p.p.m.; and a single[10] hydroxyl proton signal near 4 p.p.m. due to OH of water, sulfuric acid, and succinic acid. Utilizing the integrals (average of six integrations) for the benzylic protons of acid and anhydride, and that for the benzene ring protons as an internal standard for the total number of moles of anhydride and diacid, in conjunction with the known gravimetric composition of the sample before equilibration, the values of the mole fraction equilibrium constants, K_X, were calculated. (A refers

$$K_X = \frac{(X_A)(X_{H_2O})}{X_D}$$

to anhydride, D to diacid.) Typical values of K_X obtained in this way as equilibrium was approached from the two sides were I (X = H), 0.27 ± 0.02 *vs.* 0.25 ± 0.02; I (X = CH_3), 0.30 ± 0.02 *vs.* 0.31 ± 0.02; and I (X = Cl), 0.124 ± 0.009 *vs.* 0.117 ± 0.009. In the case of I (X = OCH_3) the equilibrium could not be approached from the anhydride side because of the failure to obtain anhydride free from acid (see Preparation of Compounds).

Results

The constants, K_X, and derived thermodynamic quantities for the equilibria are presented in Table I.

Table I

Equilibrium Data for 2,2-Diethyl-3-(*p*-X-phenyl) succinic Acids and Anhydrides[a]

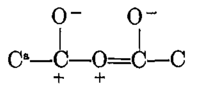
p-X	K_X	$\Delta F°$, kcal./mole	$\Delta\Delta F°$, kcal./mole
CH_3	0.31 ± 0.02	0.87 ± 0.05	−0.13 ± 0.08
H	0.26 ± 0.02	1.00 ± 0.06	0
CH_3O	0.20 ± 0.02	1.19 ± 0.07	0.19 ± 0.09
Cl	0.12 ± 0.01	1.56 ± 0.09	0.56 ± 0.11
Succinic acid[b]	$<10^{-3}$	>5	>4

[a] At 373°K. [b] The limiting values are estimated on the basis that succinic acid under similar conditions was found to exist only in the diacid form within the experimental sensitivity.

Order of magnitude estimates of data for the succinic acid–anhydride equilibrium are included in Table I to set a scale for judging the relative importance of bulk and inductive electronic effects. It is seen that substitution of three of the hydrogens in the chain of succinic acid favors the anhydride form by at least 5 kcal./mole. Since the maximum range of $\Delta\Delta F°$ is only 0.69 kcal./mole, it is clear that the effect of the substituents cannot be purely electronically inductive. The steric or bulk effect is much more important in driving the equilibrium toward the anhydride, a point already established by Lutz[5] in another system. It is also clear from the data in Table I that electron-injecting groups favor the anhydride form.

Although the temperature dependence of K_X was not measured for all compounds, its determination (using the values of K_X at 293 and 373°K.) in the cases of I (X = H) and I (X = Cl) gave the values, respectively, $\Delta H° = 4.9 \pm 0.2$ and 5.5 ± 0.3 kcal./mole and $\Delta S° = 1.05 \pm 0.05$ and 1.05 ± 0.05, giving reassurance that entropy effects are not an important part of the effect of the *para* substituent in changing the position of equilibrium.

While any theoretical explanation for the effect of electron-donating *p*-X substituents is fraught with danger because the data only show an increase in relative stability of the anhydrides with electron-donating *p*-X substituents, it seems not unreasonable to focus attention on effects of electron donation on the stability of the anhydride form, assuming that the substituent has little effect on that of the diacid.[11] Anhydrides are electrophilic reagents, Lewis acids in the sense of the contributing structure



$$C^a\text{—}\overset{O^-}{\underset{+}{C}}\text{—}O\text{=}\overset{O^-}{\underset{+}{C}}\text{—}C$$

and electron density increase in the vicinity of C^a would be expected to diminish the $^+C\text{–}O^-$ bond moment with resultant decrease in the energy resulting from unfavorable juxtaposition of bond dipoles. The data may be taken to support such an interpretation.

Acknowledgment.—The authors are indebted to the National Science Foundation (G9476) and the Air Force Office of Scientific Research (AFOSR 62-116 and AF49-638-1272) for their generous support of this investigation. We also wish to express our great appreciation to Dr. Lois J. Durham of these laboratories for her help with the proton magnetic resonance spectral analyses.

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[10] Rapid exchange of hydroxyl protons in the strongly acidic medium is responsible for the single OH signal: J. D. Roberts, "Nuclear Magnetic Resonance. Applications to Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Chapter 4.

[11] The fact that the equilibria were established in a medium 0.02 *M* in sulfuric acid removes ionization of the acid as a factor for consideration.

Oxidation of β-Pinene with Lead Tetraacetate[1]

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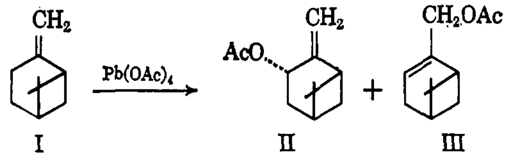
The oxidation of β-pinene (I) with lead tetraacetate in benzene and in acetic acid leads to formation of two monoacetate products in significant amount. These have been identified as *trans*-pinocarvyl acetate (II) and myrtenyl acetate (III).



The oxidation in acetic acid at 60° was previously carried out by Matsubara,[2] and he reported the monoacetates to be myrtenyl acetate (9% yield based on unrecovered β-pinene) and perilla acetate (4%). In this study, however, we have found that the two major monoacetates formed in the β-pinene oxidation in acetic acid at room temperature are myrtenyl acetate (12%) and *trans*-pinocarvyl acetate (10%). Distillation of all volatile components of the product mixture followed by gas chromatography studies of the fractions revealed that the acetic acid oxidation system is complex and many higher boiling products are formed. Careful duplication of Matsubara's

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[1] Presented in part at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964.

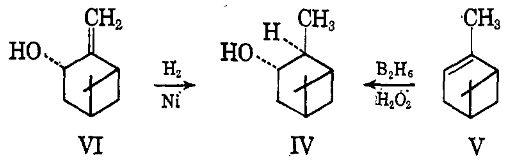
[2] Y. Matsubara, *J. Chem. Soc. Japan*, **75**, 894 (1954); *Chem. Abstr.*, **49**, 9568e (1955).

procedure (at 60°) still resulted in formation of *trans*-pinocarvyl acetate.

Oxidation in benzene at room temperature also led to myrtenyl acetate (10.5% yield) and *trans*-pinocarvyl acetate. The yield of the latter, however, increased dramatically from 10% in acetic acid to 46% in benzene. The volatile higher boiling products were outweighed by the monoacetate products by over 30-fold, whereas in acetic acid the monoacetate fraction was outweighed by the volatile higher boiling components by over 3-fold.

Assignment of structure to the major product of β-pinene oxidation in benzene was accomplished by its conversion to *trans*-pinocarveol. Transesterification of the acetate was effected by action of sodium methoxide in methanol. The resulting alcohol was shown to be *trans*-pinocarveol by comparison of its infrared spectrum and gas chromatographic retention times (on two different columns) with those of an authentic sample. Action of methanolic sodium methoxide on the other acetate converted it to an alcohol which was shown to be myrtenol. Application of the same procedure to the acetates formed in the oxidation in acetic acid showed that, again, these acetates were *trans*-pinocarvyl acetate and myrtenyl acetate.

The structural assignments for the two isomeric pinocarveols were originally made by Schmidt[3] but were challenged by Bose in 1955.[4] Recent work of Zweifel and Brown,[5] however, strongly supports the original structure assignments of Schmidt. They have shown that the same alcohol, isopinocampheol (IV), is formed from the two-step hydroboration–oxidation reaction (diborane followed by hydrogen peroxide) with α-pinene (V) as is formed from nickel-catalyzed hydrogenation of *trans*-pinocarveol (VI). Considerations based on the known stereospecificity of the hydroboration–oxidation sequence and on related work using β-pinene led them to conclude that the hydroxyl and the *gem*-dimethyl groups in isopinocampheol bear a *trans* relationship to each other. Thus, the structure of *trans*-pinocarveol must also bear this same *trans* relationship.



The most useful gas chromatographic column for separation of the acetates and alcohols encountered in this work was a hyprose column similar to that described previously.[6] A didecyl phthalate column[7] was also used with some success, but retention times were considerably longer than with hyprose. The possibility of troublesome rearrangements occurring at the operating temperatures of the columns (130–155°) was ruled out by comparison of infrared spectra of samples before and after preparative gas chromatography.

Table I compares the results obtained with the two columns. The two acetates had longer retention times than the alcohols on didecyl phthalate but shorter retention times on hyprose. Clearly, separation of the alcohols was better than that of the acetates on both columns.

TABLE I

RELATIVE RETENTION RATIOS OF ACETATES AND ALCOHOLS IN GAS CHROMATOGRAPHY

Compd.	Didecyl phthalate[a]	Hyprose[b]
trans-Pinocarveol	1.00[c]	1.00[d]
Myrtenol	1.34	1.64
trans-Pinocarvyl acetate	1.83	0.82
Myrtenyl acetate	1.97	0.89

[a] 148° and 45 cc./min. [b] 151° and 100 cc./min. [c] 27.5 min. [d] 11.8 min.

Neither *trans*-pinocarvyl acetate nor myrtenyl acetate rearranged even when heated with acetic acid under conditions more drastic than those used in the oxidation. Thus, it appears that the two acetates were formed independently of each other in the oxidation of β-pinene and not by allylic rearrangement.[8,9]

As was mentioned before, the oxidation in acetic acid leads to a much more complex reaction mixture than is found when the oxidation is carried out in benzene. Gas chromatography of the higher boiling volatile fractions revealed that each contained several different components. The low total yield of monoacetates in the acetic acid oxidation is probably a result of initially formed products undergoing further oxidation and addition of acetic acid. The situation is similar to the α-pinene–lead tetraacetate reaction, where a much higher yield of monoacetate is obtained in benzene than in acetic acid.[10]

Oxidation of esters with lead tetraacetate in acetic acid has previously been found to yield carbon dioxide.[11] In this work, however, a β-pinene oxidation in acetic acid in which any gaseous products would be passed into ascarite tubes gave no detectable amount of carbon dioxide.

Oxidation of β-pinene with lead tetraacetate in benzene followed by deacetylation and fractional distillation of the resulting alcohols provides a useful synthetic route to pure *trans*-pinocarveol.

Experimental

Gas Chromatography and Infrared Spectroscopy.—A Wilkens Aerograph A-90-S gas chromatograph with either a Brown-Honeywell Electronik or a Sargent SR recorder was employed for analysis. Separations were made with either a hyprose or didecyl phthalate column. The first of these contained 20% by weight of hyprose on hexamethyldisilazane (HMDS)-treated Chromosorb W (60–80 mesh) packed into a 10 ft. × 0.25 in. stainless steel column. The other column contained 25% of didecyl phthalate on HMDS-treated Chromosorb W (60–80 mesh) packed into a 6.5 ft. × 0.25 in. stainless steel column. Infrared spectra were run on a Perkin-Elmer Model 21 recording infrared spectrophotometer. All samples were run neat between salt plates.

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Materials.—Lead tetraacetate was obtained from K and K Laboratories, Inc., dried by suction filtration with a rubber dam, and stored overnight in a vacuum desiccator over potassium hydroxide. β-Pinene (95–98% pure, $[\alpha]^{21.5}_{\mathrm{D}}$ $-17.1°$) was obtained by distillation of commercial β-pinene (K and K, 76%) through a 24-in. spinning-band column. Purity was determined by gas chromatographic analysis on didecyl phthalate.

Oxidation in Benzene.—β-Pinene (33.0 g., 0.242 mole) in dry benzene (300 ml.) was added to a stirred suspension of lead tetraacetate (106.0 g., 0.239 mole) in dry benzene (450 ml.) over a 30-min. period at room temperature. The reaction was carried out in the absence of direct light. After stirring for an additional hour, the lead diacetate precipitate was filtered. The filtrate was then mixed with water (600 ml.) and no lead dioxide was precipitated indicating total consumption of oxidant. The benzene layer was separated and washed with two 600-ml. portions of water. The benzene was distilled from the dried solution (magnesium sulfate), and the product mixture was fractionally distilled through a spinning-band column.

Unreacted β-pinene (4.6 g., 0.034 mole) was recovered by distillation at *ca.* 15 mm. Continued distillation gave a total of 23.0 g. (0.118 mole, 57% yield based on unrecovered β-pinene) of monoacetate, b.p. 47–55° at 0.30 mm. Gas chromatography of the several fractions obtained showed two major products: *trans*-pinocarvyl acetate (46%) and myrtenyl acetate (10.5%).

Collection of pure samples was achieved by gas chromatography of appropriate fractions. The infrared spectrum of *trans*-pinocarvyl acetate showed the expected bands for ester carbonyl (1745 cm.$^{-1}$) and disubstituted alkene (1658 and 905 cm.$^{-1}$). Myrtenyl acetate showed infrared absorption for ester carbonyl (1748 cm.$^{-1}$) and trisubstituted alkene (1661 and 800 cm.$^{-1}$).

***trans*-Pinocarveol and Myrtenol.**—Several acetate fractions obtained from lead tetraacetate oxidation of β-pinene in benzene were combined to give a mixture estimated to contain 87% *trans*-pinocarvyl acetate and 11% myrtenyl acetate. A solution of this mixture (24.5 g., 0.126 mole) and sodium (0.4 g.) in methanol (400 ml.) was heated to its boiling point. Methanol and the methyl acetate formed in the transesterification were then distilled from the solution, over a 6-hr. period, until a negative ester test was observed with ferric hydroxamate reagent[12]; about 250 ml. of distillate was obtained. The remaining solution was poured into water (400 ml.), and that mixture was then extracted with three 150-ml. portions of ether. The combined ether extracts were dried over magnesium sulfate.

The ether was removed, and the mixture of alcohols was distilled *in vacuo* through a spinning-band column (18 in. long). Five fractions were obtained yielding a total of 17.2 g. (0.113 mole, 90%) of alcohols. Gas chromatographic analysis, on hyprose, of the fractions showed them to contain *trans*-pinocarveol (77%) and myrtenol (10%). Fractions 2, 3, and 4 (13.8 g.) each contained *trans*-pinocarveol of greater than 95% purity. Fraction 3 was pure *trans*-pinocarveol, b.p. 38° at 0.30 mm.; the *p*-nitrobenzoate derivative was recrystallized from methanol to give white platelets, m.p. 93–94°, lit. m.p. 91–92°,[3] 93.5–94.5°.[13] The infrared spectrum of this fraction showed O–H absorption at 3370 cm.$^{-1}$ and typical disubstituted alkene absorption at 1650 and 893 cm.$^{-1}$. The spectrum was identical with the infrared spectrum of authentic *trans*-pinocarveol.[14] The gas chromatographic retention times of the two samples on hyprose and on didecyl phthalate were also identical. Optical rotation of the alcohol (fraction 3) was $[\alpha]^{22.5}_{\mathrm{D}}$ $+64.9°$ (*c* 0.80, chloroform). The infrared spectrum and gas chromatographic retention times for fraction 3 differed considerably from those of *cis*-pinocarveol.[15]

The acetate prepared by acetylation of known *trans*-pinocarveol, using sodium acetate and acetic anhydride, and the major acetate product of lead tetraacetate oxidation of β-pinene were also shown to be identical by comparison of their infrared spectra and retention times on didecyl phthalate.

Gas chromatographic separation of fraction 5 gave a pure sample of the minor alcohol product of the transesterification. The infrared spectra and gas chromatographic retention times on hyprose and on didecyl phthalate of this alcohol and authentic myrtenol were identical. The infrared spectrum of myrtenol shows O–H absorption at 3330 cm.$^{-1}$ and trisubstituted alkene absorption at 1661 and 800 cm.$^{-1}$.

Oxidation in Acetic Acid.—β-Pinene (27.7 g., 0.204 mole) in glacial acetic acid (50 ml.) was added dropwise for 1 hr. to a stirred suspension of lead tetraacetate (83.6 g., 0.189 mole) in glacial acetic acid (200 ml.) containing acetic anhydride (6 g.). During the addition the reaction mixture was kept at room temperature, and it gradually clarified to a yellow solution. Stirring was continued for an additional hour. The reaction solution was then poured into ether (800 ml.). The resulting precipitate dissolved in the following water wash (400 ml.); no lead dioxide was observed. Additional washings with two 200-ml. portions of water, six 200-ml. portions of 5% sodium bicarbonate, and two 250-ml. portions of water were employed. The ether solution was dried over magnesium sulfate.

The ether was removed and the remaining liquid was distilled through a spinning-band column (18 in.). An unreacted β-pinene fraction (4.71 g.) was obtained by distillation at *ca.* 15 mm. Distillation of the remainder at lower pressure yielded 10.55 g. of distillate, b.p. 49–73° at 0.40 mm. Gas chromatographic analysis on hyprose indicated that the yields of *trans*-pinocarvyl acetate and myrtenyl acetate were 10 and 12%, respectively (based on unrecovered β-pinene). The chromatograms also showed the presence of four other components in lesser amount.

The major monoacetate products were found to be *trans*-pinocarvyl acetate and myrtenyl acetate by transesterification, as described above, to the alcohols. Purification of these was carried out by preparative gas chromatography. Comparison of retention times on two columns and their infrared spectra with known samples confirmed them to be *trans*-pinocarveol and myrtenol.

A similar reaction carried out under a nitrogen stream with incorporation of ascarite tubes was found to yield no carbon dioxide.

Attempted Rearrangement of Acetates.—Two samples (each 0.50 g.) containing *trans*-pinocarvyl acetate (49%) and myrtenyl acetate (48%) were dissolved in glacial acetic acid (10 ml.) containing acetic anhydride (0.1 g.). These solutions were then heated at 60° for 1- and 4-hr. periods, respectively. The solutions were then cooled and worked up in the usual way. After removal of the ether, the acetates were subjected to the transesterification procedure. Ether solutions of the resulting alcohol mixtures were analyzed by gas chromatography. Two blanks were also analyzed; one of these had been carried through the entire procedure as the above samples (without heating), and the other had simply been deacetylated. All four samples contained the same relative amounts of *trans*-pinocarveol and myrtenol. A similar experiment with nearly pure *trans*-pinocarvyl acetate also showed no indication of rearrangement.

Acknowledgment.—The authors would like to express appreciation to Mr. G. S. Fisher of the Naval Stores Station, U. S. Department of Agriculture, for authentic samples of *trans*-pinocarveol and myrtenol. They also express their gratitude to Mr. L. O. Sell for the infrared spectra determinations and Mr. A. D. Darling for his assistance.

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(15) *cis*-Pinocarveol was prepared by aluminum isopropoxide reduction of pinocarvone[3]: m.p. 45–46° lit.[3]: m.p. 51°; *p*-nitrobenzoate, m.p. 103.5–104.5°, lit.[3] m.p. 104°.

The Reaction of Benzal Chloride with Lithium

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Recently several reports on the generation of phenylcarbenoids by α-elimination have appeared in which