3-Nitro-4-picoline.—A mixture of 6.88 g. (0.04 mole) of the crude mixed 3- and 5-nitro-2-chloro-4-picoline and 13.4 g. (0.11 mole) of benzoic acid was placed in a 500-ml., three-necked flask fitted with a condenser, stirrer and thermometer. The reaction mixture was heated over a wire gauze by a burner to 150°. The burner was removed and 10 g. (0.16 mole) of copper powder (Baker purified) was added in small portions so that the temperature was maintained between 150–160°. After about half of the copper had been added, the temperature began to drop. The rest of the copper was added and heat was applied to keep the temperature at 150° for 15 minutes. The set-up was rearranged for steam distillation and, after the mixture had cooled, 50 ml. of 20% sodium carbonate solution was added slowly. The carbon dioxide produced in this neutralization was liberated only very slowly and the flask had to be heated cautiously with the burner until the evolution of gas was complete. Steam was passed into the mixture until about 300 ml. of distillate had been collected. The distillate was extracted with two 100-ml. portions of ether, the ethereal solution was dried over magnesium sulfate and the 3-nitro-4-picoline was precipitated as the hydrochloride by passing dry hydrogen chloride into the filtered solution. The yield of 3-nitro-4-picoline hydrochloride, m.p. 176–177°, was 3.07 g. (44%). The free base, 3-nitro-4-picoline, could be obtained quantitatively from the hydrochloride by neutralization with alkali. For storage purposes the hydrochloride was found to be much more stable than the free base, which, when pure, is a yellow oil that darkens rapidly on standing.

This reaction could be carried out using glacial acetic acid in place of benzoic acid. Such a procedure had the advantage of giving a liquid reaction mixture that was more readily neutralized when the reaction was complete. The yields obtained using acetic acid were often as good as those with benzoic acid, but the benzoic acid method was found to be more reliable. The dechlorination with benzoic acid was run using ten times the above amounts in a 1-l. vessel. The yield was 32%.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Friedel–Crafts Acylations with Trimethylsilylbenzoyl Chlorides

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Successful acylations of toluene with *m*- and *p*-trimethylsilylbenzoyl chlorides and aluminum chloride have been accomplished. Similarly, anisole has been acylated with *p*-trimethylsilylbenzoyl chloride in the presence of stannic chloride. The corresponding trimethylsilyl phenyl ketones were obtained in fair to good yields, as the principal reaction products. No apparent cleavage of the trimethylsilyl group was detected under the reaction conditions employed. *o*-Trimethylsilylbenzoyl chloride, when reacting under Friedel–Crafts conditions with anisole and with toluene, gave resinous materials as principal products. Structure proofs for all the silicon-containing ketones are described.

Attempts to carry out Friedel–Crafts reactions involving aromatic silicon compounds have met with little success or have resulted in fairly low yields. Thus, the attempted alkylation of diphenyldichlorosilane in the presence of anhydrous aluminum chloride yielded silicon tetrachloride, phenyltrichlorosilane, and ethyl derivatives of benzene.[1] The principal reaction of tetraphenylsilane in chloroform with aluminum chloride is that of cleavage, resulting in an 80% yield of silicon tetrachloride.[1] Similarly, tetrabenzylsilane under these conditions yields silicon tetrachloride.[1] Attempted acylations of phenyltriethylsilane in the presence of aluminum chloride yielded benzene, hexaethyldisiloxane, and the corresponding ketones in which the triethylsilyl group had been displaced by the acyl group.[2] The best yields obtainable in the acetylation of 2-trimethylsilylthiophene and 2-trimethylsilylfuran with iodine as catalyst were 13 and 25%, respectively, of the desired ketones.[3]

In previous work from this Laboratory on the hydrogen chloride cleavage of *m*- and *p*-substituted phenyltrimethylsilanes[4] an empirical correlation was attempted between the ease of cleavage of *m*- and *p*-substituted phenyltrimethylsilanes and Hammett sigma constants.[5] This correlation suggested that side-chain reactions of substituted phenyltrimethylsilanes could be carried out involving acidic or electrophilic reagents with a minimum of cleavage of the trimethylsilyl group, if the substituent had a sigma value of *ca.* +0.4 or greater.

Accordingly it became of interest to attempt the preparation of the isomeric trimethylsilylbenzoyl chlorides, to treat them under Friedel–Crafts conditions, and to determine whether the principal reaction was that of scission of the silicon–carbon bond or that of acylation. The acid chloride group would presumably have a σ-value similar to a carboxyl and thus be in the neighborhood of +0.4 or greater.

In accord with these predictions the three isomeric trimethylsilylbenzoyl chlorides were prepared from the corresponding acids using thionyl chloride with little cleavage of the silicon–carbon bond. Likewise acylations with the *m*- and *p*-trimethylsilylbenzoyl chlorides were attended with practically no cleavage with either stannic chloride or aluminum chloride as catalysts. Attempted acylations with *o*-trimethylsilylbenzoyl chloride resulted in the formation of high-boiling polymeric material. It seems likely that the proximity of the trimethylsilyl group to the carbonium ion intermediate in the ortho case may have favored cleavage especially since the desired acylation is so disfavored by steric requirements. However, the ortho ketones (with anisole and toluene) were prepared easily enough through the appropriate organocadmium reagent and *o*-trimethylsilylbenzoyl chloride, although extensive purification was necessary. These ketones were quite sterically hindered as evidenced by their failure to form phenylhydrazones.

The structure of the ketones obtained from the

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(1) W. E. Evison and F. S. Kipping, *J. Chem. Soc.*, 2774 (1931).

(2) B. N. Dolgov and O. K. Panina, *Zhur. Obschei Khim.* (*J. Gen. Chem.*), **18**, 1293 (1948); (*C. A.*, **43**, 2177 (1949).

(3) R. A. Benkeser and R. B. Currie, THIS JOURNAL, **70**, 1780 (1948).

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

(5) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 184.

acylation of toluene and anisole with *m*- and *p*-trimethylsilylbenzoyl chorides was proved by synthesizing these compounds independently and comparing their melting points. The synthesis was accomplished by treating the Grignard reagent of *m*- or *p*-substituted phenyltrimethylsilane with either *p*-tolunitrile or *p*-methoxybenzonitrile.

Infrared absorption spectra of all the silicon ketones show a strong carbonyl band at 6μ.

Experimental

***p*-Trimethylsilylbenzoic Acid.** (A) **From *p*-Bromophenyltrimethylsilane.**—*p*-Trimethylsilylbenzoic acid, m.p. 117–118°, was prepared in 66% yield from 0.186 mole of *p*-bromophenyltrimethylsilane[6] by the method of Roberts, *et al.*[7]

(B) **From *p*-Chlorophenyltrimethylsilane.**—To 8.35 g. (1.19 g. atoms) of finely-cut lithium suspended in 600 ml. of ether and under a nitrogen atmosphere was added with stirring, 100 g. (0.54 mole) of *p*-chlorophenyltrimethylsilane[6] in 150 ml. of ether over a two-hour period. The mildly exothermic reaction was stirred for a total of 7 hours. It was then allowed to stand overnight and carbonated the next morning by pouring on powdered Dry Ice. After the carbonated mixture had warmed to room temperature, it was acidified with dilute hydrochloric acid, and the layers were separated. The ethereal layer was then extracted with an equivalent amount of dilute sodium hydroxide solution. The basic extracts were combined, filtered, cooled by the addition of pieces of ice, and then acidified carefully with dilute hydrochloric acid. There was obtained 31.8 g. (39% based on recovered *p*-chlorophenyltrimethylsilane) of *p*-trimethylsilylbenzoic acid, m.p. 117–118°.

***p*-Trimethylsilylbenzoyl Chloride.**—*p*-Trimethylsilylbenzoic acid (30 g., 0.154 mole) was refluxed with 100 ml. of thionyl chloride for 1.5 hours. The excess thionyl chloride was distilled off at atmospheric pressure and then under water aspirator vacuum. The crude acid chloride was distilled to yield 29.4 g. (90%) of *p*-trimethylsilylbenzoyl chloride, boiling at 75–76° (1 mm.), $n^{20}\text{D}$ 1.5315.

Anal. Calcd. for $C_{10}H_{13}ClOSi$: Si, 13.19. Found: Si, 13.09.

Anilide was crystallized from 90–100° petroleum ether as needles, m.p. 142–142.5°.

Anal. Calcd. for $C_{16}H_{19}NOSi$: Si, 10.42. Found: Si, 10.0.

***p*-Trimethylsilylbenzoyl Chloride and Anisole. First Run.**—To a stirred solution of 4.00 g. (0.019 mole) of *p*-trimethylsilylbenzoyl chloride, 2.7 g. (0.025 mole) of anisole and 75 ml. of dry benzene protected from moisture was added 4.95 g. (0.019 mole) of anhydrous stannic chloride over a five-minute period. During this time and for an additional half hour, the temperature was maintained at 10–15°. The reaction mixture was then allowed to warm up to 25° and stirred at this temperature for an additional six hours. The wine-red reaction mixture was hydrolyzed by pouring it upon a solution of 10 ml. of concd. hydrochloric acid and 50 ml. of cold water. This mixture was placed in a separatory funnel and vigorously shaken in order to discharge the red color. The layers were separated; the organic layer was washed once with water, and then separated and dried over Drierite. This mixture was filtered, and the benzene was stripped off. Distillation of the residue through a short distilling head yielded a first fraction boiling at 77–80° (0.8 mm.), $n^{20}\text{D}$ 1.5380; and a second fraction boiling at 168–170° (0.8 mm.), which consisted of a clear yellow oil weighing 2.9 g. This oil crystallized after standing a week. The refrigerated ethanolic solution, when seeded with a crystal of the ketone, yielded crystals melting at 53.5–54°.

Anal. Calcd. for $C_{17}H_{20}O_2Si$: Si, 9.87; C, 71.79; H, 7.09. Found: Si, 9.79; C, 71.80; H, 7.53.

The first fraction was redistilled to yield 1.2 g. of pure *p*-trimethylsilylbenzoyl chloride, boiling at 75–76° (1 mm.), $n^{20}\text{D}$ 1.5315.

Phenylhydrazone.—Crystallized once from 95% ethanol, it melted at 129–134°; recrystallized, m.p. 145.5–146.5°.

Anal. Calcd. for $C_{23}H_{26}N_2OSi$: N, 7.48. Found: N, 7.83.

The yield of *p*-trimethylsilylphenyl *p*-methoxyphenyl ketone based upon recovered acid chloride was thus 78%, representing a 70% conversion.

Second Run.—A second run was carried out similar to the first except that the reaction mixture was stirred for 13 hours at 20–25°. Distillation yielded 4.28 g. (80%) of an oil which soon solidified upon seeding. This material melted at 53.5–54°. No forerun of the acid chloride was detected.

***p*-Trimethylsilylphenyl *p*-Methoxyphenyl Ketone.**—This compound was prepared by an adaptation of the method of Hauser, *et al.*[8]

To the Grignard reagent prepared from 8 g. (0.035 mole) of *p*-bromophenyltrimethylsilane and 1.02 g. (0.042 g. atom) of magnesium turnings in 65 ml. of ether was added 4 g. (0.03 mole) of *p*-methoxybenzonitrile dissolved in 15 ml. of ether. Stirring and refluxing were continued for four hours, and the reaction mixture was then allowed to stand overnight. It was hydrolyzed by the addition of dilute hydrochloric acid, and the ether was distilled off on a hot water-bath. The aqueous mixture was then refluxed for about an hour and allowed to cool. This mixture was extracted with ether, the ether layer was separated and dried over Drierite and, after filtration, the ether was stripped off. Distillation of the residue at 0.5 mm. yielded 2.81 g. (33%) of an oil boiling at 161–162°. This oil when dissolved in warm 95% ethanol, placed in a refrigerator and seeded, yielded after two crystallizations, 1.6 g. of *p*-methoxyphenyl *p*-trimethylsilylphenyl ketone, m.p. 53.5–54°. A mixed m.p. with the ketone obtained from the Friedel–Crafts reaction was not depressed.

***p*-Trimethylsilylbenzoyl Chloride and Toluene. First Run.**—To a solution of 2.58 g. (0.019 mole) of anhydrous aluminum chloride and 75 ml. of *sym*-tetrachloroethane stirred and cooled to 0° and protected from moisture was added dropwise a solution of 4.00 g. (0.019 mole) of *p*-trimethylsilylbenzoyl chloride, 2.3 g. (0.025 mole) of toluene and 20 ml. of *sym*-tetrachloroethane over a half-hour period. Stirring was then continued at ice-bath temperatures for four hours, whereupon the ice-bath was removed and the wine-red solution was further stirred at 20–25° for three more hours. It was then hydrolyzed by pouring it upon a mixture of *ca.* 75 g. of ice and 25 ml. of concd. hydrochloric acid. The layers were separated when the ice had melted, and the organic layer was washed once with water, once with sodium bicarbonate solution, and once with water, after which the separated organic layer was dried over Drierite. After filtration and stripping off of the tetrachloroethane under water aspirator vacuum, the residue was distilled through a short distilling head to yield 3.37 g. of light yellow oil boiling at 130–140° (0.5 to 1 mm.). Upon redistillation of this oil there was obtained 0.89 g. of material boiling at 78–88° (0.8 mm.) and 1.97 g. (39%) of ketone which boiled at 150° (0.8 mm.). This latter fraction when dissolved in a small amount of 95% ethanol and placed in a refrigerator, solidified after a week to yield crystals melting at 43–44°.

Second Run.—In another run using the same quantities of materials, the reaction mixture was kept at 0 to 5° and stirred for 13.5 hours. After working up the reaction mixture as in the first run, there was obtained upon distillation, a fraction boiling at 81–91° (0.5 mm.), $n^{20}\text{D}$ 1.5300, which weighed 1.23 g., and a second fraction boiling at 150–160° (0.5 mm.), weighing 1.80 g.

The lower boiling fraction was treated with aniline to yield after two crystallizations from 90–100° petroleum ether, a product melting at 142–142.5°. A mixed m.p. with *p*-trimethylsilylbenzanilide was not depressed.

Based on the amount of recovered acid chloride, there was thus obtained a 49% yield of ketone, representing a 69% conversion.

Third Run.—To a mixture of 2.58 g. (0.019 mole) of powdered anhydrous aluminum chloride and 75 ml. of dry toluene cooled by an ice-bath and protected from moisture was added with stirring a solution of 4.00 g. (0.019 mole) of *p*-trimethylsilylbenzoyl chloride in 15 ml. of toluene. Addition was completed in 10 minutes. The reaction mixture was then stirred at ice-bath temperatures for four hours, whereupon the ice-bath was removed and stirring was continued at 25–30° for an additional 29 hours. The light

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(6) C. A. Burkhard, THIS JOURNAL, **68**, 2103 (1946).

(7) J. D. Roberts, E. A. McElhill and R. Armstrong, *ibid.*, **71**, 2923 (1949).

(8) C. R. Hauser, W. J. Humphlett and M. J. Weiss, *ibid.*, **70**, 426 (1948).

green reaction mixture was then poured on ice containing 25 ml. of concd. hydrochloric acid. After the ice had melted, the layers were separated, and the organic layer was washed once with water, once with sodium bicarbonate solution, once with water, and then dried over Drierite. After filtration and removal of the solvent, distillation yielded 3.41 g. (66%) of colorless oil boiling at 148–150° (0.5 mm.). When this oil was seeded and placed in a refrigerator, it soon solidified to yield a product melting at 42–44°, which when recrystallized melted at 43–44°.

Anal. Calcd. for $C_{17}H_{20}OSi$: Si, 10.45. Found: Si, 10.0.

Phenylhydrazone.—The phenylhydrazone of the above ketone, when crystallized once from 95% ethanol, melted at 126–129°; crystallized twice it melted at 133–135°; crystallized a third and fourth time it melted at 137–138°. Another form melted at 128.5–129°; when this m.p. was checked three months later, it melted at 131–133°.

Anal. Calcd. for $C_{17}H_{26}N_2Si$: N, 7.81. Found: N, 7.79.

***p*-Trimethylsilylphenyl *p*-Tolyl Ketone.**—This ketone was prepared in the same manner as *p*-trimethylsilylphenyl *p*-methoxyphenyl ketone. From 4.0 g. (0.0175 mole) of *p*-bromophenyltrimethylsilane, 0.51 g. (0.021 g. atom) of magnesium and 1.17 g. (0.01 mole) of *p*-tolunitrile in 60 ml. of ether was obtained upon distillation 1.70 g. (64%) of *p*-trimethylsilylphenyl *p*-tolyl ketone boiling at 159–162° (0.5 mm.). After two crystallizations from cold 95% ethanol, there was obtained a crystalline material melting at 44–44.5°. A mixed m.p. with the ketone obtained from the Friedel–Crafts reaction was not depressed.

***o*-Tolyltrimethylsilane.**—This compound was prepared by an adaptation of the method of Clark, *et al.*[9]

First Run.—To 12.7 g. (0.554 g. atom) of molten sodium in a mixture of 40 ml. of toluene and 40 ml. of xylene under a nitrogen atmosphere was added, with vigorous stirring, a mixture of 31.6 g. (0.25 mole) of *o*-chlorotoluene and 29.8 g. (0.275 mole) of trimethylchlorosilane over a one-hour period. Addition was such that rapid refluxing was obtained. Stirring and refluxing were continued for an additional half hour when all the reactants had been added. The reaction mixture was then allowed to cool and was filtered under nitrogen pressure through a glass wool plug.

Second Run.—In a similar run, a mixture of 50.6 g. (0.4 mole) of *o*-chlorotoluene and 47.7 g. (0.44 mole) of trimethylchlorosilane was added to 19.3 g. (0.84 g. atom) of molten sodium in 75 ml. of toluene and 100 ml. of xylene. Addition required 80 minutes. The reaction mixture was refluxed for half an hour and then cooled and filtered.

The first and second runs were combined and distilled to yield 71.8 g. (68%) of *o*-tolyltrimethylsilane boiling at 196° (750 mm.).

Oxidation of *o*-Tolyltrimethylsilane. With Chromium Trioxide.—Oxidation of *o*-tolyltrimethylsilane with chromium trioxide by the method of Lewis and Gainer,[10] and in glacial acetic acid under various conditions resulted in negligible yields of the desired *o*-trimethylsilylbenzoic acid.

With Potassium Permanganate.—The following procedure, adapted with modifications from the method of Brumfield,[11] resulted in the best yields obtainable with varying concentrations and temperatures.

To 28.0 g. (0.17 mole) of *o*-tolyltrimethylsilane dissolved in 300 ml. of glacial acetic acid was added a small portion of 83.5 g. (0.53 mole) of potassium permanganate. The reaction mixture was warmed to *ca.* 35°, whereupon the temperature began rising spontaneously. The remainder of the permanganate was then added portionwise over a half-hour period, while the temperature of the reaction mixture was maintained at 45–50° by the occasional application of an ice-bath. This temperature was maintained for an additional six hours, and the reaction mixture was then allowed to stand overnight. It was distilled under water aspirator vacuum at a bath temperature of 80–90°. When the contents of the flask were almost dry, 200 ml. of water was added and steam distillation was continued under reduced pressure. The first distillate and the steam distillate were combined and neutralized with solid potassium carbonate. This mixture was then extracted several times with portions of ether, and the ether extracts were combined, filtered, and the ether was evaporated off. There was recovered 7.28 g. of *o*-tolyltrimethylsilane, n^{20}_{D} 1.5028.

The black paste remaining in the flask was slurried with 300 ml. of water and then made basic with solid potassium carbonate. This mixture was thoroughly mixed and warmed to *ca.* 60–70° and then filtered with suction. The filtrate was decolorized with a small amount of solid sodium bisulfite, chilled, and then acidified carefully with hydrochloric acid. The resulting white precipitate was filtered and dried. The black residue was similarly treated two more times before no further acid was obtained. The yield of *o*-trimethylsilylbenzoic acid was thus 5.11 g., m.p. 97.5–98.5° (21.4% based on recovered *o*-tolyltrimethylsilane).

***o*-Trimethylsilylbenzoic Acid.**—The following preparation of *o*-trimethylsilylbenzoic acid is an adaptation of a procedure of Gilman and Arntzen.[12]

A mixture of 53.2 g. (0.27 mole) of *o*-bromobenzoic acid and 200 ml. of anhydrous ether was cooled to −75° with the aid of an insulated Dry Ice–trichloroethylene-bath. Under a nitrogen atmosphere was then added, with vigorous stirring, 0.53 mole of *n*-butyllithium[13] in 300 ml. of ether over a 25-minute period; the second 150 ml. was added a little more rapidly than the first. The reaction mixture was stirred for an additional ten minutes after which time 61 g. (0.56 mole) of trimethylchlorosilane in 100 ml. of ether was added over a 15-minute period, while a bath temperature of −75 to −70° was maintained. There was no apparent precipitation of lithium chloride at this time nor an hour afterward. The cold bath was then liberally replenished with Dry Ice, and the reaction mixture was permitted to stir and slowly warm up overnight. The temperature of the reaction mixture the next day was *ca.* 10°. The cold bath was removed, and stirring was continued for a few hours at room temperature. Color Test I[14] was negative at this point. The reaction mixture was hydrolyzed with dilute hydrochloric acid; sufficient acid was added to ensure that the aqueous layer was acidic. The layers were separated, and the ethereal layer was extracted with a dilute aqueous solution containing 0.3 mole of sodium hydroxide. The basic extract was filtered, cooled in an ice-bath, and acidified carefully with concd. hydrochloric acid. The resulting precipitate was filtered with suction and washed twice with 25-ml. portions of cold water. The crude, air-dried product weighed 40 g. and melted at 73–82°.

Crystallization of a small portion of the crude product from cyclohexane yielded crystals melting at 130–141°, indicating the presence of unreacted *o*-bromobenzoic acid. After several trials, it was found that the two acids could be separated rather easily by the use of petroleum ether, in which solvent *o*-bromobenzoic acid is practically insoluble whereas *o*-trimethylsilylbenzoic acid is extremely soluble. The crude acid was therefore placed in a Soxhlet apparatus and extracted with 35–37° petroleum ether for five hours. The petroleum ether extract was then evaporated to dryness; the residue melted at 90–95°. Crystallization from aqueous acetic acid (approx. 2 vol. acetic acid to 1 vol. water) yielded 25.3 g. of needle-like crystals, m.p. 97–98.5°; recrystallization of a small portion of this product yielded crystals melting at 98–98.5°. A mixed m.p. with a sample obtained by the oxidation procedure showed no depression.

The residue in the Soxhlet thimble weighed 7.8 g. and melted at 142–145°. Crystallization from benzene yielded 6.9 g. of material melting 148.5–149°; a mixed melting point with *o*-bromobenzoic acid was not depressed.

Based on recovered *o*-bromobenzoic acid, there was obtained a 57% yield of *o*-trimethylsilylbenzoic acid.

***o*-Trimethylsilylbenzoyl Chloride.**—*o*-Trimethylsilylbenzoic acid (25 g., 0.13 mole) was refluxed with 75 ml. of freshly distilled thionyl chloride for one hour. The excess thionyl chloride was then distilled off first at atmospheric pressure and then under water aspirator vacuum. The residue was distilled to yield 24.22 g. (88%) of *o*-trimethylsilylbenzoyl chloride boiling at 66–67° (0.5 mm.), n^{20}_{D} 1.5360.

Anal. Calcd. for $C_{10}H_{13}ClOSi$: C, 56.45; H, 6.16; Si, 13.19. Found: C, 56.71; H, 6.40; Si, 12.7.

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[9] H. A. Clark, A. F. Gordon, C. W. Young and M. J. Hunter. This Journal, **73**, 3798 (1951).

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

[11] P. E. Brumfield, Ph.D. Thesis, Purdue University, 951.

[12] H. Gilman and C. E. Arntzen, This Journal, **69**, 1537 (1947).

[13] R. G. Jones and H. Gilman, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 352.

[14] H. Gilman and F. Shultz, This Journal, **47**, 2002 (1925).

Anilide.—Crystallization from 90–100° petroleum ether yielded needles melting at 129.5–130°.

Anal. Calcd. for $C_{16}H_{19}NOSi$: N, 5.20. Found: N, 5.36.

Amide was crystallized from 90–100° petroleum ether, m.p. 124.5–125°.

Anal. Calcd. for $C_{10}H_{15}ONSi$: N, 7.25. Found: N, 7.26.

***o*-Trimethylsilylbenzoyl Chloride and Anisole. First Run.**—Using the same amounts of materials and a similar procedure as in the *p*-acid chloride case, *o*-trimethylsilylbenzoyl chloride was treated with anisole for 15 hours at 25–30°. During this time, the initially yellow reaction mixture progressively acquired an orange color, and when stirring was discontinued, two phases separated: a lower bright red layer, and an upper yellow layer. The mixture was hydrolyzed by pouring it upon a solution of 10 ml. of concd. hydrochloric acid and 50 ml. of cold water and agitated vigorously in order to discharge the red color. The layers were separated and the organic layer was washed once with water, aqueous sodium bicarbonate solution, water, and then dried over Drierite. Upon filtration, the solution was stripped of benzene, and the residue was distilled at 0.5 mm. through a short distilling head. There was obtained 0.83 g. of material boiling at 65–66°, n^{20}_{D} 1.5360; *ca.* 0.3 g. boiling up to 148°; and 1.8 g. of a dark viscous material boiling over 200°.

The lowest boiling fraction was treated with ammonium hydroxide to yield the amide melting at 124.5–125° when recrystallized from ligroin. This amide did not depress the melting point of *o*-trimethylsilylbenzamide.

The middle fraction was dissolved in a small amount of ethanol and placed in a refrigerator. No crystallization occurred after a two-month period.

Second Run.—Since there was a possibility of polymerization occurring during the distillation process, a second run was carried out similar to the first, except that after stripping off the benzene solvent, the residue was dissolved in warm 95% ethanol and placed in a refrigerator. Crystallization did not occur after 7 weeks.

***o*-Trimethylsilylbenzoyl Chloride and Toluene. First Run.**—To 60 ml. of dry *sym*-tetrachloroethane protected from moisture and cooled in an ice-bath was added 2.58 g. (0.0194 mole) of anhydrous aluminum chloride. To this solution was then added a solution of 4.00 g. (0.019 mole) of *o*-trimethylsilylbenzoyl chloride and 2.3 g. (0.025 mole) of toluene in 15 ml. of *sym*-tetrachloroethane over a 25-minute period. The ice-bath was removed and stirring was continued at 25–30° for 15 hours. The reaction mixture was then poured on ice-water containing 25 ml. of concd. hydrochloric acid, and worked up as described for the anisole case. The *sym*-tetrachloroethane solvent was stripped off under water aspirator vacuum, and the residue was distilled through a short distilling head at 0.5 mm. There was obtained a fraction boiling 101–120° and another fraction boiling at 130–139°, each weighing approximately 0.5 g. The third fraction consisted of a viscous resinous material weighing 2 g. and boiling over 220° with decomposition.

The two lower boiling fractions could not be crystallized.

Second Run.—A second run was carried out with 2.58 g. of aluminum chloride, 4.00 g. of *o*-trimethylsilylbenzoyl chloride and 75 ml. of toluene. Stirring was continued at 25–30° for 38 hours. Hydrolysis was carried out as above, and the toluene was then stripped off. The residue was dissolved in ethanol and placed in a refrigerator. No crystallization was observed after 7 weeks.

Bis-*p*-methoxyphenylcadmium and *o*-Trimethylsilylbenzoyl Chloride.—*p*-Methoxyphenylmagnesium bromide was prepared from 7.85 g. (0.042 mole) of *p*-bromoanisole and 1.2 g. (0.05 g. atom) of magnesium turnings in 60 ml. of ether. After filtration under nitrogen to remove excess magnesium, this Grignard reagent was cooled with the aid of an ice-bath, whereupon there was added 4.2 g. (0.023 mole) of anhydrous cadmium chloride. The ice-bath was removed, and stirring was continued about two hours at room temperature. At this point, Color Test I[14] was negative. The excess ether was stripped off with the aid of a hot water bath, and to the residue was added 50 ml. of dry benzene. To this stirred suspension was added 3 g. (0.0138 mole) of *o*-trimethylsilylbenzoyl chloride in 20 ml. of benzene over a three-minute period. Stirring and gentle refluxing were then continued for about four hours, after which time the reaction mixture was cooled in ice and hydrolyzed with dilute sulfuric acid. The layers were separated, and the organic layer was washed once with water, sodium bicarbonate solution, water, and then separated and dried over Drierite. Upon filtration and stripping off of the benzene, the residue was taken up in ethanol and allowed to crystallize in a refrigerator. There was obtained 2.50 g. of crystalline material melting at 67–74°. Attempts to sharpen the m.p. by recrystallization from ethanol were not successful; petroleum ether (90–100°), proved to be a better crystallizing solvent. The warm petroleum ether solution however, still exhibited a milky hue, which could not be removed by filtration. This solution was therefore diluted further with petroleum ether and passed through a 20 by one cm. column consisting of an intimate mixture of $^2/_3$ part Celite and $^1/_3$ part activated alumina. The resulting solution was concentrated and permitted to crystallize. There was obtained 2.0 g. of material melting at 70–70.5°; a subsequent crystallization did not raise the m.p.

Anal. Calcd. for $C_{17}H_{20}O_2Si$: C, 71.79; H, 7.09. Found: C, 71.71; H, 7.29.

Bis-*p*-tolylcadmium and *o*-Trimethylsilylbenzoyl Chloride.—In a preparation similar to that preceding from the same molar amounts of materials, there was obtained from bis-*p*-tolylcadmium and *o*-trimethylsilylbenzoyl chloride, 3.15 g. of crystalline material melting at 64–70°. Purification by chromatography and crystallization as above yielded 2.2 g. of crystals melting at 76–76.5°.

This compound exhibited a reversible photocoloration. When exposed to ultraviolet light or sunlight, it rapidly became pink in color, and then became colorless when kept in the dark for a short while.

Anal. Calcd. for $C_{17}H_{20}OSi$: C, 76.08; H, 7.51. Found: C, 76.65; H, 7.50.

The phenylhydrazone of either *p*-methoxyphenyl *o*-trimethylsilylphenyl ketone or *p*-tolyl *o*-trimethylsilylphenyl ketone would not form after standing for two weeks.

Infrared Absorption Spectra.—Infrared absorption spectra[15] were determined with a Perkin–Elmer Double Beam Recording Infrared Spectrophotometer, Model 21, in carbon tetrachloride solution, equipped with a 0.1-mm. sodium chloride cell.

Absorption spectra of *p*-tolyl *p*-trimethylsilylphenyl ketone, *p*-tolyl *o*-trimethylsilylphenyl ketone, *p*-methoxyphenyl *p*-trimethylsilylphenyl ketone and *p*-methoxyphenyl *o*-trimethylsilylphenyl ketone showed the presence of a carbonyl band at 6 μ in all cases.

***m*-Trimethylsilylbenzoic Acid.**—This acid was prepared as described by Roberts, *et al.*[7]

***m*-Trimethylsilylbenzoyl Chloride.**—*m*-Trimethylsilylbenzoic acid (6.7 g., 0.0345 mole) was refluxed one hour with 25 ml. of thionyl chloride and then worked up as in the ortho and para cases. Upon distillation there was obtained 5.1 g. (70%) of *m*-trimethylsilylbenzoyl chloride boiling at 70° (0.5 mm.), n^{20}_{D} 1.5252.

Anal. Calcd. for $C_{10}H_{13}ClOSi$: Si, 13.19. Found: Si, 13.0.

Anilide.—Crystallized from 90–100° petroleum ether and decolorized with Norite, it formed shiny platelets, m.p. 127–127.5°.

Anal. Calcd. for $C_{16}H_{19}NOSi$: N, 5.20. Found: N, 5.35.

***m*-Trimethylsilylbenzoyl Chloride and Toluene.**—A mixture of 60 ml. of toluene, 4.00 g. of *m*-trimethylsilylbenzoyl chloride and 2.58 g. of aluminum chloride was stirred for 23 hours at *ca.* 25°. It was then hydrolyzed and worked up as described previously. After the excess toluene had been stripped off, the residue was taken up in warm ethanol and refrigerated; crystallization occurred after this solution had stood for 22 days. There was obtained 2.2 g. (43%) of material melting at 40–42°. Recrystallization from ethanol yielded a product melting at 43–44°.

Anal. Calcd. for $C_{17}H_{20}OSi$: C, 76.08; H, 7.51. Found: C, 76.16; H, 7.50.

Phenylhydrazone.—The phenylhydrazone separated as an oil.

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[15] Infrared absorption spectra were determined by Mr. Phillip A. Kinsey.

Semicarbazone.—Recrystallized from *ca.* 80% ethanol, the semicarbazone melted at 184–185° (cor.).

Anal. Calcd. for $C_{18}H_{23}N_3OSi$: N, 12.92. Found: N, 13.09.

***m*-Bromophenyltrimethylsilane.**—*m*-Bromophenyltrimethylsilane was prepared by an adaptation of a procedure of Gilman and Melvin.[13] *n*-Butyllithium[13] (0.132 mole) was added to a stirred solution of *m*-dibromobenzene in 100 ml. of ether over a ten-minute period. Occasional application of an ice-bath was necessary in order to prevent excessive refluxing. When all the butyllithium had been added, stirring was continued at room temperature for an additional 25 minutes. To this reaction mixture was then added a solution of 14.1 g. (0.13 mole) of trimethylchlorosilane and 50 ml. of ether over a 10-minute period. Stirring was continued for two hours at room temperature and refluxing for an additional half hour. The reaction mixture was then hydrolyzed with dilute hydrochloric acid. The ethereal layer was separated, washed once with water, separated, and then dried over Drierite. After the ether had been stripped off, the residue was distilled to yield 5.1 g. (17%) of a material boiling at 96–97° (5 mm.), $n^{20}D$ 1.5290.

Anal. Calcd. for $C_9H_{13}BrSi$: Si, 12.24. Found: Si, 12.1.

***p*-Tolyl *m*-Trimethylsilylphenyl Ketone.**—Two grams (0.0088 mole) of *m*-bromophenyltrimethylsilane in 30 ml. of ether was refluxed with 0.26 g. (0.011 g. atom) of magnesium turnings for four hours. This Grignard reagent was filtered under nitrogen, and to the filtrate was added 0.59 g. (0.005 mole) of *p*-tolunitrile in 10 ml. of ether. Refluxing was continued for four more hours, the mixture was hydrolyzed and worked up as in the preparation of *p*-tolyl *p*-trimethylsilylphenyl ketone. Distillation of the residue at 0.5 mm. yielded 1.1 g. (82%) of material boiling at 130–131°. This fraction was taken up in warm ethanol and refrigerated. There was obtained a crystalline material melting at 40–42°. Recrystallization yielded a product melting at 43–44°. A mixed m.p. with the ketone prepared through the Friedel–Crafts reaction was not depressed.

LAFAYETTE, IND.

NOTES

The Isolation of *trans*-3,5-Dimethoxystilbene from Tall Oil

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3,5-Dimethoxystilbene has been isolated from several natural sources[1,2] and Erdtman[1c] has shown by a study of their ultraviolet spectra that 3,5-dihydroxystilbene and its methyl ethers occur naturally only in the *trans* form.

In the course of some work on the unsaponifiable constituents of tall oil fatty acids, there was obtained by batch vacuum refractionation of unsaponifiables extracted from commercial tall oil fractionation heads,[3] a fraction boiling at 203–208° (4 mm.) which showed a strong absorption near 300 mμ. From this fraction 3,5-dimethoxystilbene was isolated as its picrate and identified by its physical properties and those of several of its derivatives and by oxidation to benzaldehyde, benzoic acid and 3,5-dimethoxybenzoic acid.

3,5-Dimethoxystilbene shows strong absorption at 300 mμ.[4] Since only one other unsaponifiable fraction (b.p. 170–171° at 4 mm.) showed an appreciable absorption in this region, and since the absorption of that fraction was such that $k_{300} = {}^1/_2(k_{280} + k_{320})$ (approximately), where k is the specific absorptivity, it was assumed that a linear background absorption should give satisfactory values for *trans*-3,5-dimethoxystilbene content. Therefore, the formula

$$\%\ trans\text{-3,5-Dimethoxystilbene} = 100\ \frac{k_{300} - 0.5(k_{280} + k_{320})}{38.5}$$

was derived from k values obtained with pure 3,5 dimethoxystilbene ($k_{280} = 78.8$; $k_{300} = 119$; $k_{320} = 82.2$) and used to determine the *trans*-3,5-dimethoxystilbene content of crude and distilled tall oil and of tall oil rosin.

The quantity of *trans*-3,5-dimethoxystilbene present in the unsaponifiables of crude and distilled tall oil is appreciable (*cf.* Table I). It is interesting to note that tall oil rosin,[5] unlike wood and gum rosins, contains no detectable amounts of *trans*-3,5-dimethoxystilbene.

TABLE I

trans-3,5-DIMETHOXYSTILBENE CONTENT OF TALL OIL AND TALL OIL DISTILLATION PRODUCTS

	% *trans*-3,5-Dimethoxystilbene In unsaponifiables	In product	Unsaponifiables in product, %
Crude tall oil[5]	7.4	0.54	7.3
Distilled tall oil[5]	18.0	.32	1.8
Tall oil rosin[5]	Not detected[a]	..	5.0

[a] Estimated lower limit of detection, 0.02%.

Experimental

Ultraviolet absorption spectra were obtained using a Beckman spectrophotometer, Model DUV, and a Cary automatic recording spectrophotometer, Model 11.

Isolation of *trans*-3,5-Dimethoxystilbene.—An unsaponifiable fraction from tall oil, boiling at 203–208° (4 mm.) and weighing 0.597 g. in ethanol was treated with a saturated ethanolic picric acid solution. The yellow picrate which crystallized immediately was collected after standing overnight, 0.633 g., m.p. 109–110°, unchanged on recrystallization from ethanol. The picrate was cleaved by partition between benzene and dilute ammonia. The residue from the benzene solution solidified after standing two days, m.p. 55°. After two recrystallizations from ethanol, large colorless needles melting at 57° were obtained; boiling point 206° (3.8 mm.), $n^{25}D$ (supercooled melt) 1.5600.

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(1) (a) H. Erdtman, *Svensk Papperstidn.*, **46**, 226 (1943); (b) *Svensk Kem. Tid.*, **56**, 95 (1944); (c) *ibid.*, **56**, 134 (1944).

(2) R. F. B. Cox, THIS JOURNAL, **62**, 3512 (1940).

(3) Arizona Chemical Co., 30 Rockefeller Plaza, New York 20. N. Y.

(4) Spectrum to be published in *Applied Spectroscopy*, Vol. 8.

(5) Tall Oil Rosin, as defined under the Naval Stores Act (Regulations for the Administration and Enforcement of the Naval Stores Act, Feb. 8, 1952, paragraphs 160.2 and 160.305.)