5-Cholestene-3β,26-diol (II). A. From Sodium Borohydride Reduction of Cholesterol 26-Hydroperoxide (I).—Compound I (10 mg) in 5 ml of methanol was cooled to 0° and sodium borohydride (50 mg) was added. After 5 min the excess sodium borohydride was destroyed by the addition of a few drops of acetic acid. The mixture was stirred with 10 ml of water and the product was extracted with methylene chloride. The methylene chloride extract was dried ($MgSO_4$) and concentrated to afford 4.0 mg of 5-cholestene-3β,26-diol (II): mp 169–170° [*cf.* mp 168–173° for (25*RS*)-26-hydroxycholesterol,[10] mp 169–171°[6]]; ir (KBr) 3300 cm^{-1} (OH); R_c 0.47 (magenta); r_T 3.18 and 2.27 on 3% QF-1 and 3% OV-1, respectively, identical with the r_T of an authentic sample of (25*RS*)-26-hydroxycholesterol.[6]

B. From Thermolysis of I.—Samples of 100–200 μg of the 26-hydroperoxide I in 10 μl of ethanol were injected into the flash heater zone (270°) of the gas chromatograph (6 mm i.d., 3% OV-1). The decomposition products were collected in glass capillaries by methods described earlier.[9b] After five successive collections sufficient materials were accumulated for further chromatographic and spectral identification purposes. Thus the least mobile sterol with R_c 0.47 (magenta), r_T 3.18 and 2.27 on 3% QF-1 and 3% OV-1, respectively, was identified as 5-cholestene-3β,26-diol (II) by comparison of its chromatographic data with those of an authentic sample. The structure was further confirmed by mass spectral analysis, which gave the correct molecular ion at *m/e* 402 (10).

3β-Hydroxy-5-cholesten-26-al (III).—Preparative gas chromatography of cholesterol 26-hydroperoxide gave in addition to 26-hydroxycholesterol II a comparatively more mobile component, R_c 0.87 (orange-red), r_T 3.83 and 1.88 on 3% QF-1 and 3% OV-1, respectively. The reverse mobile behavior of this compound on the selective 3% QF-1 column suggested the presence of a carbonyl group. By analogy with the thermal decomposition of cholesterol 24-hydroperoxide which afforded the 24-keto sterol as the major product[2b] this component was tentatively assigned as 3β-hydroxy-5-cholesten-26-al (III). This structural assignment was further supported by its mass spectral data which gave the expected molecular ion at *m/e* 400 (70), and by ir spectroscopy (KBr) 1720 cm^{-1} (CHO).

27-Nor-5-cholestene-3β,25ξ-diol (V). A. From Thermolysis of I.—A third major thermal decomposition product of the 26-hydroperoxide I, obtained from preparative gas chromatography, was identified as 27-nor-5-cholestene-3β,25ξ-diol (V) by comparison of its chromatographic data with those of an authentic sample: R_c 0.47 (magenta); r_T 2.30 and 1.53 on 3% QF-1 and 3% OV-1, respectively. Its mass spectrum showed the molecular ion at *m/e* 388 (8).

B. From 27-Nor-3β-hydroxy-5-cholesten-25-one.—Nor-25-ketocholesterol (4.0 mg) dissolved in 0.5 ml of methanol was treated with an excess of sodium borohydride (25 mg). The course of the reduction was followed by tlc. After all the starting material had disappeared a few drops of acetic acid was added followed by 10 ml of water. The product was extracted with methylene chloride, dried ($MgSO_4$), and concentrated to give a colorless product. Recrystallization of the product from hexane–ethyl ether gave 1.8 mg of 27-nor-5-cholestene-3β,25-diol (V): mp 159–169° (*cf.* lit.[11] mp 158–168°); R_c 0.47 (magenta); r_T 2.30 and 1.53 on 3% QF-1 and 3% OV-1, respectively; ir (KBr) 3300 cm^{-1} (OH).

27-Nor-5-cholesten-3β-ol (IV). A. From Thermolysis of I.—The most mobile thermal decomposition product of the 26-hydroperoxide I, isolated *via* preparative gas chromatography, was identified as 27-nor-5-cholesten-3β-ol (IV) by comparison of its spectral and chromatographic properties with those of an authentic sample: R_c 0.97 (magenta); r_T 0.86 and 0.84 on 3% QF-1 and 3% OV-1, respectively. Mass spectral analysis gave a molecular ion at *m/e* 372 (100).

B. From 27-Nor-5-cholestene-3β,25-diol (V).—Nor-5-cholestene-3β,25-diol (3.0 mg) was selectively converted to the 25-monotosylate upon treatment with 20 mg of *p*-toluenesulfonyl chloride in 0.5 ml of dry pyridine. The reaction was monitored by tlc and when most of the starting material had disappeared, anhydrous ether (3 ml) was added followed by lithium aluminum hydride (200 mg). The mixture was refluxed for 5 hr, followed by the addition of 10 ml of water. The product was extracted with methylene chloride. Gas chromatographic analysis of the methylene chloride extract revealed the presence of two major components, 27-norcholesterol (IV, 50%) and 27-nor-5-cholestene-3β,25-diol (V, 30%), together with a small amount of norcholestene.[12] The product mixture was separated by preparative tlc and recrystallization from hexane–ethyl ether to afford 1.2 mg of 27-nor-5-cholesten-3β-ol (V): mp 127–131° (*cf.* lit.[11] mp 132°); R_c 0.97 (magenta); r_T 0.86 and 0.84 on 3% QF-1 and 3% OV-1 respectively; ir (KBr) 3300 cm^{-1} (OH).

Registry No.—I, 23652-97-3; II, 13095-61-9; III, 32557-11-2; IV, 4420-91-1; V, 7548-79-0.

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Poly-α,α,2,3,5,6-hexafluoro-*p*-xylylene

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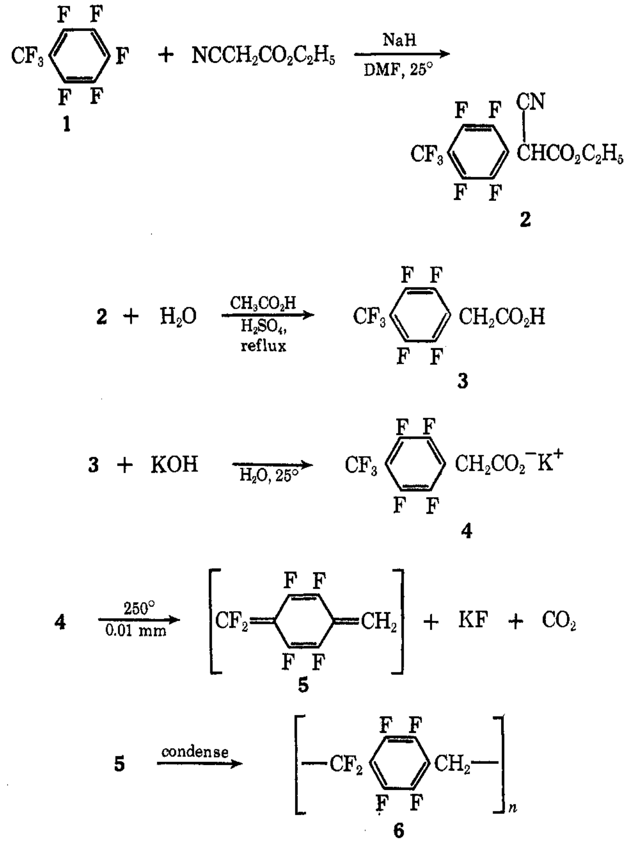
Poly-α,α,2,3,5,6-hexafluoro-*p*-xylylene (6) is formed by pyrolyzing potassium (4-trifluoromethyl-2,3,5,6-tetrafluorophenyl)acetate (4) under vacuum. The highly reactive intermediate, α,α,2,3,5,6-hexafluoro-*p*-xylylene (5), is transported, in the gas phase, to a cool surface where it condenses and immediately polymerizes.[1] The polymer was obtained as a clear



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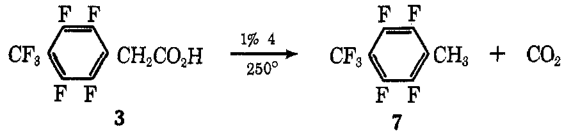
[1] Poly-*p*-xylylenes are commonly prepared by generating the monomeric *p*-xylylenes in the gas phase and condensing them to give polymers: L. A. Errede and M. Szwarc, *Quart. Rev., Chem. Soc.*, **12**, 301 (1959); W. F. Gorham, *J. Polym. Sci.*, **4**, 3027 (1966).

film on the inside of the condenser. It was swollen slightly with acetone but did not dissolve. An X-ray diffraction pattern shows well-defined lines indicating a high degree of crystallinity which is common with poly-*p*-xylylenes.[1] Whether the polymer units were joined head to tail or head to head and tail to tail was not determined. The polymer begins absorbing strongly in the ultraviolet at 300 nm.

Sodio ethyl cyanoacetate reacts readily with **1** to give ethyl (4-trifluoromethyl-2,3,5,6-tetrafluorophenyl)cyanoacetate (**2**).[2] Only one isomer was isolated, presumably the para isomer. Toward nucleophilic substitution on an aromatic system, trifluoromethyl is strongly, perhaps exclusively, para directing.[3] The trifluoromethyl group also increases the rate of aromatic nucleophilic substitution relative to fluorine, 10^3 times,[4] which accounts for the ease with which **2** is prepared. Acidic hydrolysis of **2** to **3** was used instead of basic hydrolysis because of the sensitivity of the highly fluorinated nucleus to nucleophilic attack.

Pyrolysis of alkali salts of fluorinated aliphatic acids leads to olefins. For instance, pyrolysis of sodium heptafluorobutyrate gives hexafluoropropene in high yield.[5] In the present instance the reaction has been extended from a 1,2 elimination to a 1,6 elimination.

The free acid, **3**, was thermally stable to its boiling point at 250°. Addition of a small amount of **4** to the boiling **3** caused loss of CO_2 to give **7**. Heating **4** in dimethylacetamide at 120° resulted in the formation of **7** also. The source of protons necessary to form **7** from **4** in the latter case was not investigated.



Experimental Section

Ethyl (4-Trifluoromethyl-2,3,5,6-tetrafluorophenyl)cyanoacetate (2).—Ethyl cyanoacetate (22.6 g, 0.20 mol) was added to 5.0 g (0.21 mol) of sodium hydride suspended in 75 ml of dimethylformamide keeping the reaction temperature at 25 ± 5°. When hydrogen evolution ceased, 23.6 g (0.10 mol) of octafluorotoluene (**1**) was added, maintaining the temperature at 25 ± 5°. The solution was stirred for 15 min after adding **1**. The reaction mixture was poured into 300 ml of ice water and extracted with 100 ml of ether. The ether phase was discarded; 30 ml of concentrated hydrochloric acid was added to the aqueous phase and extraction was performed with three 50-ml portions of ether. Evaporation of ether and distillation of residue gave 28 g (85% yield) of **2**, bp 107–113° (1.5 mm), mp 48–51°.

Anal. Calcd for $C_{12}H_6F_7NO_2$: C, 43.78; H, 1.84; F, 40.40; N, 4.26. Found: C, 44.08; H, 2.08; F, 39.86; N, 4.67.

(4-Trifluoromethyl-2,3,5,6-tetrafluorophenyl)acetic Acid (3).—Ethyl (4-trifluoromethyl-2,3,5,6-tetrafluorophenyl)cyanoacetate (28 g, 0.085 mol) was added to 50 ml of water, 50 ml of acetic acid, and 80 ml sulfuric acid and the mixture was heated at reflux for 5 hr. The mixture was poured into 500 ml of water and cooled to 5° overnight. The solid was filtered off to give 20 g (85% yield) of product, mp 60–70°. Recrystallization from *n*-hexane gave 18 g of **3**, mp 77–80°.

Anal. Calcd for $C_9H_3F_7O_2$: C, 39.15; H, 1.09; F, 48.17. Found: C, 39.04; H, 1.22; F, 49.52.

Methyl (4-Trifluoromethyl-2,3,5,6-tetrafluorophenyl)acetate.—To a mixture of 35 ml of methanol, 20 ml of benzene, and 1 ml of concentrated H_2SO_4 was added 9.8 g (0.034 mol) of **3**. The mixture was heated to reflux and the water was collected in a Dean–Stark trap. When the reaction was finished the reaction mixture was cooled and extracted with water. The organic phase was dried over Drierite and distilled to give 6.0 g (0.021 mol, 60% yield) of methyl (4-trifluoromethyl-2,3,5,6-tetrafluorophenyl)acetate, bp 90–100° (10 mm).

Anal. Calcd for $C_{10}H_5F_7O_2$: C, 41.39; H, 1.74; F, 45.84. Found: C, 41.37; H, 1.89; F, 45.74.

Potassium (4-Trifluoromethyl-2,3,5,6-tetrafluorophenyl)acetate (4).—(4-Trifluoromethyl-2,3,5,6-tetrafluorophenyl)acetic acid, 4.7 g (0.017 mol), was suspended in 25 ml of water, two drops of phenolphthalein indicator solution was added, and then 50% KOH solution was added to give a faint pink end point. The water was removed under reduced pressure at 25°. The dry residue was dissolved in 15 ml of acetone, filtered, and heated to boiling. Ethylene dichloride was added to the cloud point. Cooling gave 5.0 g (93%) of white needles, mp 222° dec. The salt was heated at 100° for 5 hr at 0.001 mm pressure and then analyzed.

Anal. Calcd for $C_9H_2F_7O_2K$: C, 34.40; H, 0.64; F, 42.33; K, 12.44. Found: C, 34.20; H, 0.57; F, 42.37; K, 12.48.

Poly-α,α,2,3,5,6-hexafluoro-*p*-xylylene (6).—Two grams of **4**, evacuated to a pressure of 0.01 mm, was heated in a 250° bath. The gases were led through a condenser cooled with Dry Ice. A thin film of polymer (0.1 g) formed on the inside of the condenser tube. The film was removed by wetting with acetone. It was 0.04 mm thick, clear, and pliable. An X-ray diffraction pattern on the film dried at 100° (0.001 mm) shows definite lines indicating crystallinity. Differential thermal analysis under nitrogen shows a small endothermic process starting at 421°. The sample showed no weight loss after 20 min at 400°. At 500° for 20 min it showed a 17% weight loss.

Anal. Calcd for $(C_8H_2F_6)_n$: C, 45.30; H, 0.95; F, 53.75. Found: C, 45.17; H, 0.83; F, 53.71.

α,α,α,2,3,5,6-Heptafluoro-*p*-xylene (7).—Ten grams (0.036 mol) of **3** was heated to 250° with no noticeable decomposition. It was allowed to cool and 0.10 g of **4** was added and then reheated to 250°. Seven grams of material distilled over at 135°. Redistillation gave 5.1 g (60%), bp 135–136° (705 mm), of **7**. The mass spectrum had a strong parent ion peak at *m/e* 232 and a base peak at *m/e* 163 (parent ion minus CF_3).

Anal. Calcd for $C_8H_3F_7$: C, 41.39; H, 1.31; F, 57.30. Found: C, 41.15; H, 1.39; F, 57.25.

One-half gram of **4** was heated to 120° in *N,N*-dimethylacetamide. Gas was evolved which gave a precipitate with barium hydroxide solution. After gas evolution ceased the mixture was poured into water and a dark liquid settled to the bottom. Vpc analysis (Dowfax 9N9 on Chromosorb W, 100°) showed only one volatile component, **7**. The mass spectrum was identical with that of **7** prepared in the previous experiment.

Registry No.—**2**, 32251-53-9; **3**, 32304-29-3; **3** methyl ester, 32251-56-2; **4**, 32251-54-0; **6**, 32218-15-8; **7**, 778-35-8.

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The Configuration of D-Alanyl-D-cycloserine Confirmed

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In an earlier report,[3] we described the synthesis of the dipeptide, D-alanyl-D-cycloserine (**1**), but the basis

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[1] Abstracted from the M.S. thesis presented to the University of Georgia Graduate School by Mr. C. S. Levine.

[2] To whom inquiries should be directed.

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