18, 37.0 min; alcohols **8** and **9**, 42.4 min. None of the starting materials or products were lost by other reactions to give nonvolatile products.

After a 1-min reaction, the ratio of cyclohexanone to cyclohexanol was 82.9:17.1, respectively. At the same time, the ratio of ketone **18** to the mixture of alcohols **8** and **9** was 18.5:81.5, respectively. After 2 min, the above ratios were 78.8:21.2 and 13.1:86.9. After 10 min, these ratios were 68.8:31.2 and 3.1:96.9. The relative rates were calculated by the equation below[45]

$$\frac{k_x}{k_y} = \frac{\log \frac{[X]_f}{[X]_i}}{\log \frac{[Y]_f}{[Y]_i}}$$

where i and f indicate initial and final. The relative rates were 8.97 after 1 min, 8.53 after 2 min, and 9.38 after 10 min.

The average relative rate for reduction of pentacyclodecanone **14** to cyclohexanone was 8.96 ± 0.43. Since the absolute rate for reduction of cyclohexanone at 0° is $1.61 \times 10^{-2}\ M^{-1}\ \text{sec}^{-1}$,[37] the calculated rate for **18** is $0.144 \pm 0.007\ M^{-1}\ \text{sec}^{-1}$.

Equilibration of *syn* 8 and *anti* 9 Alcohols.—According to the procedure of Wilcox and coworkers,[46] the reaction mixtures were made up in heavy-walled Pyrex tubes which were then frozen at −196° and sealed *in vacuo*. Each tube contained 100 mg (0.68 mmol) of alcohol, 300 mg (1.47 mmol) of aluminum isopropoxide, 20 μl (0.27 mmol) of acetone, and 2 ml of 2-propanol. The tubes were placed in a constant temperature oil bath at 120° and removed for analysis after the appropriate intervals. The reactions were worked up by pouring the contents of the tube into 5 ml of 5 *N* hydrochloric acid. This mixture was then diluted with water and the alcohols were extracted with two 20-ml portions of ether. The combined ether extracts were washed with water and dried ($MgSO_4$). The alcohols were recovered by evaporation of the ether and sublimation of the residue at 100° (0.5 mm). The recovery of the alcohols was *ca.* 75% in each run. The sublimate was analyzed by nmr. The two carbinol C–H (C-6) absorption peaks for **8** and **9** at −4.04 and −4.28 ppm, respectively, were recorded six times for each equilibration sample. The areas of the peaks were obtained by plainmeter integration and averaged. The results of these analyses are given in Table VI.

TABLE VI

ALUMINUM ISOPROPOXIDE EQUILIBRATION OF *syn* ALCOHOL 8 AND *anti* ALCOHOL 9

Starting alcohol	Equilibration time, hr	Distribution (%)[a] *syn* 8	Distribution (%)[a] *anti* 9
syn 8	95	51.2	48.8
	137	50.0	50.0
	169	50.3	49.7
anti 9	95	50.5	49.5
	168	50.0	50.0

[a] The range of precision in these values is ± 1%.

Registry No.—**8**, 20446-30-4; **9**, 20446-31-5; **10**, 20446-32-6; **14**, 20446-33-7; **15**, 20446-34-8; **18**, 20446-29-1; **19**, 20446-35-9; **21**, 20440-15-7.

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[45] G. A. Russell, "Technique of Organic Chemistry," Vol. VIII, Part I, 2nd ed, S. L. Friess, E. S. Lewis, and A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1961, p 343.

[46] C. F. Wilcox, Jr., M. Sexton, and M. F. Wilcox, *J. Org. Chem.*, **28**, 1079 (1963).

Equilibration of *p*-Menthadienes in Acid and Base[1]

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Conditions are described for equilibrating the *p*-menthadienes with acid or base without getting appreciable amounts of the aromatization product, *p*-cymene. The equilibrium composition is given, and rate constants for the interconversions observed in acid and base are recorded and compared.

A great many studies have been reported involving acid-[3] and base-catalyzed[4] isomerizations of various substances to mixtures containing *p*-menthadienes. However, due to complicating side reactions, especially aromatization, equilibrium among the *p*-menthadienes appears to have been reached only in one case, involving potassium *t*-butoxide in dimethyl sulfoxide at 50°, which gave a 5:3:1 ratio of II, III, and V, respectively.[4c] In this study, only the three main constituents were identified, and the only rate constants given are for disappearance of starting materials. We wish to report a fuller analysis of the equilibrium composition, conditions for achieving it in acid and base with <10% of side reactions, and rate constants for many of the possible interconversions of the isomers.

Equilibrium was first reached with potassium *t*-butoxide in *t*-butanol at 200° for 8 hr. Starting from α-terpinene (II), 3,8-*p*-menthadiene (IV), or γ-terpinene (V), gas phase chromatography (gpc) gave virtually the same trace. Preparative gpc of the mixture in one case followed by spectral analysis and derivatization of the components showed the equilibrium mixture at 200° to contain the six isomers shown in Scheme I in the percentages indicated (relative to total diene = 100%; in a typical case, 1% of menthenes and 7% of *p*-cymene were also present). The stability order observed for the *p*-menthadienes can be rationalized in terms of the intrinsic stabilities of double bonds in various menthenes (Δ3 > 1Δ > Δ8 > the other three

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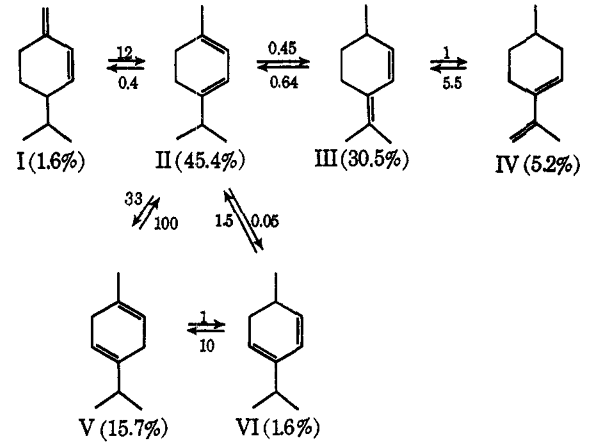
[1] Taken in part from the B.S. Thesis of H. P. Klein, University of Illinois, 1963, and the M.S. Thesis of E. J. Salacinski, University of Arizona, 1966; presented at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967.

[2] Alfred P. Sloan Fellow, 1967–1969.

[3] For example, (a) O. Wallach, *Ann.*, **239**, 34 (1887); (b) W. A. Mosher, *J. Amer. Chem. Soc.*, **69**, 2139 (1947); (c) R. C. Palmer and A. F. Wicke, Jr., U. S. Patent 2,799,717; (d) J. Vergese, *J. Sci. Ind. Res.* (India), **18B**, 263 (1959); (e) E. von Rudloff, *Can. J. Chem.*, **39**, 1 (1961); (f) Y. Watanabe, *Kogyo Kagaku Zasshi*, **65**, 1573 (1962); (g) G. L. K. Hunter and W. B. Brogden, Jr., *J. Org. Chem.*, **28**, 1679 (1963); (h) M. I. Goryaev, V. I. Shabalina, and A. D. Dembitskii, *Dokl. Akad. Nauk SSSR*, **158**, 155 (1964); (i) G. Valkanas and N. Iconomou, *Pharm. Acta Helv.*, **39**, 441 (1964); (j) R. E. Wrolstad and W. G. Jennings, *J. Chromatog.*, **18**, 318 (1965).

[4] (a) H. Pines and H. E. Eschinazi, *J. Amer. Chem. Soc.*, **77**, 6314 (1955); (b) H. Pines and L. Schaap, *ibid.*, **79**, 2956 (1957); (c) S. Bank, C. A. Rowe, Jr., A. Schriesheim, and L. A. Naslund, *J. Org. Chem.*, **33**, 221 (1968).

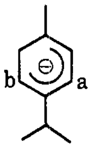
SCHEME I[a]



[a] Equilibrium percentages and rate constants (relative to V → II = 100; the absolute value for this rate constant was $4.5 \pm 0.5 \times 10^{-2}$ sec^{-1}) for isomerization of *p*-menthadienes at 200° with potassium *t*-butoxide in *t*-butanol.

positions[5]) coupled with small resonance energies for the cisoid conjugated dienes and *larger* resonance energies for the transoid conjugated dienes I and III.[6] Especially noteworthy is III, which in spite of having both double bonds in unfavorable positions on the menthane carbon skeleton, possesses sufficient resonance energy to be the second most stable isomer.

Rate constants for many of the interconversions were obtained by matching concentration *vs.* time curves for the observed dienes in kinetic runs starting from II, IV, and V, using an analog computer. Scheme I is based on the assumption that all the interconversions proceeded *via* pentadienyl carbanion intermediates. The rate constants for reactions leading to and from VI are considerably less certain than the others; since II and V equilibrate much more rapidly than VI forms, it is not clear how much VI is coming from each. The values given in Scheme I for the rate constants involving VI were based on the assumption that the pentadienyl carbanion VIII would protonate about eight times as fast at a as at b;[7] they gave a satisfactory fit. The largest rate constants, for the interconversion of II with V, are large partly because U-shaped pentadienyl anions are involved rather than the other shapes,[8] and partly because there are *two* good routes, one involving deprotonation at a secondary site to VIII and reprotonation at another secondary site, and the other involving similar reactions with IX as the intermediate.



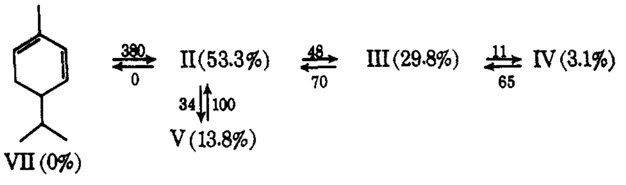
VIII

IX

Having thus learned the equilibrium composition from experiments in base, and noting that none of the many final compositions reported from acid-catalyzed isomerizations[3] comes very close to the equilibrium composition, it was decided to see if conditions could be found for equilibrating in acid without extensive side reactions. In addition, the rate constants for approach to equilibrium, which could be very different since the intermediates were now carbonium ions instead of carbanions, were of interest.

After trying several other conditions, essentially those of Palmer and Wicke[3c] were used. α-Phellandrene (VII) was stirred vigorously under nitrogen at 67° with twice its weight of 50% aqueous sulfuric acid, and samples were withdrawn occasionally for analysis. After 32 hr, the values in Scheme II, quite close to those in Scheme I, had been obtained. The minor components I and VI were undoubtedly present again in amounts under 2%, but were ignored in the acid study. The percentages of the four major components were approaching values close to the limiting values found in base (*e.g.*, the concentration of II was decreasing from its maximum value of 72.4% at 7 hr). The reaction was worked up at this point and the identities of the major products verified by preparative gas chromatography and spectral analysis. *p*-Menthadienes still comprised 93% of the mixture; 5% *p*-cymene and 2% menthenes had also been formed. For the determination of the rate constants in Scheme II, with an analog computer, the equilibrium values obtained at 200° were used; though the equilibrium values at 67° no doubt differ from those at 200° owing to entropy differences, they may not differ by much more than the experimental error in the values.

SCHEME II[a]



[a] 32-hr percentages and rate constants (relative to V → II = 100; the absolute value for this rate constant was $2.0 \pm 0.3 \times 10^{-5}$ sec^{-1}) for isomerization of *p*-menthadienes at 67° with 50% aqueous sulfuric acid.

Although it was originally hoped that, under mild acidic conditions starting with a conjugated *p*-menthadiene, other conjugated dienes (formed *via* allylic carbonium ion intermediates) would be formed much faster than unconjugated dienes, it is readily seen from Scheme II that the unconjugated diene V is formed from II almost as rapidly as the conjugated diene III is formed from II. Thus, unlike the situation in base, in which there is a rate difference of about 10^6 between isomerizations proceeding *via* allylic anions and pentadienyl anions,[8,9] there must be a small difference

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(5) H. Pines and H. E. Eschinazi, *J. Amer. Chem. Soc.*, **78**, 1178 (1956).

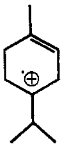
(6) R. B. Bates, R. H. Carnighan, and C. E. Staples, *ibid.*, **85**, 3030 (1963).

(7) Cyclohexadienyl anion protonates 8 times as fast at the central carbon as at each end: R. B. Bates, R. H. Carnighan, and C. E. Staples, *ibid.*, **85**, 3032 (1963).

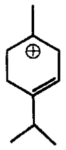
(8) R. B. Bates, R. H. Carnighan, and C. E. Staples, *ibid.*, **85**, 3031 (1963); this extra stability is probably due to homoconjugation, since the alternative explanation involving better chelation of the U shape seems to be ruled out by kinetic studies showing that KO*t*-Bu and LiO*t*-Bu give the same relative rate constants for the interconversions of the hexalins (S. S. Bratcher, M.S. Thesis, University of Arizona, 1967).

(9) A. Schriesheim, C. A. Rowe, Jr., and L. Naslund, *J. Amer. Chem. Soc.*, **85**, 2111 (1963).

between the allylic carbonium ion intermediates and the tertiary homoallylic carbonium ions X and XI.



X



XI

As expected, the relative rate constants in acid and base differ considerably. Using the analog computer and the rate constants in Scheme I and II, curves for approach to equilibrium in acid and base from each of the dienes were drawn. The major differences result from the very rapid equilibration between II and V in base (*via* a U-shaped pentadienyl anion); if II were desired from V, for example, base would be chosen since with it a mixture containing 74% V and 26% II can be obtained, whereas in acid, V never gets appreciably above its equilibrium value of 45%, and by the time it is close to that value, 10% of III has formed.

A general advantage of base for diene isomerizations, that of fewer and slower side reactions, holds to some extent for the *p*-menthadienes, since aromatization is faster relative to isomerization in acid, at least under our conditions. A big advantage of acid in the *p*-menthadiene case is that the system can be entered from alcohols such as α-terpineol[3e] and isomeric hydrocarbons such as the readily available pinenes.[3a–d,f,i]

Experimental Section

The α-phellandrene (VII) used was Eastman practical grade, purified by preparative gas phase chromatography (gpc) on Carbowax 20M to 98% purity, contaminated with 2% α-terpinene (II). Samples of α-terpinene (II) and γ-terpinene (V) obtained from the Glidden Co. contained several per cent *p*-cymene as the only noticeable impurity and were used without purification, as was the 3,8-*p*-menthadiene (IV) obtained from the Hercules Powder Co.

For gpc analyses, Carbowax 20M on water- or base-washed firebrick at 110–140° was used unless otherwise stated.

Equilibration in Base.—A mixture of 6% potassium in *t*-butanol under nitrogen was stirred until all of the metal had reacted, and to 10 g of this solution was added 9 g of the diene to be equilibrated. The equilibrations were performed by heating sealed tubes (nitrogen atmosphere) containing 1-cm^3 portions of these solutions to 200° for 8 hr. The tubes were quenched in ice water, opened, and the contents poured into sodium chloride solution. The hydrocarbons were extracted with ether, and the ether solution was washed twice with salt water to remove *t*-butanol. After drying over potassium carbonate, the ether was allowed to evaporate at room temperature under a nitrogen stream and the residual oil was analyzed. The equilibrated samples starting from II, IV, V, VII, and a 3:1 mixture of VII and I had virtually the same nmr spectra and gpc patterns. Even after 30 hr, menthadienes still comprised 96% of the hydrocarbon mixture; the remainder consisted of *p*-cymene (3%) and menthenes (1%). The equilibrium menthadiene composition given in Scheme I was determined by integration of the gpc curve obtained by equilibrating VII for 30 hr. Several equilibrated samples were put through a preparative gpc column and all hydrocarbon fractions were collected and analyzed by nmr and uv. Maleic anhydride adducts were prepared from the cisoid dienes II and VI. Retention times in minutes were as follows: a menthene, 8.8; VI, 10.4; another menthene, 13.2; II, 16.8; I, 19.8; V, 23.4; IV and *p*-cymene, 27; III, 30.3. The relative amounts of IV and *p*-cymene were determined from the intensity of the absorption at 233.5 mμ in the sample collected at 27 min; *p*-cymene does not absorb there, but it was necessary to correct for the absorption due to III, a contaminant in the collected sample.

Kinetic runs were made at 200 ± 0.1° starting from II, IV, and V. Tubes were removed and analyzed at various time intervals, and the resulting composition–time curves were matched as well as possible on an analog computer using Scheme I. The best rate constants thus obtained are given in Scheme I.

Equilibration in Acid.—To 8.0 g of α-phellandrene (VI) under nitrogen in a bath maintained at 67.0 ± 0.03° was added 15.3 g of 50% sulfuric acid, and the paddle stirrer was started. When a sample was to be removed for analysis, the stirrer was momentarily stopped and the sample was taken with a syringe from the upper layer. The sample was squirted into 10% sodium hydroxide solution and the hydrocarbons were extracted by washing three times with ether. The ether solution was washed twice with water and the ether was evaporated.

After 32 hr, the relative amounts of the various *p*-menthadienes were changing very little, although the *p*-cymene and menthene concentrations continued to rise from their values of 5% and 2%, respectively. The gpc trace looked strikingly similar to that obtained from the base equilibrations, and mixed gpc confirmed the correspondence in retention times for the components of the two samples. Samples of the equilibrium mixture (composition given in Scheme II) were put through the preparative gpc as before; various spectral methods confirmed the similarity in composition of the equilibrium mixtures obtained in acid and in base.

A kinetic study of this reaction gave the rate constants in Scheme II. The concentration of IV, the only menthadiene which was not well separated on Carbowax, was determined by gpc on a second packing, silicone rubber, rather than by the uv method mentioned above. VII had a retention time of 16.1 on Carbowax. The retention times in minutes for the major components on silicone rubber at 150° were VII, 10.3; II and *p*-cymene, 10.6; IV and V, 12.5; III, 14.4.

Registry No.—I, 555-10-2; II, 99-86-5; III, 586-63-0; IV, 586-67-4; V, 99-85-4; VI, 586-68-5; VII, 99-83-2.

Acknowledgment.—We thank the Glidden Co. for generous gifts of α- and γ-terpinenes, the Hercules Powder Co. for 3,8-*p*-menthadiene, and the Petroleum Research Fund and National Science Foundation for financial support.