reaction mixture was decolorized with sulfur dioxide, the aqueous solution was made strongly acid with concentrated hydrochloric acid and was extracted continuously with ether for 24 hours. The ethereal extract was dried with magnesium sulfate, was concentrated and the residue was distilled. After a small amount of bromodifluoroacetic acid had distilled, 42 g. of 1,4-dibromo-1,1,4,4-tetrafluoro-2,3-butanediol boiling at 80–82° (1 mm.) and solidifying immediately was obtained. Sublimation at 0.25 mm. from an oil-bath at 70° gave colorless crystals melting at 74–75°.

Anal. Calcd. for $C_4H_4O_2Br_2F_4$: C, 15.00; H, 1.26; Br, 49.95. Found: C, 15.05; H, 1.57; Br, 50.01.

Smaller quantities of this same compound were isolated in oxidations of the dibromotetrafluoro-2-butene at 20° as described previously. Infrared analysis showed absorption in the 3.0 μ region consistent with the diol structure The fluorine n.m.r. spectrum[8] at a temperature above the melting point showed a doublet centered at +752 c.p.s. relative to trifluoroacetic acid at zero and was consistent with the proposed structure. Alkaline permanganate oxidation of the 1,4-dibromo-1,1,4,4-tetrafluoro-2,3-butanediol in aqueous solution gave bromodifluoroacetic acid, identified as the *p*-chlorophenylammonium salt, m.p. 112–113°, alone or in admixture with a known sample of the salt.

1,2,3,4-Tetrachloro-1,1,4,4-tetrafluorobutane.[6]—To a solution of 93.5 g. of 1,1,4,4-tetrafluoro-1,3-butadiene[9] in 25 ml. of methylene chloride was added slowly by distillation 106 g. of chlorine. The reaction flask was cooled in ice and a condenser cooled with solid carbon dioxide–acetone was used to condense the low-boiling reactants. After the addition of the chlorine was complete, the temperature was increased gradually to 85° during the course of two hours. The fraction boiling at 72–74° (60 mm.) weighed 184 g.

Anal. Calcd. for $C_4H_2Cl_4F_4$: C, 17.95; H, 0.75; Cl, 52.93; F, 28.37; mol. wt., 268. Found: C, 17.94; H, 1.16; Cl, 52.81; F, 28.30; mol. wt., 270.

1,2,4-Trichloro-1,1,4,4-tetrafluoro-2-butene.—A mixture of 1,2,3,4-tetrachloro-1,1,4,4-tetrafluorobutane, 120 g. of 85% potassium hydroxide and 400 ml. of water was gradually brought to reflux and heated under reflux gently for 8 hours. The reaction mixture was steam distilled, and the organic layer was separated and dried. The yield of halogenated butene boiling at 100–102° was 64 g. Infrared absorption was observed at 3.2 (=CH), at 6.0 (C=C), and at 8–9 μ (strong absorption characteristic of C–F). The fluorine nuclear magnetic resonance spectrum was consistent with the 2-butene structure.

(8) The authors wish to thank Dr. Harlan Foster for the nuclear magnetic resonance determinations.

(9) J. L. Anderson, U. S. Patent 2,743,303, issued April 24, 1956.

1,2,2,3,4-Pentachloro-1,1,4,4-tetrafluorobutane.—A mixture of 66 g. of 1,2,4-trichloro-1,1,4,4-tetrafluoro-2-butene and 21 g. of chlorine was gradually heated to 60° during the course of 6 hours. A solid carbon dioxide–acetone cooled condenser was used to condense the chlorine. Fractionation of the reaction product gave 92 g. of 1,2,2,3,4-pentachloro-1,1,4,4-tetrafluorobutane boiling at 90° (49 mm.).

Anal. Calcd. for C_4HCl_5F: Cl, 58.65. Found: Cl, 58.62, 58.73.

1,2,3,4-Tetrachloro-1,1,4,4-tetrafluoro-2-butene.—A vigorously stirred mixture of 70 g. of 1,2,2,3,4-pentachloro-1,1,4,4-tetrafluorobutane, 60 g. of 85% potassium hydroxide and 200 ml. of water was refluxed gently for five hours. The organic material was recovered by steam distillation and the organic layer was separated, dried, and fractionated. The fraction boiling at 94° (215 mm.) weighed 38 g.

Anal. Calcd. for $C_4Cl_4F_4$: Cl, 53.35. Found: Cl, 53.40, 53.68.

1,2,2,3,3,4-Hexachloro-1,1,4,4-tetrafluorobutane. (a) **From 1,2,3,4-Tetrachloro-1,1,4,4-tetrafluoro-2-butene.**—A mixture of 38 g. of tetrachlorotetrafluoro-2-butene and 12 g. of chlorine was illuminated with a RS sun lamp for 10 hours. During this time, a condenser cooled with solid carbon dioxide–acetone was used to condense the chlorine. Fractionation of the reaction mixture gave 1,2,2,3,3,4-hexachloro-1,1,4,4-tetrafluorobutane, b.p. 102° (28 mm.), $n^{25}D$ 1.4581; reported[3] b.p. 125–126° (76 mm.), $n^{28}D$ 1.457.

Anal. Calcd. for $C_4Cl_6F_4$: Cl, 63.17. Found: Cl, 63.14, 63.27.

(b) **From 1,1,4,4-Tetrafluoro-1,2,3-butatriene.**—The tetrafluorobutatriene obtained by adding 28.6 g. of 1,4-dibromo-1,1,4,4-tetrafluoro-2-butene to a mixture of 100 g. of 85% potassium hydroxide and 7 ml. of water at 140–150° as previously described was passed into a solution of 28 g. of chlorine in 100 ml. of carbon tetrachloride at −20°. After addition of the tetrafluorobutatriene was complete, the reaction mixture was allowed to warm to room temperature and illuminated for 30 minutes with a RS sun lamp. Distillation of the reaction mixture gave 20 g. of a fraction boiling at 102° (28 mm.), $n^{25}D$ 1.4582. The infrared spectra of the two samples of hexachlorotetrafluorobutane were identical. They were also the same as the published infrared spectrum[4] for 1,2,2,3,3,4-hexachloro-1,1,4,4-tetrafluorobutane[3] prepared by an alternate method.

Acknowledgment.—Helpful discussions with Dr. R. E. Putnam of this Laboratory are gratefully acknowledged.

WILMINGTON 98, DEL.

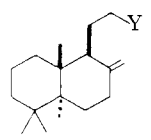
COMMUNICATIONS TO THE EDITOR

TOTAL SYNTHESIS OF A β-AMYRIN DERIVATIVE, OLEAN-11,12;13,18-DIENE (V)

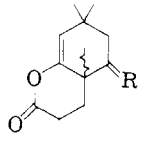
Sir:

The β-amyrin (oleanane) series of pentacyclic triterpenes has not previously been reached by total synthesis despite the possibility of a relatively simple synthetic route involving the coupling of A/B and D/E ring moieties and subsequent closure of ring C. Such a synthesis has now been accomplished via terminal stages which are as follows. Reaction of the Grignard reagent derived from the (+)-bromide I with (±) enol lactone II afforded an oily mixture of epimeric tricyclic diketones (III) ($\nu_{max}^{CS_2}$ 1706 cm.$^{-1}$) which was converted using potassium *t*-butoxide to a mixture of epimeric conjugated ketones (IV), $\nu_{max}^{CS_2}$ 1668, 1606 cm.$^{-1}$, λ_{max}^{EtOH} 252 mμ (ε 14,600) (C, 84.53; H, 11.52). Treatment of IV with methyllithium produced the expected C_{30} tertiary alcohol mixture which was subjected (without separation) to acid-catalyzed cyclization using hydrogen chloride–acetic acid (saturated) at 25° for 20 hours and 55°

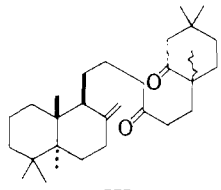
for 3 hours. Extensive chromatography afforded olean-11,12;13,18-diene (V),[1] m.p. 218°, mixture m.p. 218° with an authentic sample (of m.p. 219°), $[\alpha]^{25}D$ −65° as compared to −66° for authentic material[2] and ultraviolet and infrared spectra identical with those of pure olean-11,12; 13,18-diene [ultraviolet: $\lambda\lambda\lambda_{max}^{hexane}$ 242, 250, 259 mμ (ε 26,670, 29,860, 19,710)]. The yield of V was poor (*ca.* 2%), somewhat less than that (*ca.* 10%) for the onoceradiene → pentacyclosqualene conversion.[3,4] However, isolation of V was greatly facilitated by its characteristic and intense ultraviolet absorption.



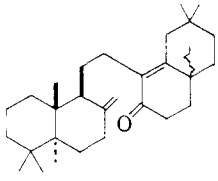
I, Y = CH_2Br
VII, Y = COOH
VIII, Y = CH_2OH



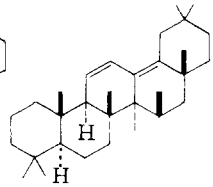
II, R = H_2
XIV, R = O



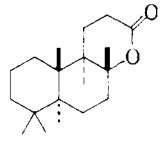
III



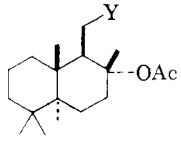
IV



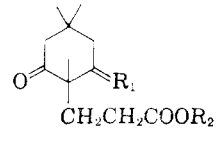
V



VI



IX, Y = CHO
X, Y = CH_2OH
XI, Y = CH_2CN



XII, R_1 = O, R_2 = CH_3
XIII, R_1 = O, R_2 = H
XV, R_1 = H_2, R_2 = H

The synthesis of the (+)-bromide (I) was accomplished by two different procedures. In the first (+)-ambreinolide[5] (VI) was converted by hydrolysis, methylation (CH_2N_2) dehydration ($POCl_3$–C_5H_5N) and saponification to the olefinic acid VII, m.p. 113–115°, $[\alpha]^{20}D$ +52.1° (C, 76.95; H, 10.94). Reduction of VII ($LiAlH_4$) afforded the liquid alcohol VIII, b.p. 150° (0.4 mm.), $[\alpha]^{20}D$ +33.3° ($CHCl_3$), $\nu_{max}^{CS_2}$ 890, 1645 cm.$^{-1}$ (C, 81.95; H, 12.14), which was transformed via the tosylate to the bromide I (LiBr–acetone). The acid VII was also prepared from the acetoxyaldehyde IX[4] via the corresponding alcohol (X) ($NaBH_4$), brosylate and cyanide (XI), m.p. 84–86°, $[\alpha]^{20}D$ − 10.1° (C, 75.10; H, 10.02; N, 4.62). Treatment of the acetoxy nitrile XI with quinoline at reflux and then basic hydrolysis gave the acid VII.

The (+)-enol lactone II was prepared from 2,5,5-trimethylcyclohexane-1,3-dione[6] via the diketoester XII (methyl acrylate–potassium *t*-butoxide) and the acid XIII, m.p. 109–113° (C, 63.73; H, 7.98; neut. equiv., 218) (acid hydrolysis). The enol lactone XIV, m.p. 95–97° (C, 69.29; H, 7.88), $\nu_{max}^{CS_2}$ 1765, 1720, 1675 cm.$^{-1}$, obtained by the action of phosphorus pentachloride on XIII, was hydrogenated (platinum–acetic acid) to the keto acid XV, m.p. 68–70° (C, 68.00; H, 9.23 which was converted (PCl_5) to II, m.p. 64–65° (C, 74.25; H, 9.40), $\nu_{max}^{CS_2}$ 1755, 1673.

This work was supported in part by the National Science Foundation.

(1) J. Green, N. Mower, C. W. Picard and F. S. Spring, *J. Chem. Soc.*, 527 (1944).

(2) All rotations measured in chloroform; m.p.'s determined with a micro hot-stage.

(3) D. H. R. Barton and K. H. Overton, *J. Chem. Soc.*, 2639 (1955).

(4) E. J. Corey and R. R. Sauers, THIS JOURNAL, **81**, 1739 (1959).

(5) For total synthesis see P. Dietrich and E. Lederer, *Helv. Chim. Acta*, **35**, 1148 (1952).

(6) E. G. Meek, J. H. Turnbull and W. Wilson, *J. Chem. Soc.*, 811 (1953).

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RECEIVED AUGUST 17, 1959

THE REACTION OF PERCHLORYL FLUORIDE WITH ENOL ETHERS

Sir:

This communication describes the novel reaction between enol ethers and perchloryl fluoride to produce fluorinated ketones.[1] In the absence of acids, the fluorine atom of perchloryl fluoride appears to be electrophilic and reacts with the negative center established at the α-carbon atom by the unshared electrons of the alkoxy group. For example, brief treatment of 1-ethoxycyclohexene in pyridine with $FClO_3$ at 0°, followed by dilution with water and acidification, gave 2-fluorocyclohexanone, b.p. 83–83.5° (20 mm.); $n^{25}D$ 1.4432; found; C, 62.25; H, 7.81; F, 16.69; dinitrophenylhydrazone, m.p. 139–140°.

In the steroid series, the respective 3-ethoxy-Δ^2-compounds treated with $FClO_3$ in pyridine for two minutes at room temperature with subsequent hydrolysis produced I, II and III in yields of 75 to 90%. Acidic methanolysis of III gave IV. The same compounds are obtained from perchloryl fluoride and the corresponding steroid enamines, and IV is identical with fluorodihydrotestosterone obtained from the 2-hydroxymethylene steroid.[2] Fluorination at position 2 was established by conversion of I to the 2,4-dinitrophenylhydrazone of 1-cholesten-3-one,[3] whereas α-orientation of fluorine in I is indicated by optical rotatory dispersion[4] and n.m.r. spectrum.[5]

(1) The analogous reaction of steroid "enamines" with $FClO_3$ was reported recently from this laboratory by R. B. Gabbard and E. V. Jensen, *J. Org. Chem.*, **23**, 1406 (1958).

(2) J. Edwards and H. J. Ringold, THIS JOURNAL, **81**, 5262 (1959). We are grateful to Dr. Ringold for sending us a sample of his material.

(3) J. J. Beereboom, C. Djerassi, D. Ginsburg and L. F. Fieser, *ibid.*, **75**, 3500 (1953).

(4) C. Djerassi, I. Fornaguera and O. Mancera, *ibid.*, **81**, 2383 (1959).

(5) E. J. Corey, private communication.