

The Conversion of 1-Phenyl-2-isopropylcyclopropane to 1,1,2-Trimethylindan.—While stirring, 14.4 g. of 1-phenyl-2-isopropylcyclopropane was run into 30 ml. of 90% sulfuric acid. Within a half hour the temperature rose to 40° after which it was maintained at 35° for one hour. The residual oil was removed by adding 25 ml. of ligroin, separating from the acid, washing the ligroin layer twice with 5-ml. portions of cold, concentrated sulfuric acid, steam distilling, separating the volatile oil, removing the ligroin by distillation through a short Widmer column, and distilling the residue. This gave 3.2 g. of 1,1,2-trimethylindan, b. p. 203°, d_{20}^{25} 0.919, n_{20}^{25} 1.5137.

Analyses.¹¹ Calculated for $C_{12}H_{16}$: C, 89.9; H, 10.1. Found (1-phenyl-2-isopropylcyclopropane): C, 89.7; H, 10.1. Found (1,1,2-trimethylindan): C, 89.7; H, 10.2.

Oxidation of 0.46 g. of the product obtained above by

(11) These analyses were performed by Mr. Saul Gottlieb, Columbia University.

the method of Price, Davidson and Bogert⁴ yielded 0.30 g. of the ketone acid (V) which when recrystallized from water melted at 156°. This did not depress the melting point of an authentic sample of the acid melting at 158°. Both samples gave iodoform when treated with sodium hypiodite.

Summary

1. 1-Phenyl-2-isopropylcyclopropane is rearranged by 90% sulfuric acid to 1,1,2-trimethylindan.

2. Under similar conditions 1-phenyl-2-methylcyclopropane and 1-phenyl-2-ethylcyclopropane undergo polymerization.

3. Cyclopropanes obey the modernized Markovnikov rule.

BROOKLYN, N. Y.

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[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE OF AGRICULTURE AND APPLIED SCIENCE]

The Isolation of Stigmasterol and β -Sitosterol from the Common Bean, *Phaseolus vulgaris*

BY ARNOLD C. OTT¹ AND CHARLES D. BALL

The content of the "crude fat" of the common or navy bean, *Phaseolus vulgaris*, has been reported by various workers² to be between 1.4 and 2.36%. Grimme³ submitted values for certain physical and chemical constants of the oil among which was an unsaponifiable matter percentage of 5.85. Likiernik⁴ appeared to be the only worker to have isolated sterols from any part of the bean. He obtained from the seed coats two substances named by him paraphytosterol and phasol. In harmony with the work of Anderson and Shriner⁵ paraphytosterol would appear to be γ -sitosterol, while phasol, m. p. 189–190°, $[\alpha]_D + 30.6^\circ$, is either a mixture or has not been identified with any of the better known sterols. Attention has been focused on the ether soluble portion of the navy bean by the recent observation of Bowman,⁶ who maintains that the bean oil retards the digestion of soluble starch by pancreatic amylase *in vitro*.

In the present work the bean oil, "ether extract," has been found to represent about 2.6% of the bean, of which 5.0 to 6.0% was unsaponifiable matter. This unsaponifiable matter consisted of 55 to 60% crude sterols. Stigmasterol made up about one-fourth of the sterols, while β -sitosterol was found to be present to the extent of 5 to 7% of the total sterols. The separation of the stigmasterol was based on the insolubility of the

tetrabromide while the β -sitosterol was obtained from the mother liquors after debromination and fractional crystallization as acetates. No sterols corresponding to α -sitosterols appeared to be present in any appreciable amount. After irradiation the unsaponifiable matter had a vitamin-D activity of about 700 U. S. P. units per g. of unsaponifiable matter, thus indicating the presence in very small amount or amounts of irradiatable sterol or sterols.

Experimental

1. **Extraction of the Beans.**—Forty kg. of the common bean, *Phaseolus vulgaris*, was ground in a hammer mill and extracted six times by cold ethyl ether. The extract was filtered and the solvent distilled off in an atmosphere of carbon dioxide. The yield was 0.83 kg. of yellow oil, which represented 1.9% of the original beans.

2. **Saponification.**—To the entire lot of the oil 4 liters of ethanol and 1 liter of 50% potassium hydroxide were added. The mixture was stirred on the steam-bath for two hours. Water was then added and the unsaponifiable matter was exhaustively extracted from the soaps with "Skellysolve B." The combined extracts were concentrated to 50% concentration of oil and then washed free from alkali. The remainder of the solvent was evaporated; yield, 48.7 g. of a yellow, semi-solid oil. This quantity represented about 5.9% of the crude oil.

3. **Preparation of Crude Sterols.**—The entire lot of unsaponifiable material was taken up in petroleum ether, b. p. 40–60°, and steam passed into the solution until saturation nearly occurred. The solution was then allowed to stand overnight. The first fraction of crystals, designated Fraction I, consisted of 22.5 g. of colorless crystals; m. p. 138–144°; $[\alpha]_D^{25} - 44.0^\circ$ (35.4 mg., 2.1 ml. chloroform, $l = 1$ dm., $\alpha_D^{25} - 0.742^\circ$, average reading). The Liebermann-Burchard reaction was strongly positive. The mother liquor was evaporated to 300 ml. and allowed to stand for twenty-four hours in the cold. The result was Fraction II, which consisted of 7.2 g. of crystals, m. p. 128–131°; $[\alpha]_D^{25} - 38.0^\circ$ (38.6 mg., 2.1 ml. chloroform, $l = 1$ dm., $\alpha_D^{25} - 0.698^\circ$, average reading). A third fraction of about 2 g. was obtained from the mother liquors of

(1) Present address: Hercules Powder Co., Wilmington, Del.

(2) (a) Atwater and Bryant, *U. S. Dept. Agr. Off. Exp. Sta. Bul.*, 28 Rev. (1906); (b) Peterson and Churchill, *THIS JOURNAL*, 43, 1180 (1921); (c) Eichelberger, *ibid.*, 44, 1407 (1922).

(3) Grimme, *Pharm. Zentr.*, 52, 1141 (1911).

(4) (a) Likiernik, *Ber.*, 24, 187 (1891); (b) Likiernik, *Z. physiol. Chem.*, 15, 426 (1891).

(5) Anderson and Shriner, *THIS JOURNAL*, 48, 2976 (1926).

(6) Bowman, *Science*, 98, 308 (1943).