

(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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The preparation of ethyl 4-formylphenoxyacetate (I) from 4-formylphenoxyacetic acid and ethyl alcohol has been reported.<sup>1</sup> 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<sup>2</sup> 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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### The Chlorination of Phenyltrimethylsilane<sup>1</sup>

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It has been shown that at 80° the relative reactivities of the  $\alpha$ - and  $\beta$ -hydrogen atoms of cumene towards a chlorine atom are 12.8:1.<sup>2</sup> It would be of interest if similar data on the reactivities of the hydrogen atoms of the silicon analog of cumene, phenyltrimethylsilane, were available. Since silicon-hydrogen bonds usually are weaker than carbon-hydrogen bonds,<sup>3</sup> 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 phenyltrimethylsilyl radical.<sup>4</sup> In fact, towards the highly selective peroxy radical the  $\alpha$ -hydrogen atom of cumene is about 200 times as reactive as the  $\alpha$ -hydrogen atom of phenyltrimethylsilane, presumably because of this resonance effect.<sup>5</sup>

When phenyltrimethylsilane was photochemically chlorinated in the liquid phase at 80° we observed that substitution at the  $\alpha$ -position occurred 30 times as readily as substitution at the  $\beta$ -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.<sup>6</sup> Presumably ionic substitution by chlorine occurs in a similar manner involving

(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<sup>-1</sup>) is 10 kcal. mole<sup>-1</sup> less than the carbon-hydrogen bond energy of methane (90.8 kcal. mole<sup>-1</sup>) [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).

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

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