m.p. 88–92°) precipitated from the cloudy solution. Sublimation gave 4.7 g. (80.1%) of pure material, m.p. 91–92°.[7]

Dehalogenation of the crude dibromoacenaphthene by this same procedure gave an over-all yield of 67% from acenaphthene.

The picrate was obtained as orange crystals, m.p. 201–202°.[8]

Bromination (in ether) gave 1,2-dibromoacenaphthene, m.p. 121–123°.[5]

B. **From 1-Acenaphthenyl Acetate.**—A solution of 1 g. (0.006 mole) of 1-acenaphthenyl acetate[9] in 20 ml. of acetic acid was dropped into a Pyrex column (57 cm. long and 15 mm. in diameter) packed to a depth of 47 cm. with $^3/_{32}$ inch Pyrex helices. The internal temperature of the column was maintained at 480 ± 10°. The drop rate was such that the addition required 2 hours (*ca.* 2 drops per min.). Nitrogen was passed through the column throughout the addition at a rate (measured at room temperature) of 11 l. per hour. The pyrolysate (collected in a trap cooled by a Dry Ice–acetone-bath) was poured into 40 ml. of water. The crystalline material (0.67 g.) which formed slowly was separated after 3 hours and sublimed. The yield of pure (m.p. 91–92°)[7] acenaphthylene was 0.65 g. (71%).

---

(7) A. Behr and W. A. Van Dorp, *Ber.*, **6**, 753 (1873).

(8) A. Behr and W. A. Van Dorp, *Ann.*, **172**, 263 (1874).

(9) J. Cason, "Organic Syntheses," Vol. 21, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 1.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WASHINGTON
SEATTLE, WASHINGTON

An Alkaline Hydrolysis of Trichloromethylphosphonic Esters

BY IRVING S. BENGELSDORF[1]

RECEIVED JUNE 1, 1955

The acidic hydrolysis of dialkyl trichloromethylphosphonates, $CCl_3P(O)(OR)_2$, proceeds without cleavage of the carbon–phosphorus bond to yield the expected trichloromethylphosphonic acid.[2] The only alkaline hydrolytic study of these esters is reported by Yakubovich and Ginsburg who employed an aqueous solution of 1.4 *N* barium hydroxide at 60–80°[2b,3]; cleavage of the carbon–phosphorus bond was observed and symbolized by the following indefinite equation.

$$CCl_3P(O)(OR)_2 \xrightarrow[Ba(OH)_2]{H_2O} CCl_3H + H_3PO_4 + 2ROH \quad (A)$$

This proposed hydrolytic scheme must proceed *via* the dialkyl phosphate anion after the chloroform is liberated. Helleiner and Butler,[4] however, have recently shown that only a small proportion (0.1–0.4%) of the total phosphorus of phosphate diesters is converted to inorganic phosphate during hydrolysis with barium hydroxide. The observation, therefore, by Yakubovich and Ginsburg[3] that the barium hydroxide hydrolysate gives a yellow precipitate with ammonium molybdate reagent is not a definite proof that phosphoric acid is a major hydrolytic reaction product.

In addition, saponification equivalent data, as determined in this work by refluxing the esters with 0.5 *N* ethanolic potassium hydroxide solution, revealed that the alkaline hydrolytic scheme in 95% ethanol as the solvent can be more complex than as proposed above. This is due to two factors; (i) chloroform itself is attacked further by alkali,[5] and (ii) the dialkyl phosphate anion, $(RO)_2(O)PO^-$, although hydrolyzable by acids, is resistant toward further alkaline hydrolysis.

Plimmer and Burch have shown that the dialkyl phosphate anion, whether it is derived from a dialkyl phosphoric acid or a trialkyl phosphate, is resistant toward alkaline hydrolysis.[6] In addition, Toy[7] and Dvornikoff and Morill[8] have observed that the alkaline hydrolysis of pyrophosphoric esters stops at the dialkyl phosphate anion stage.

$$(RO)_2P(O)O(O)P(OR)_2 + 2^-OH \longrightarrow 2(RO)_2(O)PO^- + H_2O \quad (B)$$

The stoichiometry of the ethanolic alkaline hydrolysis, therefore, strongly suggests that dialkyl trichloromethylphosphonates are hydrolyzed according to the following reaction sequence (Eqn. C-E); the over-all reaction is represented by Eqn. F.

$$2(RO)_2(O)PCCl_3 + 2OH^- \longrightarrow 2CCl_3H + 2(RO)_2(O)PO^- \quad (C)$$

$$2CCl_3H + 2OH^- \longrightarrow 2H_2O + 2CCl_2 + 2Cl^- \quad (D)$$

$$2CCl_2 + 5OH^- \longrightarrow CO + HCOO^- + 4Cl^- + 2H_2O \quad (E)$$

$$2(RO)_2(O)PCCl_3 + 9OH^- \longrightarrow CO + HCOO^- + 2(RO)_2(O)PO^- + 6Cl^- + 4H_2O \quad (F)$$

This hydrolytic scheme is verified by the following observations: (1) The observed saponification equivalents of the esters are in close agreement with the expected values, *i.e.*, $^2/_9$ of the molecular weight.

(2) At the start of the hydrolysis, the presence of chloroform is indicated by a positive phenyl isonitrile test; at the end of the hydrolysis, this test is negative, *i.e.*, chloroform is absent.[9]

(3) Formate and chloride ions, respectively, are shown to be present in the hydrolysate, by the production of a violet coloration with chromotropic acid, and the precipitation of silver chloride.

(4) Phosphate ion is absent in the alkaline hydrolysate, for no precipitation is observed when it is treated with a nitric acid–ammonium molybdate solution.[10] If the alkaline hydrolysate, however, is further hydrolyzed with acid, then the test for

---

(1) General Electric Research Laboratory, Schenectady 5, N. Y.

(2) (a) A. Ya. Yakubovich, V. A. Ginsburg and S. P. Makarov, *Doklady Akad. Nauk S.S.S.R.*, **71**, 303 (1950); (b) A. Ya. Yakubovich and V. A. Ginsburg, *ibid.*, **82**, 273 (1952); (c) P. C. Crofts and G. M. Kosolapoff, THIS JOURNAL, **75**, 5738 (1953); (d) A. Ya. Yakubovich and V. A. Ginsburg, *J. Gen. Chem. U.S.S.R.*, **24**, 1465 (1954); (e) I. S. Bengelsdorf and L. B. Barron, THIS JOURNAL, **77**, 2869 (1955).

(3) A. Ya. Yakubovich and V. A. Ginsburg, *J. Gen. Chem. U.S.S.R.*, **24**, 2250 (1954).

(4) C. W. Helleiner and G. C. Butler, *Can. J. Chem.*, **33**, 705 (1955).

(5) Chloroform, according to experimentally determined saponification equivalents, is hydrolyzed as

$$2CCl_3H + 7OH^- \longrightarrow CO + HCOO^- + 6Cl^- + 4H_2O$$

The observed saponification equivalent is equal to $^2/_7$ of the molecular weight. The kinetics of this reaction are reviewed and discussed by J. Hine, THIS JOURNAL, **72**, 2438 (1950). Excellent evidence that dichlorocarbene, CCl_2, is an intermediate in the alkaline hydrolysis of chloroform recently has been advanced by W. von E. Doering and A. K. Hoffmann, THIS JOURNAL, **76**, 6162 (1954).

(6) R. H. A. Plimmer and W. J. N. Burch, *J. Chem. Soc.*, 279 (1929).

(7) A. D. F. Toy, THIS JOURNAL, **72**, 2065 (1950).

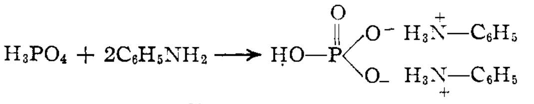
(8) M. N. Dvornikoff and H. L. Morill, *Anal. Chem.*, **20**, 935 (1948).

(9) F. W. Bennett, H. J. Emeleus and R. N. Haszeldine, *J. Chem. Soc.*, 3598 (1954), report that whereas trifluoromethylphosphonic acid, $CF_3P(O)(OH)_2$, is not cleaved by alkali, trifluoromethylphosphonous acid, $CF_3P(OH)_2$, gives fluoroform when it is so treated.

(10) This observation is not necessarily contradictory to the findings of Yakubovich and Ginsburg,[3] because Helleiner and Butler[4] have shown that although barium hydroxide liberates little phosphate from phosphate diesters, sodium hydroxide is even less effective in this respect.

phosphate ion becomes positive, and phosphoric acid can be isolated as its dianilinium salt.

$$^{-}OP(O)(OR)_2 + 3HCl \longrightarrow H_3PO_4 + 2RCl + Cl^-$$



$$H_3PO_4 + 2C_6H_5NH_2 \longrightarrow HO-P(=O)(O^-\ \overset{+}{H_3N}-C_6H_5)(O^-\ \overset{+}{H_3N}-C_6H_5)$$

Experimental

The Preparation of the Esters.—Dimethyl and diethyl trichloromethylphosphonate were prepared by the interaction of carbon tetrachloride with the respective trialkyl phosphite.[2e]

Alkaline Hydrolysis of Diethyl Trichloromethylphosphonate.—A solution of the ester (2.5 g.) and potassium hydroxide (2.8 g.) in 30 ml. of ethanol was refluxed for two hours. Aliquot portions of the hydrolysate were treated as follows: (a) Aniline was added and the solution was heated. There was no odor of phenyl isonitrile. Heating a mixture of the original ester, potassium hydroxide and aniline, however, produces the isonitrile odor immediately.

(b) Hydrochloric acid was added, followed by magnesium metal. After the evolution of hydrogen had ceased, chromotropic acid (4,5-dihydroxy-2,7-naphthalenedisulfonic acid, disodium salt) and sulfuric acid were added. The formation of a pink-violet color indicated the presence of formaldehyde in the hydrolysate. The color was only observed if the hydrolysate was first reduced with the magnesium–acid combination (reduction of formic acid to formaldehyde).[11]

(c) Acidification with nitric acid, followed by silver nitrate, gave an immediate precipitate of silver chloride.

(d) Nitric acid and an ammonium molybdate solution were added. There was no evidence of precipitation.

The remaining alkaline hydrolysate was then refluxed with hydrochloric acid for six hours. The hot solution was treated with charcoal, filtered, and the filtrate was evaporated to dryness. The residual material, A, immediately gave a precipitate of yellow phosphomolybdate when it was treated as in (d) above.

Treatment of an ethereal extract of the above residue, A, with aniline, produced dianilinium phosphate (platelets from abs. ethanol, m.p. 182–183° dec.). The salt had the correct phosphorus content (10.8%) and neutralization equivalent (141) as compared to an authentic sample.[2e]

Saponification Equivalents.—Ten ml. of a standard ethanolic potassium hydroxide solution (3 g. of KOH in 100 ml. of 95% ethanol) were pipetted into an empty flask and into a flask containing the ester or chloroform (b.p. 61.5°). Both solutions were refluxed for two hours and then titrated with a standard hydrochloric acid solution. The difference between the two titration values was indicative of the actual base consumed.

TABLE I

SAPONIFICATION EQUIVALENTS (TWO HOURS AT 80°)

Compound	Mol. wt.	Saponification equivalent Calcd.	Saponification equivalent Observed
$CHCl_3$	119.4	34.12	35.01, 35.04
$(CH_3O)_2(O)PCCl_3$	227.4	50.54	53.5, 54.6, 56.0
$(C_2H_5O)_2(O)PCCl_3$	255.5	56.77	57.3, 58.6, 59.2

The observed values, in all cases, are greater than the calculated. This could be due to either (a) a slight loss of the volatile chloroform during the hydrolysis, or (b) an incomplete hydrolysis, or both. Plimmer and Burch,[6] for example, found that the hydrolysis of only one ethyl group is only 92% complete in triethyl phosphate after 30 hours treatment with 2 *N* alkali. This resistance of triethyl phosphate toward alkaline hydrolytic agents was confirmed by subjecting it to the same hydrolytic conditions as described in Table I; it was only 20% hydrolyzed.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
LOS ANGELES 24, CALIFORNIA

---

[11] F. Feigl, "Spot Tests," Vol. 2, 4th Ed., Elsevier Publishing Co., Houston, Texas, 1954, pp. 245–246.

Steroidal Cyclic Ketals. XVII.[1] The Synthesis of 6β-Hydroxyprogesterone

BY SEYMOUR BERNSTEIN, WILLIAM S. ALLEN, CARL E. LINDEN AND JASPER CLEMENTE

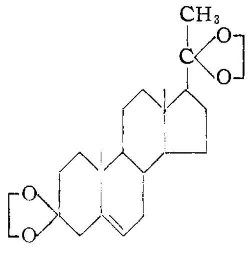
RECEIVED SEPTEMBER 2, 1955

Treatment of cholesterol with osmium tetroxide has been reported to produce an 81% yield of cholestane-3β,5,6α-triol.[2] Thus a stereospecific attack occurred on the rear-side of the molecule. No mention was made in this work of the possible formation of coprostane-3β,5,6β-triol. The formation of the latter would require a frontal attack. With this work in mind it was decided to study the reaction of a Δ^5-3-ketal (in particular, the bis-ethylene ketal I of progesterone) with osmium tetroxide. The results obtained form the basis of this report.

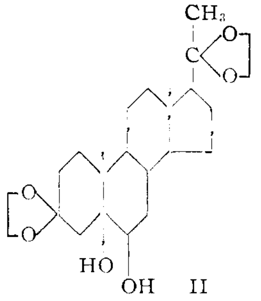
The bis-ethylene ketal I of progesterone on reaction with osmium tetroxide gave in approximately 50% yield pregnane-5,6β-diol-3,20-dione 3,20-bis-ethylene ketal (II). (The structure of the latter was proven by a subsequent transformation (*vide infra*).) No allopregnane-5,6α-diol-3,20-dione 3,20-bis-ethylene ketal could be isolated. Nevertheless, it is apparent that a 3-ethylene ketal grouping has an important influence on the stereochemistry of osmylation of a Δ^5-double bond.

Subsequent hydrolysis of the 5,6β-diol II with 90% (v./v.) acetic acid afforded in 65% yield the known Δ^4-pregnene-6β-ol-3,20-dione (6β-hydroxyprogesterone) (III).[3] Hydrolysis with glacial acetic acid gave a 60% yield of III. These transformations represented a novel synthesis of the latter.

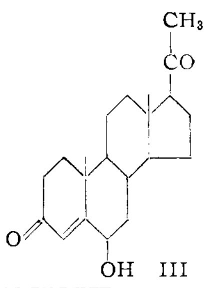
Hydrolysis of the 5,6β-diol II in methanol with 8% (v./v.) sulfuric acid resulted in the known allopregnane-3,6,20-trione (IV).[3] The rearrangement



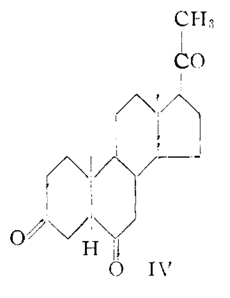
I



II



III



IV

---

[1] Paper XVI, S. Bernstein, M. Heller and S. M. Stolar, THIS JOURNAL, **77**, 5327 (1955).

[2] V. Prelog and E. Tagmann, *Helv. Chim. Acta*, **27**, 1867 (1944); see also, M. I. Uschakow and A. I. Tjutenberg, *Chem. Zentr.*, **110**, **II**, 4489 (1939); R. Criegee, B. Marchand and H. Wannowius, *Ann.*, **550**, 130 (1942).

[3] C. P. Balant and M. Ehrenstein, *J. Org. Chem.*, **17**, 1587 (1952); C. Amendola, G. Rosenkranz and F. Sondheimer, *J. Chem. Soc.*, 1226 (1954).