

although rather large, are probably well within the accuracy of the data. It should be borne in mind that certain of the "measured" free energy values given actually represent results that were obtained on materials in the solid or liquid phase, and free energies of vaporization of considerable magnitude had to be estimated in order to convert the values to the gas phase where resonance energies are applicable. These estimates introduce an uncertainty of at least 2 kilocalories in some instances.

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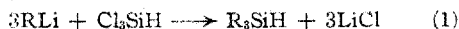
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Tetra-2-naphthylsilane

BY HENRY GILMAN AND CECIL G. BRANNEN

In connection with studies on steric hindrance in arylsilanes, we have synthesized tetra-2-naphthylsilane. This is of interest because of a generalized comment^{1a} that four naphthyl or tolyl groups can be bonded to silicon. Four tolyl groups have been attached to silicon,^{1b} but none of the compounds reported has an *ortho* substituent, which is of most significance in steric studies. There appears to be no reference concerning tetra-*o*-tolyl- or any tetranaphthyl-silane. Furthermore, experiments designed to bond four *o*-tolyl radicals to silicon have demonstrated² that the fourth group is introduced with difficulty.

We have found that tetra-2-naphthylsilane can be easily prepared by treating silicon tetrachloride, ethyl silicate, or trichlorosilane, respectively, with 2-naphthyllithium. The reactions involved in the preparation from trichlorosilane possibly proceed³ through the formation of tri-2-naphthylsilane



2-Naphthyllithium was made both by the direct method⁴ from 2-bromonaphthalene and lithium metal and by halogen-metal interconversion⁵ of 2-bromonaphthalene with *n*-butyllithium. The former method introduces colored impurities into the product which are difficult to eliminate by the ordinary techniques, while the latter method introduces the coupled product, 2,2'-binaphthyl, which is extraordinarily difficult to remove completely. Higher yields were obtained by treating silicon tetrachloride with 2-

naphthyllithium prepared by the direct method and purifying the product by chromatography.

Preliminary experiments indicate that the preparation of tetra-1-naphthylsilane proceeds with considerable difficulty, probably largely because of steric hindrance.

Experimental

All temperatures are uncorrected unless otherwise noted.

Tetra-2-naphthylsilane: (a) From Silicon Tetrachloride and 2-Naphthyllithium Made by the Direct Method.—A 0.39 *N* solution of 2-naphthyllithium in ether was made from 10 g. (0.048 mole) of 2-bromonaphthalene⁶ and 7 g. (0.1 g. atom) of lithium by the usual method, the yield (96%) being determined by acid titration.⁷ Two grams (0.018 mole) of silicon tetrachloride in about 50 ml. of dry ether was added to the organolithium reagent with stirring. After refluxing for ten minutes the mixture was poured into dilute hydrochloric acid, the inorganic salts removed by extraction, and the organic layer steam-distilled. The residue was extracted with about 400 ml. of petroleum ether (b. p. 60–80°) and this extract was poured through a 4 × 20 cm. column of alumina.⁸ The colored material was not eluted after development with 1 l. of solvent. The eluant was reduced to a small volume to obtain 5.1 g. (81%) of the pure silane, m. p. 216–217° (cor.).

*Anal.*⁹ Calcd. for C₄₀H₂₄Si: Si, 5.22. Found: Si, 5.29, 5.20.

(b) From Silicon Tetrachloride and 2-Naphthyllithium Made by Halogen-Metal Interconversion.—To a solution of 10 g. (0.048 mole) of 2-bromonaphthalene, m. p. 57–58°, in 50 ml. of dry ether was added 0.048 mole of *n*-butyllithium¹⁰ in 46 ml. of ether keeping the internal temperature at 5°. After stirring for fifteen minutes, 1.5 g. (0.0088 mole) of silicon tetrachloride in 15 ml. of ether was added dropwise maintaining the temperature at 5°. Color Test I¹¹ was positive even after stirring for two hours at 5° followed by refluxing thirty minutes. The mixture was poured into dilute hydrochloric acid; the organic layer was extracted with water and steam-distilled. The residue was extracted with petroleum ether (b. p. 60–80°). In four crops, 2.40 g. (51%) of the crude silane, m. p. 202–205°, was isolated. Recrystallization from ethanol-ethyl acetate (1:1) gave 2.10 g. (42%) of the pure silane, m. p. 216–217° (cor.).

(c) From Ethyl Silicate.—An ethereal solution of 20.7 g. (0.1 mole) of 2-bromonaphthalene and 0.1 mole of *n*-butyllithium were mixed under the usual conditions⁵ at 5°. After stirring for ten minutes, 1.9 g. (0.009 mole) of ethyl silicate, b. p. 164° at 740 mm., in 20 ml. of dry ether was added dropwise and the mixture refluxed for fifteen hours. The mixture was worked up as in (b) using the same solvent for crystallization. 2,2'-Binaphthyl, 0.40 g. (6%), melting point and mixed melting point with an authentic specimen, 188–189° (cor.), separated first; then came an impure fraction, m. p. 150–160°; followed by 1.90 g. (40%) of the crude silane, m. p. 203–205°. Recrystallization of the crude silane gave 1.2 g. of material, m. p. 216–217° (cor.), which showed no depression when mixed with the material from (a).

Chromatographic adsorption of the petroleum ether extract failed to achieve a separation. Fractional crystallization of the solid present in the eluant showed this material to contain binaphthyl and the silane.

(d) From Trichlorosilane.—2-Naphthyllithium was made in the same manner as in (b) using the same quanti-

(6) Prepared in 55% yield in essential accordance with the directions of Newman and Wise, *ibid.*, **63**, 2847 (1941).

(7) Gilman, Wilkinson, Fishel and Meyers, *ibid.*, **45**, 150 (1923).

(8) Fisher Scientific Company, 80–200 mesh.

(9) See Gilman, Hofferth, Dunn and Melvin, *ibid.*, **72**, in press (1950).

(10) Gilman, Beel, Brannen, Bullock, Dunn and Miller, *ibid.*, **71**, 1499 (1949).

(11) Gilman and Schulze, *ibid.*, **47**, 2002 (1925).

(1) (a) Burkhard, Rochow, Booth, and Hartt, *Chem. Reviews*, **41**, 105 (1947); (b) Polis, *Ber.*, **18**, 1540 (1885).

(2) Unpublished studies by Dr. G. N. R. Smart.

(3) Gilman and Massie, *This Journal*, **68**, 1128 (1946); Meals, *ibid.*, **68**, 1880 (1946); Gilman and Melvin, *ibid.*, **71**, 4050 (1949).

(4) Gilman, Zoellner and Selby, *ibid.*, **54**, 1957 (1932).

(5) Gilman and Moore, *ibid.*, **62**, 1843 (1940).

ties of material and 2.70 g. (0.02 mole) of trichlorosilane in 10 ml. of ether was added dropwise. After stirring for ten minutes, the mixture was poured into dilute acid and worked up as described in (b). Crystallization from ethyl acetate gave 4.3 g. (40%) of the pure silane, m. p. 216–217° (cor.), which gave no depression of melting point when mixed with the material from (a) and (b), respectively.

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Secondary Amine Salts of Some Thiophenols

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In some recent studies in this Laboratory involving the condensation of formaldehyde and secondary amines with thiophenols, it was noted that if the secondary amine was first mixed with the thiophenol, an appreciable amount of heat

morpholine salts, are insoluble in ether. All are appreciably soluble in water, but their aqueous solution soon becomes cloudy due to hydrolysis.

Experimental

The 1-thionaphthol was obtained from a sample of a rubber peptizing agent RPA No. 4 that contained about 30% by weight of this thiophenol and which was kindly furnished us by Mr. M. A. Youker of E. I. du Pont de Nemours and Company. The fraction distilling at 145–147° at 13 mm. pressure was collected as the desired material. All the other chemicals used in this investigation were of the practical grade and were obtained from the Eastman Kodak Company, Rochester, N.Y.

Five grams of the thiophenolic compound was dissolved in 20–25 ml. of the appropriate solvent (see Table I). An equivalent amount of the amine was then added to this solution and the resulting mixture was cooled to 15–20° in an ice-bath. After crystallization was complete, the salt was removed by filtration, was washed with small portions of ether and was then dried in a vacuum desiccator. These salts were recrystallized from ether, benzene, 95% ethyl alcohol or dioxane, as is indicated in Table I.

TABLE I
SALTS OF SECONDARY AMINES AND SOME THIOPHENOLS

Salts of <i>p</i> -thiocresol	Solvent used in prep.	Solvent used in recryst.	Yield, %	Color of crystals	M. p., °C.	Formula	S Analyses, %			Specific conductivity × 10 ⁴	
							Calcd.	Found	Found	Aque- ous sol.	95% alcohol sol.
Diethylamine ^a	Dioxane	Benzene	72	Colorless	51–52	C ₁₁ H ₁₉ SN	16.24	15.63	15.52	5.99	
Piperidine	Ethyl alc.	Ethyl alc.	89.5	Colorless	137–138	C ₁₃ H ₁₉ SN	15.31	15.42	15.59	6.75	1.14
Morpholine	^b	alc.	94	Colorless	71.5	C ₁₁ H ₁₇ OSN	15.17	15.27	15.30	5.43 ^d	
Salts of 2-thionaphthol											
Diethylamine ^c	Dioxane	Dioxane	89	Yellow	107	C ₁₄ H ₁₉ SN	13.73	13.92	13.71	4.74	
Piperidine	Dioxane (40 ml.)	Dioxane	91	Yellow	139–140	C ₁₃ H ₁₉ SN	13.47	13.24	13.03	6.05	1.74
Morpholine	Dioxane	^d	28.5	Yellow	86–87	C ₁₄ H ₁₇ OSN	12.96	13.18	12.85	3.29 ^d	
Salts of 1-thionaphthol ^e											
Diethylamine	Dioxane	Dioxane	93.5	Cream	99–102	C ₁₄ H ₁₉ SN	13.73	13.84	13.88	5.50	
Piperidine	Ethyl alc. (50 ml.)	Ethyl alc.	68	Cream	145–149	C ₁₃ H ₁₉ SN	13.47	13.41	13.13	4.74 ^f	1.61
Morpholine	Dioxane	Dioxane	47	Cream	95–96	C ₁₄ H ₁₇ OSN	12.96	12.90	12.83	3.23 ^d	

^a This salt appears to sublime at about 127°. ^b This salt was prepared by the direct union of morpholine and *p*-thiocresol. ^c This salt appears to sublime at about 101°. ^d This salt was not recrystallized. Melting point of crude salt did not change on recrystallization. ^e It has been shown in this laboratory that the 1-thionaphthol from the source used also contained some 2-thionaphthol. This may explain why the melting points of these salts were not too sharp. See Grillo, Levin, Green and Bashford, *THIS JOURNAL*, 72, 1863 (1950). ^f An 0.008 *M* solution was used. ^g A saturated solution was employed.

was generated and a crystalline precipitate was formed. It was decided to investigate these precipitates on the supposition that they were salts.

Previously, Kraus and White¹ dissolved thiophenol in liquid ammonia and obtained a white crystalline precipitate, which they assumed was the ammonium salt of thiophenol. It was insoluble in petroleum ether and gradually decomposed on standing in the air with the evolution of ammonia. Gordy and Stanford² observed that white crystalline solids are formed when piperidine, cyclohexylamine and triamylamine are mixed with thiophenol. These were believed to be salts but were not further studied.

From the results of our investigation, we feel that there is sufficient evidence to indicate that the products of the interaction of the thiophenols and the secondary amines are true salts. The compounds obtained, with the exception of the

One hundredth molar aqueous solutions of the salts were prepared and their conductivities were determined. If the salts were not soluble to this extent, saturated solutions were employed. The equivalent conductivity of the aqueous solutions of the diethylamine and the piperidine salts of *p*-thiocresol agreed closely with the conductivity of the aqueous solutions of the free amines. (We found specific conductivity of diethylamine to be 6.08×10^{-4} and piperidine to be 6.86×10^{-4} .) Saturated aqueous solutions of the thiols gave no measurable conductivity in the conductivity apparatus used by us. From these results we have concluded that these salts are rapidly and nearly completely hydrolyzed in an aqueous solution.

The conductivities of the piperidine-thiol compounds were then determined in a 95% ethyl alcohol solution. Such a solution has a sufficiently large dielectric constant that the salts should ionize, while hydrolysis in this solvent should be slower than in water. A measurable conductivity of these salts in the alcohol solution was obtained, whereas solutions of the thiols and the amines in this solvent gave no measurable conductivity in our apparatus.

Analyses, physical properties and conductivity data are summarized in Table I.

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(1) Kraus and White, *THIS JOURNAL*, 48, 768 (1928).

(2) Gordy and Stanford, *ibid.*, 68, 467 (1940).