$CHClCO_2C_2H_5$ (III) as the principal product (64% yield).

The structure assigned to III is supported by elemental analysis and by its infrared spectrum. The compound exhibited a strong carbonyl absorption at 1760 cm^{-1} (liquid film), a shift from the frequency range (1750–1735 cm^{-1})[3] for the carbonyl group of normal saturated esters, but typical of esters having an electron-withdrawing group α to the C=O.[4-6] Further evidence for structure III is found in the work of Sweeney,[7] who obtained this compound by the sodium ethoxide-catalyzed reaction of II with ethanol and further characterized the ester by conversion to the anilide. The physical properties of our compound are in excellent agreement with those given by Sweeney.

The formation of III could be postulated as follows:

$$\underset{\text{I}}{CF_3CHClCClF_2} \xrightarrow{\text{KOH}} \underset{\text{II}}{(CF_3CCl{=}CF_2)} \xrightarrow{C_2H_5OH}$$

$$\underset{\text{IV}}{(CF_3CHClCF_2OC_2H_5)} \xrightarrow{OC_2H_5^-} \underset{\text{III}}{CF_3CHClCO_2C_2H_5}$$

It has been demonstrated[8] that conversions of the type I→IV proceed *via* an olefin intermediate rather than by a displacement (Williamson) reaction. Further reaction of a saturated α-difluoro ether with an alcohol in a basic medium often produces an ortho ester,[9] which, in turn, may be hydrolyzed to the ester with concentrated sulfuric acid.[10] The ether may be converted directly to the ester with this reagent.[10,11] Tarrant and Brown[9] observed, however, that when $CF_2{=}CCl_2$ was refluxed with ethanol and potassium hydroxide, ethyl dichloroacetate was obtained. We were unable to detect any saturated ether or ortho ester. It was also found that II, prepared from I, using aqueous alkali,[2] could be converted to III using Sweeney's procedure[7] (sodium ethoxide in absolute ethanol); the yield, however, was only 35%.

EXPERIMENTAL

Reaction of 1,2-dichloro-1,1,3,3,3-pentafluoropropane with potassium hydroxide in ethanol. In a 200-ml., round-bottomed flask, fitted with a reflux condenser to which a Dry Ice trap was attached, was placed 50 g. (0.246 mole) of 1,2-dichloro-1,1,3,3,3-pentafluoropropane and a solution of 14 g. (0.25 mole) of potassium hydroxide in 100 ml. of absolute ethanol. The mixture was heated under reflux for 6 hrs. No material was found in the trap. The reaction mixture was washed with water, dried over Drierite, and distilled. Thirty grams (64%) of ethyl 2-chloro-3,3,3-trifluoropropionate, b.p. 128–129°, n_D^{20} 1.3635, d_4^{20} 1.322, were obtained. Sweeney[7] reported, b.p. 118° (630 mm.), n_D^{20} 1.3636, d_4^{20} 1.322. The compound possessed a strong absorption band at 1760 cm^{-1} (C=O).

Anal. Calc'd for $C_5H_6ClF_3O_2$: C, 31.51; H, 3.17. Found: C, 31.47; H, 3.42.

Reaction of 2-chloro-1,1,3,3,3-pentafluoropropene with sodium ethoxide in ethanol. A 500-ml., 3-necked, round-bottomed flask was equipped with a stirrer, a condenser cooled with a Dry Ice-trichloroethylene mixture, and an addition tube. In the flask was placed a solution containing 4.6 g. (0.2 g.-atom) of sodium in 200 ml. of absolute ethanol. Then (50 g., 0.3 mole) of redistilled 2-chloro-1,1,3,3,3-pentafluoropropene (b.p. 7°),[2] was placed in an ampule which was attached to the addition tube. The olefin was allowed to boil into the reaction mixture, which was kept at room temperature and stirred continuously. The addition proceeded during 3 hours. Stirring was continued for an additional 2 hours. Starting material (20 g.) was recovered in a trap, cooled with Dry Ice-trichloroethylene, which was attached to a Friedrichs' condenser after the addition was complete. The reaction mixture was washed with water, dried over Drierite, and distilled. There was obtained 12 g. (35%) of ethyl ester, b.p. 128.5–129°, n_D^{20} 1.3630. An unidentified higher-boiling residue (b.p. *ca.* 160–170°), was also obtained in a 6-g. amount.

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(3) Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley and Sons, Inc., New York, N.Y. 1954, p. 153.

(4) Rasmussen and Brattain, *J. Am. Chem. Soc.*, **71**, 1073 (1949).

(5) Rappaport, Hauptschein, O'Brein, and Filler, *J. Am. Chem. Soc.*, **75**, 2695 (1953).

(6) Hampton and Newell, *Anal. Chem.*, **21**, 914 (1949).

(7) Sweeney, Ph.D. Thesis, University of Colorado (1952).

(9) Tarrant and Brown, *J. Am. Chem. Soc.*, **73**, 1781 (1951).

(8) Tarrant and Young, *J. Am. Chem. Soc.*, **75**, 932 (1953).

(10) Young and Tarrant, *J. Am. Chem. Soc.*, **71**, 2432 (1949).

(11) Young and Tarrant, *J. Am. Chem. Soc.*, **72**, 1860 (1950).

Preparation of 1-Phenoxyethyl Acetate

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1-Phenoxyethyl acetate was first prepared by Gershtein and Shostakovskii[2] in 49% yield by heating vinyl phenyl ether with acetic acid for 8–10 hours at 200–210° in an autoclave; later by Adelman[3] in 44% yield by the reaction of phenol with vinyl acetate at 25° in the presence of copper resinate, mercuric acetate, and sulfuric acid.

We obtained 1-phenoxyethyl acetate in 85% yield by refluxing a mixture of vinyl phenyl ether, acetic acid or acetic anhydride, and dimethylaniline.

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(2) Gershtein and Shostakovskii, *Zhur. Obshchei Khim.*, **18**, 1989 (1948); *Akad. Nauk S.S.S.R., Inst. Org. Khim., Sintezy Org. Soedinenii, Sbornik*, **2**, 19 (1952): *Chem. Abstr.*, **43**, 3786 (1949); *Chem. Abstr.*, **48**, 580 (1954).

(3) Adelman, U. S. Patent 2,579,411 (1951); *Chem. Abstr.*, **46**, 11226 (1952).

EXPERIMENTAL[4]

A mixture of 120 g. of vinyl phenyl ether,[5,6] 150 g. of acetic acid, and 150 g. of dimethylaniline was refluxed for 2.5 hours under nitrogen. The reaction mixture was decomposed with cold dilute hydrochloric acid, extracted with ether, and distilled at 20 mm. through a 23-plate Fenske-type column to give 152 g. of 1-phenoxyethyl acetate (85% yield) plus 4 g. of recovered vinyl phenyl ether. The following constants were obtained on a heart cut of the material: b.p. 119°/20 mm., n_{D}^{25} 1.4870, d_4^{25} 1.0715, t_f $-10.76° \pm 0.01$[7] (calc'd mole-% purity, 99.2–99.6).

Anal. Calc'd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71; Mol. wt., 180. Found: C, 66.44; H, 6.74; Mol. wt., 182.

Alkaline hydrolysis was accomplished by boiling 9 g. of 1-phenoxyethyl acetate for 1 hour with 45 cc. of 10% aqueous potassium hydroxide under a 50-cm. Vigreux column. Acidification of the pot residue gave 4.1 g. (87% yield) of crude phenol, identified as phenoxyacetic acid; m.p. and mixture m.p. 97–98°. The aqueous distillate contained acetaldehyde, identified as its dimedon derivative; m.p. and mixture m.p. 139–141°. [Attempts to determine the saponification equivalent of 1-phenoxyethyl acetate by standard procedure (refluxing for 2 hours with an excess of 0.7 *N* base, followed by back-titration) gave the low value of 165 instead of the theoretical 180].

Acid hydrolysis was accomplished by refluxing 1 g. of 1-phenoxyethyl acetate for 2 hours with a mixture of 2 g. of 2,4-dinitrophenylhydrazine, 15 cc. of concentrated sulfuric acid, and 150 cc. of 95% ethanol. One gram of crude acetaldehyde dinitrophenylhydrazone (81% yield) was obtained: m.p. and mixture m.p. of once-crystallized material 166–168°.

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[4] All melting and boiling points are uncorrected; t_f is corrected.

[5] Insinger, U. S. Patent 2,615,050 (1952); Brit. Patent 656,556 (1951); *Chem. Abstr.*, **46**, 8149 (1952).

[6] Shostakovskii and Burmistrova, *Akad. Nauk S.S.S.R., Inst. Org. Khim., Sintezy Org. Soedinenii, Sbornik*, **2**, 48 (1950); *Chem. Abstr.*, **48**, 627 (1954).

[7] t_f = freezing temperature determined by extrapolation of freezing curve; temperature measured by platinum resistance thermometer and G-2 Mueller bridge which had been certified by the National Bureau of Standards.

Marine Sterols. II. 24-Methylenecholesterol in Molluscs

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A new sterol, 24-methylenecholesterol, has recently been isolated from two species of the class pelecypoda, oyster, *Ostrea virginica* and clam, *Saxidomus giganteus.*[1] From the viewpoint of the comparative biochemistry of sterols it was of interest to further investigate the occurrence of 24-methylenecholesterol in pelecypoda.

This paper reports the occurrence of 24-methylenecholesterol in three other members of the same class, scallop, *Pecten caurinus*, cockle, *Cardium corbis*, and in a commercially prepared crude sterol mixture from mussel *Modiolus demissus.*[2]

The chromatographic pattern of *p*-phenylazobenzoyl (azoyl) esters of scallop, cockle, and mussel sterols resembled that of oyster and clam. The minor top zone ($\Delta^{5,7}$-sterol) was absent, zone 1 consisted of 24-methylenecholesterol, zone 2 of a diunsaturated, and zone 3 of a monounsaturated sterol.

The identity of these bands with the corresponding bands in the chromatogram of oyster and clam sterol azoyl esters was indicated by a comparison of the infrared spectra of the free sterols.

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EXPERIMENTAL[3]

Preparation of crude sterols. Commercially packed frozen scallop muscle (6.58 kg.) was ground up with an equal weight of sodium sulfate and the mixture was shaken with two 15 l. portions of petroleum ether (b.p. 65–110°). By evaporation of the solvent 8.0 g. of fat were obtained. Further shaking with the same volume of chloroform yielded 32.8 g. (total fat 0.62%). The fat was saponified for 2 hours in 10% ethanolic potassium hydroxide and the non-saponifiable matter, 9.4 g. (23.0%) of yellow solid, was dissolved in methanol. Cooling precipitated 6.49 g. (69.0%) of sterols melting at 130–132°, recrystallized m.p. 132–133° $[\alpha]_{\text{D}}^{22}$ $-37.7°$. The addition of water to the non-saponifiables supernatant precipitated 390 mg. of sterols, m.p. 124–126°.

In the case of cockle the entire contents of the shell (278 g.) were extracted with three 1000-ml. portions of acetone; when the solvent was evaporated and the remaining water suspension was extracted with ether, 7.5 g. (2.7%) of fat were obtained. Phosphatides were precipitated by the addition of magnesium chloride to an acetone solution of the fat. Saponification for 2 hours in 10% ethanolic potassium hydroxide yielded 950 mg. (12.7%) of non-saponifiable matter. Recrystallization from methanol gave 390 mg. (41.1%) of sterols m.p. 129–131°, $[\alpha]_{\text{D}}^{22}$ $-30.6°$.

Mussel sterols were obtained by recrystallization of the commercially prepared, crude sterol mixture.[2]

Chromatography. p-Phenyl azobenzoyl esters of scallop, cockle and mussel sterols were chromatographed on silicic acid-Celite employing the same technique as in the case of oyster and clam.[1,4]

Scallop esters separated into three closely running bands of approximately equal intensity. There was 34.6% of 24-methylenecholesterol. Because of the relatively low concentration of zone 2 (16.7%), cockle sterols appeared to separate into only two nearly equally intense bands, but after the chromatogram had been extruded a faint band appeared be-

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[1] Idler and Fagerlund, *J. Am. Chem. Soc.*, **77**, 4142 (1955).

[2] Bergmann and Ottke, *J. Org. Chem.*, **14**, 1085 (1949).

[3] Melting points are uncorrected. Optical rotations were measured by means of a Rudolph precision polarimeter. Infrared spectra were recorded of solid films with a Perkin-Elmer doublebeam infrared spectrophotometer.

[4] Idler and Baumann, *J. Biol. Chem.*, **195**, 623 (1952).