Experimental[5]

Cholesteryl Tetrahydropyranyl Ether.—A slurry of 5.00 g. (13 mmoles) of cholesterol and 20 ml. of dihydropyran was treated with two drops of concentrated hydrochloric acid and shaken vigorously for five minutes. At the end of this time all of the steroid had dissolved. After standing 12 hours at room temperature, the semi-solid mass was diluted with ether and processed as previously described.[2b] The solid residue was recrystallized from ethanol to give 5.01 g. (82%) of the ether, m.p. 151.5–152.5°. Recrystallization raised the melting point to 154.5–155.5°, $[\alpha]^{23}\text{D}$ −35.9° in chloroform.

Anal. Calcd. for $C_{32}H_{54}O_2$: C, 81.62; H, 11.56. Found: C, 81.80; H, 11.56.

3β-Hydroxy-Δ⁵-homocholenic Acid.—A solution of 1.00 g. (2.40 mmoles) of 3β-acetoxy-Δ⁵-cholenic acid in 10 ml. of dry benzene and 4 ml. of oxalyl chloride was heated at 50° for two hours. The solution was then concentrated to dryness at 50° *in vacuo*. Two 10-ml. portions of dry benzene were added and distilled under reduced pressure to remove the last traces of oxalyl chloride. The acid chloride, in 10 ml. of dry benzene, was added dropwise to a stirred solution of diazomethane (prepared from 1.1 g. of nitrosomethylurea) in 60 ml. of methylene chloride. After standing 12 hours, the solution was filtered, concentrated at reduced pressure and the residue treated with 100 ml. of methanol and freshly precipitated silver oxide (prepared from 10 ml. of 10% silver nitrate solution). The solution was slowly brought to reflux temperature, refluxed for one hour, treated with Norit, filtered and concentrated. The residue was refluxed with 5.00 g. of potassium hydroxide in 50 ml. of methanol and 40 ml. of water under a nitrogen atmosphere. The solution was filtered and acidified with concentrated hydrochloric acid. The suspension after standing for 12 hours, was centrifuged and dried overnight at 60°. The crude product weighed 0.72 g. (72%). After two recrystallizations from methanol–water, the acid melts from 197.6–199.2°. Hattori[6] reported a m.p. of 210–215°.

Anal. Calcd. for $C_{25}H_{40}O_3$: C, 77.23; H, 10.38. Found: C, 77.52; H, 10.53.

For conversion to the methyl ester the crude acid may be used.

Methyl 3β-Hydroxy-Δ⁵-homocholenate.—An ethereal solution of the crude acid was added slowly to an excess of diazomethane in ether at 0°. The solution was allowed to come to room temperature and the excess diazomethane removed with a slight excess of formic acid. The ethereal solution was washed with dilute sodium bicarbonate solution and water, dried and concentrated. The crude ester was chromatographed on alumina. After developing with benzene, the ester was eluted with 1% methanol in benzene. Recystallization from methanol gave 80% of white plates, m.p. 85.6–87.0°.

Anal. Calcd. for $C_{26}H_{42}O_3$: C, 77.32; H, 10.52. Found: C, 77.04; H, 10.24.

Methyl 3β-Hydroxy-Δ⁵-homocholenate Tetrahydropyranyl Ether.—Concentrated hydrochloric acid (two drops) was added to a solution of 0.63 g. of the methyl homocholenate in 10 ml. of dihydropyran with vigorous shaking. The reaction solution was allowed to stand for 24 hours and then processed in the usual fashion.[2b] The crude material was recrystallized from ethanol–water, yield 0.20 g. (30%), m.p. 92.5–93.0°, $[\alpha]^{25}\text{D}$ −36.6° in chloroform.

Anal. Calcd. for $C_{31}H_{48}O_4$: C, 76.81; H, 9.98. Found: C, 76.93; H, 10.40.

3β-Hydroxy-Δ⁵-norcholesten-25-one Tetrahydropyranyl Ether.—A solution of 1.00 g. (2.6 mmoles) of norolone in 20 ml. of dihydropyran was prepared by gentle warming and then carefully cooled to room temperature. Concentrated hydrochloric acid (0.4 ml.) was added dropwise to this solution over a period of four minutes with vigorous agitation. After the addition of each drop of acid, the solution was shaken until the blackish precipitate, which formed, redissolved. The solution was allowed to stand for 48 hours and then processed in the usual fashion.[2b] The first recrystallization gave a sirupy mixture which was best separated by centrifugation. After two more recrystallizations from alcohol–water, the product melted at 104.9–106.2°. The yield was 0.71 g. (57%), $[\alpha]^{28}\text{D}$ −28.6° in chloroform.

Anal. Calcd. for $C_{31}H_{50}O_3$: C, 79.11; H, 10.69. Found: C, 79.45; H, 10.85.

Hydrolysis of Cholesteryl Tetrahydropyranyl Ether.—A solution of 1.00 g. (2.12 mmoles) of cholesteryl tetrahydropyranyl ether and 0.05 g. of *p*-toluenesulfonic acid in 15 ml. of ethanol was refluxed for one hour, concentrated to half volume, diluted with water and cooled. Filtration gave 0.80 g. (97%) of lustrous plates, m.p. 146.0–147.5°. Concentrated hydrochloric acid may also be used as catalyst, though the yield is somewhat lower.

Acetolysis of the Ether to Cholesteryl Acetate.—A solution of 4.00 g. (8.15 mmoles) of the pyranyl ether in 25 ml. of acetic acid was refluxed for 24 hours, concentrated under reduced pressure and the residue dissolved in ether. The ethereal solution was washed with dilute sodium carbonate solution and saturated sodium chloride solution, dried and concentrated. The solid acetate was recrystallized twice from methanol to give 2.57 g. (70.5%) of cholesteryl acetate, m.p. 113.1–113.8°, undepressed upon admixture with an authentic sample. Acetic anhydride as solvent gave almost identical results. When the reaction time was cut to three or four hours, a mixture of unchanged ether and cholesteryl acetate was obtained, which melted at 95.5–97.0° after sintering at 92° (unchanged by repeated recrystallization), $[\alpha]^{23}\text{D}$ −40.9° in chloroform. The optical rotation was intermediate between that of the ether, −35.9°, and that of the acetate, −47.5°. An equimolar mixture of the ether and the acetate, thrice recrystallized from methanol, melted at 95.0–97.1°, $[\alpha]^{21}\text{D}$ −38.0° in chloroform.

Cyclohexyl Tetrahydropyranyl Ether.—Three drops of concentrated hydrochloric acid were added dropwise to a solution of 20.0 g. (0.2 mole) of cyclohexanol in 35 ml. of dihydropyran and the reaction allowed to stand overnight. The solution was then diluted with ether and worked up as usual. After 2.07 g. of forerun, 30.68 g. (82.5%) of the ether was obtained, b.p. 94–95° (5 mm.), $n^{25}\text{D}$ 1.4642.

Anal. Calcd. for $C_{11}H_{20}O_2$: C, 71.68; H, 10.95. Found: C, 71.83; H, 10.80.

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Reaction of Wijs Iodine Number Reagent with the *exo*-Isomer of Endomethylenetetrahydrophthalic Anhydride

BY C. H. HELBING

In connection with research on cyclopentadiene, *endo*-3,6-endomethylenetetrahydrophthalic anhydride was converted to the *exo*-isomer by a process which in its essential details followed that reported by Alder and Stein, *et al.*[1] The *endo*-isomer was prepared from cyclopentadiene and maleic anhydride in methyl ethyl ketone at 20–40°.

The iodine number determined by the Wijs method,[2] which utilizes iodine monochloride, on the *exo*-isomer was substantially the theoretical value as calculated for 3,6-endomethylenetetrahydrophthalic anhydride (154.7). The iodine number determined in the same manner on the *endo*-isomer was substantially zero. A determination on a known mixture gave about the expected result with the assumption that the *exo*-form reacts with iodine monochloride and the *endo*-form does not. This information should be useful in determining the isomers present in cyclopentadiene adducts.

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[5] All melting points are corrected. All boiling points are uncorrected. All analyses are by the Microanalytical Laboratory of the Dept. of Chemistry, Univ. of California

[6] J. Hattori, *J. Pharm. Soc. Japan*, **58**, 548 (1938).

[1] K. Alder, G. Stein, Wolfgang Eckardt, Rudolf Freiherr v. Buddenbrock and Stephan Schneider, *Ann.*, **504**, 216 (1933); *C. A.*, **27**, 5311 (1933).

[2] ASTM: D 555-41-9.

Experimental details are given in Table I.

TABLE I

Isomer	M.p., °C.	Iodine number Found	Iodine number Calcd.
endo	151–162[a]	3.4	154.7
exo	142–145	151.9	154.7
Mixture 69% *endo* 31% *exo*	118–133	49.6	49.4

[a] This melting point was taken on *endo*-3,6-endomethyleneetetrahydrophthalic anhydride which was fused and allowed to resolidify. The crystals of the *endo*-isomer which separated from methyl ethyl ketone as reaction product of maleic anhydride and cyclopentadiene melted at 164° before fusion.

We wish to thank Mr. E. F. Berger for iodine number determinations.

PAINT DIVISION RESEARCH LABORATORY
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Preparation of Organopolysilanes

BY HENRY GILMAN, TSE CHENG WU, HOWARD A. HARTZFELD, GERALD A. GUTER, ARTHUR G. SMITH, JACK J. GOODMAN AND SCOTT H. EIDT

The silicon–silicon bond is in general much less stable than the carbon–carbon bond (Si–Si, 45 kcal./mole; C–C, 80 kcal./mole[1]). While the length of the carbon–carbon chain is almost unlimited, the silicon–silicon chains known at the present time are relatively short. In the polysilane series the longest silane ever reported[2] is Si_6H_{14}. Silicon chlorides from $SiCl_4$ to Si_6Cl_{14} are well known.[3] Schwarz and co-workers[4,5] reported the preparation of $Si_{10}Cl_{22}$ and $Si_{25}Cl_{52}$ by heating $SiCl_4$ in a hydrogen and in a nitrogen atmosphere, respectively.

The organosubstituted silicon chains which have been made are rather small. Although there are a few known hexasubstituted disilanes, no octasubstituted trisilane has been reported. Schumb and Saffer[6] treated octachlorotrisilane with phenylmagnesium bromide, and they obtained a mixture of tetraphenylsilane and hexaphenyldisilane instead of octaphenyltrisilane. The aryl organosilicon chains of greater length which have been reported were prepared by the action of sodium on diphenyldichlorosilane and closely related compounds. By this method Kipping and co-workers[7a] were able to isolate two compounds with the formula $(C_6H_5)_8Si_4$ and two other substances with the formulas $[(C_6H_5)_2Si]_n$, with n having a value of 6 or 8. Recently, Burkhard,[7b] using a similar procedure, showed in an interesting study that polydimethylsilanes can be prepared from dimethyldichlorosilane and sodium.

We are now reporting a new approach for the syntheses of organopolysilanes. When two moles of triphenylsilylpotassium is treated with one mole of diphenyldichlorosilane in ether, octaphenyltrisilane is formed. When one mole of triphenylsilylpotassium is treated with one mole of diphenyldichlorosilane, pentaphenylchlorodisilane can be isolated. Pentaphenylchlorodisilane is an interesting compound because compounds of this type may be coupled to form organopolysilanes by doubling the length of the silicon chain.

$$(C_6H_5)_3SiSi(C_6H_5)_3 \xrightarrow{\text{Na-K}} 2(C_6H_5)_3SiK$$

$$2(C_6H_5)_3SiK + (C_6H_5)_2SiCl_2 \longrightarrow (C_6H_5)_8Si_3 + 2KCl$$

$$(C_6H_5)_3SiK + (C_6H_5)_2SiCl_2 \longrightarrow (C_6H_5)_3SiSi(C_6H_5)_2Cl + KCl$$

Experimental

Triphenylsilylpotassium.—In a previous paper from this Laboratory[8] there was described the preparation of triphenylsilylpotassium from hexaphenyldisilane and sodium–potassium alloy. (Due precautions should be exercised in the preparation and handling of this alloy.) Since then we found that the amount of ether used as a solvent affected the initiation of the reaction. In general an increase in the amount of solvent used increased the time for the appearance of the color of the organosilicon–metallic compound. After some studies the following procedure worked satisfactorily, and it has been checked more than twenty times.

In a dry three-necked flask fitted with a Trubore glass blade stirrer, a gas inlet tube, and a glass stopper were placed 4 g. (0.0077 mole) of hexaphenyldisilane,[9] 1 ml. of sodium–potassium alloy (1:5) and 10 ml. of anhydrous ether, after the flask had been swept with dry, oxygen-free nitrogen. The slurry was stirred vigorously at room temperature. Usually, after 5 to 10 minutes a greenish-yellow color began to form, indicating the start of the reaction. About 30 minutes later a distinct tan mixture was formed. Then 50 ml. of anhydrous ether was added to the reaction mixture against a stream of nitrogen.[10] The mixture was stirred at room temperature for about 20 hours. At the end of this period a suspension with a color ranging from dark greenish-brown to tan was formed. Mercury was added (caution!) dropwise to the reaction mixture until a liquid amalgam was formed. The amalgam was then stirred with the reaction mixture for one and one-half hours in order to dissolve all the excess sodium–potassium alloy. The triphenylsilylpotassium suspension was separated from the liquid amalgam by forcing it through a glass tubing by the pressure of nitrogen into a dry nitrogen-filled dropping funnel. Color Test I[11] for the clear supernatant liquid was negative, whereas the precipitate gave an intense bluish-violet color in both organic and aqueous layers of the Color Test.

Octaphenyltrisilane.—A triphenylsilylpotassium suspension prepared according to the procedure described in the last paragraph was added fairly rapidly to 1.5 g. (0.0059 mole) of diphenyldichlorosilane dissolved in 20 ml. of anhydrous ether (in a nitrogen atmosphere). Some heat was evolved, and there was very little color change. The reaction mixture was stirred for 9 hours at room temperature. Color Test I[11] at this stage was positive (bluish-green), probably due to the slight excess of triphenylsilylpotassium present. The reaction mixture was filtered by suction. The gray residue was boiled 30 minutes with 50 ml. of dry benzene and filtered hot. On standing, a small amount of white precipitate was formed. This was removed by filtration. The solids melted at about 270° to form a turbid

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[1] K. S. Pitzer, THIS JOURNAL, **70**, 2140 (1948).

[2] A. Stock and C. Somieski, *Ber.*, **49**, 111 (1916).

[3] See, for example, J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. VI, Longmans, Green and Co., New York, N. Y., 1940, p. 960 ff.

[4] R. Schwarz and H. Meckbach, *Z. anorg. u. allgem. Chem.*, **232**, 241 (1937).

[5] R. Schwarz and C. Danders, *Chem. Ber.*, **80**, 444 (1947).

[6] W. C. Schumb and C. M. Saffer, Jr., THIS JOURNAL, **61**, 363 (1939).

[7a] F. S. Kipping and J. E. Sands, *J. Chem. Soc.*, **119**, 830, 848 (1921); F. S. Kipping, *ibid.*, **123**, 2590, 2598 (1923); *ibid.*, **125**, 2291 (1924).

[7b] C. A. Burkhard, THIS JOURNAL, **71**, 963 (1949).

[8] H. Gilman and T. C. Wu, THIS JOURNAL, **73**, 4031 (1951).

[9] Hexaphenyldisilane was prepared according to the method described by H. Gilman and G. E. Dunn, *ibid.*, **73**, 5077 (1951). It appears desirable to extend the reflux period to about 12 hours.

[10] It was observed that if the remainder of the ether was added before about 30 minutes, the yellow color which had formed faded away. It took some time for the reappearance of the color.

[11] H. Gilman and F. Schulze, THIS JOURNAL, **47**, 2002 (1925).