

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 was 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

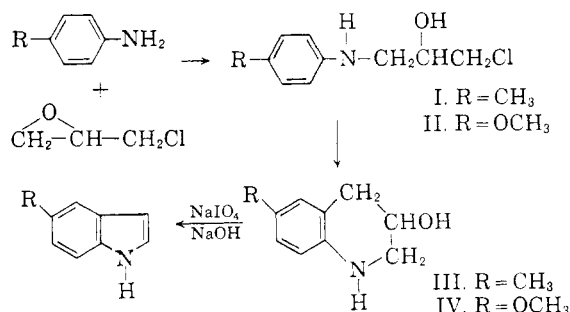
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Recently, a new indole synthesis involving periodate oxidation of substituted tetrahydroquinolin-

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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been described previously, but a more convenient method was developed. *p*-Toluidine (4.00 g.) was dissolved in 500 ml. of warm water and epichlorohydrin (3.30 ml.) was added over a 15-min. period while the temperature was held at 35–40°. The solution was stirred and the temperature held at 35–40° for 2 hr. When the mixture began to get cloudy, seed crystals of the product were added. The mixture was allowed to stand 20 hr., and the product (I) was recovered and washed with cold water, 5.37 g. (72%), m.p. 79–81° (lit. 81–82°). Although a larger excess of epichlorohydrin gave greater yields, the product was not as pure.

N-(γ -Chloro- β -hydroxypropyl)-*p*-anisidine (II). This compound was prepared by the procedure used for the synthesis of I except that *p*-anisidine was condensed with epichlorohydrin (10% excess). The product was obtained as an oil. It was extracted with bromobenzene and used without purification for the synthesis of IV.

1,2,3,4-Tetrahydro-6-methyl-quinolin-3-ol (III). Compound I (3.78 g.) was dissolved in bromobenzene (450 ml.) and diethylaniline (3.00 ml.) added. The mixture was boiled under reflux for 48 hr. The product was extracted with 5% hydrochloric acid (100 ml.), and the extract washed with benzene. The acidic extract was made basic with sodium hydroxide, and a benzene extraction carried out. The benzene extract was dried over anhydrous sodium sulfate and passed over an alumina column. The column was washed with benzene, and the product eluted with benzene ether and ether. Although recrystallization of eluted product was possible, further purification was best achieved by converting III to its hydroiodide salt using a mixture of butanol (20 ml.), hydroiodic acid (5 ml.) and ether (150 ml.). The salt was recovered, and washed with ether 2.74 g. (50%).

A purified sample of the hydroiodide salt melted at 237–239° with some decomposition.

Anal. Calcd. for C₁₀H₁₄NOI: neut. equiv., 291. Found: neut. equiv., 292.

Neutralization of an aqueous solution of the hydroiodide salt gave III, which was recrystallized from hexane for analysis, m.p. 101.5–103°.

Anal. Calcd. for C₁₀H₁₄NO: C, 73.59; H, 8.03; N, 8.58. Found: C, 73.77; H, 8.26; N, 8.58.

It was possible to follow the cyclization of I to III by mixing an aliquot (1 ml.) from the reaction mixture with benzene (5 ml.) and 5% hydrochloric acid (3 ml.). The aqueous layer was added to a mixture of 6*N* sodium hydroxide (4 ml.) and 1.28% sodium periodate (4 ml.). The indole that was formed was steam distilled out of the mixture, and aliquot parts of the distillate in 50% alcohol were analyzed. A sample (2 ml.) was mixed with 2.5% alcoholic dimethylaminobenzaldehyde solution (1 ml.) and 6*N* hydrochloric acid (1 ml.), and the absorption at 570 m μ was determined. Although the procedure is not a good method of analyzing for III, it gives some measure of the amount of cyclization occurring in the reaction.

1,2,3,4-Tetrahydro-6-methoxy-quinolin-3-ol (IV). This compound was prepared from a bromobenzene solution of II. The bromobenzene extract obtained from the reaction of *p*-anisidine (4.60 g.) and epichlorohydrin (3.0 ml.) was adjusted to a volume of 900 ml. of bromobenzene, and the residual water distilled with a small amount of bromobenzene. Diethylaniline (6 ml.) was added, and the mixture was boiled under reflux for 48 hr. The product was isolated by chromatography in a manner similar to the isolation of III. The product was recrystallized from a mixture of benzene and hexane, 1.30 g. (19.5%), m.p. 73.5–74.5°. An analytical sample melted at 75°.

Anal. Calcd. for C₁₀H₁₃NO₂: C, 67.02; H, 7.31; N, 7.82. Found: C, 66.95; H, 7.03; N, 7.79.

5-Methylindole. Compound III was oxidized by periodate using essentially the procedure previously reported.¹ A solution of III (200 mg. in 35 ml. of ethanol) and a solution of sodium periodate (626 mg. in 35 ml. of water) were added at about the same rate over a 1.5-hr. period to 100 ml. of an 8% sodium hydroxide solution, and 5-methylindole steam-

distilled from the reaction mixture as soon as it was formed. A small amount of 5-methylindole crystallized in the steam distillate which had been saturated with salt, m.p. 57.5–58° (lit. 58.5°), but a more efficient recovery was obtained by extracting the indole with ether, removing the ether, extracting the product with a small volume of hot water and adding the hot solution to a saturated, aqueous picric acid solution. The orange-red picrate was recovered, 121 mg. (27%), m.p. 145–148°, with some decomposition (lit. 151°).

5-Methoxyindole. Compound IV was oxidized by the same method that was used for the oxidation of III. The red picrate of 5-methoxyindole was obtained in 10% yield, m.p. 142–144° with some decomposition (lit. 145°).

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Some Properties of Benzenesulfonyl Peroxide

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The published chemistry of benzenesulfonyl peroxide consists of one paper¹ describing its preparation and another² describing its decomposition in water to form phenol, sulfuric acid, and (probably) benzenesulfonic acid. We now wish to report our unsuccessful attempts to improve the unsatisfactory yields in its preparation and the results of some exploratory work involving its use as a polymerization initiator and concerning the products of its decomposition in benzene.

Adaptations of several procedures for the preparation of benzoyl peroxide^{3–6} involving interaction of benzenesulfonyl chloride and sodium peroxide or hydrogen peroxide failed to give isolable amounts of the sulfonyl peroxide. Benzenesulfonyl chloride failed to react with the urea hydrogen peroxide complex³ and formed only the sulfonamide with the hydrogen peroxide dicyclohexylamine complex.⁷

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