Hydrochloride.—A solution of the base in the calculated amount of 1 *N* hydrochloric acid was concentrated *in vacuo*. The residual salt was purified by crystallization from acetone. It forms colorless needles melting at 198–199°.

Anal. Calcd. for $C_{19}H_{21}N_3 \cdot HCl$: C, 69.60; H, 6.76; N, 12.82. Found: C, 69.36; H, 7.03; N, 12.47.

6,7-Dimethyl-4-phenyl-2-dimethylaminomethyl-3,4-dihydroquinazoline (XVI).—6,7-Dimethyl-4-phenyl-2-dimethylaminomethylquinazoline (XV) (0.8 g.) was hydrogenated in 50 cc. of methanol at room temperature and atmospheric pressure in the presence of 5 g. of wet Raney nickel, until about 1 mole of hydrogen was absorbed. The mixture was filtered, concentrated, the residue dissolved in ether and filtered again. The ether solution was concentrated *in vacuo*, and the residue crystallized from a mixture of ether and petroleum ether. The yield was 0.3 g. (37%). After recrystallization from a mixture of ether and petroleum ether, the product forms colorless prisms melting at 125–126°. It gives a melting point depression with the starting material.

Anal. Calcd. for $C_{19}H_{23}N_3$: C, 77.77; H, 7.90. Found: C, 77.71; H, 7.86.

Dihydrochloride.—An alcoholic solution of the base was neutralized with two moles of hydrochloric acid, and concentrated *in vacuo*. The salt was purified by crystallization from acetone or from a mixture of methanol, acetone and petroleum ether. It forms white prisms melting at 235–236° dec. The product turns pink on exposure to light.

Anal. Calcd. for $C_{19}H_{25}N_3Cl_2$: C, 62.30; H, 6.87; N, 11.47. Found: C, 62.31; H, 7.17; N, 11.38.

A Mixture of 6,7-Dimethyl-4-phenyl-2-dimethylaminomethylquinazoline and 6,7-Dimethyl-4-phenyl-2-dimethylaminomethyl-3,4-dihydroquinazoline by Hydrogenation of 6,7-Dimethyl-2-dimethylaminomethyl-4-phenylquinazoline 3-Oxide.—6,7-Dimethyl-2-dimethylaminomethyl-4-phenylquinazoline 3-oxide (XIV) (8.1 g.) dissolved in 200 cc. of methanol was hydrogenated in the presence of 10 g. of wet Raney nickel at atmospheric pressure and room temperature. After the absorption of 1.1 moles of hydrogen, the solution was filtered, concentrated *in vacuo* and the residue crystallized from ether. Thus 4.5 g. of crude 6,7-dimethyl-4-phenyl-2-dimethylaminoquinazoline (XV) was obtained melting at 100°. The product was purified by crystallization or by conversion into the hydrochloride. It was identical with the compound described above. The mother liquors obtained after the separation of the crude base contained the dihydroquinazoline XVI which was isolated as crude dihydrochloride melting at 221–228° (1.4 g.). In addition 1.2 g. more of crude quinazoline XV hydrochloride was obtained.

Oxidation of 6,7-Dimethyl-4-phenyl-4-dimethylaminomethyl-3,4-dihydroquinazoline (XVI) to 6,7-Dimethyl-4-phenyl-2-dimethylaminomethylquinazoline (XV).—A solution of 0.6 g. of 6,7-dimethyl-4-phenyl-4-dimethylaminomethyl-3,4-dihydroquinazoline (XVI) in 10 cc. of benzene was stirred vigorously at room temperature with a solution of 1.4 g. of potassium ferricyanide and 1.3 g. of potassium hydroxide in 30 cc. of water. After 2 hours the benzene solution was separated and the water layer extracted with some ether. The organic layers were combined, concentrated and the residue crystallized from a mixture of ether and petroleum ether. It yielded 0.16 g. of 6,7-dimethyl-4-phenyl-2-dimethylaminomethyl-quinazoline (XV) melting at 109–110°. The product gave no melting point depression with an original sample and a considerable depression with the starting material. In addition, 0.13 g. of the hydrochloride of 6,7-dimethyl-4-phenyl-2-dimethylaminomethylquinazoline (XV) was obtained in crystalline form.

NUTLEY 10, N. J.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

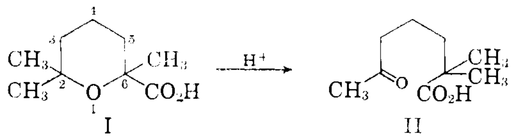
The Acid-catalyzed Rearrangement of Cinenic Acid. IV. Synthesis and Rearrangement of 6-Carboxy-6-ethyl-2,2-dimethyltetrahydropyran

BY JERROLD MEINWALD AND JOHN THOMAS OUDERKIRK

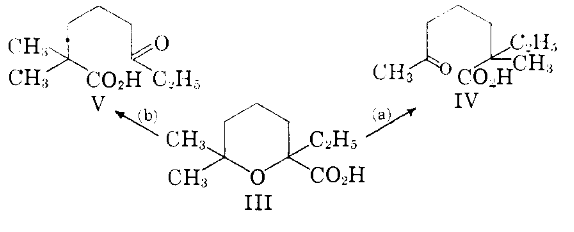
RECEIVED MAY 23, 1959

A synthesis of 6-carboxy-6-ethyl-2,2-dimethyltetrahydropyran (III) is described. This acid undergoes a reaction analogous to the cinenic acid rearrangement, giving rise to 2,2-dimethyl-6-oxoöctanoic acid (V), whose structure was proved by independent synthesis. This transformation can be rationalized only in terms of a carboxyl transfer process.

The rearrangement of cinenic acid (I) to geronic acid (II) was first observed by Rupe and Liechtenhan.[1] Early attempts to rationalize the transformation were based on the implicit assumption that an alkyl migration (2 → 6) was taking place.[1,2] More recently it was suggested that II could form from I by means of a carboxyl transfer (6 → 2).[3] In this Laboratory, two series of experiments were undertaken in parallel to decide between these alternatives. The first of these studies, involving the rearrangement of isotopically labeled cinenic acid, has already been described.[3] The second provides the subject of the present communication.



The ambiguity in recognizing the migrating group in the cinenic acid to geronic acid transformation would vanish if the rearrangement of a homologous compound such as 6-carboxy-6-ethyl-2,2-dimethyltetrahydropyran (III) were studied. Thus, whereas alkyl migration (a) would yield IV, carboxyl transfer (b) would give rise to the easily distinguishable isomer V.



The synthesis of 6-carboxy-6-ethyl-2,2-dimethyltetrahydropyran (III) was carried out as outlined in Chart 1. The key intermediate, 7-methyl-6-octen-3-one (VIII), was prepared by two independent routes. The first of these was convenient

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[1] H. Rupe and C. Liechtenhan, *Ber.*, **41**, 1278 (1908).

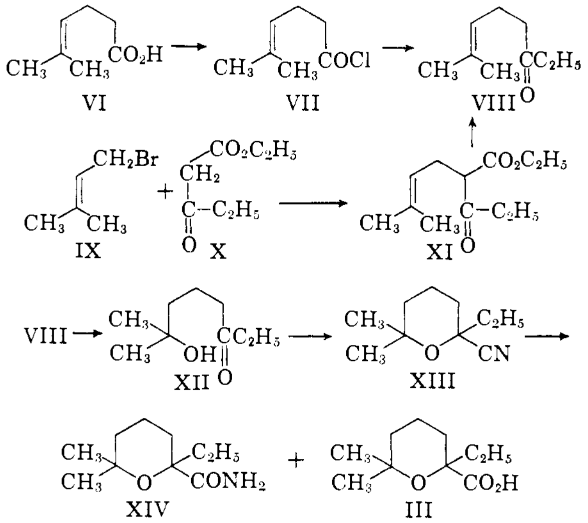
[2] H. Rupe and H. Hirschmann, *Helv. Chim. Acta*, **16**, 505 (1933).

[3] J. Meinwald, THIS JOURNAL, **77**, 1617 (1955).

at first because a supply of the requisite starting material, 5-methyl-4-hexenoic acid (VI), had already been prepared in this Laboratory.[3] However, difficulty in obtaining the acid chloride VII pure, and the low yield in the subsequent reaction with diethylcadmium made this path to VIII less attractive than the alternate route described below.

Ethyl β-oxovalerate (X) was prepared from ethyl cyanoacetate and ethylmagnesium iodide using the procedure of Anderson.[4] Alkylation with 2-methyl-4-bromo-2-butene (IX), obtained by addition of hydrogen bromide to isoprene,[5] gave a good yield of 4-carbethoxy-7-methyl-6-octen-3-one (XI). Base hydrolysis of XI followed by acid-catalyzed decarboxylation gave the desired ketone VIII in excellent yield; VIII prepared in this way was identical with that prepared by the diethylcadmium technique.

CHART 1



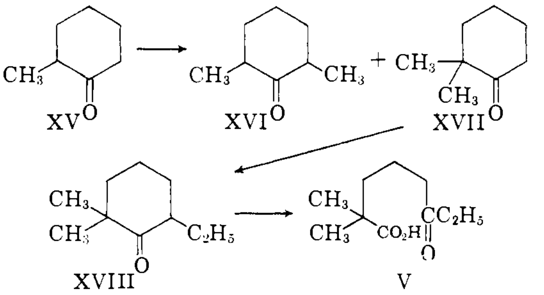
Hydration of VIII using 35% sulfuric acid gave rise to the corresponding ketol, 7-methyl-7-hydroxy-3-octanone (XII). Treatment with anhydrous hydrogen cyanide gave the nitrile XIII, easily recognized by the appearance of a 4.50 μ (nitrile) band and the disappearance of both hydroxyl and carbonyl absorption in the infrared. The hydrolysis of this nitrile to the desired acid III was carried out using the procedure previously developed for the successful hydrolysis of α-cinenic nitrile.[3] The major product (60%) was found to be the amide XIV, while only a small yield (30%) of the expected acid III was obtained. This acid proved to be a hygroscopic liquid at room temperature. It formed a crystalline hydrate when exposed to moist air. Attempts to improve the hydrolysis technique were unsuccessful, and the amide was uncommonly resistant to further hydrolysis. These difficulties undoubtedly stem from the large degree of steric hindrance in the region of the amide grouping.

The rearrangement of III proceeded smoothly in concentrated sulfuric acid solution at room temperature. The crude product was separated into neutral and acid fractions, and a portion of the acidic material was treated with sodium hypoiodite. No iodoform was obtained, indicating that the methyl ketone IV was not present. This result gave a preliminary indication that carboxyl migration, leading to V, had occurred. Since the quantity of available rearrangement product was expected to be small, an independent synthesis of V was carried out simultaneously with the work described above. This allowed a direct comparison between the rearrangement product and an authentic sample of 2,2-dimethyl-6-oxoöctanoic acid (V).

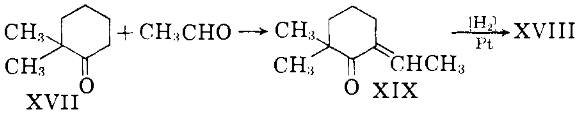
The synthesis of V proceeded as outlined in Chart 2. The methylation of 2-methylcyclohexanone is complicated by the formation of both symmetrical and unsymmetrical isomers (XVI and XVII). Thus, Haller investigated this reaction using sodamide and methyl iodide, and described the product as a 17:3 mixture of XVI and XVII.[6] The separation of this mixture *via* semicarbazones or oximes proved tedious and wasteful. A more elegant route from XV to XVII, involving the use of isopropoxymethylene blocking group, has been described by Johnson and Posvic.[7] Although we have found this procedure to give XVII in about 30% yield, a shorter process seemed desirable.

A simple route from XV to XVII, consisting of (1) alkylation with sodamide and methyl iodide, (2) formylation of the crude product with ethyl formate and sodium ethoxide, (3) separation of neutral from acidic products and (4) slow distillation of the alkaline solution of hydroxymethylene derivative of XVII, was found to produce XVII in 40% over-all yield.[8]

CHART 2



Considerable difficulty was encountered in the ethylation of XVII to give 6-ethyl-2,2-dimethylcyclohexanone (XVIII). A number of direct alkylations leading to low yields of XVIII were carried out. Equally unrewarding were attempts to prepare XVIII *via* the steps shown below. The chief difficulty in this case was the poor yield in the aldol condensation leading to XIX. The best results were finally obtained by treatment of XVII with potassium *t*-butoxide and ethyl iodide.



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[4] G. Anderson, I. Halverstadt, W. Miller and O. Roblin, THIS JOURNAL, **67**, 2197 (1945).

[5] H. Staudinger, W. Kreis and W. Schelt, *Helv. Chim. Acta*, **5**, 750 (1922).

[6] A. Haller and R. Cornubert, *Bull. soc. chim.*, **41**, 367 (1927).

[7] W. Johnson and H. Posvic, THIS JOURNAL, **69**, 1361 (1947).

[8] After the completion of this work, essentially the same technique was described by F. E. King, T. J. King and J. G. Topliss, *J. Chem. Soc.*, 919 (1957).

The synthesis of V was completed by chromic acid oxidation of XVIII. The keto-acid was found to have an infrared spectrum essentially identical to that shown by the acidic rearrangement product produced from III. 2,4-Dinitrophenylhydrazones of the two samples had identical infrared spectra and an undepressed mixture melting point. These results establish the reality of the carboxyl transfer path for the rearrangement of III, and are in accord with conclusions reached on the basis of the C^{14} work for the case of cineic acid itself.

Acknowledgment.—The authors are grateful to the National Science Foundation for a research grant in support of the program of which this investigation was a part.

Experimental[9]

The following compounds were prepared by methods already described: 5-methyl-4-hexenoic acid,[3] ethyl β-oxovalerate[4] and 2-methyl-4-bromo-2-butene.[5]

5-Methyl-4-hexenoyl Chloride (VII).[10]—A solution of 3.5 g. of 5-methyl-4-hexenoic acid and 4 ml. of thionyl chloride in 20 ml. of absolute benzene was refluxed for one hour. The benzene and excess thionyl chloride were removed under vacuum and the crude product distilled, yielding 2.0 g. (58%) of VII, b.p. 77–80° (4.4 mm.).

7-Methyl-6-octen-3-one (VIII) (Method A).—A Grignard reagent was prepared under nitrogen in the standard fashion from 3.7 g. of magnesium ribbon and 17.0 g. of ethyl bromide. When the addition was complete the mixture was refluxed for one hour. After cooling the reaction mixture, 12.9 g. of anhydrous cadmium chloride was added, and the mixture stirred at room temperature until reaction was complete as indicated by testing with Michler ketone.[11] The ether was replaced by anhydrous benzene and a solution of 10.8 g. of VII in 20 ml. of benzene was added dropwise. The mixture was refluxed for two hours, then cooled and decomposed with ice and concentrated sulfuric acid. The organic layer was separated and the aqueous layer extracted with benzene. The extracts were combined with the organic layer, washed successively with water, dilute sodium carbonate, and water, and finally dried over magnesium sulfate. Purification by distillation gave 5.9 g. (57%) of 7-methyl-6-octen-3-one, b.p. 94° (32 mm.), $n_D^{22.9}$ 1.4409, infrared maximum at 5.85 μ.

Anal. Calcd. for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 76.84; H, 11.31.

The semicarbazone and 2,4-dinitrophenylhydrazone were prepared in the usual manner and had melting points of 122–124° and 64.5–65.5°, respectively.

Anal. Calcd. for $C_{10}H_{19}N_3O$; C, 60.88; H, 9.71; N, 21.30. Found: C, 61.03; H, 9.76; N, 20.97. Calcd. for $C_{15}H_{20}N_4O_4$: C, 56.24; H, 6.29; N, 17.49. Found: C, 56.37; H, 6.38; N, 17.60.

4-Carbethoxy-7-methyl-6-octen-3-one (XI).—Ethanolic solutions of 144 g. of ethyl β-oxovalerate and 127 g. of 2-methyl-4-bromo-2-butene were added in that order to a solution prepared by dissolving 23 g. of sodium in 400 ml. of absolute ethanol. The reaction mixture was refluxed for two hours and allowed to stand overnight.

After approximately 200 ml. of ethanol was distilled off, the reaction mixture was poured into water and the organic layer removed. The aqueous portion was extracted with ether and the ether extracts were combined with the organic layer. After washing with water, the ethereal solution was dried over magnesium sulfate. Distillation yielded 173 g. (82%) of XI, b.p. 103–106° (4 mm.). The infrared spectrum had strong, well resolved bands at 5.73 and 5.83 μ characteristic of a ketoester.

Anal. Calcd. for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 67.87; H, 9.76.

7-Methyl-6-octen-3-one (Method B).—A mixture of 95.4 g. of XI and 450 ml. of a 5% sodium hydroxide solution was stirred for three hours at room temperature by which time a single phase remained. The basic solution was extracted once with ether and then acidified with 50% sulfuric acid and held at vigorous reflux for one hour. The reaction mixture was extracted with ether, and the extract washed with sodium carbonate solution and water. After drying, the solvent was removed to yield 57 g. (90%) of VIII which could be used directly in the next step.

2-Carboxy-2-ethyl-6,6-dimethyltetrahydropyran (III).—In a tube previously flushed with dry nitrogen, a mixture of 15 g. of 7-methyl-6-octen-3-one and 150 g. of 35% sulfuric acid was shaken for 9 hours at room temperature and allowed to stand overnight at 10°. The mixture was made distinctly alkaline with 10% sodium hydroxide, without allowing the temperature to rise above 10°. Sufficient water was added to dissolve the solid which had precipitated and the aqueous portion was extracted with six portions of ether. After washing with water, the extract was dried over sodium carbonate. The solvent was removed and the crude product distilled from sodium carbonate to yield 9.4 g. (56%) of 7-methyl-7-hydroxy-3-octanone, b.p. 99–102° (3 mm.). It showed intense absorption at 2.95 μ (hydroxyl) as well as at 5.85 μ (carbonyl). An additional 2.1 g. of crude product was obtained by continuous ether extraction of the aqueous portion. The once-distilled XII was treated with hydrogen cyanide in a sealed tube as described by Rupe,[1,3] to give the nitrile XIII (infrared absorption at 4.50 μ; disappearance of hydroxyl and carbonyl absorptions).

The hydrolysis of XIII to yield III was carried out as previously described.[1,3] The major product (60%) was the amide XIV, m.p. 78–79°, which was characterized by its infrared spectrum and by its elementary analysis.

Anal. Calcd. for $C_{10}H_{19}O_2N$: C, 64.83; H, 10.34; N, 7.56. Found: C, 64.79; H, 10.44; N, 7.73.

The acidic product from the hydrolysis showed infrared absorption typical of an acid (sharp peak at 5.84 μ and general absorption in the 2.8–3.4 μ region). Its water solution was acidic. Several attempts at elementary analysis yielded data which fell between those calculated for $C_{10}H_{18}O_3$ and $C_{10}H_{18}O_3 \cdot H_2O$.

Anal. Calcd. for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74. Calcd. for $C_{10}H_{20}O_4$: C, 58.80; H, 9.87. Found: C, 60.42; H, 9.73.

The acid when dry was a liquid but quickly formed a solid hydrate when exposed to the atmosphere.

Rearrangement of 2-Carboxy-2-ethyl-1,6-dimethyltetrahydropyran.—To 10 ml. of ice-cold concentrated sulfuric acid was added 0.9 g. of the hydrate of III. A light straw color developed after a few minutes. The reaction was allowed to proceed for 27 hours and was then quenched with ice-water. The organic material was taken up in ether and separated into acidic and non-acidic fractions. A yield of 0.32 g. (35%) of 2,2-dimethyl-6-oxoöctanoic acid was obtained. A 2,4-dinitrophenylhydrazone, m.p. 124–125°, was prepared. The infrared spectrum of this material was indistinguishable from that of a sample prepared by independent synthesis. A mixture melting point showed no depression.

2,2-Dimethylcyclohexanone (XVII) (Method A).—The procedure of Johnson and Posvic was used and the yield of 2,2-dimethylcyclohexanone reported by these authors was obtained.[7]

2,2-Dimethylcyclohexanone (Method B).—To a slurry of 23 g. of sodamide in 300 ml. of anhydrous ether was added slowly 57 g. of 2-methylcyclohexanone. The mixture was held at reflux until the reaction was complete, as indicated by no further evolution of ammonia. Methyl iodide (85 g.) was added at a rate sufficient to maintain reflux. After three hours of additional refluxing, the reaction mixture was cooled and decomposed with water and dilute acid. The aqueous portion was extracted with ether and this material added to the organic layer of the reaction mixture. The ethereal solution was washed with sodium thiosulfate solution and water, then dried, and the solvent removed under reduced pressure. The crude product could be used directly in the next step.

Purification of Crude XVII.—To a cooled solution of 12.6 g. of the crude ketone in 125 ml. of anhydrous benzene were added 10.8 g. of commercial sodium methoxide and 14.8 g. of ethyl formate. The system was flushed with

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(9) Melting points are uncorrected. Infrared spectra were obtained using a Perkin-Elmer double beam model 21 instrument.

(10) H. L. Simon, A. Kaufmann and H. Schinz, *Helv. Chim. Acta*, **29**, 1133 (1946).

(11) H. Gilman, "Organic Chemistry, An Advanced Treatise," John Wiley and Sons, Inc., New York, N. Y., 1938, p. 496.

nitrogen, protected with a calcium chloride tube, and then cooled. A heavy white precipitate formed very quickly and the reaction mixture was left overnight. To work up, ice-water was added, and the organic layer was extracted with 5% sodium hydroxide solution. The aqueous layer, after dilution to 160 ml., was added to the basic extract, which was then extracted once with ether and slowly distilled. The distillate, which was collected until 50 ml. had been gathered after the condensing vapors gave a single phase, was saturated with salt and extracted with ether. The ether extract was washed with water and dried over magnesium sulfate. Removal of the ether gave 2,2-dimethylcyclohexanone which was purified by distillation to give 5.3 g. (40%, based on XV) of pure XVII, b.p. 80–82° (38 mm.), $n^{21.0}\text{D}$ 1.4481. The identity of the product was demonstrated by its oxidation to α,α-dimethyladipic acid and by its infrared spectrum, which showed carbonyl absorption at 5.87 μ as reported by Corey.[12]

2,2-Dimethyl-6-ethylcyclohexanone (XVIII) (Method A).—A series of experiments were performed in an attempt to ethylate XVII substantially by the methylation procedure described above. A variety of bases (commercial sodium amide, freshly prepared sodium amide, lithium amide), ethylating agents (ethyl iodide, diethyl sulfate), solvents (ether, benzene) and reflux times (5–72 hours) were used. In each case, distillation of the crude product gave a fraction of pure starting material and a small amount of higher boiling mixture which contained some of the desired compound.

2,2-Dimethyl-6-ethylcyclohexanone (Method B).—A solution of potassium *t*-butoxide was prepared by dissolving 7.9 g. of potassium in 250 ml. of anhydrous *t*-butyl alcohol. To this solution were added 12.6 g. of 2,2-dimethylcyclohexanone and 62.4 g. of ethyl iodide. After the reaction had subsided the mixture was allowed to stand for at least three hours. The solid phase was filtered off, and most of the solvent removed under vacuum. The product was poured into 250 ml. of water, extracted with ether and after washing with dilute acid and water, was dried and partially purified by distillation. Pure XVIII was most easily obtained by conversion of the high boiling portion to a semicarbazone. Recrystallization and regeneration in the usual way gave XVIII, b.p. 110° (30 mm.), $n^{22.6}\text{D}$ 1.4550.

A semicarbazone and a 2,4-dinitrophenylhydrazone were prepared and had melting points of 182–184° and 114–116°, respectively.

Anal. Calcd. for $C_{11}H_{21}ON_3$: C, 62.52; H, 10.02; N, 19.89. Found: C, 62.87; H, 10.08; N, 20.21. Calcd. for $C_{16}H_{22}O_4N_4$: C, 57.47; H, 6.63; N, 16.76. Found: C, 57.87; H, 6.65; N, 17.02.

2,2-Dimethyl-6-oxoöctanoic Acid (V).—To a solution of 7.7 g. of 6-ethyl-2,2-dimethylcyclohexanone in 100 ml. of glacial acetic acid was added 6.7 g. of chromic anhydride at a rate sufficient to maintain the reaction mixture at a temperature of 35–45°. After all the anhydride had been added this temperature was held for 1.5 hr. and then most of the solvent was removed under vacuum at a bath temperature no greater than 50°. The crude product was poured into brine and extracted with ether. The acidic materials were extracted with aqueous sodium hydroxide. The basic extract was acidified, and the organic portion extracted with ether. The acidic product was purified by distillation to give 1.5 g. (16%) of V, b.p. 162–163° (1.5 mm.), neutralization equivalent 180 (calcd. 186).

A 2,4-dinitrophenylhydrazone, m.p. 124–125°, was prepared and a mixed melting point with the same derivative of the rearrangement product of III showed no depression. The infrared spectra of the two 2,4-dinitrophenylhydrazones were indistinguishable.

Anal. Calcd. for $C_{16}H_{22}O_6N_4$: C, 52.45; H, 6.05; N, 15.29. Found: C, 52.64; H, 5.40; N, 15.06.

ITHACA, N. Y.

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[12] E. Corey, T. Topie and W. Wozniak, THIS JOURNAL, **77**, 5415 (1955).

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF CORNELL UNIVERSITY AND THE BROOKHAVEN NATIONAL LABORATORY]

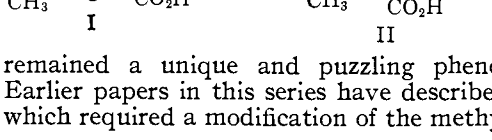
The Acid-catalyzed Rearrangement of Cinenic Acid. V. Evidence for a Decarbonylation–Recarbonylation Mechanism

BY JERROLD MEINWALD, HO CHIEN HWANG, DAVID CHRISTMAN AND ALFRED P. WOLF

RECEIVED MAY 23, 1959

A series of steps involving the loss and subsequent recapture of carbon monoxide is suggested to account for the carboxyl group transfer characteristic of the cinenic acid rearrangement (I → II). This reaction sequence is compatible with all earlier observations, and can be supported by analogies at every stage. The participation of carbon monoxide is indicated by an experiment in which the rearrangement, carried out in the presence of excess carbon monoxide, gave a significantly increased yield of geronic acid (II). Rearrangement in the presence of C^{14}-labeled carbon monoxide yielded labeled geronic acid. The possibility that this incorporation is due to exchange of the carboxylic carbon of either the starting material I or the product II with the externally supplied carbon monoxide is excluded by appropriate control experiments.

Introduction.—The rearrangement of α-cinenic acid (I) to geronic acid (II) was discovered by Rupe and Liechtenhan over a half century ago.[1] Even at that time the transformation appeared unusual, because it seemed to involve a long range migration of a methyl group (implicit in equation 1). As recently as 1952 this rearrangement remained a unique and puzzling phenomenon.[2] Earlier papers in this series have described results which required a modification of the methyl migration theory.[3,4] It is the purpose of the present paper to outline a rational mechanism for the cinenic acid rearrangement, and to present experimental evidence supporting this new mechanism.



I II (1)

Discussion.—The demonstration by two discrete lines of evidence that the cinenic acid rearrangement involves a carboxyl-group transfer rather than a methyl migration[3,4] has led us to a more careful consideration of the mechanistic details of this unusual process. Our original hypothesis, which served to motivate the reinvestigation of the problem, involved the series of steps shown below in Chart I. The key feature in this postulated scheme is the formation of the electron-deficient species A, in which an oxygen atom with an open

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[1] H. Rupe and C. Liechtenhan, *Ber.*, **41**, 1278 (1908).

[2] H. Dahn and T. Reichstein, *Helv. Chim. Acta*, **35**, 1 (1952).

[3] K. Meinwald, THIS JOURNAL, **77**, 1617 (1955).

[4] J. Meinwald and J. T. Ouderkirk, *ibid.*, **82**, 480 (1960).