

pathway to 2,4,5-trichloro-*C*¹³⁶-phenol was through hydrolysis.²

EXPERIMENTAL

*2,4,5-Trichloro-C*¹³⁶-phenol. The compound¹ 1,2,4,5-tetrachloro-*I-C*¹³⁶-benzene (84.8 mg., 0.39 mmol., specific activity 20.8 μ c./mmol.) and 2 ml. of 5*M* sodium hydroxide in methanol³ were sealed in a Pyrex test tube (1.4 \times 14 cm.). The atmosphere in the tube was dry nitrogen. The tube was put in a Parr high-pressure bomb together with sufficient methanol to equalize the pressure within the tube. The bomb was heated without shaking for a total of 5 hr.^{4,5} and then cooled as rapidly as possible under tap water. Fifty min. was required for the temperature of the bomb to reach the operating temperature of 160°.

As soon as the bomb was cool, the tube was removed. Sodium chloride was visible as a precipitate in the bottom of the tube. The contents were quantitatively transferred to a steam distillation apparatus (commonly used for Kjeldahl nitrogen determinations) and any unreacted starting material or such by-products as trichloroanisole, or both, were removed by steam distillation. None of these compounds were found in the first 30 ml. of distillate. The reaction mixture was then acidified with dilute sulfuric acid and again steam distilled until 60 ml. of distillate had been collected. The 2,4,5-trichloro-*C*¹³⁶-phenol sublimed very rapidly. The distillate was extracted with methylene chloride, and the extracts were dried over a minimal amount of anhydrous magnesium sulfate.

The 2,4,5-trichloro-*C*¹³⁶-phenol was isolated by evaporating the solvent through a column of glass tubing 0.6 \times 84 cm.⁷ The yield of product was 69 mg. (89%); the specific activity was 15.6 μ c./mmol. The m.p. of the product was 66° (for unlabeled compound, lit.² 66°). The infrared absorption spectrum of the compound was identical with that of unlabeled 2,4,5-trichlorophenol, and a mixed m.p. with an authentic specimen thereof showed no depression in melting point.

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(2) W. S. W. Harrison, A. T. Peters, and F. M. Rowe, *J. Chem. Soc.*, 235 (1943).

(3) 1.1*M* Potassium hydroxide in Carbitol was also investigated as a hydrolyst, but this system was not nearly so efficient as the methanolic sodium hydroxide in the conversion.

(4) During the course of preliminary work it was found that the effect of reaction time on the yield of product was quite marked: as the time of reaction increased beyond the optimum of 5 hr., the yield decreased. This showed that the product was being subjected to hydrolysis or methanolysis, or both, resulting in the formation of polyphenols and some or all of their methyl esters. However, the method of isolation was such that these by-products could not have been detected, and no attempt was made to isolate them.

(5) Trichloroanisole is to be expected as a by-product in the methanolic sodium hydroxide hydrolysis of 1,2,4,5-tetrachlorobenzene. Holleman⁶ found the anisole derivative, but he used a higher temperature (180° instead of 160°) and a longer time (12 hr. instead of 5 hr.). No trichloroanisole was detected when the shorter reaction time and lower temperature were used.

(6) A. F. Holleman, *Rec. trav. chim.*, **39**, 736 (1920).

(7) It was found in preliminary work that the use of a 1.4 \times 20-cm. Vigreux column resulted in a loss of 5–6 mg. of product.

Aryl and Aryl-alkyl Isocyanosilanes¹

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Alkylisocyanosilanes have been prepared by Eaborn² and by McBride and Beachell.³ While the present work was in progress, the first arylisocyanosilane, triphenylisocyanosilane, was reported by Bithner and co-workers.⁴ The structure of these compounds has been the subject of some controversy. The "iso" structure was favored by Eaborn and by McBride and Beachell. Infrared studies have been made by Bithner and co-workers who suggest that the trialkyl compounds are temperature-dependent equilibrium mixtures of the normal and isocyanide forms. Linton and Nixon⁵ studied isotopic shifts in the CN-stretching frequency of the trimethyl compound and concluded that this compound is the normal rather than the isocyanide. The Raman spectra of the trimethyl compound permitted no definite differentiation.⁶

This paper reports the preparation of diphenyldiisocyanosilane, dimethylphenylisocyanosilane, and the recently described triphenylisocyanosilane. The molar refractions of the first two compounds (dimethylphenylisocyanosilane is a liquid and diphenyldiisocyanosilane a low-melting solid with a strong tendency to supercool) are much closer to the calculated values for isocyanides than for normal cyanides.

The aryl and aryl-alkyl isocyanosilanes, like the alkyl compounds, are, with the exception of the triphenyl compound, extremely susceptible to hydrolysis and react violently with water. Triphenylisocyanosilane did not hydrolyze appreciably on standing in air for 0.5 hr. The great reactivity of the compounds is also shown by the reaction of diphenyldiisocyanosilane with the phenyl Grignard at the temperature of refluxing ethyl ether. Tetraphenylsilane was obtained in 80% yield. With diphenyldibromosilane and the phenyl Grignard under the same conditions, no tetraphenylsilane was obtained.

A new isothiocyanate, dimethylphenylsilyl isothiocyanate, and a new bromide, methylphenyldibromosilane, are described.

(1) Florida Agricultural Experiment Stations Journal Series, No. 909.

(2) C. Eaborn, *J. Chem. Soc.*, 2757 (1949); 3077 (1950).

(3) J. J. McBride, Jr., and H. C. Beachell, *J. Am. Chem. Soc.*, **74**, 5427 (1952).

(4) T. A. Bithner, W. H. Knoth, R. V. Lindsey, Jr., and W. H. Sharkey, *J. Am. Chem. Soc.*, **80**, 4151 (1958).

(5) H. R. Linton and E. R. Nixon, *J. Chem. Phys.*, **28**, 990 (1958).

(6) J. Goubeau and J. Rehying, *Z. anorg. u. allgem. Chem.*, **294**, 92 (1958).

ISOCYANOSILANES

| Compound | M.P. | B.P. | n_D^{20} | d_4^{20} | % CN | | M_R Obs. | M_R Calcd. ^a | |
|--|-----------------------|------------|------------|------------|--------|-------|------------|---------------------------|-------|
| | | | | | Calcd. | Found | | —NC | —CN |
| (C ₆ H ₅) ₂ Si(NC) ₂ ^b | 46–48° | 142°/2 mm. | 1.559932 | 1.090432 | 22.0 | 20.5 | 69.48 | 69.51 | 68.07 |
| (CH ₃) ₂ (C ₆ H ₅)SiNC | | 230–232° | 1.499828 | 0.957328 | 16.1 | 16.2 | 49.44 | 49.60 | 48.88 |
| (C ₆ H ₅) ₂ SiNC | 136–138° ^c | 210°/5 mm. | | | 9.12 | 9.05 | | | |

^a Using Auwers' [Ber., 60, 2122 (1927)] values for —NC and —CN. ^b Density and refractive index measured on super-cooled liquid. ^c Ref. 3 gives 136–138° for the b.p. of (C₆H₅)₂SiNC—obviously a typographical error.

EXPERIMENTAL

Diphenyldiisocyanosilane. To 0.055 mol. of silver cyanide was added 0.025 mol. diphenyldibromosilane. There was immediate evolution of heat and yellowing of the solid. The mixture was kept at 110–120° for 1 hr. and then distilled. The distillate, a straw-colored liquid, b.p. 135–140°/2 mm. was redistilled over a little silver cyanide. There was obtained 4.7 g. (80% of theory) of diphenyldiisocyanosilane, a pale yellow viscous liquid, b.p. 142–144°/2 mm.

Dimethylphenylisocyanosilane. To 0.11 mol. silver cyanide was added 0.10 mol. dimethylphenylbromosilane. There was immediate evolution of heat and yellowing of the solid. The mixture was heated to reflux and maintained at reflux for 2 hr. Distillation gave 12.4 g. (77% of theory) of colorless liquid, b.p. 230–232°.

Triphenylisocyanosilane. A mixture of 0.030 mol. triphenylbromosilane and 0.036 mol. silver cyanide was heated for 2 hr. at 200°. Distillation at reduced pressure gave 6.9 g. (81% of theory) of pure white solid, b.p. 210°/5 mm.

Dimethylphenylsiliconisothiocyanate. A mixture of 0.024 mol. of dimethylphenylisocyanosilane and 0.024 mol. of sulfur were heated at reflux (ca. 250°) for 0.5 hr. Distillation gave 2.2 g. (57% of theory) of straw-colored liquid, b.p. 252–254°, n_D^{20} 1.5556, d_4^{20} 1.0384, M_R calcd. 59.91; M_R obs. 59.81.

An identical product was obtained in 60% yield by the reaction of dimethylphenylchlorosilane with silver thiocyanate.

Methylphenyldibromosilane was prepared in 18% yield by the reaction of phenylmagnesiumbromide with methyltribromosilane in ethyl ether. The pure compound had b.p. 140–144°/60 mm., n_D^{20} 1.5537, d_4^{20} 1.599, Br, calcd. 57.2%; found: 57.2%.

Reaction of diphenyldiisocyanosilane with phenylmagnesiumbromide. When 0.01 mol. diphenyldiisocyanosilane in 15 ml. of ether was added dropwise with stirring to 0.030 mol. phenylmagnesiumbromide in 25 ml. ether, a very vigorous reaction occurred. After addition was complete, the mixture was stirred under reflux for 1 hr. After working up in the usual way, there was obtained 2.77 g. (81% of theory) of tetraphenylsilane, m.p. and mixed m.p. 233–234°. When this reaction was run using a 25% deficiency of the phenyl Grignard, a 61% yield of tetraphenylsilane was obtained.

This high reactivity is in contrast to the reactivity of diphenyldibromosilane with excess phenylmagnesiumbromide under the same conditions. No tetraphenylsilane was formed.

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Synthesis of 1,2,3,4-Tetrahydroquinolin-3-ols

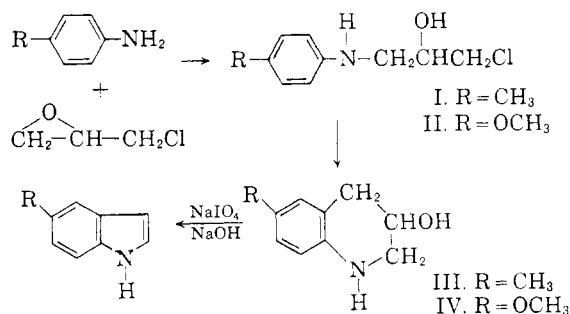
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Recently, a new indole synthesis involving periodate oxidation of substituted tetrahydroquinolin-

3-ols was reported.¹ The tetrahydroquinolin-3-ols were conveniently prepared by condensing α - and β -naphthylamine with epichlorohydrin. We have found that if substituted anilines, such as *p*-toluidine and *p*-anisidine, are used in place of the naphthylamines, a modified procedure is required.

The reaction of the amines with epichlorohydrin actually involves two reactions, and since *p*-toluidine readily adds to epichlorohydrin to give I,² the step giving difficulty is the cyclization of I to a substituted tetrahydroquinolin-3-ol (III). In studying the conversion of I to III, we found that relatively dilute reaction mixtures are necessary and that adding a base such as diethylaniline helps to prevent the formation of undesirable by-products. For example, a cyclization yield of 50% was obtained by heating a 0.042*M* solution of I with an equivalent amount of diethylaniline in boiling bromobenzene for 48 hr.



When *p*-anisidine was treated with epichlorohydrin, II was obtained as an oil. Therefore, it was more convenient to prepare IV without isolating II.

Periodate oxidation of III and IV led to the picrates of 5-methylindole and 5-methoxyindole, respectively, although in the case of 5-methoxyindole the yield was but 10%.

EXPERIMENTAL

N-(γ -Chloro- β -hydroxypropyl)-*p*-toluidine (I). The synthesis of this compound² and analogous compounds³ has

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- (2) P. Cohn and P. Friedlaender, *Ber.*, **37**, 3034 (1904); N. N. Vorozhtsov, Jr., and S. I. Kutkevichus, *Zhur. Obschei. Khim.*, **27**, 2152–2160 (1957).
- (3) H. L. Yale, E. J. Pribyl, W. Braker, F. H. Bergein, and W. A. Lott, *J. Am. Chem. Soc.*, **72**, 3715 (1950); B. J. Ludwig, W. A. West, and D. W. Farnsworth, *J. Am. Chem. Soc.*, **76**, 2893 (1954).