

**Dinitrate Ester:**  $n_D^{20}$  1.4688,  $d_{20}^{20}$  1.191. *Anal.* Calcd. for  $C_{11}H_{18}N_2O_8$ : C, 43.14; H, 5.92; N, 9.15. Found: C, 42.95; H, 6.08; N, 8.82.

**Monoallyl Pentaerythritol Ether:** b.p. 148–150° (1 mm.),  $n_D^{20}$  1.4843,  $d_{20}^{20}$  1.135, was obtained in 35% yield. *Anal.* Calcd. for  $C_8H_{16}O_4$ : C, 54.53; H, 9.15. Found: C, 54.50; H, 9.12.

**Trinitrate Ester:**  $n_D^{20}$  1.4797,  $d_{20}^{20}$  1.373. *Anal.* Calcd. for  $C_8H_{16}N_3O_{10}$ : C, 30.87; H, 4.21; N, 13.50. Found: C, 31.01; H, 3.93; N, 13.53.

**Monopropyl Pentaerythritol Ether.**—A solution of 35.2 g. of monoallyl pentaerythritol ether in 400 ml. of 95% ethanol was hydrogenated at room temperature and atmospheric pressure, using 0.2 g. of platinum oxide. The product was distilled at 125° (1 mm.),  $n_D^{20}$  1.4662,  $d_{20}^{20}$  1.096. *Anal.* Calcd. for  $C_8H_{16}O_4$ : C, 53.91; H, 10.18. Found: C, 53.57; H, 10.25.

**Trinitrate Ester:**  $n_D^{20}$  1.4654,  $d_{20}^{20}$  1.332. *Anal.* Calcd. for  $C_8H_{16}N_3O_{10}$ : C, 30.67; H, 4.83; N, 13.42. Found: C, 30.67; H, 4.77; N, 13.65.

**Dipropyl Pentaerythritol Ether.**—A solution of 25 g. of diallyl pentaerythritol in 175 ml. of 95% ethanol was hydrogenated at room temperature and atmospheric pressure, using 0.2 g. of platinum oxide. The product was distilled at 115° (1 mm.),  $n_D^{20}$  1.4461,  $d_{20}^{20}$  0.993. *Anal.* Calcd. for  $C_{11}H_{24}O_4$ : C, 59.97; H, 10.98. Found: C, 59.83; H, 11.06.

**Dinitrate Ester:**  $n_D^{20}$  1.4470,  $d_{20}^{20}$  1.144. *Anal.* Calcd. for  $C_{11}H_{22}N_2O_8$ : C, 42.57; H, 7.15; N, 9.03. Found: C, 42.59; H, 7.15; N, 9.15.

**Monoglycerol Pentaerythritol Ether.**—A mixture of 15 g. of monoallyl pentaerythritol ether, 100 ml. of 95% ethanol and 0.015 g. of osmium tetroxide dissolved in 5 ml. of water was placed in a three-necked flask equipped with a stirrer and dropping funnel. The temperature of the mixture was adjusted to 20° and 100 g. of cold 3% hydrogen peroxide was added dropwise with slow stirring. The reaction mixture was maintained at 0° overnight, then concentrated and subjected to molecular distillation. The distillate formed sugar-like crystals which softened at 55° and melted at 59–61°. *Anal.* Calcd. for  $C_8H_{16}O_6$ : C, 45.71; H, 8.64. Found: C, 45.91; H, 8.63.

**Pentanitate Ester:** m.p. 54.5–55.0°;  $n_D^{20}$  1.531, 1.520;  $d_{20}^{20}$  1.57. *Anal.* Calcd. for  $C_8H_{16}N_5O_{16}$ : C, 22.03; H, 3.00; N, 16.09. Found: C, 22.15; H, 2.97; N, 15.92.

**Diglycerol Pentaerythritol Ether.**—Diglycerol pentaerythritol ether was prepared by hydroxylating diallyl pentaerythritol ether. The method of preparation was similar to that used for the preparation of monoglycerol pentaerythritol ether from monoallyl pentaerythritol ether. The product crystallized after molecular distillation, m.p. 72.5–74.0°, softening at 69°, when heated rapidly (Fisher-Johns melting point apparatus). *Anal.* Calcd. for  $C_{11}H_{24}O_8$ : C, 46.47; H, 8.51. Found: C, 46.67; H, 8.43.

**Hexanitate Ester:**  $n_D^{20}$  1.4878,  $d_{20}^{20}$  1.540. *Anal.* Calcd. for  $C_{11}H_{18}N_6O_{20}$ : C, 23.83; H, 3.27; N, 15.16. Found: C, 23.96; H, 3.08; N, 14.87.

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## Functional Aromatic Silanes

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The preparation of aromatic silane derivatives containing nuclear substituted functional groups has been the subject of a series of recent investigations.<sup>1–6</sup>

Roberts, McElhill and Armstrong<sup>1</sup> described the

(1) J. D. Roberts, E. A. McElhill and R. Armstrong, *THIS JOURNAL*, **71**, 2925 (1949).

(2) J. L. Speier, *ibid.*, **74**, 1003 (1952).

(3) R. A. Benkeser and P. E. Brumfield, *ibid.*, **73**, 4770 (1951).

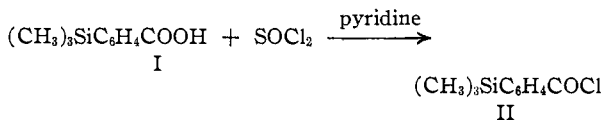
(4) D. W. Lewis and G. C. Gainer, *ibid.*, **74**, 2931 (1952).

(5) B. N. Dolgov and O. K. Panina, *Zhur. Obshchei Khim. (J. Gen. Chem.)*, **13**, 1129 (1948); *C. A.*, **43**, 1737 (1949).

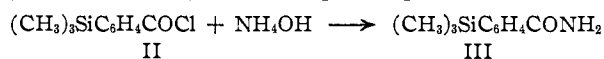
(6) A. J. Barry and J. W. Gilkey, U. S. Patent 2,601,237 (1952).

preparation of *m*- and *p*-trimethylsilylbenzoic acid (I) via the Grignard reaction as well as by means of the corresponding lithium derivative.

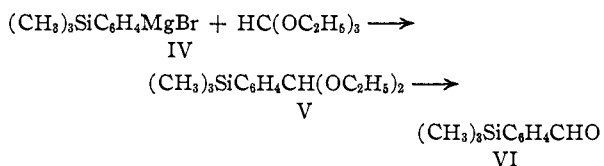
In the present investigation the preparation of the *p*-trimethylsilylbenzoyl chloride (II) and the corresponding amide (III) was undertaken. The synthesis of the *p*-trimethylsilylbenzoyl chloride presented somewhat of a problem because of the well-known tendency of silyl groups connected to an aromatic ring to undergo cleavage in acid medium particularly at elevated temperatures. It therefore became necessary to adopt a procedure using mild conditions and working if possible at low temperatures. This was accomplished by using thionyl chloride in the presence of pyridine as a hydrohalogen acceptor



The above reaction required less than ten minutes and the resulting acid chloride reacted with an excess of cold concd. ammonium hydroxide which yielded instantly the corresponding amide (III).



Silicon-containing aromatic aldehydes have hitherto not been reported in literature. *p*-Trimethylsilylbenzaldehyde (VI) was prepared by reaction of *p*-trimethylsilylphenylmagnesium bromide (IV) with ethyl orthoformate followed by hydrolysis of the resulting acetal (V)



The acetal was not isolated in pure form but was used directly in the hydrolysis step to yield the aldehyde (VI). Remarkable is the fact that *p*-trimethylsilylbenzaldehyde can be steam distilled from an acid solution without undergoing cleavage of the C (phenyl)–Si bond.

The synthesis of silicon-containing phenols is of very recent origin. Gilman and Nobis<sup>7</sup> in 1950 reported several unsuccessful attempts to prepare *o*- and *m*-trimethylsilylphenol by various methods and concluded that such phenols were unstable structures.

Sunthakar and Gilman,<sup>8</sup> however, succeeded in preparing trimethyl- and triphenylsilylnaphthols by the reaction of chlorosilanes with the corresponding naphthyllithium compounds.

After the present work was completed Speier<sup>2</sup> reported the successful synthesis of *o*- and *p*-trimethylsilylphenol by the reaction of *o*- and *p*-chlorophenoxytrimethylsilane with sodium and trimethylchlorosilane. The same investigator also reported that magnesium could not be used in place of sodium when used with *p*-bromophenoxytrimethylsilane.

(7) H. Gilman and J. F. Nobis, *THIS JOURNAL*, **72**, 2629 (1950).

(8) S. V. Sunthakar and H. Gilman, *ibid.*, **72**, 4884 (1950).

