Oxidation of Terpene Compounds with tert-Butyl Chromate. VI.
Oxidation of Terpinolene

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On oxidation of terpene hydrocarbons with *tert*-butyl chromate[1-5] it was recognized that the active methylene group adjacent to a double bond in a molecule was mainly oxidized to α, β-unsaturated carbonyl. Among diene terpene hydrocarbons, only D-limonene has been researched and the oxidation products were rather more complicated than in the cases of α-pinene[1,5], D-carvomenthene[2,5] and D, L-α-terpinyl acetate[4]; D-limonene was oxidized to D, L-carvone, D-isopiperitenone, piperitenone and carvacrol. This report is concerned with the oxidation of terpinolene (I) which has an active methylene group at $C_{(3)}$ position situated between two double bonds.

Results and Discussion

The oxidizing agent was prepared in a manner similar to that in the previous reports[3,4] from chromic anhydride and *tert*-butyl alcohol, glacial acetic acid and acetic anhydride being added.

Experiment 1.—The mole ratio of sample to chromic anhydride was 1 to 2. After the reaction was carried out at 10°C during 15 hr., the reaction mixture which resulted was treated with water and oxalic acid under ice-cooling to decompose the excess of the oxidant. Then the mixture was separated into a benzene and an aqueous layer. From the benzene layer was obtained a neutral brown oil which was fractionated and the constituents of which were identified.

Experiment 2.—The mole ratio of sample to chromic anhydride was 1 to 2, and the reaction was carried out at 10°C during 45 hr. The reaction mixture was treated in the same manner as in Experiment 1.

Experiment 3. — In this experiment glacial acetic acid and acetic anhydride were excluded from the oxidant. This is not the case in Experiments 1 and 2. When the oxidant was added to the sample solution at 0°C during 2 hr., the reaction was stopped and the reaction products were examined.

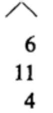
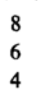
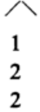
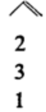
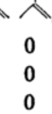
In the case of each of the above three experiments, piperitenone (II), 8-hydroxy-*p*-cymene (III), *p*-cymene (IV) and α, p-dimethylstyrene (V) were identified as constituents of the reaction products, and an unidentified carbonyl compound was also recognized.

Experiment 4.—*p*-Cymene was treated with *tert*-butyl chromate under the same condition as in Experiment 1, and small amounts of 8-hydroxy-*p*-cymene and *p*-methylacetophenone were identified as reaction products.

The above results are summarized in Table I.

In the oxidation of terpinolene with *tert*-butyl chromate, the point different from the oxidation of the other cyclic terpene compounds already reported is the aromatization of the hydroaromatic ring by dehydrogenation in addition to the oxidation of the active methylene group adjacent to a double bond. On oxidation of D-limonene and D, L-α-terpineol it has been clarified that among two active methylene

TABLE I

No. of Experiment	Sample	Reaction condition					Reaction product wt. % to sample				
		Sample : CrO_3 mole ratio	CH_3COOH wt. % to sample	$(CH_3CO)_2O$ wt. % to sample	Temp. °C	Time hr.					
1	Terpinolene	1 : 2	17	17	10	15	6	8	1	2	0
2	Terpinolene	1 : 2	50	50	10	45	11	6	2	3	0
3	Terpinolene	1 : 2	0	0	0	2	4	4	2	1	0
4	*p*-Cymene	1 : 2	17	17	25	15	0	0.8	—	0	0.2

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[1] T. Matsuura and K. Fujita, *J. Sci. Hiroshima Univ.*, **A16**, 173 (1952).

[2] K. Fujita and T. Matsuura, ibid., **18**, 455 (1955).

[3] K. Fujita, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **78**, 1112 (1957).

[4] T. Matsuura, T. Suga and K. Suga, ibid., **78**, 1122 (1957).

[5] G. Dupont, R. Dulou and O. Mondou, *Bull. soc. chim. France*, **1953**, 60.

groups adjacent to a double bond in the carbon ring the $C_{(6)}$ active methylene is predominantly oxidized in comparison with the $C_{(3)}$ active methylene. In the case of terpinolene, however, it was found that the oxidation of the $C_{(3)}$ active methylene has proceeded in exclusion of the oxidation of the $C_{(6)}$ active methylene, owing to the existence of a double bond between $C_{(4)}$ and $C_{(8)}$ atoms.

The formation of piperitenone II from terpinolene I by the oxidation of the $C_{(3)}$ active methylene is an analogous reaction to the formation of α,β-unsaturated ketone from cyclic terpene compounds such as α-pinene, limonene, carvomenthene and α-terpinyl acetate reported already. However the formation of 8-hydroxy-*p*-cymene III and *p*-cymene IV from terpinolene is due to oxidation of the $C_{(8)}$ position and dehydrogenation, which was found for the first time in the oxidation of terpinolene. An exocyclic double bond between $C_{(4)}$ and $C_{(8)}$ carbons in terpinolene seems to migrate into the carbon ring in the presence of acid to form α-terpinene[6]. It has been reported that menthene-4(8) is rearranged into menthene-3 by the action of dilute sulfuric acid solution[7]. Thus it may be considered that an exocyclic double bond of terpinolene molecule migrates into the ring to form a conjugated diene (α-terpinene) by acid reagent. Although α-terpinene was not found in the reaction products, it has reacted easily with *tert*-butyl chromate to produce a large amount of *p*-cymene[*1]. Therefore *p*-cymene in the reaction products is considered to be produced by dehydrogenation of α-terpinene which results from isomerization of terpinolene.

It would seem that 8-hydroxy-*p*-cymene has been formed from *p*-cymene by the oxidation of an active methine group at $C_{(8)}$. But this is not the case, because the result of the oxidation of *p*-cymene with *tert*-butyl chromate in the same conditions as in Experiment 1 (sample, terpinolene) has shown that *p*-cymene is virtually stable against *tert*-butyl chromate, giving only a small amount (1% to the sample) of 8-hydroxy-*p*-cymene and of *p*-methylacetophenone.

Accordingly it can not be considered that 8-hydroxy-*p*-cymene is formed via *p*-cymene.

It has been recognized that on distillation of 8-hydroxy-*p*-cymene in presence of acid (a small amount) α,p-dimethylstyrene is produced by dehydration[8], so α,p-dimethylstyrene is considered to be a secondary product formed by dehydration during the oxidation reaction or distillation of the reaction products.

On the basis of the above results and discussion the reaction course is summarized as shown in Fig. 1.

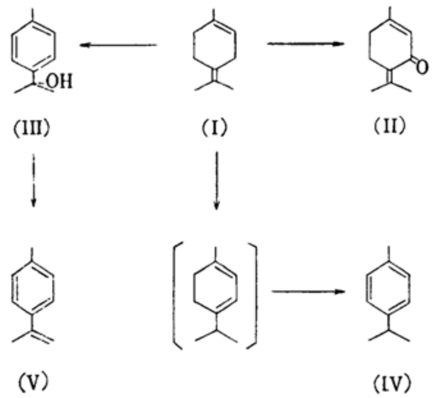

Fig. 1

Experimental

1. Oxidation of Terpinolene

1.1. Preparation of Terpinolene

Terpinolene (b. p.$_{21}$ 78.0°C, n_D^{25} 1.4859, d_4^{25} 0.8577, tetrabromide m. p. 116°C) was prepared, according to Charalton and Day's method[9] by treating α-pinene (b. p.$_{28}$ 58~59°C, n_D^{25} 1.4628, d_4^{25} 0.8548, $[\alpha]_D$ +40.62°) with 50% alcoholic solution of sulfuric acid, and by rectifying the crude product.

1.2. Oxidation and Identification of Reaction Products

1.2.1. Experiment 1

tert-Butyl chromate was prepared by adding 88 g. of chromic anhydride in small portions to 163 g. of *tert*-butyl alcohol under ice-cooling, diluting the resultant with 650 g. of benzene, and drying the resulting benzene solution on anhydrous sodium sulfate. To the solution were added 10 g. of glacial acetic acid and 10 g. of acetic anhydride just prior to the oxidation. This oxidant was added dropwise with stirring at 10°C to 60 g. of terpinolene in 60 g. of dry benzene during 1 hr., and the mixture was left to stand at 10°C for 15 hr. Then 700 cc. of water and 160 g. of oxalic acid were added under ice-cooling to the viscous reaction mixture and shaken to decompose the excess of the oxidant. The mixture was separated into a benzene layer and an aqueous one, and the latter was extracted with benzene. The combined benzene solution was washed with 10% aqueous solution of sodium carbonate and with water successively, and dried (anhydrous sodium sulfate). After removal of the solvent, 28.1 g. of a neutral brown oil was obtained.

The aqueous solution was neutralized with a sodium carbonate solution and extracted with chloroform. From the extract 7.9 g. of a dark-brown viscous oil was obtained. The sodium carbonate solution was acidified with 10% sulfuric acid solution and

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[6] O. Wallach, *Ann.*, **275**, 103 (1893).

[7] O. Wallach, *Ber.*, **39**, 2504 (1906); *Ann.*, **360**, 70 (1908).

[*1] T. Matsuura, unpublished.

[8] J. N. Borglin, D. A. Lister, E. J. Lorand and J. E. Reese, *J. Am. Chem. Soc.*, **72**, 4591 (1950).

[9] R. W. Charalton and A. R. Day, *Ind. Eng. Chem.*, **29**, 92 (1937).

extracted with chloroform, giving 18.9 g. of a dark-brown viscous oil. As neither of the above dark-brown viscous oils could be distilled under reduced pressure and also could not be crystallized, they seemed to be polymer, the further test of which was not undertaken.

The neutral oil was fractionated, giving the physical properties of Fig. 2, and then the constituents of fractions were identified.

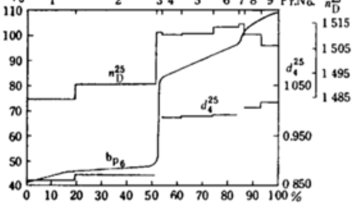

Fig. 2

(i) *p*-Cymene and α,p-Dimethylstyrene. Fractions 1 and 2 gave a tetrabromide of m. p. 116°C which was identified as terpinolene tetrabromide by admixture with an authentic sample. On the other hand, the ultraviolet absorption spectra of these two fractions showed the absorption maxima at 247 and 273 mμ which coincide with those of α,p-dimethylstyrene (247 mμ)[10] and *p*-cymene (273 mμ)[11].

Ozone was passed in a solution of 5 g. of the combined fractions 1 and 2 dissolved in 20 cc. of ethyl acetate-glacial acetic acid (6 : 2) under ice-cooling. The ozonized solution, after the solvent having been driven off under reduced pressure and 50 cc. of water being added, was steam-distilled to decompose the ozonide. The distillate was extracted with ether, and the ether extract was washed with 10% aqueous sodium carbonate solution and dried. From the ether extract thus treated, 2.1 g. of an oily product was obtained, after the solvent was driven off. The oily product was eluted through a silica gel column with petroleum benzine and ether successively, and the following two fractions, A and B, were obtained.

Fraction	Yield (g.)	λ_{max} (mμ) (absorptivity a*2)
A	1.20	254(1.42), 260(2.35), 265(2.86), 267(2.95), 273(3.34)
B	0.67	252(68.90)

Fraction A (b. p.$_{15}$ 62~64°C, n_D^{25} 1.4795, d_4^{25} 0.8552) was confirmed to be *p*-cymene from its ultraviolet spectrum. Ultraviolet absorption spectrum of fraction B coincided with that of *p*-methylacetophenone (λ_{max} ; 252 mμ)[12]. 2, 4-Dinitrophenylhydrazone m. p. 256.5~257.0°C and semicarbazone m. p. 205~206°C of fraction B were identified to be those of *p*-methylacetophenone by mixing with authentic samples. The formation of *p*-methylacetophenone by ozonolysis of fractions 1 and 2 shows the existence of α,p-dimethylstyrene. From the result of ozonolysis the amounts of *p*-cymene and α,p-dimethylstyrene in fractions 1 and 2 (unified) were calculated to be 24% and 13% respectively.

(ii) 8-Hydroxy-*p*-cymene. Infrared absorption spectra of fractions 4 and 5 showed a hydroxy band in a region of 3400 cm^{-1}, and from these fractions a phenylurethane of m. p. 118~119°C was obtained, which was identified as that of 8-hydroxy-*p*-cymene*3 by the mixed melting point determination.

Three grams of the combined fractions 4 and 5 was heated with 3 g. of powdered potassium hydrogen sulfate at 190~200°C and distilled. The distillate was extracted with petroleum benzine, and the extract was washed with 10% aqueous sodium carbonate solution, dried and eluted through a silica gel column. From the extract thus treated 0.72 g. of an oily product was obtained after the solvent was driven off. Its infrared spectrum showed absorption bands at 1630 cm^{-1} (conjugated double bond), 883 cm^{-1} (end methylene) and 816 cm^{-1} (aromatic *para* substitution), and its ultraviolet spectrum had an absorption maximum at 246 mμ. Thus the dehydration product was confirmed to be α,p-dimethylstyrene, and therefore the original alcohol to be 8-hydroxy-*p*-cymene.

(iii) Piperitenone. Ultraviolet absorption spectra of fractions 6 and 7 showed λ_{max} 242 mμ (ε : 10140) and 276 mμ (ε : 7640) which coincide with absorption maxima of piperitenone, 242 mμ (ε : 12500) and 278 mμ (ε : 7920)[13]. 2, 4-Dinitrophenylhydrazone of the above fractions melted at 183.5~184°C. This was identified as that of piperitenone by mixing with a known sample.

Fractions 8 and 9 were unified and eluted through a silica gel—plaster of paris (4 : 1) column with ether-petroleum benzine (3 : 7), and it was verified that 37% of the above unified two fractions was piperitenone.

(iv) Unidentified Carbonyl Compound. By column chromatography of fractions 8 and 9 mentioned above, a carbonyl compound was separated, which gave a 2, 4-dinitrophenylhydrazone of m. p. 216.5~217°C and ultraviolet absorption spectrum which had λ_{max} 244 mμ and 257 mμ, but it was not identified.

1.2.2. Experiment 2

tert-Butyl chromate solution was prepared, in the same way as in Experiment 1, from chromic anhydride (147 g.), *tert*-butyl alcohol (274 g.), benzene (1000 g.), glacial acetic acid (50 g.), and acetic anhydride (50 g.). This oxidant was added dropwise to 100 g. of terpinolene in 100 g. of dry benzene, and the reaction was carried out for 45 hr. at 10°C. Then the reaction mixture was treated as in Experiment 1, and 56.1 g. of a neutral oil was obtained. Piperitenone, 8-hydroxy-*p*-cymene, α,p-dimethylstyrene and *p*-cymene were found in the neutral oil*4 (cf. Table I).

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[10] M. J. Murray and W. S. Gallaway, *J. Am. Chem. Soc.*, **70**, 3867 (1948).

[11] R. T. O'Connor and L. A. Goldblatt, *Anal. Chem.*, **26**, 1726 (1954).

[12] J. Tanaka, S. Nagakura and M. Kobayashi, *J. Chem. Phys.*, **24**, 311 (1956).

[*2] The concentration is in g./l. and the cell length in cm.

[*3] 8-Hydroxy-*p*-cymene was prepared from *p*-bromotoluene and acetone by Grignard reaction (V. N. Ipatieff, H. Pines and R. C. Obberg, *J. Am. Chem. Soc.*, **70**, 2123 (1948)).

[13] R. Y. Naves, *Bull. soc. chim. France*, **1951**, 370.

[*4] Identification of the constituents in the neutral oils in 1. 2. 2 and 1. 2. 3 was carried out by the similar methods as in 1. 2. 1.

1.2.3. Experiment 3

tert-Butyl chromate solution was prepared from the same amounts of chromic anhydride, *tert*-butyl alcohol and benzene as in Experiment 1, but glacial acetic acid and acetic anhydride were excluded. Sixty grams of terpinolene in 60 g. of dry benzene was stirred with the above oxidant for 2 hr. at 0°C. Then the reaction mixture was treated as in Experiment 1, and 28.5 g. of a neutral oil was obtained. The same compounds as in Experiment 2 were confirmed to exist in the neutral oil (cf. Table I).

2. Oxidation of *p*-Cymene (Experiment 4)

To 60 g. of *p*-cymene (b.p.$_{22}$ 70.5°C, n_D^{25} 1.4860, d_4^{25} 0.8519) dissolved in benzene (60 g.) was added dropwise an oxidant solution consisting of chromic anhydride (89 g.), *tert*-butyl alcohol (166 g.), benzene (650 g.), glacial acetic acid (10 g.) and acetic anhydride (10 g.), and the reaction was carried out for 15 hr. at 25°C. Then the reaction mixture, after being treated as in the preceding experiments, gave 56.4 g. of a neutral oil which was fractionated as follows: fraction 1 (53 g., b.p.$_{25}$ 73~74°C, n_D^{25} 1.4876, d_4^{25} 0.8645), fraction 2 (0.6 g., b.p.$_4$ 46~70°C, n_D^{25} 1.5017) and residue (0.4 g.).

It was confirmed that fraction 1 was unchanged *p*-cymene by its ultraviolet spectrum measurement. Fraction 2 gave 2,4-dinitrophenylhydrazone m.p. 256°C of *p*-methylacetophenone and phenylurethane m. p. 120°C of 8-hydroxy-*p*-cymene, both of which were identified by mixing with authentic samples. An ultraviolet absorption spectrum of fraction 2 have λ_{max} 250 mμ (*a*: 20) which agrees virtually with λ_{max} 252 mμ (*a*: 117) of *p*-methylacetophenone.

Summary

Oxidation of terpinolene with *tert*-butyl chromate was carried out, and piperitenone, 8-hydroxy-*p*-cymene, *p*-cymene and α, *p*-dimethylstyrene were obtained as reaction products. In this oxidation it was found that the active methylene group at $C_{(3)}$ position in terpinolene was oxidized to a carbonyl group, and that the aromatization of carbon ring in terpinolene molecule took place. This could not be recognized in the oxidation of terpene compounds already reported by this oxidant.

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