(*b*). *1-Bromo-7-ethoxyphenazine.* When 1.0 g. of 6-bromo-4′-ethoxy-2-nitrodiphenylamine was mixed with 1.3 g. of ferrous oxalate dihydrate and 10 g. of granulated lead, heating the mixture for 12 minutes in a bath at 255–260° gave 0.63 g. product on vacuum-sublimation from the whole ground sublimation mixture at 270° and about 0.5 mm. This product had a good deal of red material in it, however, so it was again subjected to treatment with ferrous oxalate dihydrate and granulated lead, as before, giving 0.50 g. of light-yellow microcrystals, m.p. 156–157°, on purification by vacuum-sublimation at about 0.5 mm., from a bath at 270°.

Anal. Calc'd for $C_{14}H_{11}BrN_2O$: C, 55.5; H, 3.66. Found: C, 55.9; H, 3.80.

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Ethyl 4-Formylphenoxyacetate

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Received May 31, 1956

The preparation of ethyl 4-formylphenoxyacetate (I) from 4-formylphenoxyacetic acid and ethyl alcohol has been reported.[1] The product was impure, disintegrating at 100° and becoming completely liquid at 155°.

We wish to report the preparation of I from *p*-hydroxybenzaldehyde and ethyl bromoacetate using the potassium carbonate method employed by A. Robertson[2] for the *ortho* isomer. Our product, after recrystallization, melted at 42–42.5° and the analyses for it and the oxime derivative were consistent with the values calculated for I and its oxime. The infrared spectrum of the product indicated the presence of ester, arylaldehyde, and phenoxy groupings and *para* substitution.

We submit this evidence in correction of the prior literature on the compound I.

EXPERIMENTAL

Ethyl 4-formylphenoxyacetate (I). Ethyl bromoacetate (167 g.), *p*-hydroxybenzaldehyde (122 g.), potassium carbonate (138 g.), and dry acetone (500 ml.) were stirred vigorously under reflux conditions for two hours. The mixture then was poured, with stirring, into two liters of ice-water. The resulting solid was filtered, washed well with ice-water and dried (1) by pressing with a rubber dam and (2) over calcium chloride in a vacuum desiccator.

The light yellow product melted at 35–38° and amounted to 175 g. (84.1%). One crystallization from ethanol raised the m.p. to a constant 42–42.5° (uncorr.).

Anal. Calc'd for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81. Found: C, 63.53; H, 5.59.

Oxime. The oxime was prepared according to method A in Shriner and Fuson, *Identification of Organic Compounds*, Second Edition, John Wiley and Sons, New York, N. Y., 1940, page 167. The oxime (white needles from alcohol-water) melted at 61–62° (uncorr.).

Anal. Calc'd for $C_{11}H_{13}NO_4$: C, 59.19; H, 5.87. Found: C, 58.81; H, 5.60.

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(1) Elkan, *Ber.*, 19, 3042 (1886).

(2) Robertson, *J. Chem. Soc.*, 489 (1933).

The Chlorination of Phenyldimethylsilane[1]

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Received June 4, 1956

It has been shown that at 80° the relative reactivities of the α- and β-hydrogen atoms of cumene towards a chlorine atom are 12.8 : 1.[2] It would be of interest if similar data on the reactivities of the hydrogen atoms of the silicon analog of cumene, phenyldimethylsilane, were available. Since silicon-hydrogen bonds usually are weaker than carbon-hydrogen bonds,[3] it is expected that generally a chlorine atom will react with a silicon-hydrogen bond in preference to a carbon-hydrogen bond. In the case of cumene and its silicon analog this generality may not apply since the 2-phenyl-2-propyl radical undoubtedly possesses considerably more resonance stabilization than the phenyldimethylsilyl radical.[4] In fact, towards the highly selective peroxy radical the α-hydrogen atom of cumene is about 200 times as reactive as the α-hydrogen atom of phenyldimethylsilane, presumably because of this resonance effect.[5]

When phenyldimethylsilane was photochemically chlorinated in the liquid phase at 80° we observed that substitution at the α-position occurred 30 times as readily as substitution at the β-position. However, further investigation demonstrated that the substitution reaction occurred as readily in the dark as in the presence of intense illumination. Apparently an ionic substitution reaction occurred so readily that the free radical reaction was completely overshadowed. The cleavage of silicon-hydrogen bonds by bromine in the dark has been observed previously.[6] Presumably ionic substitution by chlorine occurs in a similar manner involving

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(1) Directive Effects in Aliphatic Substitutions. VIII.

(2) G. A. Russell and H. C. Brown, *J. Am. Chem. Soc.*, **77**, 4031 (1955).

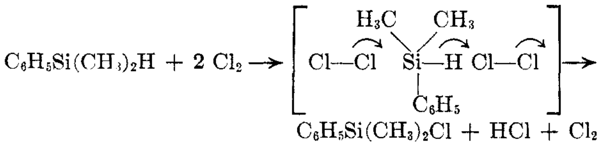
(3) Unfortunately, bond dissociation energies for various silicon-hydrogen bonds are not available. The silicon-hydrogen bond strength of silane (80.8 kcal. mole^{-1}) is 10 kcal. mole^{-1} less than the carbon-hydrogen bond energy of methane (90.8 kcal. mole^{-1}) [M. L. Huggins, *J. Am. Chem. Soc.*, **75**, 4123 (1953)].

(4) H. Gilman and G. E. Dunn, *Chem. Revs.*, **52**, 77 (1953).

(5) G. A. Russell, *J. Am. Chem. Soc.*, **78**, 1047 (1956).

(6) A. Stock and C. Somieski, *Ber.*, **50**, 1739 (1917); C. Eaborn, *J. Chem. Soc.*, 2755 (1949); W. H. Nebergall and O. H. Johnson, *J. Am. Chem. Soc.*, **71**, 4022 (1949); W. H. Nebergall, *J. Am. Chem. Soc.*, **72**, 4702 (1950).

electrophilic attack on hydrogen and nucleophilic attack on silicon.[7]



$$C_6H_5Si(CH_3)_2H + 2\ Cl_2 \rightarrow \left[Cl{-}Cl\quad \overset{H_3C\ \ CH_3}{\underset{C_6H_5}{Si}}{-}H\quad Cl{-}Cl \right] \rightarrow C_6H_5Si(CH_3)_2Cl + HCl + Cl_2$$

In both the photochemical and dark reactions of chlorine with phenyldimethylsilane it was observed that only substitution occurred; one mole of hydrogen chloride and one mole of alkyl and silyl chlorides were formed for each mole of chlorine added. This demonstrates that addition of chlorine to the aromatic ring did not occur and that cleavage of the silicon-phenyl bond by chlorine,[8] or by hydrogen chloride,[9] or the cleavage of the silicon-hydrogen bond by hydrogen chloride,[10] did not compete with the cleavage of a silicon-hydrogen bond by chlorine. If any of these reactions had occurred less than one mole of hydrogen chloride would have been formed per mole of alkyl and silyl chlorides.

The fact that the chlorination product formed in the absence of illumination could be quantitatively and easily hydrolyzed indicates that the reaction product was phenyldimethylchlorosilane and that aromatic substitution did not occur. The small amount of unhydrolyzable chloride formed in the photochemical chlorination has thus been attributed to free radical attack on the methyl groups of phenyldimethylsilane.

EXPERIMENTAL

Preparation of phenyldimethylsilane. Phenyldimethylchlorosilane was prepared by Dr. J. R. Ladd by the reaction of methylmagnesium chloride and phenyltrichlorosilane. Material boiling at 85.5° at 21 mm. was reduced by lithium aluminum hydride. To 10 g. of lithium aluminum hydride in 200 ml. of ethyl ether 128 g. of phenyldimethylchlorosilane was added over a three-hour period. The solution was refluxed for three hours before the excess lithium aluminum hydride was destroyed by ethyl acetate. The reaction mixture was poured over ice, the ether layer separated from the aqueous layer, and the aqueous layer extracted twice with 200 ml. of ether. The etheral solution was dried over sodium sulfate and distilled until a pot temperature of 85° was reached. The residue did not give a qualitative test for chlorine. The residue upon distillation through a small packed column (*ca.* 5 plates) under nitrogen gave 99 g. (97%) of phenyldimethylsilane, b.p. 57° at 20 mm., n_D^{20} 1.4988, d_4^{20} 0.876; lit.[11] n_D^{20} 1.4995, d_D^{20} 0.889.

Anal. Calc'd for $C_8H_{12}Si$: C, 70.5; H, 8.8; Si, 20.6. Found: C, 70.5; H, 9.1; Si, 20.6.

The molar refraction, 45.62, was in excellent agreement with the value of 45.73 calculated from the data of Warrick.[12]

Chlorination procedure. The chlorination procedure was similar to that used in the chlorination of cumene.[2] Phenyldimethylsilane was placed in a 200-ml. three-necked flask containing a True-Bore stirrer, a gas inlet capillary tube, and a Dry Ice condenser. The amount of chlorine used was estimated from measurement of the volume of liquid chlorine at −34°. The chlorine from a calibrated tube was allowed to vaporize into a stream of dry nitrogen and after passing through a 500-ml. gas mixing bulb was introduced in the phenyldimethylsilane through the capillary tube. The flask was maintained at 80 ± 1° by a water-bath and was illuminated by a 300-watt bulb approximately 2 inches from the flask. A large excess of nitrogen was used and after passing through the Dry Ice condenser, hydrogen chloride was removed from the nitrogen by a sodium hydroxide trap. Chlorine could not be detected in the exit gases from the chlorination flask. After the desired amount of chlorine had been introduced over a one-hour period, the solution was degassed for several hours with dry nitrogen to remove the last trace of hydrogen chloride. The sodium hydroxide trap was analyzed for chlorine content as was the chlorination product.

The chlorination product was hydrolyzed by shaking with water and the aqueous layer analyzed for chloride ion. Unreacted phenyldimethylsilane had to be completely removed from the aqueous layer since it reduced silver ion. The same amount of chloride ion was found when the hydrolysis was conducted for $^1/_2$, 2, or 24 hours.

Chlorination results. Photochlorination of 0.24 mole of phenyldimethylsilane at 80° with 0.060 ± .006 mole of chlorine yielded 0.0538 mole of hydrogen chloride. The chlorination product contained 0.0539 mole of alkyl and silyl chlorides from which 0.0523 mole of chlorine ion was immediately liberated upon hydrolysis. The remaining 0.0016 mole of chlorine was not ionized by prolonged contact with water. The hydrolyzable chloride is undoubtedly phenyldimethylchlorosilane while the unhydrolyzable chloride is most likely phenyl(chloromethyl)methylsilane.

When the above experiment was repeated in the absence of illumination the amounts of hydrogen chloride, total alkyl and silyl chlorides and hydrolyzable chloride were identical within experimental error. This result indicates that the 0.0016 mole of unhydrolyzable chloride formed in the photochemical reaction is not a product of ionic aromatic substitution, but most likely results from the attack of a chlorine atom on a methyl group of phenyldimethylsilane.

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[7] D. R. Deans and C. Eaborn, *Research*, **5**, 592 (1952); *J. Chem. Soc.*, 3169 (1954).

[8] B. O. Pray, L. H. Sommer, G. M. Goldberg, K. T. Kerr, P. A. Di Giorgio and F. C. Whitmore, *J. Am. Chem. Soc.*, **70**, 433 (1948).

[9] H. Gilman and F. J. Marshall, *J. Am. Chem. Soc.*, **71**, 2066 (1949).

[10] H. E. Opitz, J. S. Peake, and W. H. Nebergall, *J. Am. Chem. Soc.*, **78**, 292 (1956).

[11] R. A. Benkeser and D. J. Foster, *J. Am. Chem. Soc.*, **74**, 5314 (1952).

[12] E. L. Warrick, *J. Am. Chem. Soc.*, **68**, 2455 (1946).

Polynitrogen Systems from the Hydrazinocarbonic Acids. Part VII. Some Reactions of 1-Phenyl-5-methylmercaptotetrazole

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Received June 6, 1956

In connection with other work, it became of interest to examine some properties of 1-phenyl-5-

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