Anal.[18] Calcd.: Cl, 23.23. Found: Cl, 23.31, 23.34.

Relative Reactivities

Reaction with Potassium Iodide in Acetone.—The same procedure was used as previously described.[6] The usual modified second order equation, $k = {}^1/_4bt \log (5 - z)/5(1 - z)$, was used and a plot of $\log (5 - z)/5(1 - z)$ *vs.* time gave a straight line between 26 and 77% reacted for *cis*-cinnamyl chloride and between 22 and 64% reacted for *trans*-cinnamyl chloride. The data are given in Table I.

TABLE I

RELATIVE REACTIVITIES OF *cis*- AND *trans*-CINNAMYL CHLORIDE

Reaction with Potassium Iodide in Acetone at 20°

cis, rel. reactivity 17.3[a]			*trans*, rel. reactivity 11.4[a]		
Time, hr.	% reacted	*k*, hr. mole l.	Time, hr.	% reacted	*k*, hr. mole l.
0.17	26.3	4.07	0.25	21.8	2.19
.50	55.4	3.73	.50	42.9	2.56
.67	65.0	3.69	.75	59.2	2.79
.75	70.2	3.81	1.00	63.6	2.38
1.00	77.1	3.53		Av.	2.48 ± 0.19
	Av.	3.77 ± 0.14			

Cuprous Chloride-Catalyzed Acid Hydrolysis at 20°

cis

Time, hr.		1.00	2.00	3.00	4.00
% reacted		25.1	52.8	70.8	74.4

trans

Time, hr.	0.50	1.00	2.00	3.00	4.00
% reacted	10.1	24.2	53.6	85.2	92.7[b]

[a] Allyl chloride as 1.00 with $k = 0.218$. [b] Average of two runs.

It was necessary, before titration with potassium iodate, to extract the reaction mixture with chloroform to remove the cinnamyl iodide because this iodide can be titrated with potassium iodate. This added step in the analysis adversely affected the precision of the data obtained.

Reaction with Sodium Ethoxide in Ethanol.—The same procedure and mole ratios were used as in previously reported work[7] with the exception of the temperature which was 20 ± 0.1°. Only anomalous results were obtained. The reaction for each isomer apparently was about 60% complete in 10 minutes and only about 65% complete after 40 minutes.

Catalytic Hydrolysis with Cuprous Chloride in Hydrochloric Acid.—The method used was essentially the same as the previously described.[11] It was necessary to introduce the organic chloride to the reaction flask from a weighing bottle instead of by use of gelatine capsules because at the temperature used (20°) the capsules would not melt and liberate the chloride. The data obtained are given in Table I.

Summary

Both *cis*- and *trans*-cinnamyl chloride have been synthesized and the boiling point, density and index of refraction of each isomer have been determined.

The relative reactivities of these two isomers have been determined for their reaction with potassium iodide in acetone. *cis*-Cinnamyl chloride is slightly more reactive than the *trans* isomer.

Attempts to obtain similar data for their reaction with sodium ethoxide in ethanol and for their cuprous chloride catalyzed acid hydrolysis gave anomalous results.

The phenyl group apparently increased the rate of reaction for all three of these reactions.

AUSTIN, TEXAS RECEIVED MARCH 24, 1950

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[18] Chablay, *Ann. chim.*, **1**, 510 (1914).

[CONTRIBUTION FROM THE RESEARCH DIVISION, STAMFORD RESEARCH LABORATORIES, AMERICAN CYANAMID CO.]

The Dimer of α-Phenylacrylonitrile

BY HERBERT A. NEWEY[1] AND JOHN G. ERICKSON

Walker[2] has recently described the preparation of α-phenylacrylonitrile (atroponitrile) and its spontaneous conversion to a crystalline dimer, m. p. 123°, for which he proposed a cyclobutane structure. He hydrolyzed this dimer with sodium hydroxide solution to obtain a dicarboxylic acid, m. p. 204–206°. Hydrolysis of the dimer with sulfuric acid yielded a diamide which was further hydrolyzed to a dibasic acid by means of alkali; the melting points and other properties of the diamide and dibasic acid so obtained were not stated. The dimeric nitrile has also been isolated by German workers,[3] who apparently made no effort to determine its structure. We have also obtained this dimer of α-phenylacrylonitrile, m. p. 123–124°, and wish to present our observations on its chemical properties and structure.

We have found that hydrolysis of the dimer with dilute sulfuric acid yields a dibasic acid, m. p. 238–240°, which, oxidized with potassium permanganate, yields *o*-benzoylbenzoic acid. This same dibasic acid appears to have been obtained by Fittig,[4] who found that α-phenylacrylic acid is dimerized by heating to two products, melting at 237–237.5° and 206°, which he called "α- and β-isatropic" acids, respectively. Fittig also noted that, when heated above its melting point, β-isatropic acid was converted to the higher melting α-isatropic acid. He reported that oxidation of either α- or β-isatropic acid with chromium trioxide in acetic acid yielded *o*-benzoylbenzoic acid and anthraquinone, but no benzoic acid. It appears to us that Walker's dicarboxylic acid, m. p. 204–206°, is identical

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[1] Shell Development Co., Emeryville, Calif.

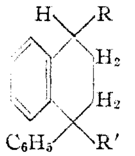
[2] Walker, U. S. Patent 2,478,990, Aug. 16, 1949.

[3] Meisenburg, I. G. report, May 20, 1938; PB 13321, frame 245. Also PB 50455.

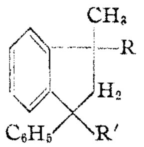
[4] Fittig, *Ann.*, **206**, 34 (1880).

with Fittig's β-isatropic acid, m. p. 206°, and that our dibasic acid, m. p. 238–240°, is identical with Fittig's α-isatropic acid, m. p. 237–237.5°.

Fittig favored structure I, R = R′ = COOH, wherein the carboxyl groups may be *cis* or *trans*



I

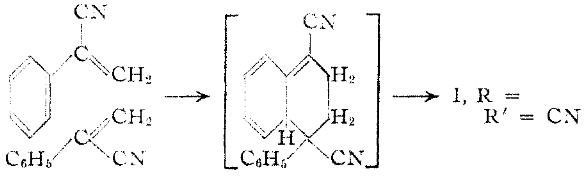


II

to each other, for α- and β-isatropic acids. This is supported by the oxidation studies of Fittig and the present authors which definitely exclude Walker's cyclobutane structure. An alternative structure II, R = R′ = COOH, not considered by Fittig, is admissible so far as the oxidation results are concerned but does not readily explain the conversion of β-isatropic acid to α-isatropic acid. This conversion can readily occur in structure I, R = R′ = COOH, where the lability of the hydrogen alpha to one of the carboxyls would allow *cis–trans* isomerization of the carboxyl groups. In view of this, we believe that Fittig's structure is correct, and that the dimeric nitrile is I, R = R′ = CN.

The infrared absorption spectrum of the dinitrile shows bands at 2220 cm.$^{-1}$ (CN group), 1600 cm.$^{-1}$ (phenyl group), 1496 and 760 cm.$^{-1}$ (*o*-phenylene structure) and 1450 cm.$^{-1}$ (methylene group). The critical point is the presence or absence of bands corresponding to the methyl group, which is present in I but absent in II. Here the spectroscopic evidence is inconclusive. There is no absorption band at 1375 cm.$^{-1}$ (CH_3 bending frequency) but such a condition is occasionally found with compounds known to possess methyl groups. At 2970 cm.$^{-1}$ there is a band which is in the correct position for the CH_3 stretching frequency. However, this might also be a C–H band, displaced because of the proximity of the C–H group (in structure I) to adjacent phenyl and cyano groups.

The dimerization of α-phenylacrylonitrile may be regarded, formally, at least, as a Diels–Alder reaction, followed by a 1,3 shift of a hydrogen atom



We have found that the hydrolysis of the dinitrile with sulfuric acid may be directed so as to yield the diamide, the diacid, or an amide-acid believed to be I, R = COOH, R′ = $CONH_2$.

Acknowledgment.—We wish to thank Dr. R. C. Gore of these laboratories for determining and interpreting the infrared absorption spectrum of the dimer. Analyses were performed by members of the Analytical and Microanalytical groups.

Experimental

α-Phenylacrylonitrile Dimer.—Walker used paraformaldehyde to prepare α-phenylacrylonitrile. The following procedure is somewhat similar but employs aqueous formaldehyde. Phenylacetonitrile (117 g., 1.0 mole), 37% formaldehyde solution (85 g., 1.0 mole of formaldehyde), ethanol (100 ml.), and 40% benzyltrimethylammonium hydroxide solution (Triton B) (2 ml.) were mixed and heated to reflux temperature. The heat of reaction was considerable and little external heating was necessary to maintain the refluxing. After ten minutes the mixture had formed two layers. It was cooled and the upper layer, containing mainly alcohol and water, was separated. Sodium carbonate (1 g.) was added to the lower layer which was heated under reduced pressure. The distillate collected at 75–195° under 2 mm. pressure was partly monomer and partly dimer; on standing it dimerized completely. Crystallization from methanol yielded 111.5 g. (86%) of product, m. p. 123–124°.

Anal. Calcd. for $C_{18}H_{14}N_2$: C, 83.69; H, 5.46; N, 10.85; mol. wt., 258. Found: C, 83.61, 83.80; H, 5.47, 5.17; N, 10.91, 11.08; mol. wt., 256 (benzene freezing point).

Our observations agree with those of Walker regarding the solubility of this substance in various solvents. However, we have found it to be considerably more stable than he suggests; it can be distilled at 408–412° at atmospheric pressure with little decomposition. Walker gives the b. p. as 185–215° (1.0–2.0 mm.); Meisenburg[3] gives 214° (12 mm.).

Experiments on the Dimerization of α-Phenylacrylonitrile.—In an attempt to determine which factors affected the rate of formation of the dimer, 3-ml. samples of the monomer were made up, containing, respectively, one drop of acetic acid, one drop of Triton B, copper wire, and a trace of hydroquinone. Each of these samples dimerized in approximately the same time as that required for a blank sample. Walker found that ultraviolet light accelerated the dimerization.

Hydrolysis of the Dinitrile to the Diamide.—α-Phenylacrylonitrile dimer (25.8 g., 0.10 mole) was mixed with sulfuric acid monohydrate (23.2 g., 0.20 mole) and heated at 90° for one hour, then poured into a solution of sodium bicarbonate. The product was filtered off, extracted with ethanol and with hot benzene, and recrystallized from acetic acid, m. p. 275°.

Anal. Calcd. for $C_{18}H_{18}N_2O_2$: C, 73.45; H, 6.17; N, 9.52. Found: C, 73.53, 73.42; H, 6.25, 6.42; N, 9.43, 9.52.

Hydrolysis of the Dinitrile to the Amide-acid.—A mixture of α-phenylacrylonitrile dimer (10.3 g., 0.04 mole) and sulfuric acid monohydrate (35 ml.) was heated at 90° for 20 hours, then diluted with water (40 ml.) and warmed briefly. The product was filtered off and recrystallized twice from acetic acid–water (2:1) to give 8.0 g. of white solid, m. p. 239–241.5°.

Anal. Calcd. for $C_{18}H_{17}NO_3$: N, 4.74; neut. equiv., 295. Found: N, 4.71; neut. equiv., 296.

Hydrolysis of the Dinitrile to the Diacid.—A mixture of α-phenylacrylonitrile dimer (30.0 g., 0.12 mole) and sulfuric acid monohydrate (100 ml.) was heated at 90° for 20 minutes. Water (20 ml.) was then added and the mixture was refluxed for two hours, allowed to cool and filtered. The precipitate was crystallized twice from acetic acid–water (2:1) to yield a white product, m. p. 238–240°.

Anal. Calcd. for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44; neut. equiv., 148. Found: C, 72.48, 72.35; H, 5.63, 5.52; neut. equiv., 150.

Oxidation of the Diacid.—A solution of the diacid (5.0 g.), sodium hydroxide (2.0 g.), and potassium permanganate (18.0 g.) in water (300 ml.) was refluxed for two hours, filtered, cooled, acidified and extracted with two

100-ml. portions of ether. Removal of the ether left 4.5 g. of red solid which was crystallized twice from water to yield 0.8 g. of the hydrate of *o*-benzoylbenzoic acid, m. p. 93–94°. Its identity was confirmed by conversion to anthraquinone.

Summary

1. It has been shown that the dimer of α-phenylacrylonitrile possesses a structure similar to that of Fittig's isatropic acids and is probably a substituted tetralin.

2. Several hydrolysis products of the dimer of α-phenylacrylonitrile are described.

STAMFORD, CONN. RECEIVED MARCH 27, 1950

[CONTRIBUTION FROM THE MULTIPLE FELLOWSHIP OF THE CORN PRODUCTS REFINING COMPANY, MELLON INSTITUTE]

Sitosterols from Corn Gluten

BY DOROTHY M. RATHMANN AND LOUISE R. MORROW

Anderson and co-workers[1] found that the "sitosterols from corn" are a complex mixture containing sitostanols and a small amount of stigmasterol in addition to α-, β- and γ-sitosterols, and that relatively more sitostanol was obtained from the endosperm than from the germ. In the commercial isolation of zein from corn gluten,[2] one stage consists in extraction of an alkaline isopropyl alcohol solution with hexane to remove the lipids. The resulting extract contains at least 95% of the oil originally present in the gluten. After washing the extract with water and evaporating off the hexane there is obtained a dark red-brown oil, known as "xanthophyll oil," about 11% of which consists of nonsaponifiables. The crude phytosterols are isolated in a yield of 8% (based on the oil), as a cream-colored solid having a sitosterol content of at least 85%. A typical batch of this sterol mixture constituted the starting material for the present investigation.

Removal of the non-steroid contaminants and some degree of fractionation (Table I) was achieved by recrystallization of the acetates which were then hydrolyzed. Further fractionation was obtained by the adsorption analysis of the *i*-sitosteryl methyl ethers. Although adsorption has been employed[3] as a means of freeing the *i*-steryl methyl ethers from unreacted sterols, there seems to have been no investigation of the method as a means of analyzing phytosterol mixtures.

In order to obtain data on the probable behavior of the ethers of the sitosterols during adsorption, *i*-cholesteryl methyl ether and cholesteryl methyl ether were prepared by the method of Stoll[4] and chromatographed. The results indicated that the recovery of both types of ethers would be high and that the *i*-steryl methyl ether would be less strongly adsorbed than the corresponding steryl methyl ether.

Chromatography of the ethers derived from the sitosterol fractions is summarized in Table II from which it is apparent that the sitosterol fraction of highest negative specific rotation yielded primarily *i*-γ-sitosteryl methyl ether (I). Intermediate fractions yielded a complex mixture of *i*-sitosteryl methyl ethers (II) and sitosteryl methyl ether (III). The sterol fraction of lowest specific rotation yielded principally episitostanol (IVA) and sitostene (V) which may have been derived from sitostanol in the course of preparing the methyl ethers.

On the basis of this preliminary investigation, it is concluded that γ- and β-sitosterols are the major components of the phytosterols from xanthophyll oil, that stigmasterol is absent, and that the content of sitostanol is much lower than was found by Anderson in corn gluten. Many small fractions have not been fully characterized. Speculations regarding the possible occurrence of the α-sitosterols are consequently not warranted.

Experimental

With the exception of the crude sitosterols, samples were dried over phosphorus pentoxide for several hours at 60° and 2 mm. pressure before being analyzed.

Specific rotations were determined at room temperature (25 ± 2°) for a chloroform solution of the compound in a 2-dm. tube, using sodium light. The concentration was 2.0 ± 0.2 g. per 100 ml. of solution. Barton and Cox[5] reported that, in the range used in the present work, the specific rotations of various sterol derivatives were independent of temperature and concentration. Consequently these data are not listed for each compound.

Carbon-hydrogen analyses were conducted by G. L. Stragand, Microchemical Laboratory, University of Pittsburgh. The infrared spectra were obtained and interpreted by R. B. Hannan, Jr., Department of Research in Chemical Physics, Mellon Institute.

Unless otherwise stated, the **acetates** were prepared by refluxing the sterol with 10 volumes of acetic anhydride for thirty minutes. The **benzoates** were obtained from the reaction of 1 weight of sterol with 1 volume of benzoyl chloride in 10 volumes of anhydrous pyridine for twenty-four hours at room temperature. After being isolated in the usual fashion, these derivatives were recrystallized from ethyl acetate.

Properties of Sitosterols from Corn Gluten.—Crude sitosterols isolated from xanthophyll oil consisted of slightly tan crystals containing 85 to 90% sitosterols (digitonin-precipitable) and having total fatty acid contents as high as 6%, depending on the method of isolation. Melting points were in the range of 125 to 135°. Recrystallization of a mixture of two such preparations from ethyl acetate gave: crop A, 74% yield, m. p. 134–136°, $[\alpha]^{26}_{\mathrm{D}}$

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[1] (a) Anderson and Moore, THIS JOURNAL, **45**, 1944 (1923); (b) Anderson, *ibid.*, **46**, 1450 (1924); (c) Anderson and Shriner, *ibid.*, **48**, 2976 (1926); (d) Anderson and Shriner, *J. Biol. Chem.*, **71**, 401 (1927); (e) Anderson, Nabenhauer and Shriner, *ibid.*, **71**, 389 (1927).

[2] Swallen, *Ind. Eng. Chem.*, **33**, 394 (1941).

[3] Fernholz and Ruigh, THIS JOURNAL, **62**, 3346 (1940).

[4] Stoll, *Z. physiol. Chem.*, **207**, 147 (1932).

[5] Barton and Cox, *J. Chem. Soc.*, 783 (1948).