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GAS–LIQUID CHROMATOGRAPHY OF TERPENES

PART II. THE DEHYDRATION PRODUCTS OF α-TERPINEOL[1]

E. VON RUDLOFF

ABSTRACT

The complex mixture of terpenes obtained on dehydrating α-terpineol with aqueous oxalic acid was almost completely separated by gas–liquid chromatography (GLC), using rapeseed oil as a new liquid phase. Terpinolene, dipentene, α- and γ-terpinene, $\Delta^{2,4(8)}$-*p*-menthadiene, and 1,8-cineole were identified as the major reaction products; three minor and seven trace constituents were also detected. One of the minor components was *p*-cymene, one an oxide, and the third an unidentified hydrocarbon. The yield of these components after different reaction times was determined by GLC. The initial dehydration gives terpinolene and dipentene in the ratio of approximately 2:1. Terpinolene is isomerized to α- and γ-terpinene, $\Delta^{2,4(8)}$-*p*-menthadiene, and the unidentified hydrocarbon, but not to dipentene. 1,8-Cineole and the other oxide are formed in a reversible reaction. Dehydration of α-terpineol with several other acidic reagents yielded mixtures of products similar to that obtained with aqueous oxalic acid. With acetic acid or acetic anhydride, however, dipentene was formed preferentially and this reaction appears to proceed via the derived acetate.

INTRODUCTION

The first comprehensive study of the dehydration of α-terpineol (I) with acidic reagents was carried out by Wallach *et al.* (1, 2), who fractionated the steam-volatile reaction products by distillation and identified some of the constituents by conversion to known derivatives. In this manner terpinolene (II), dipentene (III), α-terpinene (IV), γ-terpinene (V), and 1,8-cineole (VI) were obtained by use of aqueous oxalic, sulphuric, or phosphoric acids. Mild conditions favored the formation of terpinolene, whereas longer reaction times gave higher yields of α-terpinene. In the reaction with fused potassium hydrogen sulphate only dipentene was identified. Reaction with acetic acid containing 2% sulphuric acid caused much resinification, whereas that with aqueous formic acid resulted in little dehydration. Flawitzky (3) found that when optically active α-terpineol was heated in a sealed tube with excess acetic anhydride, large amounts of limonene (optically active III) were formed. Baeyer (4) used the reaction with aqueous oxalic acid for the preparation of terpinolene (very short reaction time) and α-terpinene, but it is doubtful whether the pure hydrocarbons can be obtained in this manner (5). Using the same reaction for the preparation of α-terpinene, Alder and Rickert (6) reported the presence of an unidentified diene, which they thought to be possibly a seven-membered ring compound. O'Connor and Goldblatt (7), in a study of the spectral properties of terpene hydrocarbons, reported the preparation of α- and γ-terpinene and $\Delta^{2,4(8)}$-*p*-menthadiene (VII) and $\Delta^{3,8(9)}$-*p*-menthadiene (VIII) by dehydration of α-terpineol

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followed by high-efficiency fractional distillation of the reaction products, but did not give experimental details for these preparations. Terpinolene was obtained by Petrů (8) in the reaction between α-terpineol and phthalic anhydride, also using short reaction times.

The products obtained in the above reactions thus appear to be rather complex mixtures of *p*-menthadienes and 1,8-cineole and it is doubtful whether all constituents have been identified. The mixtures have a boiling range from about 173–183° C, and it is very difficult to obtain pure components by fractional distillation, even when high-efficiency columns are used. It is possible that azeotropes are formed (9), and in 1891 Wallach himself (10) wrote: "experience has shown that it is especially difficult to determine the presence of other terpenes (*p*-menthadienes) when these are admixed with α-terpinene". Obviously, different analytical techniques are required for the analysis of such mixtures and gas–liquid chromatography (GLC) appears to be the ideal tool at the present time.

GAS–LIQUID CHROMATOGRAPHIC SEPARATION

Previously (11), the mixture obtained in the reaction of α-terpineol with aqueous oxalic acid was used by the author as one of the test mixtures in a study of some of the general aspects of the separation of terpenoid compounds by means of GLC. Using 6-ft×1/4-in. diameter columns with Craig polyesters, polyethylene glycol, polyphenyl ether, or squalene as liquid phase, it was shown that the mixture was composed of at least seven compounds, but the degree of separation obtained with these columns was insufficient to allow quantitative calculations or qualitative separations for preparative purposes. The investigation was therefore continued in order to find conditions which would permit a satisfactory analysis of this mixture and thus facilitate the study of the dehydration reaction itself.

There are several ways by which the chromatographic separations can be improved (12). Increasing the column length is limited by the dimensions of the apparatus and eventually by excessive retention times. The use of thinner diameter columns and smaller samples (less than the 1 to 20 μl commonly used) may also lead to increased efficiency, but requires an exceedingly sensitive detector. A third means of improving the degree of separation is by selecting a more efficient liquid phase. Of the liquid phases used for the separation of terpene hydrocarbons as described in the literature of the past year (9, 13–16), none gave better results for the mixture under consideration than were already obtained previously. In Part I (11) it was shown that squalene was a useful liquid phase and a 12-ft column did indeed give almost complete separation. However, this material is subject to fairly rapid deterioration and cannot be used above 100–120° C for any length of time. It may be reasoned that aliphatic olefins of greater stability and larger molecular weight may give equal or better results. Such compounds are readily available in the form of the triglycerides of vegetable oils, with the added advantage that a wide choice in the degree of unsaturation is available. The additional polarity due to the ester groups would be favorable in this instance, since the polyester columns partially separated peak C into two components whilst the squalene column did not (11). Superior separations were, in fact, obtained when rapeseed or olive oil were used as liquid phase. Oils having a higher degree of unsaturation, e.g. linseed or sunflower seed oil, were not as efficient, a finding which indicates that triolein itself may be very suitable as liquid phase. Columns containing rapeseed or olive oil gave reproducible results during 2 to 3 months of continuous or intermittent use at 120° C or lower, provided they were kept under helium or nitrogen at all times.

A 13-ft rapeseed oil column at 90° C was found to give almost complete separation of the components of the above mixture of terpenes with reasonable retention times. This allowed the near quantitative determination (±2 to 3%) of the nine components found to be present in the *p*-menthadiene range. Trace components (less than 0.5–1%) were also present in the camphene – *p*-menthene range (three peaks) and in the range between the *p*-menthadienes and unreacted α-terpineol (four peaks). This column, together with 12-ft polyester and polyethylene glycol and 6-ft polyphenyl ether columns, was used to determine the composition of the steam-volatile products obtained in the dehydration of α-terpineol.

EXPERIMENTAL

The gas-chromatographic equipment and procedures were those described previously (11). All columns were made up with the liquid phase on Chromosorb W (60–80 mesh) in the ratio of 1:6 (by weight). The retention times, measured from the time of injection to the initial emergence of a peak, of various terpenes on the columns used are shown in Table I. The percentage composition of a particular mixture was determined by the area under the curves. Test runs with a synthetic mixture of pure limonene, 1,8-cineole, and α-terpineol gave values within ±1.5% of the weight composition, provided the peaks did not tail. When tailing took place, as with α-terpineol on some columns, the calculated values were low by 2–3%. Duplicate runs on the same column agreed within 0.5%, but differed on different columns by as much as 3%. Preparative runs (10 to 50 mg) were carried out either on the analytical 1/4-in. diameter columns, or on a combination of a 3-ft×3/8-in. diameter silicone grease column used ahead of a 6-ft×1/4-in. polyphenyl ether column. Samples were collected with the detector current off (11), and the purity of the fractions collected was determined by injecting 1- to 3-μl aliquots into the analytical columns. At no time was there any evidence of decomposition or rearrangement of any of the components isolated. Individual components were identified by infrared and ultraviolet spectra, by retention times, and, where possible, by conversion

TABLE I

Retention times* (in minutes) of terpenes on three GLC columns

Compound	Peak No.	13-ft rapeseed oil (90° C, 59 ml He/min)	6-ft polyester (APEG) + 6-ft polyethylene glycol (80° C, 46 ml He/min)	6-ft polyphenyl ether (120 ml He/min)	
				80° C	130° C
α-Pinene	—	43.5	8.6	3.9	—
Camphene	1	55.8	11.4	5.4	1.8
β-Pinene	—	58.1	15.1	6.3	—
Oxide 1	2	77.0	22.0	8.5	2.8
α-Terpinene	3	84.7	23.7	8.9	2.9
1,8-Cineole	4	92.4	31.0	12.7	3.6
Dipentene	5	96.5	27.0	10.4	3.1
p-Cymene	6	104.7	31.0	12.7	3.6
γ-Terpinene	7	109.6	36.2	14.4	4.2
Unidentified	8	134.8	41.7	17.0	4.7
Terpinolene	9	144.8	45.7	18.6	5.1
$\Delta^{2,4(8)}$-*p*-Menthadiene	10	154.7	47.0	18.8	5.1
Unidentified	11	—	—	—	10.4
Unidentified	12	—	—	—	12.2
Unidentified	13	—	—	—	14.2
α-Terpineol	14	—	—	—	16.1
Unidentified	15	—	—	—	18.5
α-Terpinyl acetate	16	—	—	—	30.6

*Measured from the time of injection to initial emergence of the peaks.

to known crystalline derivatives by standard techniques (5, 17) or as indicated. Melting points were determined on a Leitz hot-stage microscope. Infrared and ultraviolet spectra were recorded on Perkin–Elmer Model 21 infrared and Warren Electronic Inc. Spectracord spectrophotometers, respectively, using the film or potassium bromide disk method for the former instrument.

Commercial *dl*-α-terpineol was purified by fractional distillation through a Podbielniak 8-mm diameter spinning band column until GLC analysis showed less than 1% impurities to be present. Thus purified it had n_D^{20} 1.4829 (lit. (17) 1.4813, 1.4832) and gave the phenylurethane, m.p. 112–113° C (lit. (2, 5) m.p. 113° C), in good yield. α-Terpinyl acetate was prepared by refluxing α-terpineol with excess acetic anhydride in the presence of sodium acetate for 4 to 5 hours and was purified by fractional distillation; n_D^{20} 1.4666 (lit. (17) 1.4689).

Small-Scale Dehydration Experiments

α-Terpineol (1.0 g), oxalic acid (hydrate, 4.0 g), and water (5.0 ml) were placed in a 25-ml flask which had two necks with ground-glass joints. A small reflux condenser was attached to one of the joints whilst the other one was tightly stoppered. The mixture was brought to boil and refluxed for the required length of time. The reflux condenser was then changed to the horizontal position and the mixture was steam-distilled for 20 to 30 minutes. The distillate was collected in an ice-cooled flask and, after distillation was complete, the condenser was rinsed with a small amount of ether. The steam-volatile terpenes were recovered by extraction with small amounts of ether, the ethereal solution was washed with bicarbonate solution, then with water, and was dried over anhydrous sodium sulphate. The dried solution was quantitatively transferred to a weighed 25-ml flask having a long neck, and the ether was evaporated on a water bath at 80–90° C. In blank test runs with pure limonene the recovery was 94–98% with 3–5% ether remaining. Calculation of yields and percentage composition were, therefore, based on a 96% recovery. On this basis the yields were 98–100% of theory for reaction up to 8 hours. After that losses due to resinification became marked; for example, after 12 hours, the recovery was only 76% of theory.

In experiments using other dehydrating agents the same procedure was followed. The amounts of reagent used and reaction times are shown in Tables II and III.

Isolation and Identification of Individual Components

Terpinolene (Peak No. 9)

Oxalic acid (hydrate, 160 g) and water (200 ml) were brought to boil in a 500-ml flask which was equipped with a condenser, a dropping funnel, and an inlet tube. Steam was passed through the boiling solution and α-terpineol (40 g) was added dropwise (4), the steam distillate being collected in an ice-cooled flask. After the addition was complete, the mixture was steam-distilled for a further hour. The terpene mixture was recovered as described above. The crude product (38 g) was analyzed by GLC and then fractionally distilled through the spinning band column. The fractions collected were analyzed by GLC. The ninth (3.1 g), b.p. 92.5° at 41 mm Hg pressure, was found to contain better than 90% of peak 9 and had n_D^{20} 1.4914 (lit. (7) 1.4888). The infrared spectrum resembled that reported for terpinolene (7). The ultraviolet absorption was weak and devoid of any characteristic band due to conjugation. The fraction gave in good yield a crystalline bromide, m.p. 112–115° C, recrystallized from ether–methanol, m.p. 115.0–115.8° C (lit. (2) m.p. 116° C). Found: C, 26.48%; H, 3.68%; Br, 70.24%. Calculated for $C_{10}H_{16}Br_4$: C, 26.34%; H, 3.54%; Br, 70.12%. The derived tetrol was prepared as follows: terpinolene (126 mg) was added to an ice-cold solution of tertiary butanol (10 ml) and water (10 ml)

TABLE II

Yield of steam-volatile products in the reaction with α-terpineol (1.00 g)

Reagent	Reagent (ml)	Reaction time (hr)	Total yield (g)	Percentage of individual components in volatile product															
				Peak No.															
				1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Sulphuric acid ($33\frac{1}{3}\%$)	4	1	0.85	—	1.5	28.5	5	9	6	15	1	18.5	15	—	—	—	—	—	—
Phosphoric acid (20%)	4	1	0.96	—	3	7.5	3	7.5	2.5	6	—	11	1.5	2	1.5	4.5	49	—	—
Phosphoric acid (20%)	4	4	0.88	—	4.5	10	2	8	4	8	—	12.5	3	3.5	1.5	5	38	—	—
Acetone–H_2SO_4 (20%)	2+5	1	0.85	—	3	9	4	4	—	7.5	—	8.5	2.5	4	1	6	49.5	—	—
Ethanol–H_2SO_4 (98%)	4+1	1	0.43	16	1	27	3	5	5	13	1	8	6.5	3.5	—	3.5	4	—	—
$KHSO_4$, anh.	(2 g)	1	0.86	—	1	19	4	16	5.5	15.5	—	31	6	—	—	—	—	—	—
$KHSO_4$, anh. (pyro)	(3 g)	1	0.64	11	6	2	75	—	3	—	—	2	—	—	—	—	—	—	—
Phthalic anhydride	(2 g)	1	0.54	6.5	4.5	27	10	8.5	8	13	—	19	1	—	—	—	—	—	—
Acetic anhydride	5	16	1.02	—	1	3	1	32	1.5	3	—	6	—	—	—	—	3.5	—	50
Acetic acid (98%)	5	12	0.94	—	—	0.5	1.5	16	0.5	0.5	—	6	—	—	—	—	69.5	—	5
Acetic acid (50%)	5	2	0.95	—	—	0.5	1	5.5	—	0.5	—	6.5	—	—	0.5	1.5	84	—	—
Acetic acid (50%)	5	6	0.94	—	—	1.5	3	10.5	1	1.5	—	12	—	—	2	3	58.5	—	—
Acetic acid (50%)	5	18	0.75	—	3	10	9	15	4	11	—	29	3	1.5	1.5	2	8	—	—
Acetic acid + H_2SO_4 (5%)	5	2	0.21	18	5	2	37	1	0.5	0.5	—	1	—	—	—	—	—	32	1
Acetic acid + H_2SO_4 (5%)	5	3*	0.34	7.5	12.5	—	24	4	22	—	—	1	0.5	—	—	—	—	26	—
Formic acid (98%)	4	6	0.14	13	8	—	24	—	10	—	—	1.5	—	—	—	3	31.5	5	—

*At room temperature.

TABLE III

Yield of steam-volatile components in the reaction with α-terpinyl acetate (1.00 g)

Reagent	Reagent (ml)	Reaction time (hr)	Total yield (g)	Percentage of individual components in volatile product															
				Peak No.															
				1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Acetic acid (98%)	5	18	0.56	—	—	1.5	0.5	46	—	2.5	—	21.5	—	—	—	—	4	—	29
Acetic acid + H_2SO_4 (5%)	5	3*	0.29	7	9	8	30	3	19	10	—	8	—	—	—	—	—	11	—
Acetic acid + H_2SO_4 (5%)	5	18*	0.18	12	6	2	27	2	18	4	0.5	5	—	—	—	—	—	20	—
Acetic anhydride	5	18	0.98	—	2	3	2	30	1	2.5	—	5	—	—	—	—	—	—	18
Acetic anhydride + H_2SO_4 (5%)	5	18	0.19	2.5	1	0.5	80	—	7	—	—	—	—	—	—	—	—	7.5	—

*At room temperature.

containing potassium hydroxide (0.1 g). To this was added with vigorous stirring and further cooling finely powdered potassium permanganate (0.4 g) in small aliquots. The initial permanganate color changed to black-purple, then to a dark green, and finally to a muddy brown. After complete addition and stirring for a further 10 minutes, the precipitated manganese dioxide was filtered off and the pH of the filtrate was brought to about 7 by leading in carbon dioxide. The solution was evaporated to dryness and extracted with ethanol:2-butanone (1:1 v/v). The mixture of solvents was evaporated and the residual material (192 mg) was taken up in a small volume of ethyl acetate or 2-butanone. The tetrol crystallized very slowly on keeping the solution at 0–2° C for several weeks. Recrystallization from these solvents was also very slow. Whilst the yield of crude tetrol was very good, that of crystalline material, m.p. 148–150° C (lit. (17) m.p. 149–150° C), was poor. Found: C, 58.71%; H, 9.78%. Calculated for $C_{10}H_{20}O_4$: C, 58.80%; H, 9.87%.

An aliquot of fraction 9 was purified by preparative GLC, 10 runs giving 100 mg of almost pure (99.2%) peak 9. It formed the terpinolene bromide in excellent yield and the derived tetrol more readily than the impure fraction.

Dipentene (Peak No. 5)

The first five fractions obtained in the above fractional distillation showed a high content of peak 5. These fractions were combined and redistilled to give a middle fraction containing about 80% of peak 5. This was further purified by preparative GLC, giving 98% pure peak 5. Its infrared spectrum corresponded to that of dipentene (7) and both the derived tetrabromide, m.p. 125.0–126.0° C (lit. (2, 17) m.p. 124–126° C) and tetrol, m.p. 191.5–192° C, were obtained in excellent yield. Found for the bromide: C, 26.52%; H, 3.67%; Br, 70.07% and for the tetrol: C, 58.66%; H, 9.84%.

α-Terpinene (Peak No. 3)

α-Terpineol (40 g) was refluxed with a mixture of oxalic acid (hydrate, 160 g) and water (200 ml) for 12 hours. The mixture was steam-distilled and the crude hydrocarbon mixture (29 g) recovered as above. Fractions 2 to 4 in the fractional distillation at 36 mm had a boiling point of 77–80° C and GLC analysis showed a high content of peak 3, with minor amounts of peaks 2, 4, 5, and 6 being present. Preparative GLC gave peak 3 in 95–96% purity, n_D^{20} 1.4792 (lit. (7) 1.4778). Its infrared and ultraviolet spectra corresponded to those of α-terpinene (7). No solid bromide was obtained nor did the permanganate oxidation give a derived tetrol. However, the acidified oxidation mixture on extraction with 2-butanone gave a good yield of α,δ-dihydroxy-α-methyl-δ-isopropyl adipic acid, m.p. 187–188° C (lit. (17, 18) m.p. 188–189° C). Found: C, 51.43%; H, 8.10%; neutral equivalent 115.5. Calculated for $C_{10}H_{18}O_6$: C, 51.27%; H, 7.75%; neutral equivalent 117.12. The compound melts with loss of water and forms the dilactone, m.p. 71–73° C, readily (18). The terpene gave the crystalline nitrosite, m.p. 155.5–156.5° C (lit. (2, 17) m.p. 155° C), in good yield.

γ-Terpinene (Peak No. 7)

Fractions 5 to 7 in the above fractional distillation had a boiling point of 80.5–84.5° C and showed a high content of peak 7. This was purified by GLC, when practically pure peak 7 was obtained; n_D^{20} 1.4748 (lit. (7) 1.4747). Its infrared spectrum was similar to that of γ-terpinene (7). The derived tetrol, m.p. 235–237° C (lit. (18) m.p. 237° C), was obtained in good yield. Found: C, 58.69%; H, 9.81%. This material also gave a crystalline nitrosochloride, m.p. 110–111° C, in fair yield.

$\Delta^{2,4(8)}$-p-Menthadiene (Peak No. 10)

The last two fractions in the above fractional distillation contained mainly peak 10 as well as some terpinolene (peak 9). Purification by GLC proved difficult, since these two peaks were not completely resolved. However, a small amount of peak 10, n_D^{20} 1.5030 (lit. (7) 1.5030), was obtained about 92–95% pure. The infrared and ultraviolet spectra (λ_{max} 243 mμ) corresponded to those of $\Delta^{2,4(8)}$-*p*-menthadiene (7). A nitrosite, m.p. 152–155° C, was obtained in poor yield. Pines and Eschinazi (19) report a melting point of 153–155° C for the β-nitrosite and melting points of 110°, 140–150° C for the α-nitrosite.

Oxides (Peaks Nos. 2 and 4) and p-Cymene (Peak 6)

An aliquot of the terpenoid mixture obtained in the preparation of terpinolene was oxidized exhaustively with cold, aqueous potassium permanganate. The unoxidized terpenes were recovered by extraction with ether. The dried ethereal solution was carefully evaporated and the residual material was analyzed by GLC. Peaks 2, 4, and 6 only were recorded, the major component being peak 4. The latter was isolated 95–96% pure by preparative GLC, and its infrared spectrum and retention times agreed with those of 1,8-cineole. This fraction formed the resorcinol adduct, m.p. 80–85° C (17), in fair yield. Peak 2 was not obtained pure in sufficient amount to allow positive identification. Its infrared spectrum resembled that of 1,8-cineole.

Peak 6 was also obtained only impure. However, its retention times and the ultraviolet spectrum were similar to those of *p*-cymene. Since only the other two oxides are the impurities present, there is little doubt that peak 6 corresponds to *p*-cymene.

Camphene (Peak No. 1)

The retention times of peak 1 on different columns agreed with those of camphene. α-Terpineol (40 g) was dissolved in 90% ethanol (160 ml) containing sulphuric acid (40 ml) and the mixture was refluxed for 1 hour. The steam-volatile terpenes (22 g) were recovered as before and fractionally distilled. The first fraction, b.p. 64–68° C at 20 mm pressure, contained about 80% of peak 1 and crystallized on seeding with camphene. The crystals were filtered off and recrystallized from ethanol–water, m.p. 47.5–49° C, undepressed in admixture with synthetic camphene.

Peak No. 8

This fraction was obtained only in very small amounts which were insufficient for characterization. Its spectral properties were similar to those of $\Delta^{3,8(9)}$-*p*-menthadiene (7).

RESULTS AND DISCUSSION

The amount of unreacted α-terpineol (I) and the percentage yield of the products formed in the reaction with aqueous oxalic acid after reaction times of 1/2 to 12 hours are shown in Figs. 1(*a*) and 1(*b*). Maximum yields of terpinolene (II), 1,8-cineole (VI), and oxide 1 were obtained within 1 to 3 hours and then diminished rapidly (Fig. 1(*a*)). The maximum yield of dipentene (III) was reached very quickly, decreasing only slowly after 4 to 6 hours. α-Terpinene (IV), γ-terpinene (V), $\Delta^{2,4(8)}$-*p*-menthadiene (VII), *p*-cymene, and peak 8 reached their maximum concentrations only after 8 hours, all but VII decreasing from then on. When pure II was treated under the same conditions for 6 hours, only IV, V, VII, and peak 8 were obtained (in approximately the same ratio); less than 1% of III was recorded. Thus, the four *p*-menthadienes, IV, V, VII, and peak 8, are clearly isomerization products of terpinolene. Pure limonene, under the same conditions, did not yield any isomerization or hydration products but resinified somewhat, explaining the loss of III as the reaction proceeds. Under similar conditions 1,8-cineole (VI) gave a product having the same chromatographic spectrum as was obtained for the reaction product obtained from α-terpineol (I) itself, 2–3% of I also being recorded. It

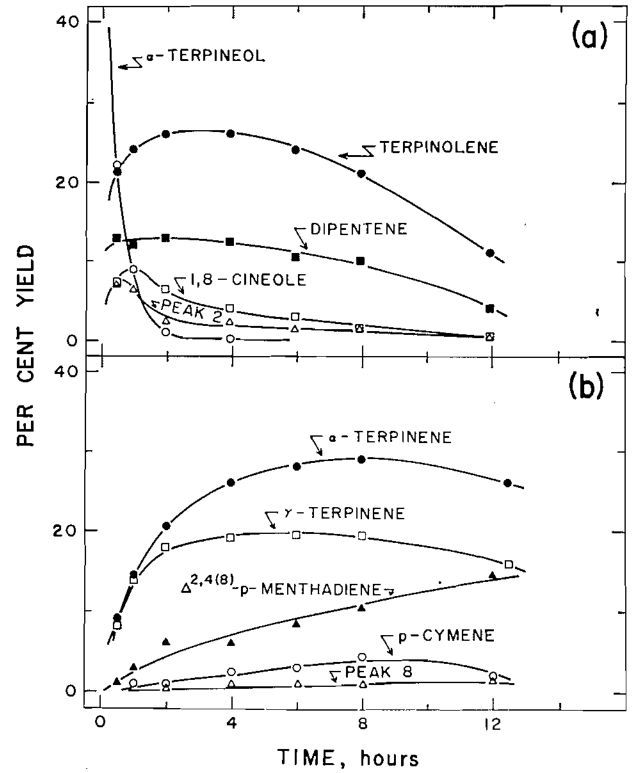

FIG. 1. Yields of individual components in the reaction of α-terpineol with aqueous oxalic acid: (*a*) initial products, (*b*) isomerization products.

can be concluded, therefore, that VI and I are in equilibrium with one another under these conditions. The similarity of the shape of the curves obtained for oxide 1 (peak 2) and VI (Fig. 1(*a*)) suggests that oxide 1 is formed in a similar reversible reaction. This could only be possible if this oxide is 2,8-cineole (dihydropinol), a finding which is further strengthened by the fact that its retention time is in good agreement with that expected for dihydropinol (as deduced from boiling points).

Thus, the reaction of α-terpineol with aqueous oxalic acid appears to proceed as follows:

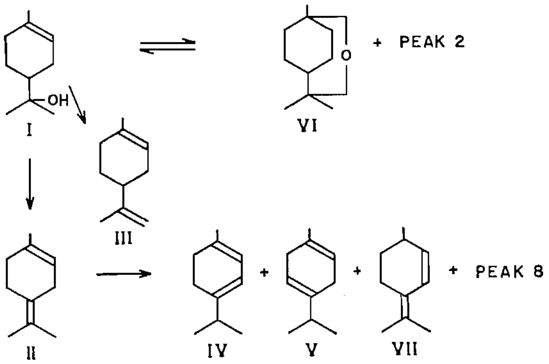

FIG. 2.

Semmler (20) has shown that alcoholic sulphuric acid isomerizes α-terpinene (IV) to V and II. Thus it is possible that these *p*-menthadienes are in a state of equilibrium under acid conditions. The above findings clearly show why it has been impossible to obtain II, IV, and V in a pure state when prepared under acidic reaction conditions.

The preferential formation of terpinolene (maximum yield about twice that of dipentene) is contrary to what would be expected from the postulate put forward by Brown *et al.* (21), according to which the exo-double bond should be formed in smaller amounts than the isopropenyl derivative. These authors quote Flawitzky (3) as having obtained limonene from I by dehydration with alcoholic sulphuric acid and use this as further evidence that tertiary alcohols of this type resist formation of an exo-double bond. Actually, Flawitzky used the alcoholic sulphuric acid to hydrate α-pinene (turpentine) to give I and the latter was then heated in a sealed tube with excess acetic anhydride to give appreciable amounts of limonene besides α-terpinyl acetate. As will be shown below, this reaction appears to be a deacetoxylation rather than a dehydration and proceeds via a different mechanism. Moreover, Brown *et al.* do not refer to the much more comprehensive studies of Wallach (1, 2), which clearly show that the exo-double bond, as in II, may be formed in substantial amounts in the acid-catalyzed dehydration. It is thus doubtful whether the olefin formation from compounds of the α-terpineol type can be included in the generalization put forward by Brown *et al.* Also, the isomerization of terpinolene does not proceed entirely according to this postulate, the exo-isomer VII being a major product besides the two endo-isomers IV and V. In a later communication, Brown (22) points out that their postulate has been misinterpreted by some workers by not considering the stability of the double bonds in cyclohexanes in conjunction with the corresponding cyclopentane derivatives. However, in the first paper, Brown *et al.* discuss the dehydration of α-terpineol and related compounds without any reference to the corresponding cyclopentanols. Recently (23), it has been shown that the whole question of the relative stabilities of methylene cycloalkanes and 1-methyl cycloalkenes is subject to some controversy.

In view of the above discrepancies, the work of Wallach and Flawitzky was repeated and the reaction with other acidic dehydrating agents was also investigated. The steam-volatile reaction products were analyzed by GLC as before and the results obtained are summarized in Table II. In the reaction with aqueous sulphuric and phosphoric acids, the reaction products had the same qualitative chromatographic spectra as that obtained with aqueous oxalic acid, confirming in essence Wallach's findings. When α-terpineol was dissolved in twice its volume of acetone and added dropwise to boiling aqueous sulphuric acid through which steam was passed (24), the steam-volatile product differed little from that obtained in the short-time reaction with aqueous oxalic acid, except that oxide 1 was produced in somewhat larger amounts and two additional peaks (11 and 13) became more prominent. Treatment with 90% ethanol – sulphuric acid (4:1 v/v) also gave a product of similar composition containing, however, a new major compound (peak 1) identified as camphene. Fused anhydrous potassium hydrogen sulphate also gave results similar to those obtained with aqueous oxalic acid, oxide formation being somewhat suppressed. This is contrary to the results Wallach obtained with "sharply dried" potassium hydrogen sulphate (2). Therefore, hydrogen sulphate was fused until fuming became extensive (pyrosulphate formation), and this was used in excess. Under these conditions I reacted to give a high yield of the oxides and camphene, but only traces of III. Thus, Wallach's findings could not be confirmed in this instance. That water is not responsible for any difference in the reaction follows from the results obtained with phthalic anhydride. Here, anhydrous conditions again give a mixture similar to that obtained with aqueous acids.

The dehydration of α-terpineol with 50% aqueous acetic acid proceeds slowly (see Table II) and allows a better study of the early stages of the reaction. II and III are distinctly the first dehydration products and the yield of the former increases much faster than that of the latter as the reaction proceeds. Oxide formation and isomerization of II is slow, making the reaction well suited for the preparation of II and III, especially so since these two *p*-menthadienes can be separated by fractional distillation. The different results obtained with glacial acetic acid (or acetic anhydride) are noteworthy (see below).

Mosher (25) proposed for the acid-catalyzed isomerization of α-pinene (X) to the *p*-menthadienes rearrangement to the intermediate carbonium ion XI. Loss of a proton leads to terpinolene (II) and dipentene (III), and (via the carbonium ion XII) to α-terpinene (IV) and γ-terpinene (V) (Fig. 3). This mixture of *p*-menthadienes is very similar to that obtained in the acid-catalyzed dehydration of α-terpineol. Thus, it is likely that α-terpineol, in the protonated form (XIII), loses the elements of water to give the same intermediate carbonium ion XI. The present findings that terpinolene isomerizes readily to IV, V, and VII, but not to III, suggest that the ion XI rearranges rapidly and irreversibly to ion XII. The formation of VII, however, demands the presence of another intermediate ion. Cyclization of the protonated alcohol (XIII) and loss of a proton would lead to 1,8-cineole (VI) in a reversible reaction.

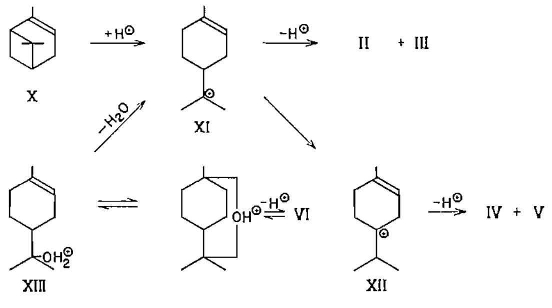

FIG. 3.

Refluxing I with excess acetic anhydride for 16 hours gave a yield of 50% α-terpinyl acetate, 32% III, and small amounts of *p*-menthadienes and oxides (see Table II), confirming, in essence, the findings of Flawitzky (3). The reaction with glacial acetic acid is similar, though the amount of α-terpineol which had reacted after 12 hours was only 30%. Since, in this reaction, I may be converted to the acetate first and this, on loss of the elements of acetic acid, could give III as the main elimination product, α-terpinyl acetate was treated in the same manner. Appreciable amounts of III, and smaller amounts of the other *p*-menthadienes, were formed (see Table III). Thus, it is possible that the preferential formation of III is due to deacetoxylation of the acetate rather than the dehydration of the parent alcohol.

Recently, Roček (26) has studied the kinetics of the dehydration of 1-methyl cyclohexanol as well as the deacetoxylation of the derived acetate, using acetic acid containing small amounts of sulphuric acid at room temperature. From the data obtained Roček concluded that both the dehydration and the deacetoxylation proceeds via the same intermediate carbonium ion and the rate-controlling step is given as the elimination of water from the protonated alcohol, or of acetic acid from the protonated ester. In the reaction of α-terpineol and its acetate with this reagent at room temperature or under reflux, appreciable amounts of camphene and the oxides, but only small amounts of the *p*-menthadienes, were obtained (see Tables II and III). The yield of steam-volatile products dropped markedly and a new peak (No. 15) in the α-terpineol range was recorded. Thus, with this reagent a third type of reaction was encountered in which the normal dehydration (or deacetoxylation) products did not survive the reaction, if these were formed at all. Similar results were also obtained when formic acid was used as dehydrating agent (Table II). Since this was no longer a normal dehydration reaction, it was not further investigated.

The presence of small amounts of *p*-cymene (peak No. 6) in most reaction products deserves some comment. Its formation in the acid-catalyzed dehydration of α-terpineol was already suspected by Wallach and Kerkhoff (2). Since the reaction conditions are not conducive to dehydrogenation, disproportionation of one or more of the *p*-menthadienes to *p*-cymene and *p*-menthenes may take place. This would account for the presence of the trace components in the *p*-menthene range.

CONCLUSIONS

The dehydration of α-terpineol with acidic reagents can occur in two different ways: (*a*) With aqueous acids, anhydrous potassium hydrogen sulphate, or phthalic anhydride, terpinolene is the major reaction product in the early stages of the reaction. About half as much dipentene and smaller amounts of 1,8-cineole and a second oxide, possibly 2,8-cineole, are also formed. As the reaction proceeds, terpinolene isomerizes to give mainly α-terpinene, somewhat less γ-terpinene and $\Delta^{2,4(8)}$-*p*-menthadiene, and a small amount of an unidentified terpene. Drastic conditions, or long reaction times, tend to cause resinification. The oxides are in equilibrium with α-terpineol and give the same reaction products on prolonged treatment. (*b*) With acetate-forming reagents, dipentene is formed preferentially. Apparently the acetate is an intermediate and subsequent loss of the elements of acetic acid favors the production of this *p*-menthadiene.

The present findings show that by proper choice of conditions the preferential formation of terpinolene, dipentene, α- and γ-terpinene, or $\Delta^{2,4(8)}$-*p*-menthadiene can be achieved. However, it is impossible to synthesize by this means any one of these *p*-menthadienes without concomitant formation of smaller amounts of several isomers. Only in very favorable instances can such mixtures be separated completely by fractional distillation. If very pure specimens of these *p*-menthadienes are required other sources must be sought, or the products obtained in the above reactions can be fractionated on a 0.01- to 0.1-g scale by preparative gas–liquid chromatography.

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