Following an intermediate fraction, there was obtained 9.5 g. (12.7%) of 4-isopropylanisole boiling all at 204°, $n^{28}D$ 1.5000 (lit.[25] b.p. 208° at 728 mm., $n^{7}D$ 1.513).

Anal. Calcd. for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 80.29; H, 9.64.

The remainder of the material had a boiling range up to 155°. Distillation fractions of 3 ml. were taken and combined into the above major fractions on the basis of their refractive indices.

2- and 4-Cyclohexylanisole.—A mixture of 0.5 mole of anisole, 0.52 mole of cyclohexanol and 400 g. of PPA was stirred at 85° for 35 min. Isolation in the usual fashion and distillation at 750 mm. yielded 68 g. (72%) of a mixture of the two isomers, b.p. 275–283°. These could not be separated by distillation, although a small amount of the pure 4-isomer (5.5% g., 5.8%) could be obtained by dissolving the mixture in 40 ml. of petroleum ether (50–60°) and cooling; m.p. 58–59° (lit.[25] 58–59°). The combined reaction products were distilled again to give 64 g., b.p. 146–150° (15 mm.). This was analyzed as a mixture of the two isomers.

Anal. Calcd. for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 81.99; H, 9.53.

2- and 4-Cyclohexylphenol.—Half-mole quantities of phenol and cyclohexanol were treated with 400 g. of PPA at 85° for 40 min. The product was isolated as above as 50.3 g. (53.7%) of a mixture of the two isomers, b.p. 155–170° (15 mm.). Fractional crystallization from ethyl acetate–petroleum ether (30–40°) and then from petroleum ether afforded 16.1 g. (17.2%) of 4-cyclohexylphenol, m.p. 129–130° (lit.[25] 131°). Further crystallization from the latter solvent yielded 20.5 g. (21.9%) of 2-cyclohexylphenol, m.p. 53–54° (lit.[25] 56–57°).

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[25] H. Lefebvre and E. Levas, *Compt. rend.*, **220**, 782 (1945); *C. A.*, **40**, 1478 (1946).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NORTH DAKOTA]

Substituted Phenylsilanes. I. The Autoxidation of *o*-, *m*- and *p*-Trimethylsilylethylbenzene[1]

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The trimethylsilylethylbenzenes have been prepared and the oxidation of these silanes with oxygen has been studied. This oxidation, carried out at 200–220° in the presence of chromic oxide and calcium carbonate, has given moderate yields of *o*-, *m*- and *p*-trimethylsilylacetophenone as well as the corresponding trimethylsilylbenzoic acids. The resulting new organosilanes have been characterized and derivatives have been prepared wherever possible.

It is well known that the methods which are available for the establishment of carbon–silicon linkages are not adapted readily to the preparation of organosilanes containing reactive functional groups. Furthermore, in the case of arylsilanes, the introduction of reactive functional groups into the aromatic ring by the usual electrophilic substitution reactions is complicated by the ease of cleavage of the aromatic carbon–silicon bond under the conditions employed in such reactions. The Friedel–Crafts acylation of phenylsilanes has been notably unsuccessful. Dolgov and Panina[2] have found that acyl halides in the presence of aluminum chloride react with triethylphenylsilane to form alkyl phenyl ketones and triethylchlorosilane rather than alkyl triethylsilylphenyl ketones.

This susceptibility of phenylsilanes to cleavage during reactions of this type has led us to an investigation of the preparation of the trimethylsilylacetophenones by methods which do not involve electrophilic reagents. This paper describes the results of an investigation of the action of oxygen on trimethylsilylethylbenzenes at elevated temperatures in the presence of chromic oxide and calcium carbonate. Apparently, only two studies of oxidation procedures as a means of introducing reactive functional groups into organosilanes have been made. Benkeser and Landesman[3] found that the mild oxidizing agent, selenium dioxide, will convert 2-acetyl-5-trimethylsilylthiophene and 2-acetyl-5-trimethylsilylfuran to the corresponding glyoxals while Lewis and Gainer[4] were able to oxidize 1,3-bis-(*p*-tolyl)-tetramethyldisiloxane to 1,3-bis-(*p*-carboxyphenyl)-tetramethyldisiloxane with chromic acid in acetic acid–acetic anhydride at low temperatures.

The trimethylsilylethylbenzenes used in this investigation were prepared by converting *o*-, *m*- and *p*-bromoethylbenzene into the corresponding organolithium reagents and treating these with trimethylethoxysilane. The yields in these preparations varied from 55% for *o*-trimethylsilylethylbenzene to 82% for the *para* isomer. When *p*-trimethylsilylethylbenzene was treated with dry oxygen at 200–214° for six hours in the presence of chromic oxide and calcium carbonate a 21% yield of *p*-trimethylsilylacetophenone and a 12% yield of *p*-trimethylsilylbenzoic acid were obtained. Increasing the reaction time to 12 hours at 209–225° gave no appreciable change in the yield. However, when the reaction mixture was illuminated with ultraviolet light, the yields of ketone and acid were increased to 25 and 15%, respectively. By means of this oxidation either with or without ultraviolet light it was possible to obtain comparable yields of *o*-trimethylsilylbenzoic acid and *o*-trimethylsilylacetophenone with the better yield of ketone (19%) being obtained when ultraviolet light was used. The oxidation of *m*-trimethylsilylethylbenzene was carried out with ultraviolet light and gave somewhat lower yields (10% of acid and 14% of ketone) than in similar reactions with the other two isomers. It would appear that temperatures of about 200° are essential in these reactions since no detectable amounts of ketone or acid were obtained when *o*-trimethylsilylethylben-

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[2] B. N. Dolgov and O. K. Panina, *Zhur. Obshchei Khim.*, **18**, 1293 (1948); *C. A.*, **43**, 2177 (1949).

[3] R. A. Benkeser and H. Landesman, THIS JOURNAL, **71**, 2493 (1949).

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

zene was treated with oxygen at 155–160° in the presence of chromic oxide and calcium carbonate even after 26 hours. An attempt was made to carry out the oxidation of *p*-trimethylsilylethylbenzene in aqueous emulsion following a procedure which has been successful with cumene and other alkylbenzenes.[5] No ketone or acid was obtained using essentially the same reaction time as in the other oxidations reported here. It is perhaps noteworthy that 23 to 38% recovery of unchanged starting material was realized in the high temperature oxidations.

Structures of *o*-, *m*- and *p*-trimethylsilylacetophenone were confirmed by their conversion, upon treatment with sodium hydroxide and iodine, to the known *o*-, *m*- and *p*-trimethylsilylbenzoic acids. The acids were converted to the corresponding amides by treatment with thionyl chloride and then with ammonia. The ketones formed 2,4-dinitrophenylhydrazones in the usual way and *m*- and *p*-trimethylsilylacetophenone formed semicarbazones. However, attempts to prepare the semicarbazone of *o*-trimethylsilylacetophenone failed to yield a crystalline derivative.

Experimental[6]

Bromoethylbenzenes.—*o*-Bromoethylbenzene and *p*-bromoethylbenzene were prepared by the bromination of ethylbenzene in the presence of iodine followed by fractionation through a Heli-Pak column of ninety theoretical plates. *o*-Bromoethylbenzene also was prepared from *o*-ethylaniline following the general procedure of Hartwell.[7] The constants for these compounds agreed with those in the literature.[8] *m*-Aminoacetophenone[9] was converted to *m*-bromoacetophenone[10] and then to *m*-bromoethylbenzene according to the procedure used by Pope and Bogert.[11]

***o*-Trimethylsilylethylbenzene.**—A solution of 175 g. (0.95 mole) of *o*-bromoethylbenzene in 300 ml. of anhydrous ether was added dropwise with constant stirring to a mixture of 13.5 g. (1.95 g. atoms) of finely cut lithium in 400 ml. of anhydrous ether. The rate of addition was such that the reaction mixture refluxed gently during the addition. When the addition had been completed and the reaction mixture had cooled to room temperature only a few small pieces of lithium remained unreacted. To this ethereal solution of *o*-ethylphenyllithium was added slowly a solution of 112 g. (0.95 mole) of trimethylethoxysilane in 200 ml. of anhydrous ether and then the mixture was refluxed for one hour. At this time Color Test I[12] was negative. The reaction mixture was hydrolyzed by the addition of water followed by the addition of dilute hydrochloric acid until two clear layers were obtained. The ether layer was removed, washed with water and dried over anhydrous sodium sulfate. After the ether had been removed by distillation, the residue was distilled through a Heli-Pak column of about forty theoretical plates. This gave 92.3 g. (55%) of *o*-trimethylsilylethylbenzene, b.p. 210–211°, $n^{20}\text{D}$ 1.5030, $d^{20}{}_4$ 0.8870; *MR* (calcd.)[13] 59.36, *MR* (found) 59.43.

Anal. Calcd. for $C_{11}H_{18}Si$: Si, 15.74. Found: Si, 15.60.

***m*-Trimethylsilylethylbenzene.**—This silane was prepared from *m*-ethylphenyllithium and trimethylethoxysilane in 0.28 mole quantity as described above for the *ortho* isomer. Rectification of the product through a small Heli-Pak column of about fifteen plates gave 38 g. (76%) of *m*-trimethylsilylethylbenzene, b.p. 202°, $n^{20}\text{D}$ 1.4914, $d^{20}{}_4$ 0.8672; *MR* (calcd.)[13] 59.36, *MR* (found) 59.59.

Anal. Calcd. for $C_{11}H_{18}Si$: Si, 15.74. Found: Si, 15.66.

***p*-Trimethylsilylethylbenzene.**—This silane was prepared from *p*-ethylphenyllithium and trimethylethoxysilane in 0.8-mole quantity as described for the *ortho* isomer. Rectification of the product through a Heli-Pak column of about 15 plates yielded 117 g. (82%) of colorless liquid, b.p. 207–208.5°, $n^{20}\text{D}$ 1.4930, $d^{20}{}_4$ 0.8672; *MR* (calcd.)[13] 59.36, *MR* (found) 59.65.

Anal. Calcd. for $C_{11}H_{18}Si$: Si, 15.74. Found: Si, 15.49.

Autoxidation of the Trimethylsilylethylbenzenes. *p*-Trimethylsilylacetophenone and *p*-Trimethylsilylbenzoic Acid.—The oxidation[14] was carried out in a 100-ml. three-necked flask, equipped with a thermometer, a gas inlet tube extending to the bottom of the flask and a modified Dean–Stark trap[15] to which two condensers were attached in series. A mixture of 35.6 g. (0.20 mole) of *p*-trimethylsilylethylbenzene, 0.5 g. of anhydrous chromic oxide and 2 g. of anhydrous calcium carbonate was placed in the reaction vessel. Dry oxygen was then passed through the gas inlet tube while the contents of the flask was heated to and held at 200–214° at a rate such that the liquid was refluxed well above the sidearm of the Dean–Stark trap. The exit gas was passed through a cold trap cooled in a Dry Ice–acetone-bath. It was found that only a negligible amount of organic material was carried through the double condenser system. The oxidation was continued for six hours. During this time approximately 2.5 ml. of water was collected and the organic liquid turned brown. The reaction mixture was filtered through a bed of Celite to remove the catalyst. The filter bed was washed with ether and the washings were added to the filtrate. The resulting ether solution was extracted with a 10% sodium carbonate solution and then dried over Drierite. The basic aqueous layer was acidified with dilute hydrochloric acid and then extracted with ether. After drying over Drierite, the ether was removed from this solution by gentle heating on a steam-bath. This left a slightly yellow crystalline residue of 3.4 g. (11.8% yield) of *p*-trimethylsilylbenzoic acid. This acid, after recrystallization from an acetic acid–water solution and then from petroleum ether (30–60°), gave white crystals, m.p. 116–117.5° (literature value[16] 117–118°). A sample of this acid was heated with thionyl chloride and then poured into aqueous ammonia. The precipitated amide was obtained, after recrystallization from aqueous ethanol, as white crystals, m.p. 158–159.5° (literature value[17] for *p*-trimethylsilylbenzamide, m.p. 155°).

The dried ether solution from which the acid had been removed was distilled to remove the ether and was then fractionated through a small jacketed Vigreux column. This gave 10.7 g. (30%) of starting material, b.p. 95–101° (17 mm.), and 5.6 g. (20.9%) of colorless liquid identified as *p*-trimethylsilylacetophenone, b.p. 135–140° (17 mm.), $n^{20}\text{D}$ 1.5170. During a second run, in which the same amounts of reactants and a reaction time of 12 hours at 209–225° were used, approximately 2.5 ml. of water was collected. After the reaction mixture was worked up as just described, there was obtained 2.5 g. (8.1%) of *p*-trimethylsilylbenzoic acid, m.p. 116–117°, 8.9 g. (25%), of starting material, b.p. 94–99° (17 mm.), and 5.9 g. (20.5%) of *p*-trimethylsilylacetophenone, b.p. 135–140° (17 mm.), $n^{20}\text{D}$ 1.5172. The ketone from these two runs was combined and rectified through a Wheeler all-glass semi-micro column of about ninety plates and gave 6.1 g. (11%) of pure, colorless *p*-trimethylsilylacetophenone, b.p. 136° (17 mm.), $n^{20}\text{D}$ 1.5170, $d^{20}{}_4$ 0.9648; *MR* (calcd.)[18] 59.87, *MR* (found) 60.30.

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(5) G. P. Armstrong, R. H. Hall and D. C. Quin, *Nature*, **164**, 834 (1949).

(6) All melting points were determined on a Kofler Micro Hot Stage, Arthur H. Thomas Company, Philadelphia, Pa. The yields have been calculated on the basis of unrecovered starting material.

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(10) L. A. Elson, C. S. Gibson and J. D. A. Johnson, *J. Chem. Soc.*, 1128 (1930).

(11) G. W. Pope and M. T. Bogert, *J. Org. Chem.*, **2**, 276 (1937).

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(16) J. D. Roberts, E. A. McElhill and R. Armstrong, THIS JOURNAL, **71**, 2923 (1949).

(17) R. A. Benkeser and H. R. Krysiak, *ibid.*, **75**, 4528 (1953).

(18) Calculated as *MR*(acetophenone) − r(C–H) + $r(\text{Si–C}_{\text{ar}})$ + $3r(\text{Si–CH}_3)$ where *MR*(acetophenone) was calculated from the density and refractive index (A. I. Vogel, *J. Chem. Soc.*, 610 (1948)), and the bond refractions are those listed in ref. 13.

Anal. Calcd. for $C_{11}H_{16}OSi$: Si, 14.60. Found: Si, 14.53.

This ketone yielded *p*-trimethylsilylbenzoic acid, m.p. 115–116°, and iodoform when it was treated with aqueous sodium hydroxide and iodine. The 2,4-dinitrophenylhydrazone of *p*-trimethylsilylacetophenone, prepared in the usual way,[19] melted at 203–207°.

Anal. Calcd. for $C_{17}H_{20}N_4O_4Si$: Si, 7.53. Found: Si, 7.44.

The semicarbazone of *p*-trimethylsilylacetophenone was prepared[19] and, after recrystallization from 50% aqueous ethanol, melted at 198–200°.

Anal. Calcd. for $C_{12}H_{19}N_3OSi$: Si, 11.25. Found: Si, 11.10.

A third experiment was carried out in which 35.6 g. (0.2 mole) of *p*-trimethylsilylethylbenzene in the presence of 2 g. of calcium carbonate and 0.5 g. of chromic oxide was oxidized with oxygen for 7.5 hours at 200–220° while the reaction vessel was exposed to ultraviolet light. During this time approximately 3 ml. of water was collected. Upon working up the reaction mixture as in the previous experiment, 4.7 g. (14.8%) of acid, m.p. 116–117°, was obtained. Rectification of the neutral fraction through a Wheeler semi-micro column gave 8.1 g. (22.8%) of starting material, b.p. 96–97°, n^{20}_{D} 1.4930, and 7.3 g. (24.6%) of colorless liquid, b.p. 136–138° (17 mm.), n^{20}_{D} 1.5165.

An attempt was made to oxidize *p*-trimethylsilylethylbenzene in aqueous emulsion following a procedure similar to that used by Armstrong, Hall and Quin for the autoxidation of cumene.[5] Oxygen was bubbled through a vigorously stirred mixture of 65 g. (0.36 mole) of *p*-trimethylsilylethylbenzene, 100 ml. of water, 1.5 g. of sodium carbonate and 0.25 g. of stearic acid at 85°. The reaction was continued for ten hours, cooled, filtered and the filtrate was extracted with ether. This ether solution was dried over Drierite, the ether was removed by distillation and the residue was fractionated through a small jacketed Vigreux column at 17 mm. After a very small forerun there was collected 54.9 g. (84%) of starting material, b.p. 97–98°, n^{20}_{D} 1.4924. No identifiable amount of higher boiling material was obtained.

***m*-Trimethylsilylacetophenone and *m*-Trimethylsilylbenzoic Acid.**—Dry oxygen was passed through a mixture of 33.6 g. (0.19 mole) of *m*-trimethylsilylethylbenzene, 0.5 g. of anhydrous chromic oxide and 2 g. of anhydrous calcium carbonate for eight hours at 205–214°. During the oxidation the flask was illuminated with an ultraviolet lamp. A total of approximately 2.75 ml. of water was collected and the final reaction mixture was dark brown. The reaction mixture was worked up in the manner described for the *para* isomer and gave 2.8 g. (10.8%) of *m*-trimethylsilylbenzoic acid, which upon recrystallization from acetic acid–water gave white crystals, m.p. 113–114° (literature value[18] 113.7–114.2°). This acid was converted by treatment with thionyl chloride and then aqueous ammonia to a white crystalline amide, m.p. 133–134° (literature value[20] 129.5–130°). Rectification of the neutral fraction through a Wheeler semi-micro column at 17 mm. gave 9.8 g. (29.2%) of starting material, b.p. 94–96°, n^{20}_{D} 1.4915, and 3.8 g. (14.8%) of *m*-trimethylsilylacetophenone, b.p. 132°, n^{20}_{D} 1.5120, d^{20}_{4} 0.9554; *MR* (calcd.)[18] 59.87, *MR* (found) 60.35.

Anal. Calcd. for $C_{11}H_{16}OSi$: Si, 14.60. Found: Si, 14.34.

When *m*-trimethylsilylacetophenone was treated with aqueous sodium hydroxide and iodine, iodoform and a white crystalline acid were obtained. Recrystallization of this acid from aqueous acetic acid gave white crystals, m.p. 113–114°. The 2,4-dinitrophenylhydrazone of *m*-trimethylsilylacetophenone was prepared in the usual way[19] and melted at 160–163°.

Anal. Calcd. for $C_{17}H_{20}N_4O_4Si$: Si, 7.53. Found: Si, 7.65.

The semicarbazone of *m*-trimethylsilylacetophenone was prepared[19] and after recrystallization from 50% aqueous ethanol melted at 166–168°.

Anal. Calcd. for $C_{12}H_{19}N_3OSi$: Si, 11.25. Found: Si, 11.29.

***o*-Trimethylsilylacetophenone and *o*-Trimethylsilylbenzoic Acid.**—Dry oxygen was passed through a mixture of 35.6 g. (0.20 mole) of *o*-trimethylsilylethylbenzene, 0.5 g. of anhydrous chromic oxide and 2 g. of anhydrous calcium carbonate for 8.5 hours at 206–210°. During the reaction approximately 1.5 ml. of water was collected and the reaction mixture turned brown. After working up the reaction mixture in the manner described for the *para* isomer, there was obtained 2.9 g. (12%) of *o*-trimethylsilylbenzoic acid which upon recrystallization from aqueous acetic acid gave white crystals, m.p. 99–100°.[21]

Anal. Calcd. for $C_{10}H_{14}O_2Si$: Si, 14.45; neut. equiv., 194. Found: Si, 14.19; neut. equiv., 193.5.

Treatment of this acid with thionyl chloride and then aqueous ammonia gave an amide. Recrystallization of this amide from aqueous ethanol gave white crystalline *o*-trimethylsilylbenzamide, m.p. 126–127.5°.[21]

Anal. Calcd. for $C_{10}H_{15}NOSi$: Si, 14.51. Found: Si, 14.25.

Rectification of the neutral fraction through an all-glass Wheeler concentric tube column at 14 mm. gave 13.4 g. (37.6%) of starting material, b.p. 92–94°, n^{20}_{D} 1.5020, and 2.6 g. (10.9%) of colorless *o*-trimethylsilylacetophenone, b.p. 116–117°, n^{20}_{D} 1.5200, d^{20}_{4} 0.9627; *MR* (calcd.)[18] 59.87, *MR* (found) 60.72.

Anal. Calcd. for $C_{11}H_{16}OSi$: Si, 14.60. Found: Si, 14.40.

This ketone gave iodoform and an acid upon treatment with aqueous sodium hydroxide and iodine. Recrystallization of the acid from acetic acid–water gave white crystalline *o*-trimethylsilylbenzoic acid, m.p. 99–100°. The 2,4-dinitrophenylhydrazone of *o*-trimethylsilylacetophenone was prepared in the usual way[19] and was found to melt at 135–137°.

Anal. Calcd. for $C_{17}H_{20}N_4O_4Si$: Si, 7.53. Found: Si, 7.73.

Attempts to prepare the semicarbazone of *o*-trimethylsilylacetophenone following the usual procedure[19] failed to give a crystalline derivative.

In a second experiment, using the same quantities of reactants, the temperature of the reaction mixture was maintained at 155–160°, while oxygen was rapidly bubbled through the reaction mixture for 26 hours. No water was collected and the appearance of the reaction mixture did not change appreciably. Fractionation of the reaction mixture gave only starting material, b.p. 95–96° (17 mm.). No higher-boiling material was obtained.

In a third experiment oxygen was bubbled through a mixture of 33.6 g. of *o*-trimethylsilylethylbenzene, 0.5 g. of chromic oxide and 2 g. of calcium carbonate for nine hours while the reaction mixture was maintained at 205–214° and was illuminated with ultraviolet light. Upon working up the reaction mixture as before, 3.3 g. (14.6%) of *o*-trimethylsilylbenzoic acid was obtained which gave white crystals, m.p. 99–100°, after recrystallization from aqueous acetic acid. Rectification of the neutral fraction at 17 mm. gave 12.9 g. (35.8%) of starting material, b.p. 96–98°, n^{20}_{D} 1.5030, and 4.2 g. (19%) of *o*-trimethylsilylacetophenone, b.p. 120–122°, n^{20}_{D} 1.5203.

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