hydrazones showed good agreement with those reported in the literature.

In preparing the semicarbazones, a solution was made of 5 g. of semicarbazide hydrochloride, 7.5 g. of sodium acetate, 20 ml. of alcohol and 20 ml. of water. Five ml. of this solution was added to 5 ml. of alcohol containing 0.5 g. of the acetal. The mixture was placed in boiling water, and water was added dropwise to the hot solution until a slight turbidity resulted. One ml. of alcohol was then added to remove the turbidity and the mixture was allowed to cool. The semicarbazone formed readily in all cases. The melting points were taken without recrystallization.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Thermal Decarboxylation of Unsaturated Acids. II

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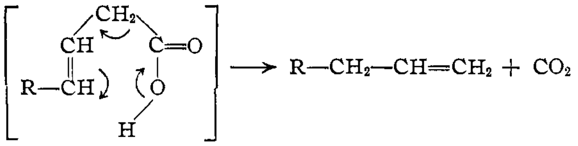
Mertenylcarboxylic acid has been synthesized and its pyrolytic decomposition studied. In each pyrolysis, a binary mixture of α- and β-pinene was produced, the composition of which depended on the particular experimental conditions employed. The results are most easily interpreted in terms of a cyclic transition state which leads to the formation of β-pinene and carbon dioxide as the primary products. α-Pinene apparently is formed by isomerization.

In an earlier paper[3] evidence was presented which indicated that many α,β-unsaturated acids undergo rearrangement to the corresponding β,γ-isomers as a preliminary step to thermal decarboxylation. The β,γ-isomer was regarded as being the more thermally unstable compound, and its decomposition into a pure Δ-olefin and carbon dioxide was explained as occurring through a cyclic transition state (I).

$R{-}CH{=}CH{-}CH_2{-}CO_2H \longrightarrow$



I

According to this view, the carbon–carbon double bond through its π-electrons serves as a base (*i.e.* an electron donor), and the analogy with the thermal decarboxylation of β-keto acids[4] becomes obvious.

Use of, and further support for, the above concept is to be found in the elucidation of the structures of morolic[5] acid and polyporenic acid A.[6]

It now seems clear that the mechanism of pyrolytic decomposition of α,β-unsaturated fatty acids (which thermally equilibrate with their β,γ-isomers) is distinctly different from that of the cinnamic acid types[7] where acid catalysis plays a major role.

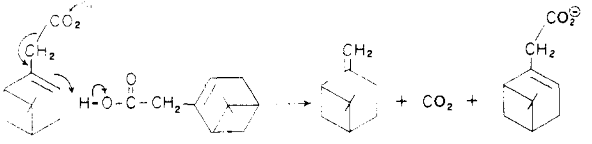
In order to gain further information on the above topic, mertenylcarboxylic acid (II) has been synthesized and subjected to elevated temperatures (190–200°) under a variety of experimental conditions. We have also studied the thermal stability of β-pinene, alone and in the presence of benzoic acid. The results are summarized in Table I.

It will be noted that although pure β-pinene is thermally quite stable at 200°, its conversion into α-pinene in the presence of carboxylic acids becomes appreciable in the temperature range 160–180°. The interconversion of α- and β-pinene has been reported earlier.[8,9]

In view of the above evidence, we have concluded that β-pinene is the sole hydrocarbon formed in the thermal decomposition of mertenylcarboxylic acid and that the α-pinene isolated results from an isomerization catalyzed by the parent acid. Consistent with this view is the fact that pyrolysis of mertenylcarboxylic in tetralin as solvent (which should markedly slow down the bimolecular isomerization) yields a binary mixture richer in β-pinene. The higher percentage of α-pinene produced when the decarboxylation occurs in the presence of added benzoic acid also is readily explained.

The catalytic effect caused by the addition of small amounts of solid sodium carbonate (prior to the thermal treatment) is especially noteworthy. The following observations seem to be pertinent: (a) in the presence of small quantities of base, decarboxylation is rapid; (b) the hydrocarbon formed is largely β-pinene; and (c) the salt formed by complete neutralization of the carboxylic acid appears to have high thermal stability.

An adequate explanation which accommodates all the above observations is found in the expression



This equation which regards the undissociated acid molecule as a necessity to the decomposition of the anion also avoids the necessity of assuming a highly energetic mertenyl carbanion as an intermediate.

Analysis of the binary mixtures of α- and β-pinene obtained in each of the above experiments

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[3] R. T. Arnold, O. C. Elmer and R. M. Dodson, THIS JOURNAL, **72**, 4359 (1950).

[4] F. H. Westheimer and W. A. Jones, *ibid.*, **63**, 3283 (1941).

[5] D. H. R. Barton and C. J. W. Brooks, *J. Chem. Soc.*, 260 (1951).

[6] T. G. Halsall and R. Hodges, *ibid.*, 3019 (1953).

[7] W. S. Johnson and W. E. Heinz, THIS JOURNAL, **71**, 2913 (1949).

[8] G. Austerweil, *Bull. soc. chim.*, [4] **39**, 690, 1643 (1926).

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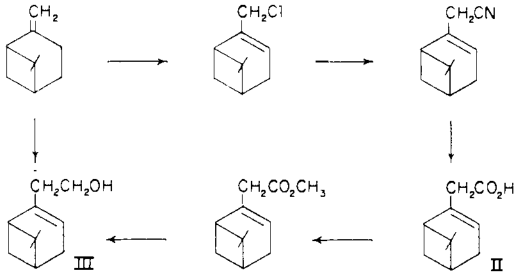
TABLE I

Compound	T, °C.	Conditions	Pinene formed %α-	Pinene formed %β-
Mertenylcarboxylic acid	190	Na_2CO_3 (10 mole% added)	2	98
Mertenylcarboxylic acid	190	Tetralin (equal wt.)	34	66
Mertenylcarboxylic acid	190	Pyrolysis, pure acid	56	44
Mertenylcarboxylic acid	190	Benzoic acid, equiv. amount added	69	31
β-Pinene	200	7 hours heating	0	100
β-Pinene	180	Benzoic acid (equal equiv. added), 7 hours heating	84	16

was accomplished by means of refractive index and infrared absorption measurements. Careful comparison of the infrared spectra taken on the binary mixtures excluded, within experimental error, the presence of any substances other than α- and β-pinene. No acid-catalyzed Wagner–Meerwein rearrangement products (*i.e.* camphene, etc.) were in evidence.

Mertenylcarboxylic acid (II) was prepared as indicated below. Proof of its structure was confirmed by conversion to nopol (III) by means of lithium aluminum hydride.



Although Tishchenko and co-workers[10] were able to prepare mertenylcarboxylic acid by carbonation of the Grignard reagent from mertenyl chloride, this method proved unsatisfactory in our hands.

An attempt is being made currently to prepare specifically deuterated β-pinene from deuteromertenylcarboxylic acid.

Experimental

Mertenylcarbonitrile.—A well-stirred mixture of mertenyl chloride (50 g.) and anhydrous cuprous cyanide (27.5 g.) was heated for 8 hr. at a carefully regulated temperature of 85–90°.[11] The dark reaction product was triturated exhaustively with ether and the extracts were dried over magnesium sulfate. The ether was removed by evaporation and the residue distilled in a claisen flask. Careful refractionation of this distillate gave pure mertenylcarbonitrile; yield 19.5 g. (41.3%), b.p. 47–48° (0.02 mm.), $n^{25}D$ 1.4852, $[\alpha]^{28}D$ 34.12°.

Anal. Calcd. for $C_{11}H_{15}N$: C, 82.0; H, 9.38. Found: C, 81.93; H, 9.35.

Mertenylcarboxylic Acid.—The above nitrile (19.3 g.), potassium hydroxide (8.25 g.), water (20 ml.) and ethanol (80 ml., 95%) was heated at the boiling point of the solution until evolution of ammonia was no longer detected. This required 4–5 days. The ethanol was removed by distillation at diminished pressure and the residue was diluted with water and extracted with ether. The resulting aqueous phase was cooled to 0°, and, while being held at that temperature, acidified to *p*H 4 with hydrochloric acid (4%). The oil which separated was not removed, and the whole was extracted with ether and the latter solution dried over magnesium sulfate. Removal of the ether and fractionation of the residue gave pure mertenylcarboxylic acid; yield 8.5 g. (41%), b.p. 95° (0.05 mm.), $n^{25}D$ 1.4941, $[\alpha]^{28}D$ 18.36° (in 95% ethanol).

Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.33; H, 8.95. Found: C, 73.02; H, 8.95.

Methyl Mertenylcarboxylate.—The acid (20 g.) was converted into its methyl ester by treatment with diazomethane in ether solution. Evaporation of the ether and fractionation of the residue gave methyl mertenylcarboxylate; yield 14 g. (65%), b.p. 42–44° (0.03 mm.), $n^{25}D$ 1.4749.

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.20; H, 9.32. Found: C, 74.03; H, 9.69.

Nopol.—To a stirred solution of lithium aluminum hydride (3.8 g.) in anhydrous ether (75 ml.) was added a solution of methyl mertenylcarboxylate (14 g.) in anhydrous ether (100 ml.) at such a rate that gentle reflux was maintained. Stirring, following completion of the addition, was continued for 4 hr., and the mixture was decomposed by water. The aluminum oxide was removed by filtration and nopol obtained by fractionation of the ethereal layer; yield 8.9 g. (74%), b.p. 89° (2.8 mm.), $n^{25}D$ 1.4918, $[\alpha]^{25}D$ 28.2°. The infrared spectrum of this material was identical with that of a purified sample of commercial nopol.[12] Similarly, the 3,5-dinitrobenzoates (m.p. 67.5–68.5°) prepared from each of these samples of nopol were identical.

Anal. Calcd. for $C_{18}H_{20}O_6N_2$: N, 7.77. Found: N, 7.91.

Nopyl Tosylate.—This substance, which was used in the present work to identify nopol, has been employed in impure form as a useful intermediate[13] and has now been prepared in pure crystalline form.

Nopol (100 g.) and anhydrous pyridine (190 g.) were dissolved in anhydrous ether and cooled to −5°. *p*-Toluenesulfonyl chloride (126 g.) was added portionwise to the well-stirred solution so that the temperature was kept at −5 to −10°. The temperature of the mixture was allowed to rise to 20°, and stirring was continued for 4 hr. The reaction mixture was poured into ice-water (3 l.). Ether was added and the whole was shaken vigorously to effect separation. The ether layer was washed with hydrochloric acid, then water and dried over magnesium sulfate. Evaporation of the ether layer and recrystallization of the crystalline residue from pentane gave pure nopyl tosylate; yield 130 g. (66%), m.p. 49–50°.

Anal. Calcd. for $C_{18}H_{24}SO_3$: C, 67.47; H, 7.55. Found: C, 67.49; H, 7.87.

Decarboxylation of Mertenylcarboxylic Acid.—All decarboxylations were carried out in an alembic flask at 190° in such a way that the mixed α- and β-pinenes formed distilled from the reaction mixture. In a typical run, mertenylcarboxylic acid (40.3 g.) was held at 190°, and from this there distilled a mixture of α- and β-pinene; yield 17.7 g., $n^{25}D$ 1.4688. An infrared spectrum showed bands attributable only to α- and β-pinene. Constants for the pure hydrocarbons employed as standards for analyzing the mixtures were (1) α-pinene, b.p. 155–156°, $n^{25}D$ 1.4629; (2) β-pinene, b.p. 165–166°, $n^{25}D$ 1.4757.

NEW YORK, N. Y.

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[10] D. Tishchenko, N. Persiantseva and V. Foliadov, *Zhur. Obshchei Khim.*, **22**, 1829 (1952).

[11] Maintenance of this temperature was found in repeated experiments to be critical. At temperatures slightly above 90°, an exothermic reaction occurred and the yield of nitrile was substantially lower. The resulting product consisted of an inseparable mixture of α,β- and β,γ-unsaturated nitriles as shown by a double absorption peak for —C≡N at 2260 and 2220 cm.$^{-1}$.

[12] We are indebted to Dr. J. P. Bain, The Glidden Co., Jacksonville, Florida, for a generous gift of nopol.

[13] G. F. Hennion, C. C. Price and V. C. Wolff, Jr., THIS JOURNAL, **77**, 4633 (1955).