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.

Acknowledgment.—It is a pleasure to express our thanks to Dr. Darel Straub for his interest and helpful suggestions. The work reported by this communication was supported in large part by W. R. Grace and Company through a contract with the University of Florida.

---

(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

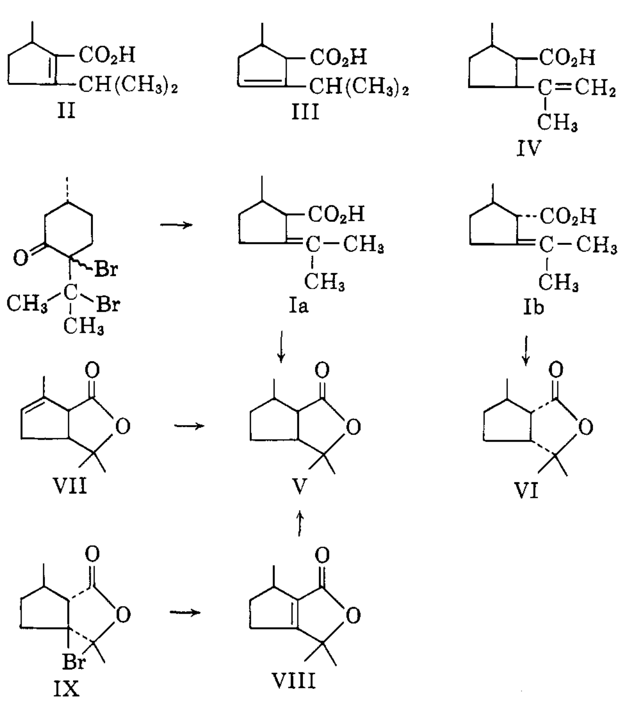
JOSEPH WOLINSKY, HAROLD WOLF, AND THOMAS GIBSON

Department of Chemistry, Purdue University, Lafayette, Indiana

Received September 6, 1962

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).

The stereochemistry assigned to the lactones V and VI and their parent pulegenic acids was suggested by the formation of lactone V, m.p. 48–49°, on catalytic hydrogenation of carvenolide (VII)[7] and lactone VIII, obtained by dehydrobromination of the bromolactone IX. Hydrogen addition should occur stereospecifically from the least hindered side of VII and VIII; this leads to the conclusion that the lactone m.p. 48–49° has a *cis–cis* configuration as depicted by V. The lactone m.p. 19°, on the assumption it possesses a thermodynamically stable *cis* ring-fusion, is formulated as *cis–trans* VI.

The course of the Favorskiĭ rearrangement reflects the likelihood that pulegone dibromide is a mixture of *cis* and *trans* isomers. Stereospecific rearrangement[8] with aqueous potassium hydroxide affords a kinetically controlled mixture of *cis*-Ia and *trans*-Ib. With sodium methoxide, on the other hand, methyl esters are produced initially and are subject to epimerization; the more thermodynamically stable *trans* ester results and is converted to *trans*-Ib during the reaction work-up.

Experimental[9]

trans-**Pulegenic Acid-Ib.**—To a stirred and cooled solution of 102 g. (0.67 mole) of (+)-pulegone ($n^{26}{}_D$ 1.4821, 95% by v.p.c.) in glacial acetic acid was added dropwise 100 g. (0.626 mole) of bromine. After stirring for 30 min. the solution was poured onto crushed ice and the resulting oily dibromide was washed with water. The combined water washings were extracted with 35–37° petroleum ether. The petroleum ether was added to the dibromide and the resulting solution was washed with dilute sodium bicarbonate solution and dried over anhydrous magnesium sulfate. Attempts to purify the dibromide led to rapid darkening and decomposition.

The dried petroleum ether solution obtained above was added dropwise to a heated and stirred solution of 105 g. of sodium methoxide in 500 ml. of methanol. The petroleum ether was distilled from the reaction as the addition proceeded. After the addition was completed and all the hydrocarbon had been distilled, the solution was kept at reflux for 2 hr. Water, 300 ml., containing 20 g. of potassium hydroxide was added and the solution was heated to reflux for 3 hr. and then steam distilled to remove neutral by-products. The cooled distilland was extracted with ether to remove polymeric products and then acidified with dilute sulfuric acid. The resulting mixture was extracted with ether. The ether solution was dried and distilled to give 66.0 g. (63%) of Ib, b.p. 105–109° (1 mm.) [lit.[5] b.p. 144–150° (11 mm.)], $n^{25}{}_D$ 1.4797, ϵ_{220} 1,566; n.m.r. 60, 66 (CH_3—CH—), 98 [(CH_3)$_2$-C=C)], 130, 140 (—CH_2—), 170, 175 (—CH—), and 696 c.p.s. (CO_2H).

cis- **and** *trans*-**Pulegenic Acids, Ia and Ib.**—Pulegone dibromide was prepared as described above except care was not taken to dry the product. The crude dibromide, from 70 g. of (+)-pulegone, was added to a heated and stirred solution of 130 g. of potassium hydroxide in 2 l. of water. The undissolved organic material floated to the top of the solution after 5 hr. After cooling and extracting with ether, the alkaline solution was acidified and worked up as described above to give 32.7 g. of Ia and Ib, b.p. 97–108° (0.5–0.7 mm.), $n^{25}{}_D$ 1.4767, ϵ_{220} 1,740; n.m.r. identical with that of Ib except for additional signals at 204 c.p.s. (—CH—) and a shift of the carboxyl proton to 624 c.p.s.

cis–trans-**Lactone VI.**—*trans*-Pulegenic acid, 27 g., was heated at reflux for 2 hr. with 200 ml. of 4:1 aqueous hydrochloric acid. The mixture was extracted with ether and the ether solution was washed free of unchanged acid with sodium bicarbonate solution. The ether solution was dried and distilled to give 19.4 g. (71%) of lactone, b.p., 74–76° (0.5 mm.). Vapor phase chromatography of this product indicated the presence of 8% of the *cis–cis*-lactone V. A sample of VI isolated by v.p.c. showed m.p. 15–19°, ν_{max} 5.70 μ, $[\alpha]^{31}{}_D = 0$, and n.m.r. 65, 71 (CH_3—CH—), 81 (CH_3—C—CH_3); and 98.4, 104.6, 145.7 and 153.4 c.p.s.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.71; H, 10.02.

cis–cis-**Lactone V. A. From** *cis*- **and** *trans*-**Pulegenic Acids.**—The pulegenic acids obtained by rearrangement of pulegone dibromide with aqueous alkali were heated with 4:1 hydrochloric acid as described above to give a liquid b.p. 82–84° (2 mm.). Repeated recrystallization from petroleum ether at −78° gave a solid m.p. 30–32° which was shown to be a mixture of V and VI. Analysis of the original product by v.p.c. indicated the presence of 60% V and 40% VI. *cis–cis*-V isolated by v.p.c. showed m.p. 47–48° $[\alpha]_D$ −75.8°, ν_{max} 5.72 μ (lit.,[1d] m.p. 50–51°, $[\alpha]_D$ −56.85°).

B. From the Unsaturated Lactone VIII.—To a solution of 0.99 g. of *cis*-Ia and *trans*-Ib in carbon tetrachloride was added 1.28 g. of bromine. The resulting solution was washed with water and sodium carbonate solution and the carbon tetrachloride was removed. The residue was crystallized repeatedly from petroleum ether at −78° and distilled evaporatively to give an oil, ν_{max} 5.65 μ, whose n.m.r. spectrum indicated the presence of a mixture of stereoisomers.

Anal. Calcd. for $C_{10}H_{15}BrO_2$: C, 48.59; H, 6.12. Found: C, 48.75; H, 5.87.

Addition of bromine to *trans*-Ib afforded a crystalline bromolactone, m.p. 30–31°; n.m.r., 77, 83 (CH_3—CH—), 87.5, 97.5 ((CH_3)$_2$C), 123, 169, and 171 c.p.s.

The mixture of stereoisomeric bromolactones obtained above was heated for 4 hr. with triethylamine in benzene. The triethylamine hydrobromide was removed and the solution was washed with water and dilute hydrochloric acid. The solvent was removed and the residue recrystallized from petroleum ether at −78° to yield a white solid, m.p. 39–39.5°. Sublimation *in vacuo* raised the melting point of VIII to 40.5–41.5° (lit.,[1b] m.p. 44–45°). The lactone VIII displayed λ_{max} 222 mμ, ε 9,170, ν_{max} 5.72 μ, and n.m.r. signals at 68, 74 (CH_3—CH—), 86.6 ((CH_3)$_2$C), 149.6, 152.2, and 170.6 c.p.s.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.22; H, 8.45.

A solution of the lactone VIII in ethyl acetate was hydrogenated using platinum oxide as a catalyst. After removing the catalyst and solvent, the residue was recrystallized from petroleum ether to give a white solid, m.p. 48.5°, $[\alpha]_D$ −77.8°, whose infrared spectrum was identical with that of the lactone V.

C. From Carvenolide VII.—Carvenolide (VII) was prepared from *d*-carvone according to the procedure described by Wallach[7] and showed m.p. 41°, $[\alpha]_D$ −183°, end absorption only in the ultraviolet, ϵ_{220} 1,000, ν_{max} 5.66 μ, and a n.m.r. spectrum, 78.8, 85.4 ((CH_3)$_2$C), 105 (CH_3—C=C—), 142 (—CH_2—), an octet centered at 187 (R_2CH—), 196.9, 207 (CO—CH—C=C), and 302 c.p.s. (CH=C—), consistent with the assigned structure VII. Hydrogenation of carvenolide in ethyl acetate using platinum oxide as a catalyst afforded a white solid, m.p. 48–49°, undepressed when mixed with lactone V, $[\alpha]_D$ −48.1° (*c* 3.12, EtOH), whose infrared spectrum was identical with that of lactone V.

---

(7) O. Wallach, *Ann.*, **305**, 245 (1899).

(8) For a recent comprehensive review of the Favorskiĭ rearrangement see A. S. Kende, *Org. Reactions*, **11**, 261 (1960).

(9) All boiling and melting points are uncorrected. Nuclear magnetic resonance spectra were measured at 60 Mc. by W. E. Baitinger with the Varian Associates V-4300-B and A-60 spectrophotometers. Chemical shifts are given with reference to tetramethylsilane. Vapor phase chromatographic separations and analyses were conducted at 185° with a 20% Carbowax 20M on firebrick column, with helium as the carrier gas. The compositions of the mixtures were determined by measuring the ratios of the individual peak areas, *cf.* M. Dimbat, P. E. Porter, and F. H. Stross, *Anal. Chem.*, **28**, 290 (1956). The microanalyses were performed by Dr. C. S. Yeh and associates.