through the sodium salt. The crystalline material melted at 135–136° and weighed 0.18 g. (26.8%).

Anal. Calc'd for $C_{12}H_7AsCl_2$: As, 25.2. Found: As, 25.1.

3-Bromodibenzarsenolic acid (I, R_1 = H, R_2 = Br). This compound was prepared from 3-aminodibenzarsenolic acid using a procedure similar to that described above for the preparation of the 2-chloro derivative. The diazonium solution in this case was added to a suspension of copper[I] bromide in concentrated hydrobromic acid. The crude product was purified by dissolution in sodium carbonate solution, and, after charcoaling the solution, was reprecipitated by the addition of excess hydrochloric acid. The compound melted at 314–315° and was obtained in 54% yield. Titration in ethanolic solution with standard alkali using Thymolphthalein as an indicator gave neutral equivalents of 341 and 337, the theoretical value being 339.

Anal. Calc'd for $C_{12}H_8AsBrO_2$: As, 22.1. Found: As, 22.0.

3-Bromo-5-chlorodibenzarsenole (II, R_1 = H, R_2 = Br, X = Cl). 3-Bromodibenzarsenolic acid (2 g.) together with 10 g. of amalgamated zinc and 100 ml. of benzene were placed in a 3-necked flask equipped with stirrer, water condenser, and dropping-funnel. Concentrated hydrochloric acid (about 50 ml.) was added slowly over a period of four to five hours until the solid had almost completely dissolved in the benzene layer, gentle warming with a water-bath being applied all the while. The benzene layer was partially evaporated to give the crystalline product in long needles weighing 0.8 g. (40%) and melting at 176°. The compound was not analyzed for arsenic.

3-Chlorodibenzarsenolic acid (I, R_1 = H, R_2 = Cl). This compound was prepared from 3-aminodibenzarsenolic acid using the procedure indicated above for the 2-chloro compound. The product was obtained in 44% yield and melted at 313–314°.

Anal. Calc'd for $C_{12}H_8AsClO_2$: As, 25.5. Found: As, 25.6.

3,5-Dichlorodibenzarsenole (II, R_2 = H; R_1, X = Cl). Finely divided 3-chlorodibenzarsenolic acid (0.2 g.) was suspended in 5 ml. of glacial acetic acid. The mixture was warmed to 80° on a water-bath and phosphorus trichloride (1 ml.) was added dropwise until a clear solution was effected. The solution then was heated for an additional 15 minutes on the water-bath and was kept in the ice chest overnight. The crystalline material was filtered and dried. The yellow compound was recrystallized from glacial acetic acid and weighed 0.1 g. (50%) and melted at 154–155°. In a similar manner, using chloroform as a reaction solvent and recrystallization medium, phosphorus tribromide converts 3-chlorodibenzarsenolic acid to *3-chloro-5-bromodibenzarsenole* (II, R_1 = H, R_2 = Cl, X = Br) in 43% yield, melting at 153°. No elemental analysis was made on these compounds.

3-Cyanodibenzarsenolic acid (I, R_1 = H, R_2 = CN). 3-Aminodibenzarsenolic acid (3 g., 0.011 mole) was diazotized at 0–5° with 1.2 g. (0.012 mole) of sodium nitrite in dilute hydrochloric acid medium. The cold diazonium solution was added dropwise to a mixture of 3.16 g. (0.034 mole) of copper[I] cyanide, 1.47 g. (0.030 mole) of sodium cyanide, and 50 ml. of water held at 60–70°. The mixture then was heated on a boiling water-bath for 20 minutes and the insoluble portion was isolated by filtration. Purification was effected by dissolution in sodium carbonate, charcoaling, and reprecipitation with hydrochloric acid. A product was obtained weighing 1.2 g. (38.7%), remaining unmelted at 360° with some decomposition.

Anal. Calc'd for $C_{13}H_8AsNO_2$: As, 26.3. Found: As, 25.9.

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Organosilanes Containing Aralkyl Groups

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Rochow's[1] tables note the physical properties of tetrabenzyl silane and a group of organosilanes containing the benzyl group in combination with a variety of short-chained alkyl groups. Recently, Maienthal, *et al.*[2] reported the preparation of diphenyldibenzylsilane and phenyltribenzylsilane. The use of triphenylbenzylsilane has been mentioned[3] but its method of preparation was not described. The compound was prepared in this laboratory[4] by the interaction of benzylmagnesium chloride and triphenylchlorosilane. Earlier,[5] it was prepared by the reaction of phenyllithium with benzyltriethoxysilane, the latter being made by the interaction of benzylmagnesium chloride and chlorotriethoxysilane.

We had prepared the two compounds reported by Maienthal, *et al.* and had also made several other organosilanes containing one or more benzyl, *beta*-phenylethyl, or *gamma*-phenylpropyl radicals in a variety of combinations. Our sample of dibenzyldiphenylsilane was found to have the same melting point as that of Maienthal and co-workers. However, our sample of phenyltribenzylsilane melted at 41–42.5° while that reported in the literature[2] melted at 130°. A second experiment in this laboratory confirmed the m.p. to be 41–42.5°.[6a] After recrystallization, the melting points of our samples became 59–60°. However, no change in the infrared spectra could be detected, thus indicating the two different melting materials to be isomorphic.[6b] The yield of tribenzylphenylsilane was improved over the 59% of viscous liquid reported by Maienthal, *et al.*[2] and a 56% yield obtained in our first experiment. The two experiments giving low yields were carried out by the reaction of three equivalents of benzylmagnesium chloride and one equivalent of phenyltrichlorosilane during a 4–8 hour heating period without any solvent. By re-

(1) Rochow, *An Introduction to the Chemistry of the Silicones*, 2nd edition, John Wiley and Sons, New York, N. Y., 1951, pp. 171–172.

(2) Maienthal, Hellmann, Haber, Hymo, Carpenter, and Carr, *J. Am. Chem. Soc.*, **76**, 6392 (1954).

(3) Gilman and Hartzfeld, *J. Am. Chem. Soc.*, **73**, 5878 (1951).

(4) Miller, Doctoral Dissertation, Iowa State College, (1950).

(5) Melvin, Doctoral Dissertation, Iowa State College, 1954.

(6a) Through the kind cooperation of Drs. Hellmann and Haber, their compound was shown to be identical with tetrabenzylsilane by a mixture melting point in their laboratories and by infrared analyses of their compound and authentic tetrabenzylsilane in this laboratory. The tetrabenzylsilane may have resulted from high temperature disproportionation of the tribenzylphenylsilane.

(6b) See Smart, Gilman, and Otto, *J. Am. Chem. Soc.*, **77**, 5193 (1955) for a report on isomeric tetra-*o*-tolylsilanes.

fluxing in a xylene solution overnight there was isolated 79.5% of the desired compound.

All other derivatives were prepared by heating a chlorosilane and a Grignard reagent after distilling most of the solvent. The chlorosilanes were all commercial products[7a] with the exception of benzyltrichlorosilane which was prepared by a method reported in the literature.[7b] The complete series of compounds having the generic formula $(C_6H_5)_{4-x}SiR_x$, where R is either *gamma*-phenylpropyl or *beta*-phenylethyl and x is 1,2,3, or 4 were prepared. In addition cyclohexyl- and *n*-dodecyl-tribenzylsilanes were prepared, as well as tri-*gamma*-phenylpropyl- and tri-*n*-octadecyl-benzylsilanes.

EXPERIMENTAL[8]

Described below is our second experiment with benzylmagnesium chloride and phenyltrichlorosilane. All other experiments were carried out in a similar manner except that a period of heating for 4–5 hours at 150–160° in the absence of solvent was employed in the place of refluxing in xylene overnight. The amount of Grignard reagent used was always in excess of the theoretical quantity to assure replacement of all available chlorine bonded to silicon. Alkyl bromides were employed to prepare all the Grignard reagents except the benzyl derivative. The results of these experiments are shown in Table I. Infrared analyses were run on all compounds and confirm the structures assigned. Of special value were the bands at 3.31 μ (aromatic C—H), 3.5 μ (aliphatic C—H) and 9.0–9.1 μ (phenyl-silicon). The ratios of the strengths of the bands mentioned conform to the relative amounts of these structures present in the compounds.

Phenyltribenzylsilane. Benzylmagnesium chloride was prepared in the usual manner from 9.6 g. (0.395 g.-atom) of magnesium turnings and 50.2 g. (45.7 ml., 0.395 mole) of benzyl chloride in 174 ml. of dry ether. The yield was indicated to be 95% by acid titration. The Grignard reagent was added, with mechanical stirring, to 19.9 g. (15.0 ml., 0.0939 mole) of phenyltrichlorosilane suspended in 50 ml. of dry ether. A dry nitrogen atmosphere was maintained at all times. The ether solution was refluxed for 4 hours after which most of the ether was distilled by adding 400 ml. of dry xylene and heating to the reflux temperature until 165 ml. of ether distilled, leaving a total volume of *ca.* 460 ml. The xylene solution was refluxed overnight. Acid titration of an aliquot showed about 0.095 mole of unreacted benzylmagnesium chloride. The calculated excess was 0.093 mole. The closeness of the two values was taken to indicate complete reaction. The reaction mixture was hydrolyzed with saturated ammonium chloride solution. The organic layer was separated, and the aqueous layer was extracted twice with 150-ml. portions of ether. After drying over sodium sulfate, the solvents were distilled. The resulting gummy oil then was distilled under reduced pressure and the fraction boiling at 229–234°/1.1 mm. was collected (23.9 g., 79.5%). Upon seeding with a few crystals (m.p. 41–42.5°) from the first experiment the whole mass crystallized to give a material (m.p. 40–42°). The melting point was raised by recrystallization from petroleum ether (b.p. 60–70°) to a constant melting point of 59–60°. Recrystallization of material from the first experiment gave white crystals (m.p. 59–60°). Mixture melting points confirmed the samples to be the same.

TABLE I
ORGANOSILANES CONTAINING ARALKYL GROUPS

Compound	Yield, %	M.p., °C.	B.p. °C.	B.p. Mm.	n_D^{20}	d_{20}^{20}	MR[b] Calc'd	MR[b] Expt'l	Analyses Silicon Calc'd	Analyses Silicon Found	Analyses Carbon Calc'd	Analyses Carbon Found	Analyses Hydrogen Calc'd	Analyses Hydrogen Found
$(C_6H_5CH_2CH_2CH_2)_4Si$	19	—	230–240	0.1	1.5623	1.001	164.8	163.8	5.57	5.61, 5.73	—	—	—	—
$(C_6H_5CH_2CH_2CH_2)_3SiC_6H_5$	52	59.5–60					6.08		6.25, 5.94		85.64	85.66	8.28	8.30
$(C_6H_5CH_2CH_2CH_2)_2Si(C_6H_5)_2$	57	—	252–253	.6	1.5930[a]	1.031[a]	137.2	138.6	6.68	6.80, 6.84	85.65	86.34	7.67	7.68
$C_6H_5CH_2CH_2CH_2Si(C_6H_5)_3$	42	62.5–64					7.61		7.58, 7.75		—	—	—	—
$(C_6H_5CH_2CH_2CH_2)_3SiCH_2C_6H_5$	26	—	214–217	.04	1.5745	1.024	155.6	153.2	5.88	5.65, 5.85	—	—	—	—
$(C_6H_5CH_2CH_2)_4Si$	28	76–76.5							6.25	6.29, 6.55	85.65	85.86	8.10	8.26
$(C_6H_5CH_2CH_2)_3SiC_6H_5$	47	62–62.7							6.68	6.92, 6.75	—	—	—	—
$(C_6H_5CH_2CH_2)_2Si(C_6H_5)_2$	40	74–74.5							7.17	7.25, 7.30	85.65	85.70	7.19	7.28
$C_6H_5CH_2CH_2Si(C_6H_5)_3$	38	146–147							7.71	7.76, 8.05	85.65	85.68	6.64	6.69
$(C_6H_5CH_2)_3SiC_6H_{11}$[c]	45	—	198–200	.25	1.5879	0.848	124.5	124.8	7.31	7.27, 7.33	—	—	—	—
$(C_6H_5CH_2)_3SiCH_2(CH_2)_{10}CH_3$	65	—	215–217	.06	1.5481	0.970	154.4	154.2	5.97	6.07, 5.87	84.18	84.34	9.85	9.87
$C_6H_5CH_2Si[CH_2(CH_2)_{16}CH_3]_3$	28	—	299–302	.005	1.4797	0.857	290.8	291.5	3.19	3.17, 3.27	83.29	82.80	13.62	13.48

[a] Temperature for index of refraction and density was 29°. [b] The calculated value of the molar refractions are based on the values of Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940) and the values of Warrick, *J. Am. Chem. Soc.*, **68**, 2455 (1946). [c] The C_6H_{11} represents the cyclohexyl radical.

(7a) Dow Corning Corp. products.

(7b) Melzer, *Ber.*, 41, 3393 (1908).

(8) All melting points are uncorrected.

(9) Silicon analyses were carried out by the procedure of Gilman, Hofferth, Melvin, and Dunn, *J. Am. Chem. Soc.*, **72**, 5767 (1950).

Anal.[9] (On compound prepared in first experiment). Calc'd for $C_{27}H_{26}Si$: Si, 7.43; C, 85.65; H, 6.92. Found: Si, 7.66, 7.61; C, 86.61, 85.91; H, 7.16, 7.24.

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1-Phenyl-4-methyl-6-pyridazone-3-carboxylic-Acid Derivatives

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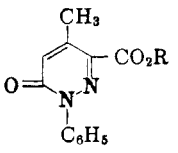
1-Phenyl-4-methyl-6-pyridazone-3-carboxylic acid (Ia), which has been made available for the first time by the rearrangement of γ-keto-β-



I

a, R = H
b, R = CH_3
c, R = C_2H_5
d, R = $N(C_2H_5)_2$
e, R = NHC_6H_5

methylglutaconic anhydride phenylhydrazone,[2] has been converted to its methyl ester (Ib), ethyl ester (Ic), N,N-diethylamide (Id), and anilide (Ie). The preparation and properties of these derivatives are recorded in this Note. All were prepared from the acid chloride which was in turn prepared from the acid.

EXPERIMENTAL

1-Phenyl-4-methyl-6-pyridazone-3-carboxylic acid chloride. One gram of 1-phenyl-4-methyl-6-pyridazone-3-carboxylic acid was warmed one hour with 15 ml. of thionyl chloride. The yellow residue remaining after removal of the excess thionyl chloride under a vacuum was recrystallized from carbon tetrachloride to give 1.1 g. of white needles melting at 135°. This chloride was used in the following reactions.

Methyl 1-phenyl-4-methyl-6-pyridazone-3-carboxylate (Ib). The acid chloride (0.5 g.) was refluxed one hour with absolute methanol. Evaporation of the solvent left a solid which was recrystallized from petroleum ether to give 0.4 g. (76.3%) of the methyl ester as white needles, m.p. 125°.

Anal. Calc'd for $C_{13}H_{12}N_2O_3$: N, 11.47. Found: N, 11.16.

Ethyl 1-phenyl-4-methyl-6-pyridazone-3-carboxylate (Ic). The acid chloride (0.5 g.) was refluxed 2.5 hours with 15 ml. of absolute ethanol. Dilution with water precipitated a solid which was recrystallized from ethyl acetate to give 0.5 g. (83.5%) of the ethyl ester as white needles, m.p. 102°.

Anal. Calc'd for $C_{14}H_{14}N_2O_3$: N, 10.85. Found: N, 10.65.

N,N-Diethyl-1-phenyl-4-methyl-6-pyridazone-3-carboxamide (Id). To a solution of 0.5 g. of the acid chloride in 25 ml. of hot toluene was added 2 ml. of diethylamine. After 0.5 hour at reflux the mixture was filtered hot to separate the amine hydrochloride and was cooled. Addition of 25 ml. of petroleum ether precipitated a crude product. On recrystallization from petroleum ether 0.4 g. (66%) of the N,N-diethylamide, m.p. 54°, was obtained.

Anal. Calc'd for $C_{16}H_{21}N_3O_3$: N, 13.85. Found: N, 13.75.

1-Phenyl-4-methyl-6-pyridazone-3-carboxanilide (Ie). To a solution of 0.5 g. of the acid chloride in 25 ml. of hot toluene was added 2 ml. of freshly distilled aniline. After one hour at reflux, the mixture was filtered hot to separate the aniline hydrochloride. On cooling the crude product precipitated. Recrystallization from a mixture of equal parts of toluene and petroleum ether gave 0.4 g. (70%) of the anilide as white needles, m.p. 259°.

Anal. Calc'd for $C_{18}H_{15}N_3O_2$: N, 13.76. Found: N, 13.89.

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A Wayward Prevost Oxidation

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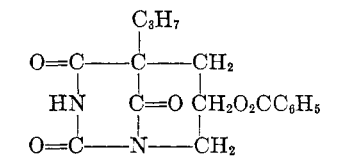
In connection with our study of central nervous system depressants, we were interested in some derivatives of 5-isopropyl-5-(2′,3′-dihydroxypropyl)barbituric acid. A likely approach to the dibenzoate of this compound appeared to be through a Prevost[1] oxidation of the commercially available 5-isopropyl-5-allylbarbituric acid using the silver benzoate-iodine complex. The product we obtained, however, did not analyze for the expected compound. It gave a blue color with alcoholic cobalt nitrate and potassium hydroxide [Mohrschulz[2] test for barbituric acid], but unlike this test for the starting material, the color disappeared with continued addition of the alcoholic potassium hydroxide. Rather the analysis corresponded to the formula



This structure can be explained by the action of the silver benzoate-iodine complex to give 5-

(1) The authors wish to acknowledge support of this research through a grant (NSF-G55) from the National Science Foundation.

(2) Wiley and Jarboe, Jr., *J. Am. Chem. Soc.*, **77**, 403 (1955).

(1) Prevost, *Compt. rend.*, **196**, 1129 (1933); **197**, 1661 (1933); Prevost and Lutz, *Compt. rend.*, **198**, 2264 (1934); Prevost and Wiemann, *Compt. rend.*, **204**, 700, 989 (1937).

(2) Mohrschulz, *Munchen med. Wochschr.*, **81**, 672 (1934).