[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF BROOKLYN COLLEGE]

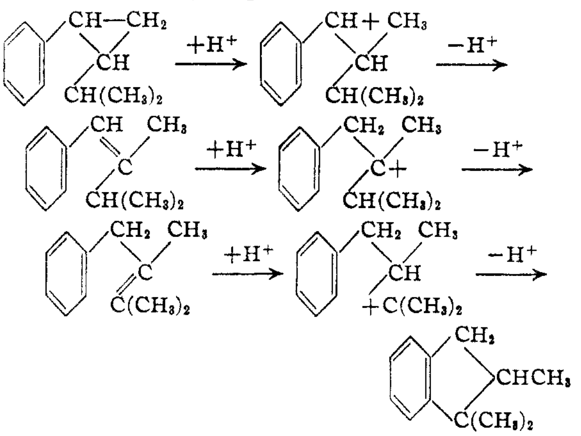
The Action of Sulfuric Acid on 1-Phenyl-2-alkylcyclopropanes[1,2]

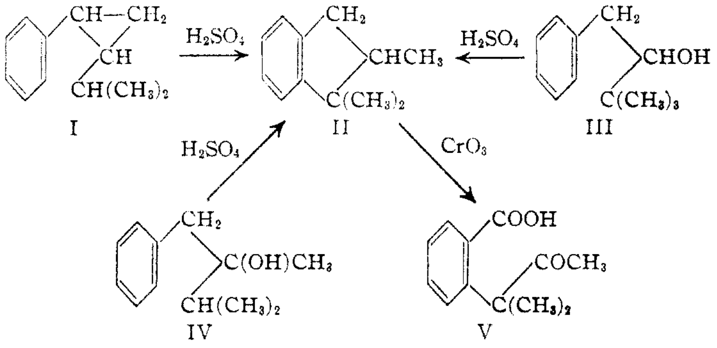
BY DAVID DAVIDSON AND JULIAN FELDMAN

Since the chemistry of the cyclopropane ring resembles that of the olefinic double bond it was of interest to compare the behavior of certain monophenylated cyclopropanes toward sulfuric acid with that of monophenylated olefins, which, if not polymerized, are converted to indans or tetralins.[3]

In the case of 1-phenyl-2-isopropylcyclopropane (I), the action of 90% sulfuric acid produced a low yield of 1,1,2-trimethylindan (II), a product previously obtained by the cyclodehydration of 1-phenyl-3,3-dimethyl-2-butanol (III)[4] and of 1-phenyl-2,3-dimethyl-2-butanol (IV).[5] This product is readily identified by its oxidation to the ketone acid (V). Treatment of 1-phenyl-2-methylcyclopropane[6] and of 1-phenyl-2-ethylcyclopropane with 90% sulfuric acid yielded gummy polymers and only traces of volatile oils.[7]

The foregoing results suggest that the attack on the 1-phenyl-2-alkylcyclopropanes by sulfuric acid begins with the opening of the cyclopropane ring by the addition of a proton to the least substituted carbon atom.[8] The resulting carbonium ion, which may also be obtained from olefins or alcohols, may then undergo its characteristic reactions; *i. e.*, addition to an unsaturated molecule (*polymerization*), decomposition to a smaller carbonium ion and an unsaturated molecule (*depolymerization*), isomerization to another carbonium ion (*rearrangement*), or decomposition into an olefin and a proton (*protolysis*). In the case of 1-phenyl-2-isopropylcyclopropane the changes shown below may be postulated.





Preliminary tests with higher homologs and with milder acid (85% phosphoric acid) indicate that isomerization to olefins actually does occur. Only with the isopropyl derivative are conditions very favorable for cyclization[3]; hence, in the other cases polymerization results.

Experimental

1-Phenyl-2-alkylcyclopropanes.—These hydrocarbons (Table I) were prepared by Kishner's method.[6,7,9] This involves the decomposition of certain pyrazolines in the presence of platinized asbestos and solid potassium hydroxide, the pyrazolines themselves resulting from the condensation of α,β-unsaturated ketones with hydrazine hydrate. The required unsaturated ketones were prepared by condensing benzaldehyde with methyl alkyl ketones in the presence of aqueous sodium hydroxide.[10] Good yields (75-80%) were obtained in each step.

TABLE I

1-PHENYL-2-ALKYLCYCLOPROPANES

R	B. p., °C.	d^{20}_4	n^{20}_D	Reference
H	174	0.940	1.5316	7
CH_3	186	.920	1.5208	6
	184–186	.925	1.5237	This paper
CH_3CH_2	203–205	.918	1.5162	This paper
$(CH_3)_2CH$	213–216	.899	1.5072	This paper

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[1] Presented before the Division of Organic Chemistry at the 100th meeting of the American Chemical Society held at Detroit, Michigan, September, 1940.

[2] This article is based on the thesis presented by Julian Feldman in partial fulfillment of the requirements for the degree of Master of Arts, Brooklyn College, 1940.

[3] Roblin, Jr., Davidson and Bogert, THIS JOURNAL, **57**, 151 (1935).

[4] Price, Davidson and Bogert, *J. Org. Chem.*, **2**, 540 (1938).

[5] Bogert and Davidson, THIS JOURNAL, **56**, 185 (1934).

[6] Kishner, *J. Russ. Phys.-Chem. Soc.*, **44**, 862 (1912); *C. A.*, **6**, 2915 (1912).

[7] Kishner, *J. Russ. Phys.-Chem. Soc.*, **45**, 950 (1913); *C. A.*, **7**, 3965 (1913), found that phenylcyclopropane was polymerized by sulfuric acid.

[8] Compare the modernized version of Markovnikov's rule (Fuson and Snyder, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1942, p. 19). The applicability of Markovnikov's rule to cyclopropanes was shown by Kishner,[6] who found hydrogen bromide to add to 1-phenyl-2-methylcyclopropane to form 1-phenyl-1-bromo-2-methylpropane.

[9] Kishner, *J. Russ. Phys.-Chem. Soc.*, **61**, 781 (1929); *C. A.*, **23**, 4698 (1929).

[10] Harries and Müller, *Ber.*, **35**, 966 (1902).

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. 208°, d^{20}_4 0.919, n^{20}D 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 the method of Price, Davidson and Bogert[4] 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 hypoiodite.

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.

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[11] These analyses were performed by Mr. Saul Gottlieb, Columbia University.

[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. OTT[1] AND CHARLES D. BALL

The content of the "crude fat" of the common or navy bean, *Phaseolus vulgaris*, has been reported by various workers[2] to be between 1.4 and 2.36%. Grimme[3] submitted values for certain physical and chemical constants of the oil among which was an unsaponifiable matter percentage of 5.85. Likiernik[4] 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 Shriner[5] paraphytosterol would appear to be γ-sitosterol, while phasol, m. p. 189–190°, $[\alpha]_D + 30.6°$, 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°; $[\alpha]^{27}_D$ −44.0° (35.4 mg., 2.1 ml. chloroform, l = 1 dm., α^{27}_D −0.742°, *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°; $[\alpha]^{26}_D$ −38.0° (38.6 mg., 2.1 ml. chloroform, l = 1 dm., α^{26}_D −0.698°, *average* reading). A third fraction of about 2 g. was obtained from the mother liquors of

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[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).