

Table I.

Compound	B.P. or M.P., ° C.	Analysis					
		Calculated			Found		
		C	H	S	C	H	S
1,1-Diethoxy-2,3-epoxybutane (I)	78.5–80.0°(20 mm. of Hg)	60.0	10.1	...	60.7	10.1	...
1,1-Diethoxy-2,3-dihydroxybutane (IIa)	94.0–95.5°(2 mm. of Hg)	53.9	10.2	...	53.8	10.5	...
1,1-Diethoxy-2,3-diacetoxybutane (IIb)	88–89°(0.5 mm. of Hg)	55.0	8.45	...	54.8	8.43	...
1,1-Diethylthio-2,3-dihydroxybutane (IIIa)	105–110°(0.3 mm. of Hg)	45.6	8.62	30.5	45.2	8.35	30.3
1,1-Diethylthio-2,3-diacetoxybutane (IIIb)	100–110°(0.2 mm. of Hg)	49.0	7.54	21.8	49.0	7.73	21.8
2,3-Diacetoxybutyraldehyde (IV) ^a	82.5–83.0°(3 mm. of Hg)	51.1	6.38	...	50.1	6.82	...
Erythro-2,2,5-trimethyl-4-carbomethoxy-1,3-dioxolane (Va)	80–82°(10 mm. of Hg)	55.2	8.10	...	55.2	8.09	...
Erythro-2,2,5-trimethyl-4-hydroxymethyl-1,3-dioxolane (Vb)	98.5–99.0°(20 mm. of Hg)	57.5	9.65	...	57.1	9.89	...
<i>p</i> -Toluenesulfonate of Vb (Vc)	53.5–54.0	56.0	6.71	10.7	56.0	7.00	10.4
		C	H	N	C	H	N
2,4-Dinitrophenylhydrazone of IV	129.5–130.5°	45.7	4.38	15.2	45.5	4.43	15.2
Tri- <i>p</i> -nitrobenzoate of erythro-1,2,3-butanetriol	179–180°	54.5	3.46	7.59	54.7	3.62	7.55

^a Glattfeld and Straitiff (1) found b.p. 87° (4 mm. of Hg).

phenylhydrazone obtained from IV has the erythro configuration also.

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Preparation and Some Reactions of the Acetylenic Alcohols from Pinonic Acid and Homoterpenylmethyl Ketone

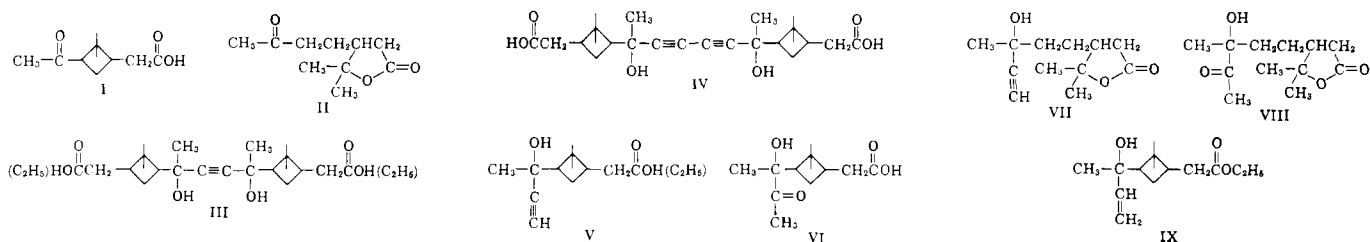
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Sodium and ethyl pinonate and homoterpenylmethyl ketone 6-keto-3-(1-hydroxy-1-methylethyl)-heptanoic acid γ -lactone, obtainable from the rearrangement of pinonic acid, were reacted with sodium acetylide. The expected products, 2,2-dimethyl-3-(1-hydroxy-1-methyl-2-propynyl)-cyclobutaneacetic acid, the ethyl ester of this acid and 6-hydroxy-6-methyl-3-(1-hydroxy-1-methylethyl)-7-octynoic acid γ -lactone were obtained in good yield. The alcohols were hydrated with mercuric sulfate giving the expected new ketones *cis-dl*-2,2-dimethyl-3-(1-methyl-2-oxopropyl)-cyclobutaneacetic acid and 6-hydroxy-6-methyl-3-(1-hydroxy-1-methylethyl)-7-oxo-octanoic acid γ -lactone. It was expected that a 1,4-glycol would result from reaction of two moles of pinonic acid with acetylene and a 1,6-glycol would result from oxidative coupling of the pinonic acid acetylenic alcohol. Negative results were obtained in both cases.

THE COMPOUND *cis-dl*-pinonic acid, 2,2-dimethyl-3-acetyl-cyclobutaneacetic acid, I, is easily obtainable from *dl*- α -pinene by permanganate oxidation or ozonolysis (4). This acid rearranges to homoterpenylmethyl ketone, 6-keto-3-(1-hydroxy-1-methylethyl)-heptanoic acid- γ -lactone, II, by action of hot aqueous mineral acids (1, 2). These ketones should react with acetylene in the presence

of basic condensing agents like ethyl levulinate, ethyl benzoylpropionate and keto fatty acids (5). The purpose of the present investigation was to study the reaction of these terpenes with acetylene, and characterize and determine some of the chemical properties of the resulting acetylenic alcohols. Two new dibasic acids, 3-(2,5-dihydroxy-3-hexynylene)-2,5-bis-2,2-dimethylcyclobu-



taneacetic acid, III, and 3-(2,7-dihydroxy-3,5-octadiynyl)-2,7-bis-2,2-dimethylcyclobutaneacetic acid, IV, were expected to result from pinonic acid.

EXPERIMENTAL

Cis-dl-2,2-dimethyl-3-(1-hydroxy-1-methyl-2-propynyl)-cyclobutane-acetic Acid, V. Sodium pinonate was prepared by adding one mole of *cis-dl*-pinonic acid to one mole of sodamide (sodium in liquid ammonia). Sodium acetylide was prepared by saturating liquid ammonia containing sodamide with acetylene (15). The sodium pinonate solution was then added dropwise to the sodium acetylide maintained at -35°C . Toward the end, a gummy solid separated and agglomerated, which made agitation difficult. A hour after completion of the addition, ammonium chloride was added. The agglomerate dissolved, and the mass became fluid. The ammonia was evaporated, and the product was taken up in ether after acidification with a little aqueous mineral acid.

Removal of the ether resulted in a crude product, in 98.6% yield, which, by ultraviolet spectrographic analyses (11) contained 7% unreacted pinonic acid leaving 91.9% yield of acetylenic alcohol. The crude recrystallized from acetone or acetonitrile resulted in 86% yield of product, m.p. $86-88^{\circ}\text{C}$. which contained less than 1% pinonic acid. By hydrogenation, using palladium on carbon in acetic acid, 2 moles of hydrogen were absorbed.

Analysis Calculated for $\text{C}_{12}\text{H}_{18}\text{O}_3$

% C		% H		Neutral Equivalent	
Calcd.	Found	Calcd.	Found	Calcd.	Found
68.54	68.60	8.63	8.42	209.30	210.26

A sample of the acetylenic alcohol after exposure to the atmosphere for 12 days, heated dry, or refluxed in benzene, water, or alcohol was not completely stable. In contrast to this, refluxing an aqueous solution of the sodium salt produced no decomposition.

Cis-dl-2,2-dimethyl-3-(1-methyl-2-oxopropyl)-cyclobutaneacetic acid, VI. Treatment of the acetylenic alcohol, V, with mercuric sulfate-formic acid mixture in accordance with Raphael (14) at 0°C . did not hydrate the ethynyl group. For this reaction, the acetylenic alcohol (0.36 mole) was added at 35°C . to 300 ml. of reagent which contained 55.9 ml. of concentrated sulfuric acid and 12.33 grams of mercuric sulfate. The batch was heated to 50°C ., then stirred until cool. Ether extraction resulted in 81% yield crude product which was purified by crystallization from acetone, m.p. $107-109^{\circ}\text{C}$.

Analysis Calculated for $\text{C}_{12}\text{H}_{20}\text{O}_4$

% C		% H		Neutral Equivalent	
Calcd.	Found	Calcd.	Found	Calcd.	Found
63.12	63.07	8.83	8.81	228.28	228.10

The keto acid gave an oxime, m.p. $144.5-146.5^{\circ}$, from 60% aqueous alcohol. Periodate oxidation of the hydroxy ketone gave *cis-dl*-pinonic acid, m.p. $104.6-106^{\circ}\text{C}$.

Ethyl Ester of V by Reaction of Ethyl Pinonate with Acetylene. Sodium acetylide was prepared from 0.52 mole sodium

metal dissolved in liquid ammonia. To this, 0.50 mole ethyl pinonate (n_D^{20} 1.4532), was added at -35°C . over a 20-minute period. Acetylene was admitted during the reaction. Ammonium chloride was added, the ammonia evaporated, and the product was taken up in ether. After removal of the ether, the residue was distilled in an 80% yield with b.p. $98-100^{\circ}/0.5$ mm. of Hg; n_D^{20} 1.4713; d_4^{20} 1.0058.

Analysis Calculated for $\text{C}_{14}\text{H}_{22}\text{O}_3$

Saponification Equivalent		Hydrogenation Equivalent	
Calcd.	Found	Calcd.	Found
238.32	237.86	119.16	117.0

Saponification of the ethyl ester with alcoholic sodium hydroxide resulted in a crude acetylenic acid which, presumably, was a mixture of *cis* and *trans* isomers since the ethyl pinonate used was such a mixture.

Analysis Calculated for $\text{C}_{14}\text{H}_{22}\text{O}_3$

Neutral Equivalent	
Calcd.	Found
210.26	210.3

Ethyl Ester of V by Direct Esterification. The acid, V, was esterified with ethanol in chloroform and the reaction catalyzed with *p*-toluenesulfonic acid. After washing, drying, and removing the solvent, an ester (n_D^{20} 1.4715), was obtained in 82% yield. A sample subjected to analyses by vapor phase chromatography resulted in separation of the ester into two parts in a ratio of about 9 to 1 with retention time of 24 and 35 minutes. Infrared spectra of each component and the original material were identical. The ester from ethyl pinonate gave the same results when similarly examined.

Analysis Calculated for $\text{C}_{14}\text{H}_{22}\text{O}_3$

Saponification Equivalent		Hydrogenation Equivalent	
Calcd.	Found	Calcd.	Found
238.32	240.2	119.16	117.8

Ethyl *cis-dl*-2,2-dimethyl-3-(1-hydroxy-1-methyl-2-propenyl)-cyclobutaneacetate, IX, by Hydrogenation. Partial reduction of the acetylenic alcohol was accomplished by use of Lindlar's catalyst (13). The product distilled at 98°C ./0.25 mm. of Hg. Hydrogenation with palladium on charcoal catalyst gave a hydrogen absorption equivalent to 78.66% double bond. Three materials—acetylenic alcohol, olefin, and alkane—were isolated by analysis with vapor phase chromatography in a ratio of 3:84:13. The major component was the desired olefin which showed strong absorbance in the infrared at 6.05 and 11.00 microns. The Lindlar catalyst used for these reductions was quite effective for the reduction of 3-hydroxy-3-methyl-1-butyne to 3-hydroxy-3-methyl-1-butene. It has not been possible to achieve similarly quantitative reductions with the acetylenic alcohols described here.

6-Hydroxy -6- methyl -3- (1- hydroxy -1-methylethyl) -7- octanoic acid- γ -lactone VII. Homoterpenylmethyl ketone, II, in liquid ammonia was added to sodium acetylide in liquid ammonia. After four hours, ammonium chloride was added and the ammonia was permitted to evaporate overnight. Work up and extraction with ether gave 68.6% yield with a product having boiling point of 140° C./0.3 mm. of Hg. Hydrogenation of the crude material using 5% palladium on carbon in acetic acid absorbed 94.2% of the calculated amount of hydrogen.

6-Hydroxy -6- methyl -3- (1- hydroxy -1- methylethyl) -7- ox-octanoic acid- γ -lactone, VIII. The crude acetylenic alcohol from homoterpenylmethyl ketone was hydrated with mercuric sulfate reagent giving 54% yield with b.p. 155° C. 0.2 mm. of Hg and m.p. 84.5–85.5° from ethylacetate. The oxime from the ketone melted at 136–138° C. (3 to 1 ethanol-water mixture).

Analyses Calculated for C₁₂H₂₀O₄

% C		% H		Saponification Equivalent	
Calcd.	Found	Calcd.	Found	Calcd.	Found
63.12	62.69	8.83	8.86	228.5	228.2

DISCUSSION

Sodium pinonate is soluble in liquid ammonia and reacts with sodium acetylide giving the expected acetylenic alcohol, V, in excellent yield. In this work, *cis-dl*-pinonic acid was used and the product had the *cis* configuration. Proof of structure was obtained by hydration of V by conventional mercuric sulfate catalyst and periodate oxidation of the hydroxy ketone, VI. The acid from this oxidation was *cis-dl*-pinonic acid.

The ethyl ester of V was prepared by reacting *dl*-ethyl pinonate with sodium acetylide and by direct esterification of the acid, V. These esters were subjected to an analysis by vapor phase chromatography. Two substances were present in the ratio of 9 to 1 with retention times of 24 and 35 minutes. The infrared spectra of each component and the original materials were identical. At this time, explanation for the presence of the second component as observed in the above analysis is not clear.

Ethyl pinonate used in this work was a 4 to 1 equilibrium mixture of *cis* and *trans* isomers. The latter appeared as a shoulder on the vapor phase chromatographic curve and was absent when a sample of methyl *cis-dl*-pinonate prepared with diazomethane was similarly analyzed (12).

Homoterpenylmethyl ketone, II, also reacted with sodium acetylide giving the acetylenic alcohol, VII, which absorbed 1.88 equivalents hydrogen and was hydrated with mercuric sulfate catalyst giving the ketone, VIII.

The ethyl ester of the acetylenic alcohol, V, on reduction with a Lindlar catalyst (13), gave the expected olefin in about 80% yield contaminated with a little acetylenic alcohol and completely reduced material. For some reason, this catalyst was less specific for conversion of this acetylenic alcohol to olefin than was obtained by reducing 3-hydroxy-3-methyl-1-butyne.

Most ketones condense with acetylene under appropriate conditions to give acetylenic glycols (7–10, 13). It was not possible to prepare the glycol, III, using the above methods.

Oxidative coupling of acetylenic alcohols is characteristic of compounds of this type (6). Zal'kind and Funduiler (17) were the first to observe this coupling reaction as the

result of air oxidation in the presence of aqueous cuprous ammonium chloride. Recently, Stansbury and Proops (16) published a method for oxidative coupling in pyridine and methanol. The ammonium salt of V was not oxidized by the first method nor was the free acid or ester oxidized by the second method.

Structural formulas for all compounds synthesized are shown in Table I.

CONCLUSIONS

Pinonic acid, a keto acid obtainable from α -pinene, was reacted with sodium acetylide in liquid ammonia. Similarly homoterpenylmethyl ketone, a keto γ -lactone obtained by the rearrangement of pinonic acid, was also reacted with sodium acetylide. The resulting acetylenic alcohols, new compounds, were obtained in good yield with little difficulty and these were conveniently converted to ketones by hydration of the acetylenic group with mercuric sulfate catalyst.

Reduction of the triple bond of the pinonic acid derivative to an olefin with Lindlar catalyst was less specific than with a simpler acetylenic alcohol.

Normally, two moles of a ketone react with one mole of acetylene to produce a 1,4-acetylenic glycol. Also most acetylenic alcohols undergo oxidative coupling using air (oxygen) and cuprous chloride producing a 1,6-diacetylenic glycol. Negative results were obtained in attempts to use pinonic acid in these reactions.

ACKNOWLEDGMENT

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