Interaction of α-Pinene with Carboxylic Acids

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The interaction of α-*d*-pinene with a series of organic acids from acetic to octanoic, under a wide range of olefin to acid ratios, yields esteric and rearrangement products after ring opening to the *p*-menthane system and ring rearrangement to the camphane system. Evidence is presented that the esterification proceeds through two distinct mechanisms one of which is highly dependent on the ionizing power and the nucleophilicity of the solution. This reaction leads to α-terpinyl esters while the esterification to bornyl and α-fenchyl esters is a reaction of zero order in the organic acid that constitutes 23.6 ± 1.5% of total product under all conditions. Furthermore, the bicyclic esters bornyl and α-fenchyl are produced in a constant ratio (bornyl/α-fenchyl = 1.6 ± 0.2). The esterification to give the terpinyl esters is explained as proceeding through solvolysis of a carbonium ion after a ring bond rupture. The esterification to give bornyl and α-fenchyl esters is considered to be the result of the filling of the vacant orbital created after a skeletal rearrangement with strain release from the pinane to the camphane skeletal system. The isomerization reaction is also suggested as following two reaction paths, one through carbonium ion intermediates producing limonene and terpinolene and the other through nonclassical intermediates with distributed charge to produce camphene and α- and β-fenchenes. For all these reactions consistent mechanistic explanations of the results are given.

Whereas the reaction of α-pinene with organic acids has received wide attention, the nature and the course of these reactions is still poorly understood. α-Pinene reportedly reacts with organic acids to yield bornyl esters and isomerization products.[1] The number of products was later enlarged to include α-fenchyl and α-terpinyl esters and the isomerization products limonene, terpinolene, and campene.[2] These findings were used by Meyer to test his stereochemical hindrance theory.[3] The reaction was interpreted in terms of the strength of the organic acid and the amount of bornyl ester formed,[4] but other workers found this to be inconsistent.[5] According to a more recent work, the reaction of α-pinene with the lower organic acids leads mainly to α-terpinyl esters, while the higher carboxylic acids produce mainly bornyl.[6]

In a preliminary publication on the reaction of α-pinene with acetic acid,[7] results were presented which show some special features of interest. The esterification reaction was found to be very sensitive to the excess of acetic acid both in the amount and kind of products. The esterification proved to be of solvolytic character with respect to α-terpinyl acetate while the formation of bornyl and α-fenchyl acetate showed an indifference to the ionizing power of the solvent. These observations were not in line with previous reports and it was thought to be desirable to further investigate the system with respect to changes in the ionizing power and the nucleophilicity of the reaction media for mixtures of α-pinene and straight-chain fatty acids from acetic to octanoic. Such information seemed useful in order to better understand the complex chemistry of terpenes, among which α-pinene has a key position and is of considerable industrial importance.

Results

The acetolysis of α-pinene was followed both kinetically and by product analysis, mainly at 150 °C over a wide range of dilution. The acetolysis, because of its key importance, was also followed at 105 °C. The methods employed for the kinetic study and the analysis of the reaction products are described in the Experimental Section.

The calculated first-order solvolysis constants at 150 °C at a dilution of organic acid to α-*d*-pinene of 4:5 (M/M), drop rapidly from acetic to butyric acid, then remain constant (Table I). This shows that from butyric acid and higher, the organic acids show a form of reactivity toward α-*d*-pinene that is independent of their molecular weight and the differences in mobility it creates. Such behavior was first observed in the esterification of organic acids with alcohols (which has led to the Newman rule of six[8]), but has not been reported for esterifications involving ring bond rupture.

Table I. Solvolysis Rate Constants of α-Pinene Giving Simple First-Order Kinetics in Organic Acid Solutions at 150°C[c]

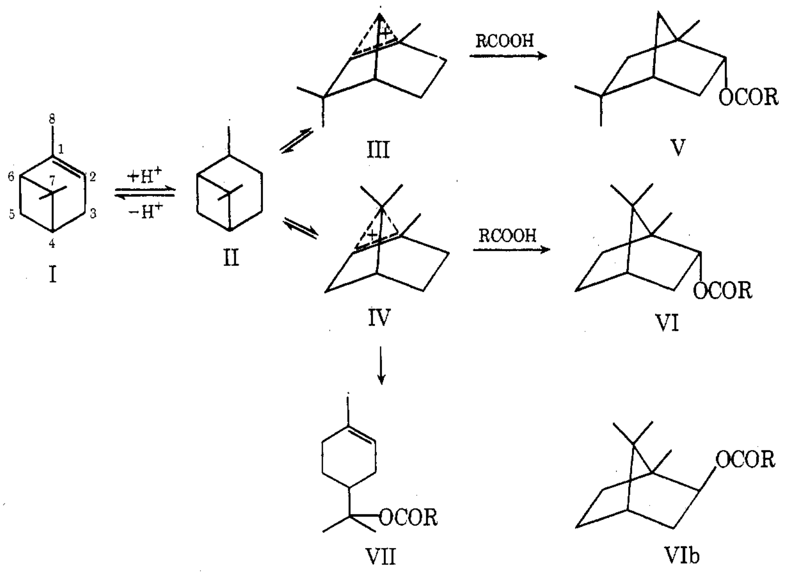
Acid	$k \times 10^4$, min	$\frac{k \text{ in acetic acid}}{k \text{ in other acids}}$ A[a]	B[b]
Acetic	120	1	1
Propionic	42	2.38	1.19
Butyric	8.9	13.3	2.02
Pentanoic	8.55	14.0	2.02
Hexanoic	8.40	14.3	2.02
Heptanoic	8.35	14.4	2.02
Octanoic	8.28	14.5	2.02

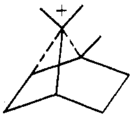
[a] In the present system. [b] In the esterification with methanol[8] at 40°C. [c] Organic acid: α-pinene, 4.5 M/M.

Apart from the effect on the solvolysis rates, the structure of the organic acids has a pronounced effect on the nature of the esterification products. While the lower acids acetic, propionic, and chloroacetic give mainly α-terpinyl esters in amounts corresponding to their relative ionizing power, which decreases in the series,[9] the acids from butyric to octanoic give total ester formation and esteric product composition that changes very little. This difference in esteric products for the different C_2 to C_8 acids refers to the α-terpinyl esters only; the amounts of bornyl and α-fenchyl esters remain practically unchanged for the whole series of acids.

In the Newman rule of six, the lower equal to all, reactivity of butyric acid and higher[8] is explained in terms of steric repulsion between the carboxylic group and the hydrogens of the sixth position in the chain. It seems, therefore that the esterification to give terpinyl esters has a different nature than the formation of bornyl and α-fenchyl esters. In the first case unhindered carboxylic groups are particularly effective while in the second the nature of the carboxylic group makes no difference.

In Table II are summarized the results for the esterification reaction using identical acid dilutions. The amount of esterification is shown to decrease from 50 to 28% between acetic acid and butyric acid and by 4% between butyric and octanoic acid. These changes in ester formation are due to

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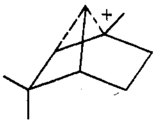
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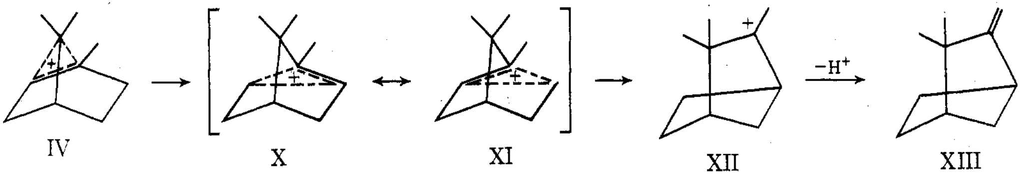

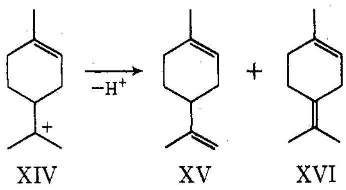

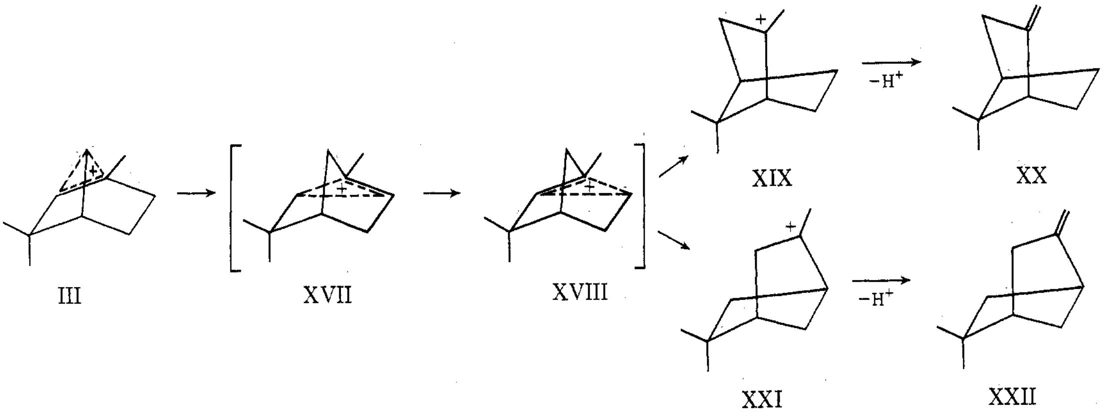

the terpinyl ester produced; the amounts of bornyl and α-fenchyl ester do not change significantly along the series.

Also characteristic is the picture given by the composition of the isomerization products (Table III). As the isomerization reaction becomes more important with the change from C_2 to C_8 acids, the isomerization products become richer in camphene (from 10% of overall reaction product with C_2 to 29% in the case of octanoic acid). Limonene, the other major isomerization product, also increases substantially from acetic acid to butyric acid and then slowly decreases. Terpinolene, which in the acid-catalyzed hydration of α-pinene in 70% aqueous acetone constitutes the major isomerization product,[10] makes only a small 5–7.5% contribution to the overall products.

The results of Tables II and III conceivably show that at equal dilutions the amount of α-terpinyl ester is related to the strength of the acid. These results, however, do not give a complete picture for the reaction system. In the interaction of α-*d*-pinene with organic acids, the product composition is also highly dependent on the degree of dilution. By changing the degree of dilution in the reaction systems of α-pinene and the acids acetic, propionic, and butyric, a strong response of different degree is observed in each case. This refers to changes in the formation of α-terpinyl esters

Table II. Solvolysis Products of α-Pinene in Organic Acid Media at 150°C

Acid	Registry no.	Organic acid/α-pinene, M/M	Esterification, %	Percent ester composition[a]		
				α-F-OCOR	B-OCOR	α-T-OCOR
Acetic	64-19-7	4.5	50.0	18.0	30.0	52.0
Propionic	79-09-4	4.5	36	25.2	42.8	32.0
Butyric	107-92-6	4.5	28	31.6	54.2	14.2
Pentanoic	109-52-4	4.5	27	32.1	56.8	11.1
Hexanoic	142-62-1	4.5	26	32.6	57.5	9.9
Heptanoic	111-14-8	4.5	24.5	33.3	58.0	8.7
Octanoic	124-07-2	4.5	24	33.6	58.5	7.9
Chloroacetic	79-11-8	4.5	35.5	25.1	43.5	31.4

[a] α-F-OCOR, α-fenchyl ester; B-OCOR, bornyl ester; α-T-OCOR, α-terpinyl ester.

Table III. Isomerization Products during Solvolysis of α-Pinene in Organic Acid Media at 150°C[a]

Acid	Isomerization %	Percent isomerization product composition			
		Cf	Fc	Lm	Tp
Acetic	50	20.1	6.6	58.5	14.8
Propionic	64	20.2	5.5	64.8	9.5
Butyric	78	26.0	5.0	60.0	9.0
Pentanoic	73	27.7	5.5	59.0	7.8
Hexanoic	74	30.9	5.3	56.7	7.1
Heptanoic	75.5	35.0	5.1	53.4	6.5
Octanoic	76	38.8	5.0	55.0	5.2
Chloroacetic	64.5	22.0	5.0	62.8	10.2

[a] Organic acid: α-pinene, 4.5 M/M.

and camphene, because in part of formation of bornyl and α-fenchyl esters, there is no significant change created by dilution. These results are included in Table IV and clearly show that in the system of α-pinene and the organic acids, the important parameters of reactivity are the ionizing power of the reaction medium and the nucleophilicity of the reagents, and not the strength of the acids. It is further concluded that in this reaction system two distinct reaction paths operate, one of which is very sensitive to the ionizing power while the other is not.

In addition to the ionizing power, the system was tested for response toward nucleophilic reagents, by adding small amounts of water to the reaction system acetic acid–α-pinene. The results obtained (Table V) show that nucleophilicity is an important factor of reactivity since 0.2–5% of added water changes the overall reactivity with an increase of 10% in the substitution products while a share of 21.5% is being taken by the alcohols. α-Terpineol is the main hydration product formed at amounts ca. 15 times higher than borneol and ca. 27 times higher than α-fenchyl alcohol.

Discussion

The bornyl (VI) and α-fenchyl (V) esters, at the same degree of dilution, make a constant part in the transformation of α-pinene (I) to products, some 23.6 ± 1.5% total reaction under variations in the kind of acid and temperature. Furthermore, the ratio of bornyl/α-fenchyl esters re-

Table IV. Effect of Solvent Dilution on Product Composition during Solvolysis of α-Pinene in Organic Acid Media at 150°C

Acid	Organic acid/α-pinene, M/M	Esterification, %	Percent ester composition			Percent isomerization product composition[a]			
			α-F-OCOR	B-OCOR	α-T-OCOR	Cf	Fc	Lm	Tp
Acetic	0.8	34	31.2	48.0	20.8	51.01	12.7	35.5	9.6
	1.9	41.5	24.6	37.6	28.8	26	9.0	52.5	12.5
	4.5	50.0	18.0	30.0	52.0	20.1	6.6	58.5	14.8
	6.75	55.0	14.9	24.2	60.9	17.5	6.9	58.8	16.8
	11.3	59.0	13.5	20.5	66.0	15.7	5.5	61.0	17.8
Propionic	1.9	31.0	29.3	48.7	22.0	29.0	5.0	58.0	8.0
	3.0	33.0	27.4	45.3	27.3	26.0	5.0	60.4	8.6
	4.5	36.0	25.2	42.8	32.0	20.2	5.5	64.8	9.5
	6.5	38.0	23.4	40.0	36.6	19.0	5.0	66.0	10.0
	9.75	40.5	22.0	37.4	40.6	17.0	5.0	67.5	10.5
Butyric	1.4	25.0	34.6	59.6	5.8	32.5	6.1	54.3	7.1
	3.0	26.0	33.0	57.0	10.0	29.2	5.5	57.5	7.8
	4.5	28.0	31.6	54.2	14.2	26.0	5.0	60.0	9.0
	7.0	29.0	30.5	54.6	14.9	24.0	5.0	61.5	9.5
	10.0	30.0	30.6	52.7	16.7	23.0	5.0	62.0	10.0

[a] Cf, camphene; Fc, fenchenes; Lm, limonene; and Tp, terpinolene.

Table V. Acetolysis of α-Pinene in the Presence of Water at 105°C[b]

Water added, %	$k \times 10^3$, min	Substitution, %	Percent solvolysis product composition[a]					
			F-OCOR	B-OCOR	α-T-OCOR	F-OH	B-OH	α-T-OH
0.75	3.35	60.8	14.5	23.0	56.7	0.2	0.4	5.2
2.5	3.6	64.8	11.0	16.0	57.4	0.5	0.9	14.4
5.0	3.8	67.5	8.0	12.0	58.5	0.7	1.4	19.4

[a] F-OH, α-fenchyl alcohol; B-OH; bornyl alcohol; α-T-OH, α-terpinyl alcohol. [b] α-Pinene:acetic acid 20:60 by weight.

mains constant (1.6 ± 0.1) under all conditions of reaction (Tables II and IV). These results can be interpreted in terms of two different reaction paths with intermediates like III and IV, for which the esterification reaction follows the skeletal rearrangement. Similar intermediates to III and IV in form of nonclassical carbonium ions have been proposed for the reaction of cis and trans α-pinanes.[11]

The esterification to bornyl and α-fenchyl esters is independent of the concentration of the organic acid and of the ionization power and nucleophilicity of the reaction medium. Therefore, it is not the result of substitution on an electron-deficient center, but a reaction of zero order on part of the acid, which develops by filling a gradually formed vacant orbital at C_6, during a skeletal rearrangement with strain release from the pinane to camphane skeletal system. The approach of the acid molecule to the C_6 carbon atom, according to the above, can be effective only from the endo side of the molecule through a bond making while an exo bond breaking is progressing. The suggestion can explain the fact that both bornyl and α-fenchyl esters are endo products. In no case was an exo product such as an isobornyl ester (VIb) detected.

In intermediates like III and IV the positive charge cannot be equally distributed among the carbon atoms of the electron-deficient three-carbon center, since the tertiary carbon atoms C_7 in IV and C_1 in III can better support a positive charge. To better demonstrate this, in another case, structures like XIII and IX have been proposed.[12] According to these postulated structures the intermediate IV resembles the products more than III, which is more like the starting material and more liable to return to it. Since esterification to give bornyl and α-fenchyl ester is not a single step but a transformation following the skeletal rearrangement, one can suggest that the ratio in which these esters are formed should be the measure of effective aptitude toward structural arrangements like IV or III. It follows that structure orientation to IV is favored over III by a factor of 1.6:1, which seems to be in accordance with the expected differences in stability of the two ionic intermediates.

Intermediate IV, because of its carbonium ion character at C_7, should be very susceptible to solvent attacks at that carbon center. Such a solvolysis on the top of the three-carbon center is highly favored because of charge location and because it relieves the strained bridge structure. Such a solvolysis with bond breaking will produce α-terpinyl esters (VII) and limonene (XV) and terpinolene (XVI). The ionic character of the intermediate IV is expected to strongly depend on the ionizing power of the reaction medium, while reaction to produce esters will additionally depend on the nucleophilicity of the reagents.[13] This is in accord with the observed solvolytic efficiency to produce α-terpinyl esters which decrease in the series acetic, chloroacetic, propionic acid (Table II). The ionic character of the carbonium ion intermediate IV is in agreement with the results obtained by adding water in the acetolysis reactions (Table V). The addition of 0.2–5% of water led to 21.5% of alcoholic products, 90.5% of which is α-terpineol. That also means that water has an efficiency for capturing the intermediate IV that is ca. 6.5 times higher than that of acetic acid. Water is a strong nucleophilic reagent widely used to test the carbonium character of reaction intermediates.[9] Its inability to promote formation of the bornyl and the α-fenchyl systems is in accordance with the foregoing proposal of a nonionic character for these transformations.

Other fates of the intermediate IV are either to return to α-pinene or to undergo skeletal transformation with release of strain to produce camphene (XIII). That camphene derives from an intermediate like IV can be seen from its competition with the α-terpinyl esters and the p-menthadienes (Tables II–IV). It decreases under conditions that promote solvolytic ring opening, such as dilution of the organic acid, and increases with the molecular weight of the organic acid. By changing the ratio of organic acid:α-pinene in acetic acid from 0.8 to 11.3 (M/M), in propionic acid from 1.9 to 9.75 (M/M), and in butyric acid from 1.4 to 10 (M/M) the amount of camphene in the overall reaction decreases from 28 to 6.4% (acetic), 20 to 10.3% (propionic), and 24.1 to 16.5% (butyric). The change in the molecular weight from acetic to octanoic at equal dilutions increases the amount of camphene formed from 10 to 28.8% (Table II). These results suggest that the formation of camphene, which results in strain release, proceeds through intermediates that do not involve heterolytic bond breaking. These changes can be formulated as in X–XI.

The camphene obtained from the isomerization of α-pinene is racemic in support of the suggestion that it is formed through symmetric intermediates like X–XI.[14]

The intermediate III also shows structural similarities with the reaction products α- and β-fenchene. These make up 2.5–8.3% of the reaction and their formation varies along with the α-fenchyl ester formation (Table IV). The reaction leading to α- and β-fenchene can be better formulated with the mechanistic scheme XVII–XVIII.

The intermediate XVII is not symmetric like the corresponding one proposed for camphene formation, and a structure assignment more consistent with the results is to have two resonating forms. These forms develop further along the two possible reaction paths leading either to α- (XXII) or to β-fenchene (XX).

Ions such as X–XI and XVII–XVIII have been proposed in a number of cases to explain reactivities in the camphanyl and norbonyl systems.[15] The occurrence of common intermediates between camphene and the fenchenes with the p-menthadienes has been demonstrated in the deamination of bornyl- and α-fenchylamines, which gave considerable ring opening.[16] From the bornyl- and α-fenchylamine deamination, the main product was α-terpineol.[17] The isobornylamine treated in the same manner gave little ring opening, which indicates special requirements for reversibility through X–XI and XVII–XVIII. These results are interpreted[17] by a series of ionic bond ruptures and bond rearrangements which are unlikely to occur and which cannot account for the deamination of the exo amines. A more consistent explanation, fitting with the present results, is a low energy reversibility of the ions X–XI and XVII–XVIII to produce the fundamental ion intermediates III–IV, which then collapse to products according to the proceedings.

By analogy the deamination of norbornylamines leads to skeletal rearrangements.[18] The deamination of the endo isomer in acetic acid gave 100% of stereospecificity for the normal but only 19% for the exo acetate and was suggested to proceed through nonclassical carbonium intermediates like X–XI and XVII–XVIII.

High-temperature isomerization of T-OH vapor has been reported to give certain amounts of camphene;[19] this, however, was later definitely reidentified as 3-menthane.[20] With this correction there is no evidence to our knowledge for the transformations from the p-menthane to the camphane bridged system. Evidently, the reaction of α-pinene to give camphene proceeds through intermediates with distributed charge without ionic bond rupture like XIV suggested for the isomerization to p-menthadienes.

According to the above suggestions and the results (Table IV), reactivity through intermediate IV is thus most favored, accounting for 80–90% of reaction products.

In a study based on product analysis rather than on a detailed kinetic study, the addition of acetic acid to α-pinene in solutions 0.2 N in sulfuric acid at 20 °C is explained with an intimate ion-pair mechanism. According to this suggestion the intimate ion pair favors elimination rather than substitution the ratio of which is said to depend on the ionization constant of the acid.

The nonclassical ion intermediates III, IV, VIII, and IX suggested by us here and elsewhere[7,11] evidently are ion pairs; however, from the results and the foregoing discussion it is rather conclusive that their reactivity does not involve collapse with bonding of the counterion but rather reaction through solvolysis and substitution. Furthermore, the addition of organic acids to α-pinene does not depend on the ionization constant of the acids[5] (Table II); the acetolysis of α-pinene gives less than 10% total esters and 90% rearranged products[21] mostly not primarily involved.[7,11]

The reaction of α-pinene with the organic acids presented above shows interesting stereochemical and mechanistic features which are unique for this natural products. Further work to demonstrate the reactivity of α-pinene with its preference for formation in nature and its structural connections with the terpenic hydrocarbons in general and the steroids in particular may be useful and interesting.

Experimental Section

α-*d*-Pinene was obtained from turpentine oil of *Pinus halepensis var.* containing α-pinene (ca. 96% by weight). After 6 h of refluxing over solid KOH and distilling through an efficient column, the α-*d*-pinene was obtained in ca. 99% GLC purity: bp 154–156 °C (770 mmHg); $n^{20}\mathrm{D}$ 1.4665; $\alpha^{20}\mathrm{D}$ +38.86°.

Organic acids were analytical grade reagents (obtained from Fluka AG, Switzerland), further purified by distillation over chromium oxide.

Kinetics. The solvolysis rates and the product analyses were determined by sampling aliquots at appropriate time intervals, using gas chromatography as the analytical method (Perkin-Elmer Model 801), equipped with ionization detector.

Product Analysis. In a typical run, the appropriate solution of α-*d*-pinene in the organic acid was divided in five to six ampules (Pyrex glass), holding 50 ml of solution each. These were inserted into a thermostated bath and were used for the determination of the course of the reaction in reaction rates and product composition. Each ampule, when withdrawn from the kinetic bath, was cooled and poured under stirring into a cold mixture of 50 ml of purified *n*-pentane and 100 ml of 5% NaOH–water solution. The *n*-pentane layer was further washed with sodium bicarbonate and carefully concentrated.[23] This was divided into three parts, A, B, and C. Part A was used for preparative chromatography, to separate the terpene fraction, which was further analyzed on macro-Golay chromatographic columns. Part B, after complete evaporation of *n*-pentane, was used to determine the saponification number using a 3-h boiling in 90% aqueous ethanolic solution of 0.3 N KOH, under standardizing conditions. Part C was used to determine by GLC the ester composition, in the ester form (case of runs in acetic and propionic acid), or in the form of alcohols after a lithium aluminum hydride reduction.[22] For the reduction part C was diluted with ether and treated with lithium aluminum hydride, under cooling. After hydrolysis with saturated aqueous ammonium chloride, the ether layer was washed with water and dried over potassium carbonate and the ether was evaporated.[23] The residue was taken up in *n*-pentane and analyzed by GLC.

In the alcohol and terpene determinations, bromobenzene was used as internal standard. The measured peak areas of terpene–alcohols and terpene–esters mixtures were corrected for the relative detector response by 1:1.1 and 1:1.08, respectively, determined by analysis of mixtures of known composition. Dehydration of alcohols and elimination in the esters were negligible under these conditions of analysis. The concentration of each was calculated by multiplying the peak height by the half-width, with correction for relative detector response. In a careful series of control experiments it was established that synthetic mixtures could be analyzed with an average error in percent of composition of terpenes 1.5%, alcohols 0.8%, and esters 1.2%.

From runs with dilution of organic acid–α-pinene (4.5 M/M), first rate constants were calculated using the expression $k = 2.303/t \log 100/x$ where x is the percent of unreacted α-*d*-pinene at time t. The amount of unreacted α-*d*-pinene was determined from the gas chromatographic analysis of the terpene mixture, through the esterification number obtained in each measurement.

Registry No.—I, 7785-70-8.

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