1956). For other examples see J. Timmermans, *ref. 4*.