indicating that reduction was not complete. The hot mixture was filtered, the insoluble portion washed with hot water, and the filtrate and washings were acidified with hydrochloric acid giving 4.5 g. of colorless oily acidic material. This product was treated with 50 ml. of 10% sodium hydroxide, and the insoluble sodium salt (3.13 g.) was separated by filtration. Acidification of the filtrate gave an oily product from which 1.56 g. (31% yield) of colorless needles, m. p. 155-161.5° (evolution of gas) was obtained by crystallization from ethyl acetate–petroleum ether (60-68°). The m. p. was not depressed on admixture with the high-melting dihydro acid III (R = H) produced by catalytic hydrogenation of the half-ester mixture (see above).

Decomposition of the insoluble sodium salt with dilute hydrochloric acid gave an oily acid which after two recrystallizations from ethyl acetate afforded 1.15 g. of the molecular compound, m. p. 170-172° (evolution of gas) with previous softening, undepressed on admixture with the original material.

The molecular compound, thus, affords a source of additional III (R = H) for the synthesis of bisdehydrodoisynolic acid. It seems probable that modification of the reduction conditions will give improved yields. A study of the cyclization of the low-melting dihydro acid III (R = H) would also be interesting.

Ultraviolet Absorption Spectra.—All determinations were made on the analytical specimens described above in 95% alcohol solution. A Beckman ultraviolet spectrophotometer was employed.

***trans*-3-Carboxy-4-(6-methoxy-2-naphthyl)-3-hexenoic Acid (VII, R = H).**—λ max 231.0 (log *E* 4.648), 332.0 (3.308). ***cis*-3-Carboxy-4-(6-methoxy-2-naphthyl)-3-hexenoic Acid (XI, R = H).**—λ max. 225.5 (log *E* 4.604), 330.5 (3.356) (plateau). **3-Carboxy-4-(6-methoxy-2-naphthyl)-4-hexenoic Acid (II, R = H).**—λ max. 234.0 (log *E* 4.763), 266.0 (3.760) (plateau), 272.5 (3.791), 320.0 (3.158), 331.0 (3.225). **High-Melting 3-Carboxy-4-(6-methoxy-2-naphthyl)-caproic Acid (III, R = H).**—λ max. 232.0 (log *E* 4.917), 252.5 (3.647), 262.0 (3.732), 271.5 (3.722), 317.0 (3.242), 331.0 (3.325). **Low-Melting 3-Carboxy-4-(6-methoxy-2-naphthyl)-caproic Acid (III, R = H).**—λ max. 232.0 (log *E* 4.913), 253.0 (3.620), 262.0 (3.720), 271.0 (3.715), 317.0 (3.214), 325 (3.172), (plateau), 331.0 (3.292). **172° Molecular Compound.**—λ max. 232.0 (log *E* 4.827), 317.5 (3.303), 331.5 (3.283). **Calculated for Equimolecular Mixture of the *trans* Hexenoic Acid VII (R = H) and the Low-Melting Dihydro Acid (III, R = H).**—λ max. 232.0 (log *E* 4.800), 316.5 (3.306), 332.0 (3.300). **Methyl 1-Ethyl-4-keto-7-methoxy-1,2,3,4-tetrahydrophenanthrene-2-carboxylate (IV, R = CH_3).**—λ max. 220.0 (log *E* 4.832), 247.0 (4.531), 315.5 (3.944), 345.0 (3.684) (plateau). **Methyl 3-Ethyl-2′-methoxy-6,7-benz-1-hydrindone-2-acetate (VIII, R = CH_3).**—λ max. 218.5 (log *E* 4.780), 245.5 (4.651), 306.5 (3.977), 351.5 (3.667). **Methyl 1-Ethyl-4-keto-6-methoxy-1,2,3,4-tetrahydroanthracene-2-carboxylate (XII, R = CH_3).**—λ max. 210.0 (log *E* 4.585), 252.0 (4.871), 300.0 (4.286), 372.5 (3.489).

Summary

Racemic α- and β-bisdehydrodoisynolic acid methyl ether have been synthesized from β-methoxynaphthalene. Friedel–Crafts acylation with propionyl chloride gave the previously known 2-propionyl-6-methoxynaphthalene, which was employed in a Stobbe condensation with diethyl succinate. Hydrogenation of the resulting mixture gave mainly one racemic form of the substituted succinic acid which on cyclization *via* the anhydride with aluminum chloride in nitromethane afforded, in addition to products of abnormal cyclization, the desired 1-ethyl-4-keto-7-methoxy-1,2,3,4-tetrahydrophenanthrene-2-carboxylic acid. Reduction of the keto group of this substance, followed by methylation of the ester with sodium triphenylmethyl and methyl iodide gave, after saponification, the mixture of α- and β-bisdehydrodoisynolic acid methyl ether, mainly the former.

Evidence for the structure of the abnormal products of cyclization (see above) has been obtained, and a linear (anthracene) analog of bisdehydrodoisynolic acid was prepared and shown to have estrogenic activity.

The mixture of isomers produced in the Stobbe condensation has been separated, and structures and configurations of the components have been assigned on the basis of ultraviolet absorption studies and chemical behavior.

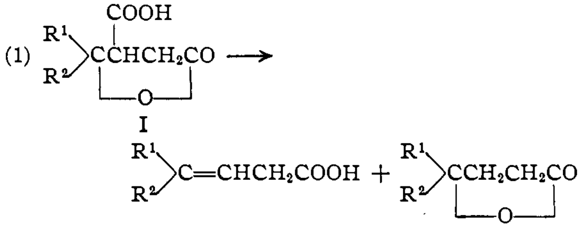
MADISON, WISCONSIN RECEIVED AUGUST 30, 1949

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Studies in Decarboxylation and Lacto-Enoic Tautomerism. IV.[1] Paraconic Acids[2]

BY WILLIAM S. JOHNSON AND RICHARD H. HUNT[3]

From the work of Fittig and his collaborators, it is well known that paraconic acids (I) lose carbon dioxide readily on heating, generally giving a mixture of an unsaturated acid and a lactone.[4] Although there is, in most of the cases, little or no evidence for the intimate structure of these products, the most likely presumption is that they are β,γ-unsaturated acids and γ-lactones as indicated in equation (1).



When R^1 = alkyl and R^2 = H (equation 1) the unsaturated acid is the main product, while with

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[1] Paper III, Johnson and Miller, THIS JOURNAL, **72**, 511 (1950).

[2] Supported in part by the Research Committee of the Graduate School from funds supplied by the Wisconsin Alumni Research Foundation.

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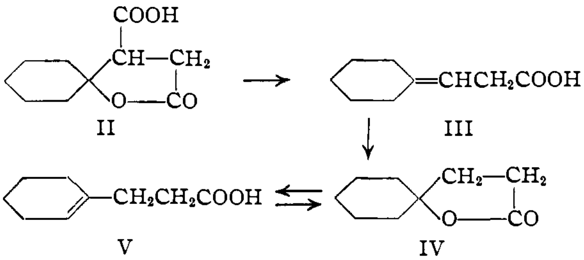
[4] Richter-Anschütz, "Chimie der Kohlenstoffverbindungen," Vol. I, 12th edition, Akademische Verlagsgesellschaft m. b. H., Leipzig. 1928, pp. 678-679.

$R^1 = R^2 = CH_3$ (the case of terebic acid)[5] the lactone is produced in preponderant but varying amounts depending upon the extent of the heat treatment, the unsaturated acid being formed in higher yields upon rapid distillation. This distinctive behavior when $R^1 = R^2 = CH_3$ is explained by the fact that the unsaturated acid readily undergoes lactonization upon heating at the boiling point, while the unsaturated acids with only one γ-alkyl group, in contrast, can generally be distilled without extensive isomerization to the lactones.[6]

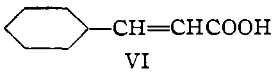
Since γ-lactones of the type considered above are not generally isomerized to the unsaturated acids under these conditions,[7] the production of the latter in the decomposition of paraconic acids suggests that the unsaturated acid is actually the primary product of decarboxylation, and hence the precursor of the lactone. Convincing support for this premise is provided by a critical study of the decarboxylation of γ,γ-pentamethyleneparaconic acid (II), which is the subject of the present communication.



The crystalline paraconic acid II was prepared in 73% yield from cyclohexanone and diethyl succinate as previously described.[8] Decarboxylation was best effected by heating the acid (m. p. 187°) with a trace of potassium acid sulfate at 215–230° for about seventy minutes. Fractional distillation at reduced pressure gave a product in 82% yield which consisted of approximately two-thirds γ,γ-pentamethylenebutyrolactone (IV) and one-third acidic material. The former was obtained crystalline and its properties compared favorably with those reported for this substance (IV) prepared by another route.[9] The nature of the liquid acidic fraction presented a more complex problem, since it contained material so susceptible to lactonization that the product obtained even immediately after careful acidification of the sodium salt in the cold had a neutral equivalent of 184 (calculated 154). If the acidification was carried out in the usual way at room temperature the neutral equivalent was 206 and after distillation at reduced pressure 220. The presence of β-cyclohexylidenepropionic acid (III) in the acidic fraction, however, was demonstrated by ozonolysis to give cyclohexanone, isolated and identified as the 2,4-dinitrophenylhydrazone. This acid (III) has been prepared by Linstead, *et al.*,[9] as a low-melting solid, which although easily lactonized could, nevertheless, be isolated in a relatively pure form from the sodium salt, and distilled at reduced pressure without lactonization. The much lower melting point of our product and its greater susceptibility to lactonization, suggested the presence of another isomeric, less stable unsaturated acid. The probable nature of this labile material follows from a consideration of the behavior of the lactone discussed below.

When the pure lactone was heated in the presence of potassium acid sulfate at 230–240° it was converted in part (12% at the most) to an unsaturated acid which yielded no cyclohexanone on oxidation with ozone or permanganate, but gave, instead, γ-ketoazelaic acid, $HOOC(CH_2)_4CO(CH_2)_2COOH$.[10] This result indicated that the acid was at least in part, β-cyclohexenylpropionic acid, V. This new acid, moreover was very susceptible to isomerization, and like the decarboxylation product, could not be obtained free of lactone. The purest material had a neutral equivalent of 177–182 (calculated 154) immediately after isolation (in the cold), and of 376 after standing for two weeks at room temperature in an acid-washed flask. When this unsaturated acid was heated at 225–235° with potassium acid sulfate the neutral equivalent rose to about 1,100 indicating about 14% acid and 86% lactone which is a ratio of the same order as that reached from the lactone. Although there remains some question as to the homogeneity of the participants, this behavior is suggestive of a lactoenoic tautomerism, IV $\rightleftarrows$ V with the equilibrium lying in the region of 85–89% in favor of the lactone at about 230°.

Since the decarboxylation of II was carried out under conditions which effect tautomerism of the lactone to the acid V as described above, the latter was undoubtedly present in the acidic fraction, and was probably responsible for the facile lactonization. Direct evidence for the presence of V in the decarboxylation product was obtained, moreover, by the isolation of some γ-ketoazelaic acid from permanganate oxidation.



VI

In addition to the acids III and V it seemed reasonable that β-cyclohexylacrylic acid VI might also be a constituent of the decarboxylation product arising from the three-carbon tautomerism III $\rightleftarrows$ VI which is known to be effected by alkali in the present case,[9] and by heat alone

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[5] Fittig and Geisler, *Ann.*, **208**, 37 (1881).

[6] See for example v. Braun and Münch, *ibid.*, **465**, 52 (1928).

[7] Linstead, *J. Chem. Soc.*, 115 (1932); Linstead and Rydon, *ibid.*, 580 (1933); Elliott and Linstead, *ibid.*, 660 (1938). For an exception see Boorman and Linstead, *ibid.*, 258 (1935).

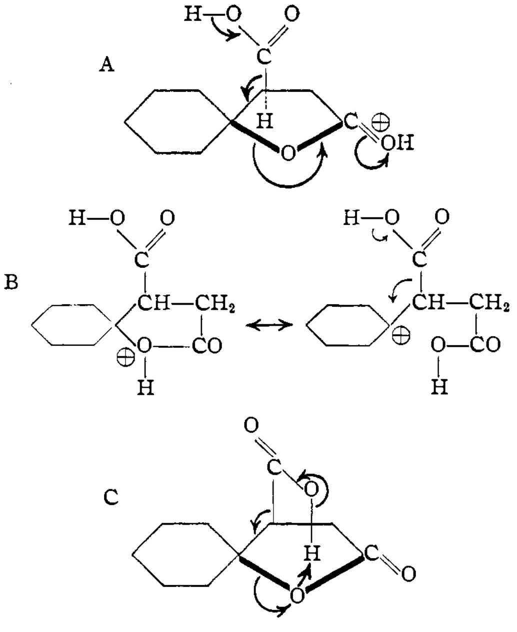
[8] Johnson, Davis, Hunt and Stork, THIS JOURNAL, **70**, 3021 (1948).

[9] Linstead, Wang, Williams and Errington, *J. Chem. Soc.*, 1136 (1937).

[10] Brown and Farmer, *Biochem. J.*, **29**, 631 (1935).

in others.[11] It was not possible, however, to prove the presence of VI. The 2,4-dinitrophenylhydrazone of the neutral product obtained by ozonolysis of the acidic fraction, was impure as compared with that derived from cyclohexylidenesuccinic acid used as a control. Although this impurity could not be isolated, it might have been due to the 2,4-dinitrophenylhydrazone of cyclohexanealdehyde which was shown to be produced readily by ozonolysis of pure VI.

The failure to detect β-cyclohexylidenepropionic acid III in the equilibrium mixture by that method which indicated its presence in the decarboxylation product, precludes the possibility that III is produced from IV, and suggests strongly, therefore, that the former is indeed the primary product of decarboxylation and the precursor of the lactone IV. The complete sequence is accordingly depicted by formulas II → V, with the possibility of the additional tautomerism III ⇄ VI. Such a scheme is entirely rational from an electronic consideration. Although the acid-catalyzed nature of the decarboxylation step has not been unequivocally proved, it is suggested by the fact that without the potassium acid sulfate it was necessary to raise the temperature to 230–250° in order to effect reaction in the same period of time. Moreover, if the apparatus (ordinarily acid-washed) was rinsed thoroughly with alkali before use, decarboxylation was even slower, an additional thirty minutes being required for complete reaction. Thus assuming the necessity of acid, various schemes for the decomposition of paraconic acids in general may be depicted, *e. g.*, A: a concerted process, or B: what is in effect an acid-catalyzed rupture of the tertiary carbon to oxygen bond to give a β-carbonium ion, the decarboxylation of which has been previously considered.[12] Scheme B, is perhaps slightly preferred, because of the good precedent for the ionization step in the conversion of IV to V which very likely involves such an ionization.[13] In any case the same primary product III is predicted by either scheme A or B. For the decomposition of the paraconic acid in the absence of a catalyst, the substance itself may be envisaged as supplying the necessary protons, either intermolecularly, providing the basis for mechanism A or B, or intramolecularly in a concerted process C.



For preparative purposes the ethyl ester of V was readily produced in 68% yield from the lactone IV by the action of thionyl chloride and ethyl alcohol followed by thermal dehydrohalogenation according to the excellent procedure of Cason, Adams, Bennett and Register.[14] The position of the double bond was shown by oxidative degradation with potassium permanganate to a crystalline half-ester of γ-ketoazelaic acid, $HOOC(CH_2)_4CO(CH_2)_2COOC_2H_5$, m. p. 69°, which upon saponification gave the known keto dibasic acid.[10] Hydrogenation of ethyl β-cyclohexenylpropionate followed by saponification gave β-cyclohexylpropionic acid, the properties of which compared favorably with material produced by perhydrogenation of cinnamic acid.

Experimental[15]

Decarboxylation of γ,γ-Pentamethyleneparaconic Acid (II).—A mixture of 20.55 g. of the paraconic acid (m. p. 185–186°) and 50 mg. of potassium acid sulfate in a 50-ml. Claisen flask was heated to 220–225° with a Wood's metal bath. Vigorous bubbling occurred during the first thirty minutes, then gradually subsided until after a total of seventy minutes when there was practically no evidence of reaction. Distillation at reduced pressure gave 13.11 g. (82% yield) of crude colorless decarboxylation product, b. p. 153–168° (21 mm.). Even after redistillation the carbon analysis of such a product was from 0.5 to 0.9% below the calculated value, apparently due to the presence of a trace of paraconic acid which was carried over in the distillation and in one instance crystallized from the distillate in quantity just sufficient to identify. The above distillate was dissolved in ether and extracted repeatedly with saturated sodium bicarbonate solution until the extract gave no cloudiness on acidification. The ether layer was washed with saturated sodium chloride and dried over anhydrous sodium sulfate. The liquid residue obtained after evaporation of the ether and drying to constant weight at water pump pressure, amounted to 8.07 g. The identity of this neutral material is described below.

The combined bicarbonate extracts were acidified with dilute hydrochloric acid and extracted thoroughly with ether. The ether solution was washed with water, saturated salt solution and dried over anhydrous sodium sulfate. The oily acidic fraction obtained by evaporation of

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[11] See for example, Linstead, *J. Chem. Soc.*, 1603 (1930).

[12] Paper II, Johnson and Heinz, THIS JOURNAL, **71**, 2913 (1949).

[13] See the rate studies of Altschul, *ibid.*, **70**, 2569 (1948), for the acid-catalyzed decomposition of *t*-butyl esters into isobutylene and carboxylic acids. It is of interest to note that this reaction is reversible and represents the intermolecular counterpart of lactoenoic tautomerisms, like IV ⇄ V; *cf.* Boorman and Linstead, *J. Chem. Soc.*, 258 (1935).

[14] Cason, Adams, Bennett and Register, THIS JOURNAL, **66**, 1764 (1944).

[15] All melting points are corrected.

the ether and drying to constant weight at water pump pressure amounted to 4.23 g. The proportion of neutral and acidic fractions of the total 12.30 g. recovered was thus 66 and 34%.

When the paraconic acid was treated as described above except that the potassium acid sulfate was not added, rapid evolution of gas did not begin until the temperature was raised to 230-250°. At this temperature the decarboxylation was essentially complete in about seventy minutes. In another run the reaction was carried out in exactly the same manner except that the reaction flask was previously washed thoroughly with dilute sodium hydroxide, then with distilled water and dried in the usual way. In this case it was necessary to continue the heating for a total of about one and three-quarter hours before the decarboxylation was essentially complete.

(*a*) *The Neutral Fraction.*—The neutral material obtained as described above from 10.2 g. of the paraconic acid was distilled through a 3-inch Vigreux column to give 3.98 g. of colorless liquid, b. p. 138.5–140° (13 mm.), $n^{25}\text{D}$ 1.4800. γ,γ-Pentamethylenebutyrolactone is reported to boil at 131-133° (10 mm.) and to melt at 20-20.5°.[9] Crystallization of the distilled material from petroleum ether (40–60°) at dry-ice temperature gave colorless crystals, m. p. 20.5–22°. On standing in the refrigerator this material changed into what was evidently a new polymorphic form, m. p. 26-27°.

Anal. Calcd. for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.04; H, 9.01.

Tests with the crude lactone demonstrated that it could not be extracted at all from an ether solution with saturated sodium bicarbonate, thus precluding the possibility that the acidic fraction from the decarboxylation contained the hydroxy acid from alkaline cleavage of the lactone.

(*b*) *The Acidic Fraction.*—The neutral equivalent of the acidic material isolated as described above was 206 (calcd. 154). After reduced pressure distillation at 18 mm. from a flask which had been cleaned in the usual manner in an acid-bath, the neutral equivalent rose to 220. A sample of the acidic fraction which was isolated from the bicarbonate extracts by cooling the solutions to −5 to 0° while being acidified (until congo red test paper changed blue), and then extracting immediately with ether, had a neutral equivalent of 184, which was essentially unchanged (179) after distillation at reduced pressure in an alkali-washed apparatus. The total product boiled at 138-144.5° (9-10 mm.) and a fraction boiling at 138.5-140.5° (9-10 mm.) was analyzed.

Anal. Calcd. for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.97; H, 9.02.

The following experiment was performed to demonstrate that the high neutral equivalents observed with the acidic fraction were really due to the presence of neutral material (presumably lactone). A sample of the acidic material obtained from a decarboxylation experiment by the technique described above for the isolation at 0° had a neutral equivalent of 186 which indicated a mixture of approximately 17% lactone and 83% acidic material of neut. equiv. 154. When 0.998 g. of this product was separated into neutral and acidic fractions with sodium bicarbonate solution, 0.135 g. (14% of total isolated) of the former and 0.831 g. (86%) of the latter were actually isolated, which is in fair agreement with the conclusion reached from the neutral equivalent.

Oxidation experiments with the acidic fraction are described below.

Isomerization Experiments. (*a*) *Of Lactone to Unsaturated Acid.*—A mixture of 6.15 g. of pure recrystallized lactone IV and 50 mg. of potassium acid sulfate was heated in an atmosphere of nitrogen at 230-240° for forty-five minutes. The product was then separated, as described above, into neutral and acidic fractions which amounted to 4.90 g. (92%) and 0.45 g. (8%), respectively. In another experiment 6.05 g. of lactone was treated similarly except that heating was continued for two and one-half hours, and this treatment gave 5.30 g. (90%) of neutral and 0.60 g. (10%) of acidic material. After five hours heating a 5.98-g. sample of lactone yielded 5.11 g. (88%) of neutral and 0.67 g. (12%) of acidic material. The lactonization and oxidation of these acidic fractions are described below.

(*b*) *Of Unsaturated Acid to Lactone.*—The acid used in these experiments was prepared by heating the pure lactone IV for four hours in the presence of potassium acid sulfate as described above, part (a). The acid isolated at 0° had a neutral equivalent of 241 indicating about 36% neutral and 64% of acidic material. After heating at 225-235° for thirty minutes in an alkali-washed flask the neut. equiv. was 298 indicating 48% neutral and 52% acidic material. The acid-catalyzed lactonization experiments were carried out by heating carefully weighed (approximately 0.2-g.) samples of the acid with portions of potassium acid sulfate obtained by evaporating to dryness an aliquot of a solution in water standardized against the alkali employed for determining the neutral equivalents. In the following experiments, the appropriate correction was made in the neutral equivalent for the amount of catalyst present. After thirty minutes at 225-235° with 0.51 mg. of catalyst, neut. equiv. 347 (56% neutral and 44% acid); after thirty minutes at 155-165° with 48.4 mg. of catalyst, neut. equiv. 846 (82% neutral, 18% acid); after thirty minutes at 225-235° with 46.0 mg. of catalyst, neut. equiv. 1,110 (86% neutral, 14% acid).

Ethyl β-1-Cyclohexenylpropionate.—A solution of 15.78 g. of pure lactone IV and 36 g. of thionyl chloride (Eastman Kodak Co. grade, redistilled) in 20 ml. of dry benzene was heated under reflux for one hour according to the procedure of Cason, *et al.*[14] The solution was then added with stirring over a period of fifteen minutes to 80 ml. of ethanol saturated with dry hydrogen chloride (at 0°). After stirring for an additional fifteen minutes the solvent was removed by distillation at reduced pressure, and the residue heated under reflux for one and three-quarters hours at 185-200°. Distillation gave 12.67 g. (68% yield) of material boiling at 108-110° (9-10 mm.) and 2.00 g. at 111-123° (9-10 mm.). The lower boiling fraction was washed with saturated sodium bicarbonate to remove dissolved hydrogen chloride, and redistilled through a short Vigreux column. The main fraction, b. p. 104.5-105° (9 mm.), had the $n^{25}\text{D}$ 1.4698, gave a negative test for halogen by the Beilstein test, and decolorized bromine in carbon tetrachloride as well as 2% potassium permanganate solution instantly.

Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.06; H, 9.79.

Hydrogenation of 2.58 g. of the above ester in 25 ml. of ethanol over 0.1 g. of platinum oxide was carried out at room temperature and atmospheric pressure. Reaction stopped after five hours, 92% of the calculated amount of gas being absorbed. The product was saponified with sodium hydroxide and the acidic material distilled through a Vigreux column to give 1.46 g., b. p. 149-150° (15 mm.), $n^{25}\text{D}$ 1.4675. A sample of β-cyclohexylpropionic acid prepared by hydrogenation of cinnamic acid in dioxane at 200° over Raney nickel distilled at 149-150° (15 mm.) and had the $n^{25}\text{D}$ 1.4617. The amide from the former sample melted at 120-120.5° and from the latter at 119-119.5°, and no m. p. depression was observed on admixture of the two derivatives.

Oxidations with Potassium Permanganate. (*a*) *Of β-1-Cyclohexenylpropionate.*—To a cooled solution of 5.61 g. of the unsaturated ester described above in 350 ml. of acetone (distilled from potassium permanganate) was added 11.3 g. of powdered potassium permanganate in portions so that the temperature of the reaction mixture remained between 2 and 4°. After addition was complete, stirring was continued for one hour at 0°, and the solvent was evaporated in a current of air. Water was added and the mixture chilled in an ice-salt-bath, and 1:1 sulfuric acid added followed by 40 ml. of saturated sodium bisulfite solution. The colorless mixture was extracted with ether from which the acidic material was separated by washing with saturated sodium bicarbonate solution. The combined bicarbonate solutions were acidified and extracted with ether. The latter ether solutions were washed with water, saturated salt solution and dried over anhydrous sodium sulfate. Evaporation of the ether gave 2.14 g. (30% yield) of crude, pale yellow waxy solid, m. p. about 61.5–64.5°, which on recrystallization from petroleum ether (60–68°) afforded 1.63 g. of colorless half ethyl ester of γ-ketoazelaic acid, m. p. 68–69.5°. Repeated recrystallization gave colorless needles, m. p. 68.8–69.4°.

Anal. Calcd. for $C_{11}H_{18}O_5$: C, 57.38; H, 7.88; neut. equiv., 230. Found: C, 57.20, 57.17; H, 7.82, 7.90; neut., equiv., 224.

The **semicarbazone** crystallized from water in the form of colorless plates, m. p. 149.5–150.5°.

Anal. Calcd. for $C_{12}H_{21}O_5N_3$: C, 50.16; H, 7.37. Found: C, 49.79; H, 7.44.

Saponification of the half-ester described above with 5% sodium hydroxide at room temperature gave crystalline keto acid which was obtained as colorless needles, m. p. 108.8–109.4° after repeated recrystallization from benzene. This m. p. is in good agreement with that (108–109°) reported by Brown and Farmer[10] for a keto acid, undoubtedly γ-ketoazelaic acid, obtained by oxidation of licanic acid.

Anal. Calcd. for $C_9H_{14}O_5$: C, 53.46; H, 6.98; neut. equiv., 101. Found: C, 53.23; H, 6.92; neut. equiv., 103.6.

The semicarbazone of the dibasic acid crystallized from water as colorless needles, m. p. 197–197.5° dec. (reported,[10] 197°).

Anal. Calcd. for $C_{10}H_{17}O_5N_3$: C, 46.32; H, 6.61. Found: C, 46.28; H, 6.45.

(*b*) *Of the Acidic Fraction from the Decarboxylation.*—A 0.5517-g. sample of the acid extracted from the decarboxylation mixture and isolated at 0° (see above) was oxidized in 30 ml. of acetone with 1.080 g. of potassium permanganate by the procedure described above, part (a). The crude semi-solid acidic product amounted to 0.097 g. which melted at 92–95° after recrystallization from benzene. Repeated recrystallization raised the m. p. to 106.5–107.5° which was not depressed on admixture with the sample of γ-ketoazelaic acid described above, part (a).

(*c*) *Of the Acidic Material Produced by Isomerization of the Lactone IV.*—A 0.3360 g. sample of the acid extracted from the mixture produced on heating the lactone IV at 225–230° over potassium acid sulfate and isolated at 0° (see above) was oxidized with 0.6110 g. of potassium permanganate by the procedure described above, part (a). The crude solid acidic product amounted to 0.070 g. and melted at 102–105° after recrystallization from benzene. Further recrystallization raised the m. p. to 106–108.5° which was not depressed on admixture with the sample of γ-ketoazelaic acid described above, part (a).

Ozonization Experiments. (*a*) *With Cyclohexylidenesuccinic Acid.*—This oxidation of an acid of known structure was performed as a control experiment. Ozone was passed into a solution of 0.211 g. of cyclohexylidenesuccinic acid[8] in 40 ml. of ethyl acetate for six hours at a rate of about 20 mg. of ozone per hour, the reaction mixture being kept at 0° by means of an ice-bath. The solution was then evaporated on a steam-bath in a current of dry air, and just before reaching dryness, 75 ml. of water and 1 g. of zinc dust were added. This mixture was heated on the steam-bath for fifteen minutes, then filtered and distilled. The distillate was collected in a flask containing 150 ml. of 2,4-dinitrophenylhydrazine reagent (prepared by dissolving 0.5 g. of 2,4-dinitrophenylhydrazine in 100 ml. of concentrated hydrochloric acid and diluting with 400 ml. of water), and the distillation was continued as long as precipitate continued to form. This treatment gave 0.068 g. (23% yield) of cyclohexanone 2,4-dinitrophenylhydrazone, m. p. 158.5–161.5°. After recrystallization from alcohol the m. p. was 159.5–161.5° and was not depressed on admixture with authentic derivative prepared from cyclohexanone.

A blank experiment conducted just as described above, but without the unsaturated acid, gave no precipitate. When methylene chloride was used in place of ethyl acetate the blank determination gave a precipitate with the 2,4-dinitrophenylhydrazine reagent, and therefore was not employed as the solvent.

An experiment carried out by distilling a suspension of 0.048 g. of cyclohexanone in 100 ml. of water and collecting the distillate in the 2,4-dinitrophenylhydrazine reagent, afforded 0.066 g. (48% yield) of derivative, m. p. 160.5–161.5°.

(*b*) *With the Decarboxylation Products.*—Ozonolysis of 1.240 g. of the mixture produced by decarboxylation of the paraconic acid was carried out as described above, part (a). The crude 2,4-dinitrophenylhydrazone amounted to 0.026 g., m. p. 135–145°. After several recrystallizations from alcohol the m. p. was raised to 159–161° and was not depressed on admixture with authentic cyclohexanone derivative.

Similar treatment of 0.189 g. of the acidic fraction isolated at 0° (see above) from the decarboxylation mixture yielded 0.050 g. of product, m. p. 146–154° which after several recrystallizations from alcohol melted at 159–161° alone or on mixing with authentic cyclohexanone 2,4-dinitrophenylhydrazone.

When either the pure lactone IV or the paraconic acid II was submitted to this ozonization treatment, no precipitate was obtained from the 2,4-dinitrophenylhydrazine reagent.

(*c*) *With the Product of Isomerization of the Lactone IV.*—The mixture produced by heating 1.493 g. of pure lactone with potassium acid sulfate at 230° for five hours was treated by the ozonization procedure described above, part (a). No precipitate formed from the 2,4-dinitrophenylhydrazine reagent. A small amount of γ-ketoazelaic acid, m. p. 105–107.5°, was isolated from the acidified residue by the procedure described in connection with the permanganate oxidation (see above).

Similar results were obtained when the acidic fraction from the isomerization was isolated before ozonization. A 0.119-g. sample gave no precipitate with the 2,4-dinitrophenylhydrazine reagent, but did afford a small amount of γ-ketoazelaic acid, m. p. 105–107°, undepressed on admixture with authentic material.

(*c*) *With β-Cyclohexylacrylic Acid.* (*VI*).—The acid was prepared from cyclohexanealdehyde and malonic acid by the procedure of Linstead, *et al.*[9] After repeated recrystallization from 40–60° petroleum ether (at dry-ice temperature) it melted at 56.5–58° (reported,[9] m. p. 59–60°). A 0.177-g. sample was submitted to the ozonization treatment described above, part (a). The precipitate amounted to 0.1475 g., m. p. 172–174°. Recrystallization from alcohol raised the m. p. to 174–175° which was not depressed on admixture with **cyclohexanealdehyde 2,4-dinitrophenylhydrazone** prepared directly from the aldehyde. The pure derivative was obtained from alcohol–ethyl acetate as bright orange crystals, m. p. 173–173.8°.

Anal. Calcd. for $C_{13}H_{16}O_4N_4$: C, 53.42; H, 5.52. Found: C, 53.70; H, 5.10.

Summary

A critical study of the decarboxylation of γ,γ-pentamethyleneparaconic acid (II) has shown that the primary product is probably β-cyclohexylidenepropionic acid (II) which undergoes fairly rapid isomerization to the lactone IV. The lactone in turn isomerizes in part to β-cyclohexenylpropionic acid (V). This step appears to be reversible, and thus represents an example of lacto-enoic tautomerism with the position of equilibrium largely in favor of the lactone.

The present findings appear to have a direct bearing on the decarboxylation of paraconic acids in general which is postulated herein as an acid-catalyzed phenomenon.

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