analytical sample, m.p. 126–127°, $[\alpha]_D$ 32° (*c* 0.86), λ_{max} 242 mμ (ε 16,092), ν_{max} 1740 cm.$^{-1}$ (acetate carbonyl), 1693 cm.$^{-1}$ (20-ketone), 1673 cm.$^{-1}$ (conjugated carbonyl), 1615 cm.$^{-1}$ (C=C of the conjugated carbonyl), and 1210 cm.$^{-1}$ (acetoxy).

Anal. Calcd. for $C_{23}H_{32}O_4$ (372.5): C, 74.16; H, 8.66. Found: C, 73.68; H, 8.83.

2α-Acetoxy-4-androstene-3,17-dione (VII).—The mixed acetates obtained by similar acetolysis of 6-bromo-4-androstene-3,17-dione (IV, 4.652 g.) were fractionally crystallized from methanol to yield 2α-acetoxy-4-androstene-3,17-dione (VII, 450 mg., 15%), m.p. 210–211.5°, $(\alpha)_D$ +138° (*c* 0.66), λ_{max} 240 mμ (ε 15,262), ν_{max} 1733 cm.$^{-1}$ (fused five-membered ring ketone and acetate carbonyl), 1680 cm.$^{-1}$ (conjugated carbonyl), 1605 cm.$^{-1}$ (C=C of the conjugated carbonyl), 1217 and 1233 cm.$^{-1}$ (acetoxy) (lit.,[8] m.p. 209–210°, $[\alpha]_D$ +146).

Anal. Calcd. for $C_{21}H_{28}O_4$ (344.4): C, 73.23; H, 8.19. Found: C, 73.20; H, 8.19.

2β-Acetoxy-4-androstene-3,17-dione (VIII).—Further fractionation of the above mother liquors from dilute methanol gave 2β-acetoxy-4-androstene-3,17-dione (VIII, 865 mg., 25%), m.p. 156–158°, $[\alpha]_D$ −8.9° (*c* 1.03), λ_{max} 242 mμ (ε 14,472), ν_{max} 1756 and 1745 cm.$^{-1}$ (acetate carbonyl and 17-ketone), 1688 cm.$^{-1}$ (conjugated carbonyl), 1620 cm.$^{-1}$. (C=C of the conjugated carbonyl), and 1225 cm.$^{-1}$ (acetoxy) (lit.,[13] m.p. 157–158°, $[\alpha]_D$ −5.9°).

Anal. Calcd. for $C_{21}H_{28}O_4$ (344.4): C, 73.23; H, 8.19. Found: C, 73.12; H, 8.11.

Saponification of 2-Acetoxy Compounds. 2α-Hydroxyprogesterone (V).—2α-Acetoxyprogesterone (II, 600 mg.) was dissolved in methanol (18.3 ml.) and dry nitrogen was bubbled through the solution. Then exactly one equivalent of methanolic potassium hydroxide (1.4 ml. of a 1 *N* solution) was added and the solution was stirred at 30° for *4 min.* Then methanol (10 ml.) containing 2 drops of water was added and stirring continued for an additional *4 min.* (total time 8 min. at 30°). The solution was then acidified with 1 *N* acetic acid (2 ml.), concentrated to one-third volume, diluted with water, chilled in an icebox, and filtered to give 2α-hydroxyprogesterone (V) which was crystallized from acetone–petroleum ether, m.p. 184–187°, $[\alpha]_D$ +188° *c* 1.09), λ_{max} 240 mμ (ε 15,474), ν_{max} 3560 cm.$^{-1}$ (hydroxyl), 1695 and 1675 cm.$^{-1}$ (20- and 3-ketones), and 1615 cm.$^{-1}$ (C=C of the conjugated carbonyl) (lit.,[4a] m.p. 182–183° $[\alpha]_D$ +199°).

Anal. Calcd. for $C_{21}H_{30}O_3$ (330.5): C, 76.32; H, 9.15. Found: C, 76.16; H, 9.52.

2β-Hydroxyprogesterone (IV).—Saponification of the 2β-acetate (III, 607 mg.) exactly as described above furnished 2α-hydroxyprogesterone (IV) in quantitative yield, m.p. 191–193°, $(\alpha)_D$ −51° (*c* 1.02), λ_{max} 242 mμ (ε 15,728), ν_{max} 3565 cm.$^{-1}$ (hydroxyl), 1695 and 1675 cm.$^{-1}$ (20- and 3-ketones), and 1625 cm.$^{-1}$ (C=C of the conjugated carbonyl).

Anal. Calcd. for $C_{21}H_{30}O_3$ (330.5): C, 76.32; H, 9.15. Found: C, 76.46; H, 9.25.

2α-Hydroxy-4-androstene-3,17-dione (X).—Controlled hydrolysis of the 2α-acetate (VII, 285 mg.) by the above-described procedure gave 2α-hydroxy-4-androstene-3,17-dione (X), crystallized from acetone–petroleum ether, m.p. 160–161°, $[\alpha]_D$ +204° (*c* 1.01), λ_{max} 240 mμ (ε 15,266), ν_{max} 3430 cm.$^{-1}$ (hydroxyl), 1738 cm.$^{-1}$ (five-membered ring ketone), 1665 cm.$^{-1}$ (conjugated carbonyl), and 1600 cm.$^{-1}$ (C=C of the conjugated carbonyl).[14]

Anal. Calcd. for $C_{19}H_{26}O_3$ (302.4): C, 75.46; H, 8.67. Found: C, 74.77; H, 8.33.

2β-Hydroxy-4-androstene-3,17-dione (IX).—Similar hydrolysis of the 2β-acetate (VIII, 533 mg.) afforded 2β-hydroxy-4-androstene-3,17-dione (IX), which crystallized from acetone–petroleum ether, m.p. 144–147°, $[\alpha]_D$ −32° (*c* 0.99), λ_{max} 242 mμ (ε 14,830), ν_{max} 3480 cm.$^{-1}$ (hydroxyl), 1735 cm.$^{-1}$ (five-membered ring ketone), 1675 cm.$^{-1}$ (conjugated carbonyl), and 1610 cm.$^{-1}$ (C=C of the conjugated carbonyl) (lit.,[13] m.p. 143–145°, $[\alpha]_D$ −36.8°).

Anal. Calcd. for $C_{19}H_{26}O_3$ (302.4): C, 75.46; H, 8.67. Found: C, 74.75; H, 8.60.

(13) R. M. Dodson, A. H. Goldkamp, and R. O. Muir, *J. Am. Chem. Soc.*, **79**, 3921 (1957); **82**, 4026 (1960).

(14) Compound X has been described as "known" by several authors.[8,11] However, a thorough search of the literature indicated that the physical constants of this compound have never been described. Therefore, this note appears to be the first to list the physical constants for 2α-hydroxy-4-androstene-3,17-dione (X).

The Synthesis of Some Quaternary Aminophosphonium Salts Containing Siloxyl, Alkenyl, and Arylalkyl Groups

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We have previously reported that *t*-butylaminodiphenylphosphine reacts with benzyl chloride and with bis(chloroethyl) ether to produce quaternary aminophosphonium chlorides.[1] We now have extended this procedure to include the reactions of 1,4-dibromobutene-2, bis(bromomethyl)tetramethyldisiloxane, *p*-fluorobenzyl chloride, and 9,10-bis(chloromethyl)anthracene with *t*-butylaminodiphenylphosphine to produce the corresponding *t*-butylaminophosphonium salts. Further, we have converted *P*-(9,10-anthracenedimethyl)-bis[*t*-butylaminodiphenylphosphonium chloride] to the corresponding hexafluorophosphate and picrate. *t*-Butylaminobenzyldiphenylphosphonium chloride was converted to the hexafluorophosphate, picrate, and borohydride. *P*-(Hexamethyldisiloxane)bis[(*t*-butylamino)diphenylphosphonium bromide], which was isolated only in the crude state, was characterized by conversion to the picrate. During the course of these experiments it was found that *t*-butylaminodiphenylphosphine reacts with ethanolic solutions of mercuric chloride and silver nitrate, respectively, to give the compounds $t\text{-}C_4H_9NHP(C_6H_5)_2 \cdot HgCl_2$ and $t\text{-}C_4H_9NHP(C_6H_5)_2 \cdot AgNO_3$.

Experimental[2]

Materials.—*t*-Butylaminodiphenylphosphine was prepared by the previously reported procedure.[3] The previously reported procedure[1] for the synthesis of *t*-butylaminobenzyldiphenylphosphonium chloride was modified by using toluene instead of benzene as solvent and by reducing the reflux time to 10 hr. By this means the yield was improved to 97%. 9,10-Chloromethylanthracene was prepared by the method of Miller, Amidon, and Tawney.[4] *p*-Fluorobenzyl chloride was obtained from Beacon Chemical Industries, Inc. Potassium borohydride was obtained from Callery Chemical Company. Bis(bromomethyl)tetramethyldisiloxane and 1,4-dibromobutene-2 were purchased from Peninsular ChemResearch, Inc. All compounds obtained from commercial sources were used as received.

Reaction of *t*-Butylaminodiphenylphosphine with RCH_2X Compounds.—The reaction of *t*-butylaminodiphenylphosphine with 9,10-chloromethylanthracene is described to illustrate the procedure used. A mixture of 5.2 g. (0.02 mole) of *t*-butylaminodiphenylphosphine and 2.8 g. (0.01 mole) of 9,10-bis(chloromethyl)anthracene in 35 ml. of dimethylformamide was stirred at reflux for 5 hr. The reaction mixture was cooled and then filtered. The yellow micro-crystalline solid was thoroughly washed with benzene and ethyl ether, and dried. The product weighed 6.5 g. (82% yield) and melted with decomposition at 279°.

This general procedure also was used for the preparation of *P*-(*p*-fluorobenzyl)(*t*-butylamino)diphenylphosphonium chloride, *P*-(1,4 - butene - 2)bis[(*t* - butylamino)diphenylphosphonium bromide], and *P*-(hexamethyldisiloxane)bis[(*t*-butylamino)di-

(1) H. H. Sisler and N. L. Smith, *J. Org. Chem.*, **26**, 4733 (1961).

(2) Analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn. Melting points and boiling points were uncorrected.

(3) H. H. Sisler and N. L. Smith, *J. Org. Chem.*, **26**, 611 (1961).

(4) M. W. Miller, R. W. Amidon, and P. O. Tawney, *J. Am. Chem. Soc.*, **77**, 2845 (1955). See also A. E. Kretov and M. R. Rovenskii, *J. Gen. Chem. USSR*, (Eng. Transl.), **30**, 667 (1960), for modifications.

TABLE I

PRODUCTS OF *t*-BUTYLAMINODIPHENYLPHOSPHINE REACTIONS AND THEIR DERIVATIVES

Compound	Yield, %	M.p., °C	C% Calcd. Found	H% Calcd. Found	N% Calcd. Found	P% Calcd. Found	X% Calcd. Found
(I) $[t\text{-}C_4H_9NHP(C_6H_5)_2(CH_2C_6H_5)]^+[BH_4]^-$	97	167° dec.)	76.04 76.06	8.60 8.43	3.86 3.85	8.53 8.38	B% 2.98 3.18
(II) $[t\text{-}C_4H_9NHP(C_6H_5)_2(CH_2C_6H_5)]^+[PF_6]^-$		139–140°	55.98 55.93	5.52 5.56	2.84 2.83		
(III) $[t\text{-}C_4H_9NHP(C_6H_5)_2(CH_2C_6H_5)]^+[OC_6H_2(NO_2)_3]^-$		104° (dec.)	60.52 59.93	4.90 5.06	9.74 9.51		
(IV) $[t\text{-}C_4H_9NHP(C_6H_5)_2(CH_2C_6H_4F)]^+[Cl]^-$	41	225° (dec.)	68.73 68.41	6.52 6.76	3.49 3.69	7.71 7.67	
(V) $[t\text{-}C_4H_9NHP(C_6H_5)_2CH_2CH{=}CHCH_2\,t\text{-}C_4H_9NHP(C_6H_5)_2]^{++}\,2Br^-$	54	129° (dec.)	59.35 59.05	6.36 6.55			Br% 21.94 21.50
(VI) $[t\text{-}C_4H_9NHP(C_6H_5)_2CH_2C_{14}H_8CH_2\,t\text{-}C_4H_9NHP(C_6H_5)_2]^{++}\,2Cl^-$	82	279° (dec.)	72.99 72.75	6.64 6.53	3.40 3.57		
(VII) $[t\text{-}C_4H_9NHP(C_6H_5)_2CH_2C_{14}H_8CH_2\,t\text{-}C_4H_9NHP(C_6H_5)_2]^{++}\,2PF_6^-$		259° (dec.)	57.14 57.37	5.20 5.34	2.78 2.62		
(VIII) $[t\text{-}C_4H_9NHP(C_6H_5)_2CH_2C_{14}H_8CH_2\,t\text{-}C_4H_9NHP(C_6H_5)_2]^{++}\,2OC_6H_2(NO_2)_3^-$		240° (dec.)	61.03 60.90	4.69 4.84	9.65 9.35		
(IX) $[t\text{-}C_4H_9NHP(C_6H_5)_2CH_2Si(CH_3)_2OSi(CH_3)_2CH_2\,t\text{-}C_4H_9NHP(C_6H_5)_2]^{++}\,2OC_6H_2(NO_2)_3^-$		164° (dec.)	53.09 53.56	5.35 5.27	9.91 10.40	5.48 5.96	
(X) $t\text{-}C_4H_9NHP(C_6H_5)_2\cdot HgCl_2$	98	216° (dec.)					Cl% 13.41 13.28
(XI) $t\text{-}C_4H_9NHP(C_6H_5)_2\cdot AgNO_3$	97	161° (dec.)			6.55 6.26		

phenylphosphonium bromide] except that toluene was used as solvent in the first case and benzene in the others. Also, the reflux period was extended to 14 hr. for the preparation of *P*-(*p*-fluorobenzyl)(*t*-butylamino)diphenylphosphonium chloride.

Preparation of Derivatives. Picrates.—The reaction of *P*-benzyl(*t*-butylamino)diphenylphosphonium chloride with picric acid is described to illustrate the procedure used in the preparation of the aminophosphonium picrates.

An aqueous solution of *P*-benzyl(*t*-butylamino)diphenylphosphonium chloride was added dropwise with stirring to an ethanolic solution of picric acid. A yellow precipitate formed. Ethanol was added with gentle warming until the product dissolved. On standing, yellow needles of the desired picrate separated.

Hexafluorophosphates.—The reaction of *P*-benzyl(*t*-butylamino)diphenylphosphonium chloride with potassium hexa-

fluorophosphate is described to illustrate the procedure used in the preparation of the aminophosphonium hexafluorophosphates.

An aqueous solution of *P*-benzyl(*t*-butylamino)diphenylphosphonium chloride was added with stirring to an aqueous solution of potassium hexafluorophosphate. A granular precipitate of the aminophosphonium hexafluorophosphate forms immediately. The precipitate was washed with water and dried in air.

Borohydrides.—The preparation of *P*-benzyl(*t*-butylamino)-diphenylphosphonium borohydride is described.

A cold solution of 2.0 g. (5 mmoles) of *P*-benzyl(*t*-butylamino)-diphenylphosphonium chloride was added with stirring to a cold solution of 0.3 g. (5 mmoles) of potassium borohydride in 25 ml. of distilled water. The product crystallized immediately. Stirring was continued for 0.5 hr. after the addition of the aminophosphonium chloride. The resultant product was filtered, and the solids were washed twice with distilled water and dried *in vacuo*. The white powder thus obtained melted with decomposition at 167° and weighed 2.0 g. (quantitative yield).

The product hydrolyzed to benzyldiphenylphosphine oxide (m.p. 191–192°) in 95% ethanol.

Physical and Analytical Data.—The physical properties, analytical data, and yields for the various syntheses are summarized in Table I.

Characteristic infrared bands, other than those already reported,[1] which were useful in identifying the various aminophosphonium salts are listed in Table II.

TABLE II. INFRARED DATA

I	2210 (w)	BH_4^-
II[5]	840 (s)	PF_6^-
V	1630 (m)	—C=C—
VI	850 (s)	—C_6H_4—
VII	840 (s)	PF_6^-
IX	1070 (w)	—Si—O—Si—

Discussion

These results suggest that the method for producing various substituted aminophosphonium salts by the *P*-alkylation of the appropriate substituted aminophosphine has a wide range of application. Furthermore, the ready conversion of various substituted aminophosphonium halides to the corresponding salts with other amines has been demonstrated. Finally, in view of the established fact that substituted aminophosphonium halides undergo hydrolysis to the corresponding substituted phosphine oxides,[6] the ready synthesis of a variety of substituted aminophosphonium halides suggests an interesting new path to complex tertiary phosphine oxides.

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(5) K. Buhler and W. Bues, *Z. anorg allgem. Chem.*, **308**, 62 (1961).
(6) H. H. Sisler, H. Ahuja, R. Drago, and N. L. Smith, *J. Am. Chem. Soc.*, **81**, 2982 (1959).

The Stereochemistry of the Pulegenic Acids

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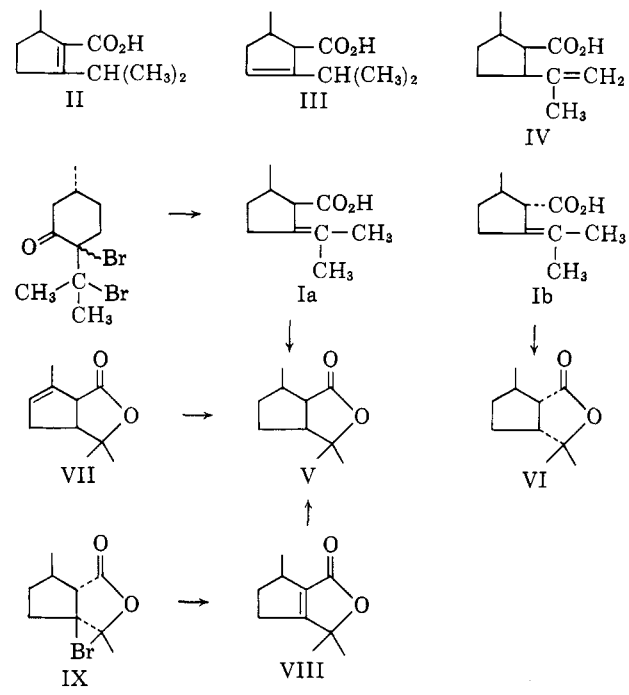
The action of alkali on pulegone dibromide is known to afford pulegenic acid, 5-isopropylidene-2-methyl-1-cyclopentanecarboxylic acid (I).[1–5] The close structural relationship between pulegenic acid and various naturally occurring alkaloids and terpene lactones suggest its use as an intermediate in the elaboration of these natural products. Consequently, we have reexamined the formation of pulegenic acid from pulegone dibromide and have found that a mixture of *cis*-Ia and *trans*-Ib is produced with aqueous potassium hydroxide, where *trans*-Ib is the predominant product when sodium methoxide is employed.

The formulation of the pulegenic acids as Ia and Ib was supported by their spectral properties. The acids showed end adsorption only in the ultraviolet and did not exhibit n.m.r. signals characteristics of vinyl protons. These observations rule out the presence of compounds II, III, and IV.



Attempts to separate acids Ia and Ib met with no success. However, the action of dilute hydrochloric acid on the acids afforded the lactones V, m.p. 48–49°, and VI, m.p. 19°, which were readily separated by vapor phase chromatography. The pulegenic acid prepared by the use of aqueous potassium hydroxide gave a lactone mixture comprised of 60% V and 40% VI, whereas the acid obtained with sodium methoxide afforded 8% V and 92% VI. The formation of identical ratios (60/40 and 8/92) of *cis*- and *trans*-2-hydroxymethyl - 3 - isopropylidene - 1 - methylcyclopentane[6] by lithium aluminum hydride reduction of the acids ensured that epimerization had not occurred during their lactonization.

(1) (a) O. Wallach, *Ann.* **289**, 349 (1895); (b) **300**, 259 (1898); (c) **327**, 125 (1903); (d) **392**, 49 (1912).
(2) O. Wallach, *ibid.*, **414**, 233 (1918).
(3) L. Bouveault and L. Tetry, *Bull. soc. chim. France*, [3] **27**, 307 (1902).
(4) H. Rupe and J. Burgin, *Ber.*, **43**, 1228 (1910).
(5) H. Rupe and K. Schafer, *Helv. Chim. Acta*, **11**, 463 (1928).
(6) J. Wolinsky, B. Chollar, and M. Baird, *J. Am. Chem. Soc.*, **84**, 2775 (1962).