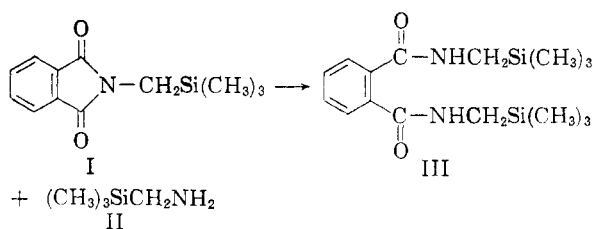


Investigation of the solid revealed that it was the diamide III. The infrared spectrum of III exhibited the characteristic amide I and II bands at 6.15μ and 6.45μ .⁷ Confirmation of the identification was obtained by the independent preparation of III from phthaloyl chloride and II.

Incomplete cleavage of I when the conditions of Ing and Manske were used would explain these results. Addition of base to the concentrated filtrates would free the amine II which in turn would react with I to yield III. However, evaporation to dryness of the acidified filtrate prior to the addition of base would complete the cleavage of I thus preventing the formation of III. That such a rationale is feasible is provided by the reaction of I and II to give a 77% yield of III.



EXPERIMENTAL⁸

N,N'-Bis(trimethylsilylmethyl)phthalamide (III). A. As a by-product from the Gabriel reaction. To a stirred solution of 125 ml. of absolute ethanol and 50.0 g. (0.215 mole) of *N*-trimethylsilylmethylphthalimide⁶ was added over a 10-min. period 10.7 g. (0.215 mole) of hydrazine hydrate. The mixture was heated under reflux for 1.5 hr., 25 ml. of concentrated hydrochloric acid added to the refluxing solution, and the heating continued for an additional 2 hr. The mixture was then cooled and filtered. The precipitate was washed several times with 6*N* hydrochloric acid and finally refluxed with 100 ml. of 6*N* hydrochloric acid, then refiltered. All acid filtrates were combined and evaporated until *ca.* two-thirds of the volume remained; two phases were observed. The concentrated filtrates were then made basic with potassium hydroxide. A white solid formed and was extracted with several portions of ether. Removal of the ether by distillation gave 13.6 g. (36%) of III, m.p. 177–178°.

Anal. Calcd. for $\text{C}_{16}\text{H}_{28}\text{Si}_2\text{N}_2\text{O}_2$: C, 57.2; H, 8.34; N, 8.35; Si, 16.6. Found: C, 57.17; H, 8.35; N, 8.37; Si, 16.8.

B. From phthaloyl chloride. To 1.00 g. (9.70 mmoles) of aminomethyltrimethylsilane was added slowly 1.00 g. (4.92 mmoles) of phthaloyl chloride followed by 7 ml. of 10% sodium hydroxide. The resulting white solid was filtered, washed with 10 ml. of water, then crystallized from 95% ethanol, yielding 2.60 g. (80%) of III, m.p. 176–177°. A mixed melting point with the material obtained as described in part A showed no depression.

C. From *N*-trimethylsilylmethylphthalimide (I) and aminomethyltrimethylsilane (II). Upon the mixing of 1.00 g. (9.70 mmoles) of II and 2.3 g. (10.0 mmoles) of I, a cloudy solution resulted, which, upon warming, solidified. Crystallization from ethanol yielded 2.5 g. (77%) of III, m.p. 177–177.5°. A mixed melting point with the sample obtained as described in part A showed no depression.

(7) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Wiley, New York, 1954, pp. 180–185.

(8) All melting points are uncorrected and were taken on a Fisher melting point stage. The infrared spectra were taken using a Beckman IR-5 recording spectrophotometer (KBr pellet). The carbon-hydrogen microanalysis was performed by the Berkeley Microanalytical Laboratory.

Aminomethyltrimethylsilane hydrochloride. The procedure described in part A was followed precisely through the combination of the acid filtrates. The combined acid filtrates were boiled to dryness and the resulting solid was then added to a potassium hydroxide solution. The resulting basic mixture was steam distilled as described by Sommer and Rockett,⁵ yielding 16.8 g. (60%) of aminomethyltrimethylsilane hydrochloride, m.p. 245–246° (lit.⁵ 242–243°).

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Studies in Organosilicon Chemistry. XLIII. An Investigation of Silicon-Containing *s*-Triazines

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Preliminary work by the writers and others has led to the conclusion that for the preparation and isolation of triazines with silyl side chains, good yields may be expected of those compounds in which an aromatic nucleus is found between triazine carbon and silicon.

Six of these compounds have been prepared through the use of the proper Grignard reagent acting on cyanuric chloride or of ammonia acting on a silicon containing product. Several new intermediates have also been prepared. For example, cyanuric chloride reacts with *p*-trimethylsilylphenylmagnesium bromide with replacement of a chlorine to give 2,4-dichloro-6-*p*-(trimethylsilylphenyl)-*s*-triazine. Dimethylallyl-*p*-bromophenylsilane was prepared by the action of *p*-bromophenyllithium on dimethylallylchlorosilane. Dimethyl-*p*-bromophenylsilane resulted from the interaction of dimethylvinylchlorosilane and *p*-bromophenylmagnesium bromide.

EXPERIMENTAL

Several intermediates were satisfactorily prepared, in accordance with methods outlined in the literature. These comprised 2-chloro-4,6-diphenyl-*s*-triazine,² trimethyl-*p*-bromophenylsilane,^{3a,b} dimethyl-*p*-bromophenylphenylsilane,⁴ and chloromethyldimethylfluorosilane.⁵

(1) Presented by the first author in partial fulfillment of the requirements for the degree of Doctor of Philosophy at The University of Buffalo. Present address: Ithaca College, Ithaca, N. Y.

(2) A. Ostrogovich, *Chem. Z.*, **36**, 3191 (1903).

(3)(a) P. J. Campagna and H. W. Post, *J. Org. Chem.*, **19**, 1749 (1954). (b) Henry Gilman, H. W. Melvin, and J. J. Goodman, *J. Am. Chem. Soc.*, **76**, 3219 (1954).

(4) J. Chatt and A. A. Williams, *J. Chem. Soc.*, 688 (1956).

(5) Dietmar Seyferth and H. P. Kogler, WADC Technical Report, 59-369 (1959).

TABLE I
 PHYSICAL PROPERTIES
 (New Compounds Only)

	B.P.	Mm.	<i>n</i>	M.P.
(CH ₃) ₂ Si(CH ₂ Cl)C ₆ H ₄ Br- <i>p</i>	100-102	0.85	(²⁵ D) 1.5531	
(CH ₃) ₂ Si(CH=CH ₂)C ₆ H ₄ Br- <i>p</i>	100	3.5	(²⁷ D) 1.5361	
(CH ₃) ₂ Si(CH ₂ CH=CH ₂)C ₆ H ₄ Br- <i>p</i>	81-84	0.3	(²⁷ D) 1.5304	
(CH ₃) ₂ Si(C ₆ H ₁₁)C ₆ H ₄ Br- <i>p</i>	90-92	0.1	(²⁷ D) 1.5178	
	104-108	15		
(CH ₃) ₂ Si(CH ₂ C ₆ H ₅)C ₆ H ₄ Br- <i>p</i>	122-125	0.1	(²⁵ D) 1.5706	
<i>p</i> -(CH ₃) ₂ Si(CH ₂ C ₆ H ₅)C ₆ H ₄ C ₆ H ₄ Br- <i>p</i>				93-95
(CH ₃) ₂ SiC ₆ H ₄ Br- <i>p</i>				91-93
Cl ₂ (NC) ₃ C ₆ H ₄ Si(CH ₃) ₃ - <i>p</i>				143.0-143.5
Cl ₂ (NC) ₃ C ₆ H ₄ Si(CH ₃) ₂ CH=CH ₂ - <i>p</i>				114.5-115.5
Cl ₂ (NC) ₃ C ₆ H ₄ Si(CH ₃) ₂ CH ₂ C ₆ H ₅ - <i>p</i>				124-127
Cl ₂ (NC) ₃ C ₆ H ₄ Si(CH ₃) ₂ C ₆ H ₅ - <i>p</i>				120-122
Cl(NC) ₃ (NH ₂)C ₆ H ₄ Si(CH ₃) ₃ - <i>p</i>				162-163
(H ₂ N) ₂ (NC) ₃ C ₆ H ₄ Si(CH ₃) ₃ - <i>p</i>				166-167
Cl ₂ (NC) ₃ C ₆ H ₄ CH ₂ - <i>p</i>				146.5-147.5

Physical properties were satisfactory, including infrared spectra and, in some cases, mixed melting points.

2,4-Dichloro-6-p-tolyl-s-triazine was prepared by treating 2.4 g. (0.1 g.-atom.) of magnesium turnings under 10 cc. of dry ether with 2 g. of *p*-bromotoluene. After the reaction had started, 15.5 g. of *p*-bromotoluene (total 0.1 mole) was added, with the customary precautions. With vigorous stirring and cooling in an ice bath, 9.2 g. (0.05 mole) of cyanuric chloride in 150 cc. of dry ether was added. After the addition had been completed, the mixture was allowed to warm to room temperature and stirred for 4 hr. The solid material was filtered off and the filtrate evaporated to dryness. The brown residue, which was a strong lachrymator, was dissolved in boiling hexane and filtered. Repeated crystallization from hexane gave 5.4 g. (45%) of colorless crystals, m.p. 146.5°-147.5°.

Anal. Calcd. for C₁₀H₇Cl₂N₃: C, 50.00; H, 2.92; N, 17.50. Found: C, 50.69; H, 3.04; N, 17.40.

The infrared spectrum showed strong bands at 1610, 1525, 1490, 1380, 1260, 1245, 1180, 1100, 855, 840, 795, 745 cm.⁻¹.

Allyldimethyl-p-bromophenylsilane. This compound was prepared using the same general technique as in the above case. The interaction of 1-bromobutane and lithium wire formed *n*-butyllithium which then reacted with *p*-dibromobenzene giving *p*-bromophenyllithium. This compound reacted with allyldimethylchlorosilane to give the product in 33% yield, b.p. 81°-84° (0.3 mm.), *n*²⁷D 1.5304. The infrared spectrum gave strong absorption at 3070, 2960, 1630, 1575, 1482, 1380, 1255, 1160, 1070, 1015, 900, 850-800, 725 cm.⁻¹.

Benzylidimethyl-p-bromophenylsilane was similarly prepared, from *p*-bromophenyllithium and benzylidimethylchlorosilane in 40.5% yield, b.p. 122°-125° (0.1 mm.), *n*²⁵D 1.5706.

Anal. Calcd. for C₁₅H₁₇BrSi; C, 59.01, H, 5.61. Found: C, 59.29; H, 6.03.

Infrared data showed bands at 3070, 3030, 2960, 2900, 1600, 1575, 1495, 1482, 1378, 1255, 1210, 1157, 1070, 1015, 850-800, 760, 725, 700 cm.⁻¹.

Vinyldimethyl-p-bromophenylsilane was prepared by the interaction of vinyldimethylchlorosilane and *p*-bromomagnesium bromide. The reacting silane had been synthesized by action of methylmagnesium chloride on methylvinylchlorosilane. Vinyldimethyl-*p*-bromophenylsilane was isolated in 21.6% yield, b.p.; 100° (2.5 mm.), *n*²⁷D 1.5361.

Anal. Calcd. for C₁₀H₁₃BrSi; C, 49.79; H, 5.43. Found: C, 50.22; H, 5.56.

Infrared data showed bands at 3050, 2960, 1575, 1482, 1407, 1378, 1250, 1072, 1012, 955, 840-800, 755, 725 cm.⁻¹.

Amyldimethyl-p-bromophenylsilane was similarly prepared by the action of methylmagnesium chloride on amyldichlorosilane followed by treatment with *p*-bromophenylmagnesium bromide, in 9.5% yield, b.p. 90°-92° (0.1 mm.), *n*²⁵D 1.5178.

Using the method of Gilman, Melvin, and Goodman^{2b} the yield was 72%.

Anal. Calcd. for C₁₃H₂₁BrSi; C, 54.72; H, 7.42. Found: C, 54.98; H, 7.33.

Infrared absorption showed at 2960, 2940, 1575, 1482, 1378, 1255, 1070, 840, 805, 725 cm.⁻¹.

Chloromethyldimethyl-p-bromosilane was prepared by the action of *p*-bromophenyllithium on chloromethyldimethylfluorosilane in 32.5% yield, b.p. 100-102° (0.85 mm), *n*²⁵D 1.5531.

Anal. Calcd. for C₉H₁₂BrClSi; C, 41.09; H, 4.60. Found: C, 40.55; H, 4.53.

Infrared bands were observed at 2950, 1575, 1482, 1377, 1255, 1070, 1022, 837, 805, 725 cm.⁻¹.

Trimethyl-p-bromoxenylsilane was synthesized by the action of *p*-bromoxenyllithium on trimethylchlorosilane in 41% yield, m.p. 91-93°.

Anal. Calcd. for C₁₅H₁₇BrSi; C, 59.01; H, 5.62. Found: C, 58.99; H, 5.83.

Infrared bands were observed at 2960, 1480, 1380, 1255, 1115, 1080, 1000, 840, 810, 760 cm.⁻¹.

Benzylidimethyl-p-bromoxenylsilane was similarly prepared from the lithium compound and benzylidimethylchlorosilane, yield 66%, m.p. 93-95°.

Anal. Calcd. for C₂₁H₂₁BrSi; C, 66.13; H, 5.55. Found: C, 65.71; H, 5.32.

Infrared bands appeared at 3010, 1600, 1495, 1480, 1380, 1255, 1210, 1150, 1115, 1075, 1000, 825, 810, 765, 700 cm.⁻¹.

2,4-Dichloro-6-p-(trimethylsilylphenyl)-s-triazine was prepared by the interaction of *p*-trimethylsilylphenylmagnesium bromide with cyanuric chloride and isolated in 15% yield, m.p. 143.0-143.5°.

Anal. Calcd. for C₁₂H₁₂Cl₂N₃Si; C, 48.50; H, 4.39; N, 14.08. Found: C, 48.58; H, 4.90; N, 13.91.

Infrared red bands were observed at 2960, 1530, 1485, 1390, 1280, 1280, 1250, 1125, 840, 795, 760, 726, 700 cm.⁻¹.

2,4-Dichloro-6-p-(vinyldimethylsilylphenyl)-s-triazine was similarly prepared from *p*-vinyldimethylsilylphenylmagnesium bromide and cyanuric chloride, with a yield of 24%, m.p. 114.5-115.0°.

Anal. Calcd. for C₁₃H₁₃Cl₂N₃Si; C, 50.32; H, 4.22. Found: C, 49.79; H, 4.28.

Infrared red bands appeared at 2950, 1535, 1485, 1390, 1320, 1285, 1250, 1125, 850, 820, 800, 775, 710 cm.⁻¹.

2,4-Dichloro-6-p-(benzylidimethylsilylphenyl)-s-triazine was prepared, under an atmosphere of nitrogen, in 6% yield, by the interaction of *p*-benzylidimethylsilylphenylmagnesium bromide and cyanuric chloride, m.p. 124-127°.

Anal. Calcd. for C₁₈H₁₇Cl₂N₃Si; C, 57.75; H, 4.58. Found: C, 57.65; H, 4.51.

Infrared absorption occurred at 3010, 2940, 1600, 1535,

1485, 1390, 1320, 1280, 1250, 1210, 1160, 1150, 1125, 850, 825, 795, 770, 700 cm^{-1} .

2,4-Dichloro-6-p-(phenyldimethylsilyl)-s-triazine. Under an atmosphere of argon, *p*-phenyldimethylsilylphenylmagnesium bromide reacted with cyanuric chloride to form the above product in 22% yield, m.p. 120–122°.

Anal. Calcd. for $\text{C}_{17}\text{H}_{15}\text{Cl}_2\text{N}_3\text{Si}$: C, 56.57, H, 4.20. Found: C, 56.12; H, 4.55.

Infrared absorption was observed at 1535, 1490, 1395, 1320, 1285, 1255, 1123, 850, 780, 710 cm^{-1} .

Reaction of 2,4-dichloro-6-p-(trimethylsilylphenyl)-s-triazine with anhydrous ammonia. In a 50 cc. Erlenmeyer flask was placed 0.5 g. (0.0017 mole) of cyanuric chloride in 20 cc. of dry ether. Dry acetone proved to be of equal value. Anhydrous ammonia was bubbled through for 15 min. A white precipitate formed almost immediately and became heavier as the reaction continued. The precipitate was filtered off. In the case of the reaction run in ether, the solvent was evaporated off and the residue recrystallized from hexane-acetone. In the case of the run carried out in acetone, after filtration, hexane was added to the filtrate at the boiling point until crystals appeared. The product appeared as colorless platelets, yields 0.43 g. (from the ether reaction), 0.40 g. (acetone). Fractional crystallization yielded two fractions, as shown below.

Fraction I: 2-amino-4-chloro-6-p-(trimethylsilylphenyl)-s-triazine, m.p. 162–163°.

Anal. Calcd. for $\text{C}_{12}\text{H}_{13}\text{ClN}_3\text{Si}$: C, 52.4; H, 5.45; N, 20.1, mol. wt. 278. Found: C, 53.20; H, 5.71; N, 19.12; mol. wt., 256.

Fraction II: 2,4-diamino-6-p-(trimethylsilylphenyl)-s-triazine, m.p. 166–167°.

Anal. Calcd. for $\text{C}_{12}\text{H}_{17}\text{N}_5\text{Si}$: C, 55.56; H, 6.61; N, 27.1; mol. wt., 259. Found: C, 55.41; H, 6.71; N, 26.96; mol. wt., 243.

Infrared absorption on both compounds showed bands at 3300, 3140, 2950, 1660, 1570, 1540, 1500, 1400, 1320, 1280, 1226, 1100, 1010, 840, 810, 730, 710 cm^{-1} .

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Two Acids Containing the Active 2-Heptyl Group

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Previous work has shown that both stereoisomers of 3-methylnonanoic acid² and 3-methylhendecanoic acid³ can be obtained optically pure by decarboxylation of the active, crystalline 2-octylmalonic and 2-decylmalonic acids, respectively. Cason and Coad⁴ discovered that this procedure failed to

(1) This work was abstracted from the Master of Science thesis of John E. Spikner submitted to the faculty at DePaul University (1952).

(2) F. S. Prout, R. J. Klimkowski, and D. E. Dickson, *J. Org. Chem.*, **24**, 826 (1959).

(3) F. S. Prout, J. Cason, and A. W. Ingersoll, *J. Am. Chem. Soc.*, **70**, 298 (1948).

(4) J. Cason and R. A. Coad, *J. Am. Chem. Soc.*, **72**, 4695 (1950).

produce pure, active 2-pentylmalonic acid needed to furnish active 3-methylhexanoic acid.

Upon repeating the malonic acid scheme^{2,3} with (–)-2-bromoheptane [$\alpha^{23}\text{D} -37^\circ$ (homogeneous)] the pure (–)-2-heptylmalonic acid [m.p. 131–132°, [α]²⁵_D –9.68° (95% ethanol)] proved to be separable from the *dl*-form (m.p. 101.5–102°) by crystallization. Decarboxylation of this acid furnished (–)-3-methyloctanoic acid, [α]²⁶_D –4.95 (homogeneous). Levene and Marker⁵ reported [α]²³_D –5.14° for this acid when resolved with quinine. The stereochemistry of these reactions has recently been reviewed by Le Goff, Ulrich, and Denney.⁶

The alkylation of ethyl methylmalonate with (–)-2-bromoheptane ($\alpha^{24}\text{D} -37^\circ$) produced the butyl (–)-2-heptylmethylmalonate with a surprisingly high rotation [α]²⁵_D –12.01° (homogeneous)]. Hydrolysis of this ester led to the (–)-2-heptylmethylmalonic acid [m.p. 100–102°, [α]²⁵_D –23.35° (95% ethanol)] which was easily obtained pure in 50% yield by crystallization from pentane. (The *dl* acid was exceedingly hard to crystallize.)

Decarboxylation of the (–)-2-heptylmethylmalonic acid gave an active 2,3-dimethyloctanoic acid, [α]²⁵_D –14.1° (homogeneous). This acid is probably antipodally pure at C-3 but is certainly partially racemic at C-2, the active site created in the decarboxylation. The rotation of the amide, [α]²⁵_D –29.1° (95% ethanol), suggests that the maximum rotatory value of 2,3-dimethyloctanoic acid is much higher than the 14° observed.

EXPERIMENTAL

All melting and boiling points were uncorrected. Densities are reported in absolute units (g./cc.). The hexane and pentane were Skellysolves B and F (b.p. 65° and 35°, respectively) sold by Skelly Oil Co., Kansas City, Mo. Elemental analyses were by Micro-Tech Laboratories, Skokie, Ill., and Drs. Weiler and Strauss, Oxford, England. Fractionations were effected through a 60-cm., heated Vigreux column having no head. Optical rotations were observed in a Rudolf Universal High Precision polarimeter through a 1 dm. tube except where noted.

(+)-2-Heptanol. *dl*-2-Heptanol was prepared in 84% yield by action of *n*-amylmagnesium bromide with acetaldehyde: b.p. 156.5–157.3°; $n^{24}\text{D}$ 1.4189; d^{25} 0.835. 2-Heptanol was converted in 82.5% yield to crude 2-heptyl hydrogen phthalate.⁷ Crystallization of a small sample from hexane gave pure half acid; m.p. 66.5–67.5°; sapon. equiv., 135, 137 (calcd. 132.1). Pickard and Kenyon⁸ reported m.p. 57–58°. The brucine salt was made from 353 g. of 2-heptyl hydrogen phthalate and 421 g. of brucine in 4 l. of acetone. Eventually systematic crystallization produced 246 g. (30%) of the desired salt; m.p. 137–138.5°; [α]²⁴_D –4.50° (95% ethanol). Pickard and Kenyon⁸ reported m.p. 137–138°, [α]_D –4.42° (ethanol). The pure brucine salt (262 g.)

(5) P. A. Levene and R. E. Marker, *J. Biol. Chem.*, **91**, 95 (1931); **95**, 19 (1932).

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(7) Cf. J. Kenyon, *Org. Syntheses*, Coll. Vol. I, 418 (1941).