

centration was estimated on the basis of equation 10, to give an approximate value of 2×10^{-3} l.² mole⁻² sec.⁻¹ for k_4 at 30°.

Values for the rate constants k_2 and k_3 were obtained at 10, 20, 30 and 40°. These results are summarized in Table IV along with the energies of

TABLE IV

SUMMARY OF THE RATE CONSTANTS AT VARIOUS TEMPERATURES AND OF THE ENTHALPIES AND ENTROPIES OF ACTIVATION

Temp., °C.	Equation 2 ^a	Equation 3 ^b
k^c	10 (2.6 ± 0.2)10 ⁻²	(0.86 ± 0.01)10 ⁻⁵
k^c	20 (4.3 ± .4)10 ⁻²	(2.2 ± .1)10 ⁻⁵
k^c	30 (9.9 ± .3)10 ⁻²	(6.7 ± .2)10 ⁻⁵
k^c	40 (13.8 ± 1.2)10 ⁻²	(14.3 ± .4)10 ⁻⁵
ΔH^\ddagger , kcal.	10.6	16.1
ΔS^\ddagger , e.u.	-28.2	-24.6

^a The units of k_2 are l.² mole⁻² sec.⁻¹. ^b The units of k_3 are l. mole⁻¹ sec.⁻¹. ^c The measure of the precision is the standard deviation of the average values used.

activation and entropies of activation calculated from them. The relatively high negative values obtained for the entropies of activation are consistent with a highly ordered transition state for each reaction.

Such actions of quaternary ammonium tribro-

midate as a nucleophilic agent which have been assumed in the explanations used here have been suggested⁹ as possible for carbon-carbon double bonds substituted with electron-withdrawing groups. Kinetic data for the addition of bromine to such unsaturated compounds in the presence of halide ions have been interpreted as showing that either a polyhalide ion is involved in a nucleophilic attack on the double bond¹⁰ or a halide ion and bromine are involved, in a concerted attack.^{10,11} In no case reported has this type of trihalide-olefin interaction been as well defined as it is in the present case. Of course, the reaction given in equation 3 might just as well have been interpreted as a concerted action of bromine and bromide on crotonic acid as far as the kinetic results were concerned. This type of behavior of polyhalides is to be contrasted with that observed¹² for tribromide ion which reacted much more slowly than bromine in the addition of *trans*-stilbene in methanol.

(9) P. B. D. de la Mare, *Quart. Revs.*, **3**, 126 (1949).

(10) P. B. D. de la Mare and P. W. Robertson, *J. Chem. Soc.*, 2838 (1950), and the references which they give.

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(12) P. D. Bartlett and D. S. Tarbell, *ibid.*, **58**, 466 (1936).

IOWA CITY, IOWA

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF COMPAGNIE PARENTO, INC.]

Preparation of α,β -Unsaturated Aldehyde Dimethyl Acetals and their Free Aldehydes

By PAUL Z. BEDOUKIAN

RECEIVED JULY 11, 1956

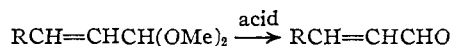
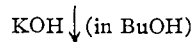
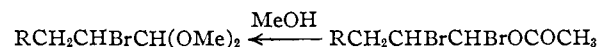
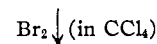
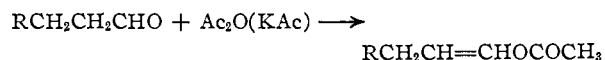
Elimination of hydrogen bromide from the α -bromoacetals of the fatty aldehydes (C-7 to C-12) gave the acetals of the corresponding α,β -unsaturated aldehydes. The free aldehydes were obtained from the acetals by acid hydrolysis. A study was made of the odor properties of these compounds. The physical properties of the enol acetates and bromoaldehyde dimethyl acetals of the saturated aldehydes are reported.

This investigation was carried out for the purpose of determining the odor characteristics of the acetals of α,β -unsaturated fatty aldehydes (C-7 to C-12) as well as those of the free aldehydes. The saturated fatty aldehydes of this series play an important role in perfume compositions and are extensively used in perfumes, cosmetics and soaps.

The preparation of α,β -unsaturated aldehydes has presented considerable difficulties and involved indirect and lengthy procedures. The present method, although it does not give high overall yields, is very convenient and is generally applicable to the conversion of any saturated aldehyde, possessing an α - and β -hydrogen, to its α,β -unsaturated analog.

The following reactions are used in preparing α,β -unsaturated aldehydes: The saturated aldehyde is converted to the enol acetate and then brominated in carbon tetrachloride. On adding methanol to the brominated mixture, the dimethyl acetal of α -bromoaldehyde is obtained in good yields. The latter on treatment with potassium hydroxide in butanol gives the unsaturated acetal which is converted to the free α,β -unsaturated aldehyde by acid hydrolysis.

The preparation of the α -bromoaldehyde dimethyl acetal of heptaldehyde has been reported.¹



Identical procedures were used in the preparation of the bromoacetals of higher aldehydes.

None of the acetals of the α,β -unsaturated aldehydes (C-7 to C-12) has been reported previously. All of the free aldehydes have been prepared by various methods but no comments have been made on their odor properties.

2-Heptenal has been prepared by the chromic

(1) P. Z. Bedoukian, *THIS JOURNAL*, **66**, 1325 (1944); P. Z. Bedoukian, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., p. 127.

TABLE I
YIELDS AND PHYSICAL PROPERTIES OF THE ENOL ACETATES, α -BROMO ALDEHYDE DIMETHYL ACETALS, α,β -UNSATURATED DIMETHYL ACETALS AND α,β -UNSATURATED ALDEHYDES (C-7 TO C-12)

		Heptanal	Octanal	Nonanal	Decanal	Undecanal	Dodecanal
Pure enol acetate from aldehyde	Yield, %	47	42	39	46	34	37
	B.p. (mm.)	88-90 (17)	95-97 (17)	110-112 (17)	126-128 (16)	133-135 (16)	111-113 (3)
	n_D^{25}	1.4300	1.4350	1.4350	1.4374	1.4420	1.4390
	d_4^{25}	0.883	0.895	0.885	0.895	0.895	0.887
α -Bromoaldehyde dimethyl acetal from enol acetate	Yield, %	78	86	83	72	85	81
	B.p. (mm.)	117-119 (17)	140-142 (26)	146-148 (23)	155-157 (17)	137-139 (4)	151-153 (4)
	n_D^{25}	1.4524	1.4530	1.4532	1.4552	1.4540	1.4552
	d_4^{25}	1.195	1.152	1.135	1.120	1.100	1.085
α,β -Unsaturated aldehyde dimethyl acetal from bromoacetal	Yield, %	55	51	55	58	52	34
	B.p. (mm.)	66-68 (11)	73-75 (13)	100-102 (16)	123-125 (18)	92-94 (2)	95-97 (2)
	n_D^{25}	1.4240	1.4332	1.4308	1.4338	1.4357	1.4372
	d_4^{25}	0.883	0.876	0.866	0.860	0.874	0.868
α,β -Unsaturated aldehyde from unsaturated acetal (slight acetal impurities)	Yield, %	45	40	62	64	62	58
	B.p. (mm.)	59-61 (18)	78-80 (9)	98-100 (12)	117-119 (22)	115-117 (10)	125-128 (10)
	n_D^{25}	1.4320	1.4220	1.4240	1.4482	1.4408	1.4442
	d_4^{25}	0.865	0.854	0.860	0.843	0.853	0.854
Semicarbazone, m.p., °C.		174 ^a	172 ^b	167 ^c	165 ^d	164 ^e	160 ^f
2,4-Dinitrophenylhydrazone, m.p., °C.		133 ^g	122 ^h	127 ⁱ	128 ^j	123 ^k	111

Melting points reported in the literature: ^a 169^{o2}; 179^{o4}; ^b 163^{o20}; ^c 163^{o8}; 160-161^{o11}; ^d 168^{o4}; 167-168^{o13}; 168.5^{o14}; 162^{o20}; ^e 161.5-162.5^{o13}; ^f 165.5-166^{o14}; 158^{o24}; ^g 131.5^{o3}; ^h 121-123^{o5}; ⁱ 124.4-125^{o8}; 126^{o12}; ^j 128.8^{o13}; ^k 122.6^{o13}

ANALYSES OF INTERMEDIATES

Compound	Mol. wt.	Adduct formula	Carbon, %		Hydrogen, %	
			Calcd.	Found	Calcd.	Found
Heptenal dimethyl acetal	158.25	C ₉ H ₁₈ O ₂	68.14	68.13	11.40	11.17
Octenal enol acetate	170.26	C ₁₀ H ₁₈ O ₂	70.48	69.72	10.64	10.37
Octenal dimethyl acetal	172.28	C ₁₀ H ₂₀ O ₂	69.65	68.92	11.68	11.84
Bromoöctenal dimethyl acetal	253.15	C ₁₀ H ₂₁ O ₂ Br	47.40	48.39	8.37	8.36
Nonanal enol acetate	184.26	C ₁₁ H ₂₀ O ₂	71.63	70.59	10.93	10.95
Nonanal dimethyl acetal	186.28	C ₁₁ H ₂₂ O ₂	70.85	70.71	11.89	11.79
Bromononanal dimethyl acetal	267.18	C ₁₁ H ₂₁ O ₂ Br	49.40	49.80	8.70	8.70
Decanal enol acetate	198.26	C ₁₂ H ₂₀ O ₂	72.63	72.66	11.17	11.14
Decanal dimethyl acetal	200.27	C ₁₂ H ₂₄ O ₂	71.89	70.46	12.07	11.86
Bromodecanal dimethyl acetal	281.18	C ₁₂ H ₂₃ O ₂ Br	51.21	52.66	8.97	9.09
Undecanal enol acetate	212.26	C ₁₃ H ₂₄ O ₂	73.49	73.33	11.45	11.50
Undecanal dimethyl acetal	214.27	C ₁₃ H ₂₆ O ₂	72.80	72.47	12.22	12.17
Bromoundecanal dimethyl acetal	295.18	C ₁₃ H ₂₅ O ₂ Br	52.85	53.31	9.22	9.50
Dodecanal enol acetate	226.26	C ₁₄ H ₂₆ O ₂	74.25	73.91	11.58	11.59
Dodecanal dimethyl acetal	228.27	C ₁₄ H ₂₈ O ₂	73.59	72.34	12.36	11.31
Bromododecanal dimethyl acetal	309.18	C ₁₄ H ₂₇ O ₂ Br	54.36	54.67	9.44	10.59
2,4-Dinitrophenylhydrazone of dodecanal	364.45	C ₁₈ H ₂₃ O ₄ N ₄	59.27	58.14	7.74	7.31

ODORS OF THE α,β -UNSATURATED ACETALS AND THEIR ALDEHYDES

	Aldehyde	Dimethyl acetal
2-Heptenal	More pungent and greener than heptaldehyde	Strong grassy green odor
2-Octenal	Grassy odor, coarser and more powerful than octanal	Strong and not unpleasant, grassy odor
2-Nonenal	Less pleasant than nonanal and more pungent and powerful	Pleasant fatty green odor, not strong
2-Decenal	Less pleasant and greener than decanal	Weak fatty odor
2-Undecenal	Strong odor similar to undecanal	Very weak sweet fatty odor
2-Dodecenal	Weaker than dodecanal	Very weak fatty note

Odor observation tests were made on 10% and 2% ethanol solutions as well as on the full strength material.

acid oxidation of the corresponding alcohol^{2,3} and dehydration of 1,4-heptanediol⁴; 2-octenal, by

(2) R. Delaby and S. Guillot-Allegre, *Compt. rend.*, **192**, 1467 (1931).

(3) C. J. Martin, A. I. Schepartz and B. F. Daubert, *THIS JOURNAL*, **70**, 2601 (1948).

(4) M. Gouge, *Ann. chim.*, **6**, 648 (1951).

the oxidation of 1-octene with cobalt acetate,⁵ by the action of allyl methyl ether on hexaldehyde in the presence of boron fluoride⁶ and by the chromic

(5) M. S. Kharasch, P. Pauson and W. Nudenberg, *J. Org. Chem.*, **18**, 322 (1953).

(6) R. I. Hoaglin and D. H. Hirsch, U. S. Patent 2,628,257; Feb. 10, 1953.

acid oxidation of the corresponding *trans*-alcohol.⁷ 2-Nonenal has been prepared by the reduction of the imide chloride of α -nonenoic acid⁸ and the hydrolysis of 1,1-dichloro-3-bromononane.^{9,10} It has also been obtained by the oxidation of the corresponding alcohol^{5,11} and by the red lead oxidation of 9,10,12-trihydroxystearic acid.¹² 2-Decenal has been prepared by the oxidation of the corresponding alcohol,¹³ dehydration of 1,4-decanediol⁴ and by the hydrolysis of the hexamethylenetetramine compound of 1-bromo-2-decene¹⁴; 2-undecenal, by the oxidation of the corresponding alcohol¹³; 2-dodecenal, by the hydrolysis of the hexamethylenetetramine compound of 1-bromo-2-dodecene.¹⁴

It is interesting to note that all of these 2-alkenals have been found to occur in nature, either in the free state in certain essential oils or as the oxidation products of fats. Thus, 2-heptenal has been found in some fat oxidation products¹⁵⁻¹⁷; 2-octenal in autoxidation products of cottonseed oil¹⁸; 2-nonenal from the oxidative fission of the hydroperoxide of methyl oleate¹⁹ and in the essential oil of *Achasma walang* Val²⁰; 2-decenal, in the essential oils of *Achasma walang* Val,²⁰ *Coriandrum sativum*²¹ and sweet orange oil from French Guinea.²² 2-Undecenal has been identified in the decomposition product of the hydroperoxide of methyl oleate²³; 2-dodecenal in the essential oil of *Eryngium foetidum* L.,²⁴ in sweet orange oil of French Guinea²² and in the essential oil of *Achasma walang* Val.²⁰

The preparation of the acetals of α,β -unsaturated aldehydes through the elimination of HBr from α -bromo acetals has been applied to the lower members of this series. Thus α -bromo-*n*-valeraldehyde gave good yields of the unsaturated acetal when heated with a large excess of potassium hydroxide.²⁵ Others have used potassium *t*-butoxide for the elimination of HBr from the bromo acetals of *n*-butyraldehyde and isovaleraldehyde.²⁶ In the present investigation, it was found convenient to boil the bromoacetal in a solution of potassium hydroxide in *n*-butyl alcohol.

(7) M. Jacobson, *THIS JOURNAL*, **75**, 2584 (1953).

(8) J. v. Braun, W. Rudolph, H. Kroper and W. Pinkernelle, *Ber.*, **67B**, 269 (1934).

(9) M. S. Kharasch, B. M. Kuderna and W. H. Urry, *J. Org. Chem.*, **13**, 895 (1948).

(10) M. S. Kharasch, U. S. Patent 2,574,832; Nov. 13, 1951.

(11) R. Delaby and S. Guillot-Allegre, *Bull. soc. chim.*, **53**, 301 (1933).

(12) J. T. Scanlan and D. Swern, *THIS JOURNAL*, **62**, 2305 (1940).

(13) C. E. Swift, R. T. O'Connor, L. E. Brown and F. G. Dollear, *ibid.*, **71**, 1512 (1949).

(14) R. Delaby, *Bull. soc. chim.*, **3**, 2375 (1936).

(15) K. T. Zilch and H. J. Dutton, *Anal. Chem.*, **23**, 775 (1951).

(16) C. J. Martin, A. I. Schepartz and B. F. Daubert, *J. Am. Oil Chemists' Soc.*, **25**, 113 (1948).

(17) A. I. Schepartz and B. F. Daubert, *ibid.*, **27**, 367 (1950).

(18) C. E. Swift, R. T. O'Connor, L. E. Brown and F. G. Dollear, *ibid.*, **26**, 297 (1949).

(19) S. Mukherjee, *Indian Soap J.*, **16**, 183 (1951).

(20) P. van Romburgh, *Rec. trav. chim.*, **57**, 494 (1938).

(21) A. J. Carlblom, *J. prakt. Chem.*, **144**, 225 (1936).

(22) Y. R. Naves, *Perfumery Essent. Oil Record*, **38**, 295 (1947).

(23) C. E. Swift, F. G. Dollear, L. E. Brown and R. T. O'Connor, *J. Am. Oil Chemists' Soc.*, **25**, 39 (1948).

(24) D. R. Koolhaas, *Rec. trav. chim.*, **51**, 460 (1932).

(25) R. Kohn and C. Grundmann, *Ber.*, **70**, 1898 (1937).

(26) S. M. McElvain, R. L. Clarke and G. D. Jones, *THIS JOURNAL*, **64**, 1968 (1942).

The yields and physical properties of the enol acetates, α -bromo aldehyde dimethyl acetals, α,β -unsaturated dimethyl acetals and α,β -unsaturated aldehydes of the aldehydes C-7 to C-12 are given below. Comments on the odor characteristics of the unsaturated acetals and their aldehydes also are given. In general, it appears that they possess powerful odors, but the odor quality as judged by experienced perfumers is not of a pleasant nature. The lower members have grassy green odors which are novel in character and may prove useful in certain perfume compositions.

Experimental

Preparation of Enol Acetate.—In all cases, the perfumery grade aldehydes were used. These aldehydes are known to be of a high degree of purity, containing only several per cent. of the corresponding alcohol and acid. The enol acetates were prepared by refluxing for 1 hr., one mole of the aldehyde, 2.5 moles of acetic anhydride and 15 g. of anhydrous potassium acetate. The reaction mixture was then allowed to cool, excess acid washed out several times with water and finally with 5% sodium carbonate solution. The resultant oil was fractionally distilled through an efficient four-foot column and the enol acetate obtained in relatively pure form.

Bromination of Enol Acetate.—One mole of enol acetate was mixed with 200 ml. of carbon tetrachloride and cooled in an ice-bath. Bromine, diluted with an equal volume of carbon tetrachloride, was added slowly with constant shaking, care being taken not to allow the temperature of the mixture to rise above 10°. The addition usually took about 20 minutes and the end-point was reached when the theoretical amount was absorbed and the bromine no longer decolorized.

Formation of Bromo Aldehyde Dimethyl Acetal.—To the brominated mixture was added 500 ml. of methyl alcohol (99.5-100%) with shaking and cooling. The mixture was allowed to stand two days with occasional shaking and then diluted with 1.5 l. of water. The separated oil was washed with 5% sodium carbonate solution until free of acid and then fractionally distilled through the column in the presence of a small amount of sodium carbonate.

Preparation of the Acetal of α,β -Unsaturated Aldehyde.—One mole of the bromoacetal was added to a mixture of 500 ml. of methanol containing 2 moles of potassium hydroxide and 500 ml. of butanol. The mixture (in some cases two layers) was gently heated in a claisen flask and the methanol allowed to distil off. When the butanol began coming off, distillation was stopped and the contents were transferred to a round-bottom flask and heated under reflux for 1 hr. in an oil-bath. During this period considerable potassium bromide precipitated out. At the end of 1 hr., the mixture was washed with water and the oil fractionally distilled through the column in the presence of several pellets of potassium hydroxide.

Hydrolysis of the Acetal.—In each case, 20 or 30 ml. of the acetal was mixed with an equal volume of 50% citric acid solution and boiled gently in a claisen flask. The methanol was allowed to distil off and when the distillate temperature reached 95°, distillation was stopped. The contents of the flask were washed with water several times and finally with 5% sodium carbonate solution. The oil thus obtained was then distilled under vacuum through a claisen flask to give the unsaturated aldehyde contaminated with small quantities of the acetal.

Formation of Derivatives.—It was found most convenient to prepare the derivatives from the acetals. The acetals obtained were of a high degree of purity and the 2,4-dinitrophenylhydrazones formed instantly while the semicarbazones were obtained within an hour. In preparing the 2,4-dinitrophenylhydrazones, a solution of 4 g. of 2,4-dinitrophenylhydrazine was made in 10 ml. of concentrated sulfuric acid to which was added 15 ml. of water. Eight ml. of this solution was added to 10 ml. of alcohol containing 0.5 g. of the acetal. The derivative precipitated instantly. It was filtered through a buchner funnel using water suction, washed with 5 ml. of cold alcohol and recrystallized from 10 to 20 ml. of alcohol. The melting points of the 2,4-dinitrophenyl-

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.

CROTON-ON-HUDSON, N. Y.

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

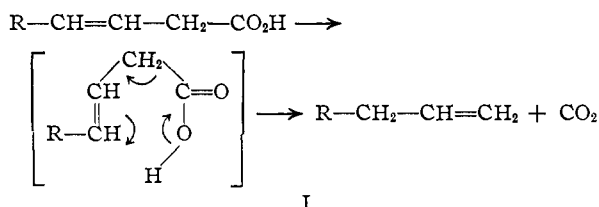
Thermal Decarboxylation of Unsaturated Acids. II

BY RICHARD T. ARNOLD¹ AND MORRIS J. DANZIG²

RECEIVED OCTOBER 3, 1956

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 paper³ 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).



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 acids⁴ becomes obvious.

Use of, and further support for, the above concept is to be found in the elucidation of the structures of morolic⁵ 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 types⁷ 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.

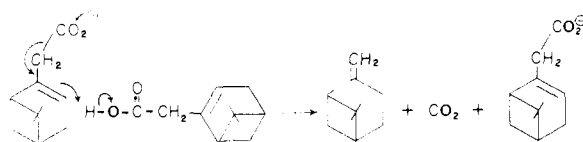
- (1) Alfred P. Sloan Foundation, Inc., New York 20, N. Y.
- (2) Du Pont Post-doctorate Fellow 1953–1954.
- (3) R. T. Arnold, O. C. Elmer and R. M. Dodson, *THIS JOURNAL*, **72**, 4359 (1950).
- (4) F. H. Westheimer and W. A. Jones, *ibid.*, **63**, 3283 (1941).
- (5) D. H. R. Barton and C. J. W. Brooks, *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).

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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