

THE CHEMISTRY OF TERPENES—I

THE EFFECT OF HYDROGEN ION CONCENTRATION AND OXYGEN UPON THE ACID CATALYSED CYCLIZATION OF CITRAL

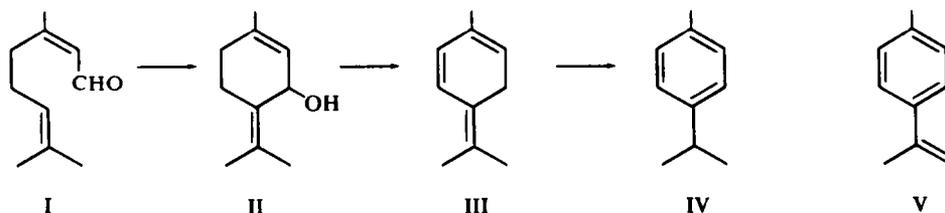
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Abstract—The acid catalysed cyclization of citral gives *p*-cymene and *p*- α -dimethylstyrene. The ratio of the arenes is dependent both upon the pH of the reaction medium and upon the presence or complete absence of oxygen. At pH 1.8 in the presence of oxygen the yield of the styrene is at a maximum to the almost complete exclusion of *p*-cymene.

SINCE Semmler's original observations in 1891 of the cyclization of citral (I) in the presence of potassium hydrogen sulphate,¹ the reaction has been studied by many workers using a variety of acidic catalysts and reaction temperatures. Under all conditions a single stable end product has been isolated and shown to be *p*-cymene (IV). The isolation of piperitenol (II)^{2,3} and of *p*-mentha-2,4(8), 6-triene (III)⁴ and confirmation of their ready conversion into *p*-cymene under acidic conditions has led to the formulation of the reaction route (I) \rightarrow (IV). This route is widely accepted and is quoted by all general organic textbooks and specialized texts on the chemistry of terpenes.⁵ Further investigations^{6,7} of the mechanism have been based upon this reaction route and have shown that the initial step involves a first order reaction with respect to the concentration of the citral and to be directly dependent upon the pH of the reaction medium. This is consistent with cyclization via a Prins type reaction involving the Δ^6 double bond and the protonated carbonyl group.



Although the reaction scheme (I \rightarrow IV) adequately rationalizes the earlier work in which classical analytical methods were used, by the use of gas-liquid chromatography we have now established that the reaction is considerably more complex. Not only does a change in the pH of the reaction medium alter the rate of the initial cyclization step but it also results indirectly in the formation of end products other than *p*-cymene.

We have also found that under an atmosphere of oxygen at pH 1.8 the predominant stable end product of the cyclization of citral is *p*- α -dimethylstyrene (V).

RESULTS AND DISCUSSION

Comparative reactions in the presence and absence of oxygen. Treatment of citral with dilute aqueous acid of pH 1.8 gave 16 detectable products (Tables 1 and 2). The presence of 14 of these compounds was found to be independent of the atmosphere above the reaction mixture and at least nine appeared to be intermediates.

Contrary to earlier reports, two major end products were detected after the reaction had been allowed to proceed to completion, i.e. when no further change in the composition of the reaction mixture could be detected. From a comparison of their spectral and gas chromatographic retention data with those of authentic samples, these compounds were shown to be *p*-cymene and *p*- α -dimethylstyrene. Unambiguous identifications of other reaction intermediates and products were made possible by the isolation of the compounds by gas chromatographic separation. Where the concentrations of the components were extremely low, tentative identification has been made on the basis of gas chromatographic retention and mass spectral data.

Loori and Cover⁹ have suggested that *p*- α -dimethylstyrene, isolated during the distillation of orange and lime oils,^{9,10} is an artefact from citral resulting from an acid catalysed cyclization followed by disproportionation of the intermediate *p*-menthatriene. The results of our experiments carried out in the complete absence of oxygen essentially support these earlier investigations. However, it is significant that, although the concentration of *p*-cymene was considerably higher than that of the styrene when the reaction was carried out in the absence of oxygen, the reverse was true when the reaction was allowed to proceed under an atmosphere of oxygen (Fig 1) and it suggests the possibility of a second mode for the formation of *p*- α -dimethylstyrene.

The preferential formation of the styrene (V) under certain reaction conditions is not due to dehydrogenation of *p*-cymene. Such a reaction requires vigorous conditions¹¹ and we have shown that *p*-cymene is recovered unchanged from acidic media under conditions encountered during the formation of *p*- α -dimethylstyrene from citral.¹² In order to rationalize the formation of the styrene in the complete absence of oxygen we are therefore led to accept Loori and Cover's suggestion of a hydrogen transfer reaction involving a *p*-menthatriene, which by analogy with earlier work,⁴ they designated as *p*-mentha-2,4(8), 6 triene (III). Although we detected only two *p*-menthatrienes with any degree of certainty, we suggest that under acidic conditions it is highly probable that four isomeric *p*-menthatrienes (III, VI-VIII), obtained by loss of a molecule of water from piperitenol (II) or isopiperitenol (IX), are in dynamic equilibrium. Disproportionation of *p*-mentha-1,3,8-triene (VI) and *p*-mentha-1,5,8-triene (VII) would lead directly to *p*- α -dimethylstyrene with simultaneous formation of α -phellandrene (X) and α -terpinene (XI), both of which were detected (Reaction Scheme 1). Hydrogen transfer involving *p*-mentha-2,4(8), 6-triene (III) could also lead to the formation of α -phellandrene. Contrary to previous reports,¹¹ we found no evidence for the formation of limonene (*p*-mentha-1,8-diene). On the basis of its mol wt and retention index the compound having a retention almost identical to that of limonene was thought to be a cyclic terpenoid ether. The

TABLE 1. REACTION PRODUCTS FROM THE ACID CATALYSED CYCLIZATION OF CITRAL AT pH 1.8 UNDER NITROGEN.*

Peak No.	Kovats Retention Index ^b	Compound	M.W. ^c	% Yields							
				2	3	4	6	8	16	22	
1	1119		---	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2	1157		---	0.0	0.0	0.0	0.5	0.6	0.5	0.6	0.5
3	1228	α -phellandrene	136	0.0	0.0	0.0	1.3	2.0	0.7	0.9	0.7
4	1248		152	2.3	3.4	4.6	1.0	0.9	0.7	0.7	0.0
5	1262		---	1.8	2.1	2.0	1.3	0.9	1.6	0.5	0.7
6	1294	a menthadiene (?)	136	1.4	1.5	2.3	1.2	1.4	0.9	0.7	0.7
7	1324	<i>p</i> -cymene	134	2.9	14.0	17.1	54.3	63.5	72.2	81.0	81.0
8	1438	a menthatriene (?)	134	0.0	0.9	1.9	0.7	0.1	0.0	0.0	0.0
9	1480	<i>p</i> -mentha-1(7),2,4(8)-triene	134	0.9	1.0	2.1	1.4	0.0	0.0	0.0	0.0
10	1498	<i>p</i> - α -dimethylstyrene	132	1.4	4.5	5.6	12.0	14.7	15.8	16.6	16.6
11	1560	linalool	154	3.5	4.4	3.8	2.1	1.8	1.6	0.0	0.0
12	1726		152	0.0	0.0	2.4	3.2	3.0	2.8	0.0	0.0
13	1749	piperitenol	152	20.0	25.1	29.1	9.2	6.5	1.4	0.0	0.0
14	1769		---	3.6	4.6	1.2	0.0	0.0	0.0	0.0	0.0
15	1796	isopiperitenol	152	10.3	9.1	8.7	4.0	0.0	0.0	0.0	0.0
16	1835	a terpenoid alcohol	152	0.8	1.9	3.0	1.2	0.0	0.0	0.0	0.0
17	1866	<i>p</i> -8-cymenol	150	1.4	4.4	5.4	3.1	2.0	0.5	0.0	0.0
<i>Unreacted Citral</i>											
	1742	citral <i>a</i>		7.7	5.1	1.4	0.0	0.0	0.0	0.0	0.0
	1783	citral <i>b</i>		42.0	18.0	9.6	3.5	2.6	0.0	0.0	0.0

* % yields were calculated using a 'Disc' integrator. Peak numbers correspond to the order in which the products were eluted. Assignments were made on the basis of spectroscopic evidence and by comparison with authentic compounds.

^b E. Kovats, *Helv. Chim. Acta*, 41, 1915 (1958). Measured at 120° on a LAC 2R-446 column.

^c Molecular weights were determined mass spectrometrically using an 'on-line' GLC-MS unit.

TABLE 2. REACTION PRODUCTS FROM THE ACID CATALYSED CYCLIZATION OF CITRAL AT pH 1.8 UNDER OXYGEN.

Peak No.	Kovats Retention Index	Compound	M.W.	1	2	3	5	6	8	16	22
			% Yields								
			Reaction Time (hours)								
1	1119		—	0.0	1.1	1.6	1.9	4.5	7.2	5.1	2.4
2	1157		—	0.0	0.5	0.6	1.0	2.9	3.0	3.1	2.1
3	1228	α -phellandrene	136	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
4	1248		152	1.1	1.8	1.9	3.8	4.5	3.1	2.8	1.9
5	1262		—	1.0	1.3	1.5	4.7	3.8	4.1	3.6	2.2
6	1294	α methandiene (?)	136	0.9	1.9	2.9	4.6	5.7	5.4	4.5	3.9
7	1324	<i>p</i> -cymene	134	0.5	2.1	2.3	5.6	5.7	6.0	5.9	7.7
8	1438	α menthatriene (?)	134	0.0	0.5	1.1	0.3	0.0	0.0	0.0	0.0
9	1480	<i>p</i> -mentha-(1(7),2,4(8))-triene	134	0.5	1.0	1.2	1.0	0.0	0.0	0.0	0.0
10	1498	<i>p</i> - α -dimethylstyrene	132	0.0	2.0	12.5	35.8	58.1	66.9	73.0	79.0
11	1560	linalool	154	1.8	2.7	3.1	4.1	0.0	0.0	0.0	0.0
12	1726		152	0.0	1.8	2.9	3.7	1.0	0.0	0.0	0.0
13	1749	piperitenol	152	10.1	12.7	21.0	3.1	0.0	0.0	0.0	0.0
14	1769		—	0.0	3.4	6.4	1.3	0.0	0.0	0.0	0.0
15	1796	isopiperitenol	152	3.7	2.6	2.4	1.8	0.0	0.0	0.0	0.0
16	1835	α terpenoid alcohol	152	0.0	1.5	1.7	3.3	0.9	0.0	0.0	0.0
17	1866	<i>p</i> -8-cymenol	150	0.0	3.9	8.0	14.5	11.2	4.0	2.0	0.8
Unreacted Citral											
	1742	citral <i>a</i>	154	15.4	9.7	7.0	2.0	0.0	0.0	0.0	0.0
	1783	citral <i>b</i>	65.0	49.5	22.0	7.5	1.7	0.3	0.0	0.0	0.0

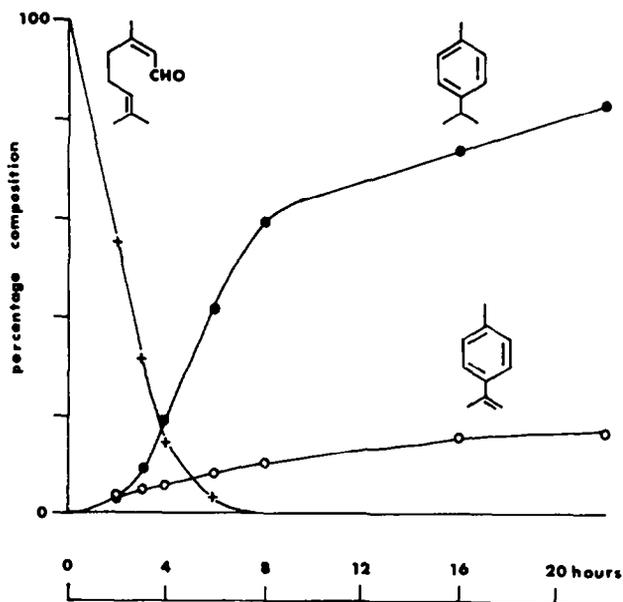


FIG. 1a. Arene formation at pH 1.8 under nitrogen.

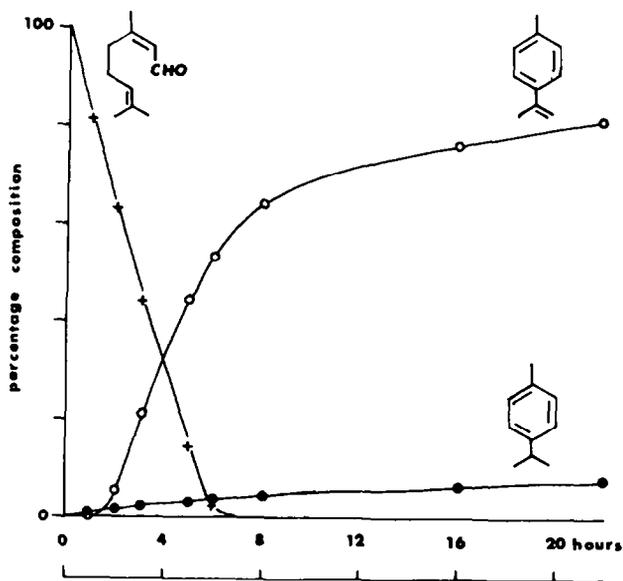
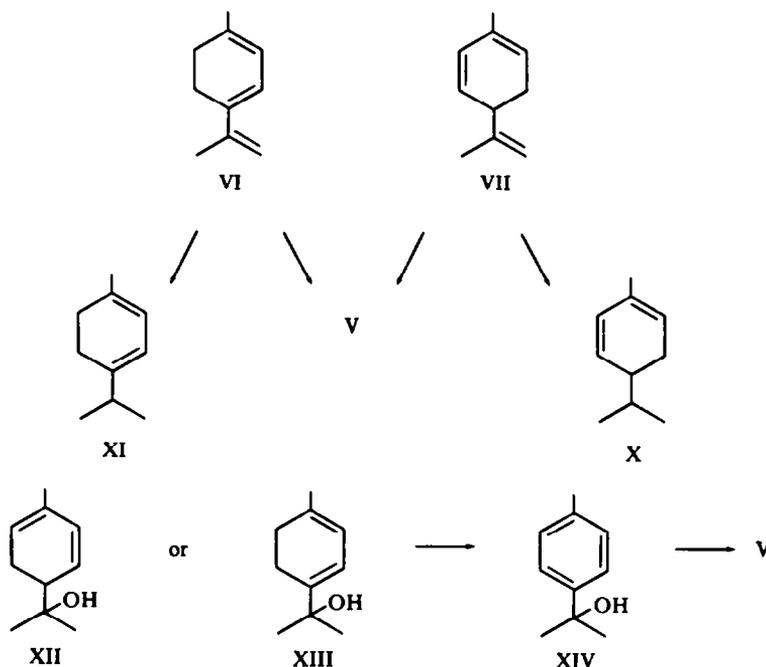


FIG. 1b. Arene formation at pH 1.8 under oxygen.

compounds having low retention indices are assumed to be *p*-menthanes and/or *p*-menthenes resulting from further hydrogen transfer reactions.

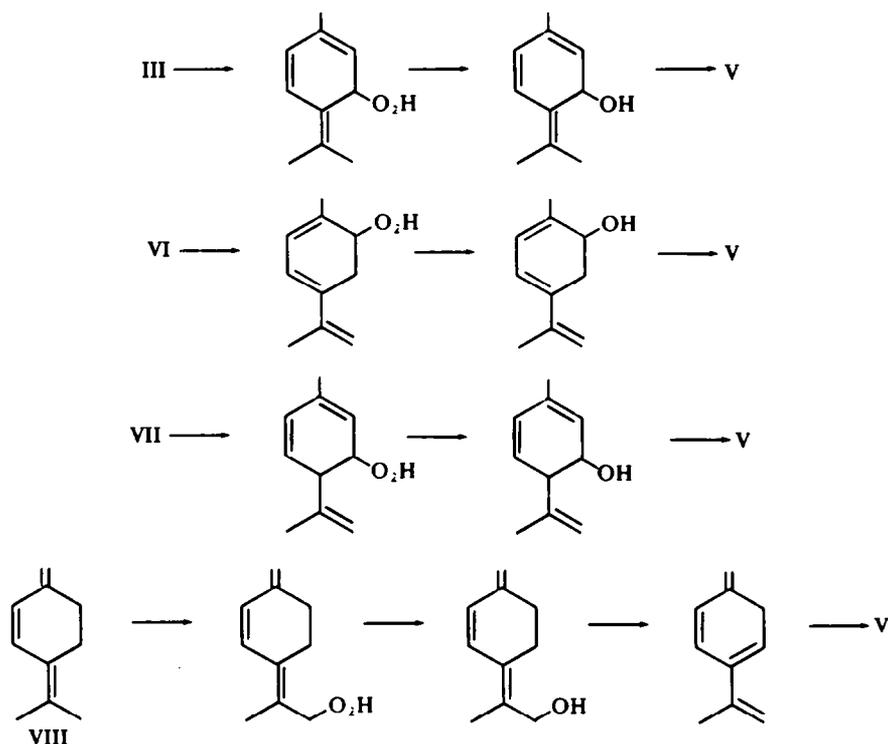


REACTION SCHEME 1.

Although there appears to be no evidence for a reaction route to *p*- α -dimethylstyrene involving disproportionation of piperitenol (II) or isopiperitenol (IX) followed by subsequent loss of a molecule of water, the alternative hydration of the *p*-menthatrienes giving *p*-menthadien-8-ols (XII and XIII) which on disproportionation yield *p*-8-cymenol (XIV) appears to be a feasible, albeit unfavourable, route to the styrene (V) (see Reaction Scheme 1). In the absence of oxygen *p*-8-cymenol is obtained in a maximum yield of *ca* 5% within the pH range 1.5 to 2.0. As we have found that the formation of the styrene from *p*-8-cymenol is irreversible under our reaction conditions,¹² the alcohol must arise from some other source.

The higher yields of *p*- α -dimethylstyrene produced in the presence of oxygen may be readily rationalized in terms of allylic oxidation. We again postulate the intermediary isomeric *p*-menthatrienes (see Reaction Scheme 2). The increased yield of *p*-8-cymenol in the presence of oxygen also results most probably from allylic oxidation of an intermediate terpene.

The effect of hydrogen ion concentration. The total number of reaction products and intermediates detected over the pH range 0.0 to 4.0 was considerably greater than the number observed at pH 1.8 (Tables 3 and 4). As the majority of additional compounds were detected in only trace concentrations at the extreme limits of the pH range, they were, in general, extremely difficult to identify. The major components were, however, the same as those observed at pH 1.8.



REACTION SCHEME 2.

Of major significance in these studies is the considerably decreased yield of *p*-cymene over the pH range 1.0 to 3.0 under the reaction conditions in which oxygen was blown continuously through the reaction mixture compared with the yield obtained when the reaction was carried out under oxygen free nitrogen. This decrease is coupled with a correspondingly increased yield of *p*- α -dimethylstyrene (Fig 2).

The competitive formation of p-cymene and p- α -dimethylstyrene. From our present investigations outlined above it is possible to postulate a complete reaction scheme which accounts for the formation of both *p*-cymene and *p*- α -dimethylstyrene and also for the intermediate terpenoid hydrocarbons and alcohols.

The variations in the relative yields of the two arenes (IV and V) may be rationalized primarily in terms of the dependence of the equilibrium constants for the reactions A, B, C and D upon the pH of the reaction medium. The relative ratio of the two arenes also depends upon the rate of the isomerization of the *p*-menthatrienes to give *p*-cymene relative to that of the disproportionation reaction, when the reaction is carried out under nitrogen, or compared with the rate of allylic oxidation of the *p*-menthatrienes in the presence of oxygen.

In general, above pH 2.5 ~ 3.0 the rate of the initial ring closure (equilibrium A) of citral leading to the formation of piperitenol (II) or isopiperitenol (IX) decreases with the increase in the pH of the reaction medium. The yields of arenes become negligible and the only products isolated are, in the main, terpenoid alcohols. In

TABLE 3. REACTION PRODUCTS DETECTED AFTER 6 HOURS FROM THE CYCLIZATION OF CITRAL IN ACIDIC MEDIA UNDER NITROGEN^a

Peak No. ^b	Kovats Retention Index	Compound	0.5	1.1	1.5	pH	2.3	2.9	3.3
1	1119				0.0	0.0	0.2	0.6	1.9
2	1157		0.5	0.2	0.8	0.4	0.2	0.0	0.0
3	1228	α -phellandrene	0.2	0.4	0.8	0.4	0.2	0.0	0.0
4	1248		3.1	2.8	1.5	0.9	0.4	0.0	0.0
5	1262		0.2	0.4	0.6	2.8	3.2	3.8	1.0
6	1294	a menthadiene	3.7	1.4	1.3	3.4	2.1	2.0	0.7
7	1324	p-cymene	0.2	0.7	1.6	3.2	2.0	1.9	0.3
8	1480	p-mentha-1(7),2,4(8)-triene	79.6	71.0	60.8	29.2	22.2	4.2	1.8
9	1498	p- α -dimethylstyrene	0.0	0.0	1.0	1.4	1.4	1.7	0.0
10	1560	linalool	10.2	19.0	22.0	12.1	5.0	1.1	0.0
11	1726		0.0	0.0	0.1	2.2	2.5	3.0	0.6
12	1749	piperitenol	0.1	0.7	0.0	3.2	2.6	2.0	1.9
13	1769	isopiperitenol	0.0	0.0	0.7	16.4	20.6	21.2	8.9
14	1796	a terpenoid alcohol	0.3	0.3	0.3	0.0	0.0	4.8	9.6
15	1835	p-8-cymenol	0.0	0.0	0.3	5.4	9.9	7.8	1.9
16	1866		0.0	0.4	1.0	0.0	0.0	1.1	0.0
17			0.3	1.9	4.5	3.6	4.5	2.3	0.0
<i>Unreacted Citral</i>									
	1742	citral <i>a</i>	0.0	0.0	0.0	3.2	4.2	7.6	12.6
	1783	citral <i>b</i>	0.0	0.2	0.7	11.6	17.7	35.0	58.5

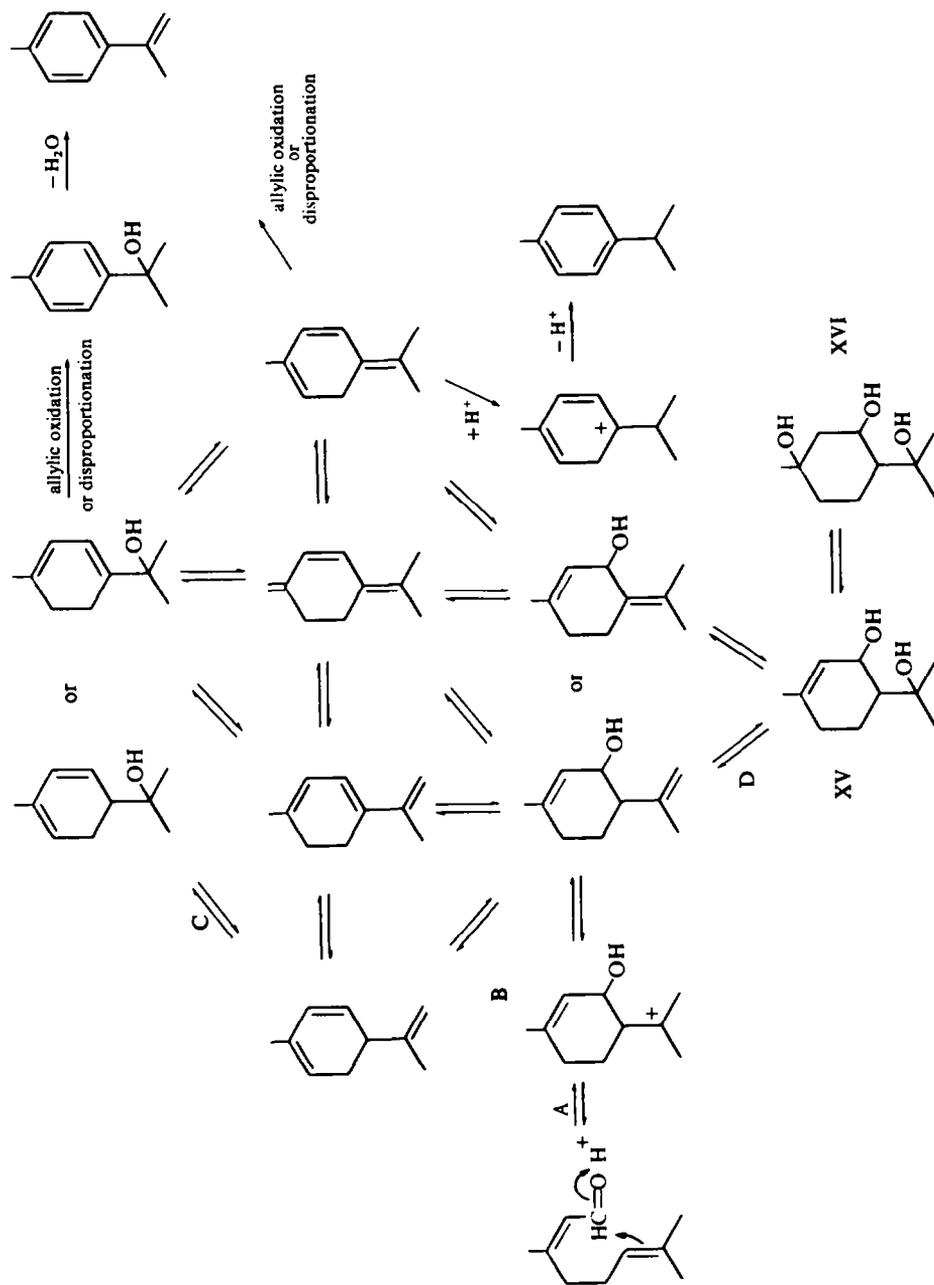
^a One compound with a retention index less than 1119 and six compounds with retention indices between 1560 and 1726 were also detected in trace amounts.

^b Peak numbers correspond to those given to the compounds listed in Tables 1 and 2.

TABLE 4. REACTION PRODUCTS DETECTED AFTER 6 HOURS FROM THE CYCLIZATION OF CITRAL IN ACIDIC MEDIA UNDER OXYGEN^a

Peak No.	Kovats Retention Index	Compound	pH							
			0.4	0.9	1.5	1.75	2.4	2.8	3.2	3.7
1	1119		0.0	0.3	0.5	1.5	1.0	0.7	0.8	0.4
2	1157		0.0	0.2	0.7	2.0	0.3	0.0	0.0	0.0
3	1228	α -phellandrene	1.4	0.3	0.1	0.0	0.0	0.0	0.0	0.0
4	1248		0.6	1.4	1.4	1.8	4.7	6.7	1.1	0.6
5	1262		0.4	0.3	0.9	0.8	0.0	0.0	0.0	0.0
6	1294	<i>a</i> menthadiene	0.0	0.5	1.7	0.8	0.8	0.7	0.0	0.0
7	1324	<i>p</i> -cymene	71.5	53.6	21.1	3.8	0.2	0.0	0.0	0.0
9	1480	<i>p</i> -mentha-1(7),2,4(8)-triene	0.0	0.0	0.0	0.0	0.9	?	?	0.3
10	1498	<i>p</i> - α -dimethylstyrene	19.8	36.9	59.5	69.0	2.2	0.5	0.8	0.3
11	1560	linalool	0.0	0.0	0.0	0.0	3.3	2.0	1.9	1.2
12	1726		0.0	0.0	1.0	2.0	2.2	1.8	?	0.0
13	1749	piperitenol	0.0	0.2	0.5	0.8	0.0	0.0	0.0	0.0
15	1796	isopiperitenol	0.0	0.0	0.0	0.0	0.0	2.0	?	0.6
16	1835	<i>a</i> terpenoid alcohol	0.3	0.9	3.4	7.0	5.3	1.4	0.9	0.6
17	1866	<i>p</i> -8-cymenol	0.6	1.7	5.6	5.6	17.3	2.3	1.5	0.0
<i>Unreacted Citral</i>										
	1742	citral <i>a</i>	0.0	0.0	0.0	0.0	11.9	4.4	22.9	22.2
	1783	citral <i>b</i>	0.3	0.2	1.1	2.3	48.9	75.5	60.7	64.5

^a Nine compounds with retention indices between 1498 and 1726 were detected in trace amounts.



REACTION SCHEME 3.

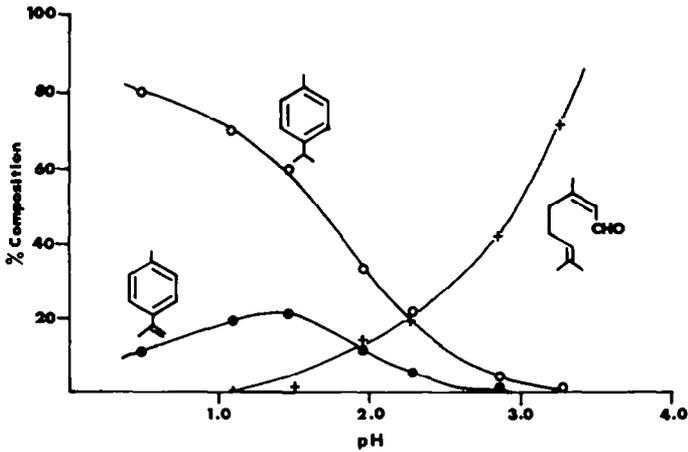


FIG. 2a. Dependence of the cymene:*p*- α -dimethylstyrene ratio upon the pH of the reaction medium in the absence of oxygen.

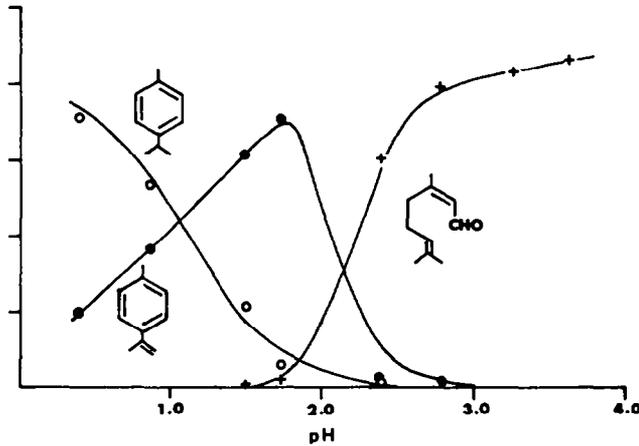


FIG. 2b. Dependence of the cymene:*p*- α -dimethylstyrene ratio upon the pH of the reaction medium in the presence of oxygen.

more acidic media of $\text{pH} < 2.5$, the rate of formation of the aromatic product increases rapidly when the reaction is carried out under nitrogen suggesting that the formation of the intermediate *p*-menthatrienes is favoured by the higher hydrogen ion concentration. The subsequent isomerization of the *p*-menthatrienes is a considerably faster reaction than the competing disproportionation reaction over the whole pH range. Between $\text{pH} 3.0$ and 1.5 the rate of formation of both arenes increases rapidly, but at the higher hydrogen ion concentrations, as the concentration of the protonated *p*-menthatriene increases, the rate of isomerization to give *p*-cymene continues to increase whilst the rate of formation of the styrene (V) appears to decrease. This suggests some specificity of the disproportionation reaction to non-protonated *p*-menthatrienes but could also be due to the extremely rapid increase in the rate of the

isomerization reaction with the decrease in the pH of the reaction medium leading to an overall decrease in the concentration of the *p*-menthatrienes.

The general effect of pH upon the rate of the isomerization of the *p*-menthatrienes also applies to reactions carried out in the presence of oxygen. However, in contrast to the disproportionation reaction, the allylic oxidation of the *p*-menthatrienes over the pH range 1.5 to 3.0 is considerably faster than their isomerization, but it appears from the decreased yields of *p*- α -dimethylstyrene at lower pH values, that by analogy with the reaction carried out in the complete absence of oxygen, the rate of isomerization of the *p*-menthatrienes increases considerably more rapidly as the pH of the reaction medium is lowered than does the rate of allylic oxidation. An alternative or additional cause for the observed decrease in the concentration of the styrene is that allylic oxidation of the protonated *p*-menthatriene is slower than the corresponding oxidation of the non-protonated species.

The formation of *p*-8-cymenol (XIV), particularly within the pH range 1.5 to 3.0, can be rationalized in terms of either the disproportionation reaction involving hydrogen transfer or by allylic oxidation of the two terpenoid alcohols, *p*-mentha-2,6-dien-8-ol (XII) and *p*-mentha-1,3-dien-8-ol (XIII). These alcohols would be expected to be in equilibrium with piperitenol (II) and isopiperitenol (IX), via the intermediate *p*-menthatrienes and their formation would be favoured when the hydrogen ion concentration of the reaction medium is low. At higher hydrogen ion concentrations (below pH *ca* 2.0) the yield of *p*-8-cymenol would be lower either as a result of its conversion into *p*- α -dimethylstyrene or due to the rapid isomerization of the intermediate *p*-menthatrienes. On the basis of Reaction Scheme 3 and its formation from piperitenol under acidic conditions (see below), the compound of molecular weight 152 with a retention index of 1835 was tentatively assigned as being either XII or XIII.

The *p*-menthendiol (XV) and the *p*-menthantriol (XVI) have both been considered to be intermediates in the formation of *p*-cymene.^{4,6} We, however, consider both compounds to be by-products and not true intermediates as the only method by which they may be converted into the aromatic end product is via their precursor, IX or II, and the *p*-menthatrienes. Although their formation would be favoured at high pH values, we failed to detect either of these alcohols at any pH over the range 0.0 to 4.0. The presence of a compound having the retention index of linalool is somewhat confusing in view of its ready isomerization to α -terpineol.¹² One must assume that it is formed by an acid catalysed isomerization of geraniol which could have been formed from citral by a hydrogen transfer reaction.

Evidence in support of Scheme 3 was provided by a study of the reaction products obtained from the rearrangements of isolated components under acidic conditions. Piperitenol (II) at pH 1.8 in the presence of oxygen gave *p*- α -dimethylstyrene, *p*-8-cymenol and the alcohol with retention index 1835 (XII or XIII) in approximately equal quantities together with a trace of isopiperitenol. Under nitrogen, the major product (> 90%) was *p*-cymene together with trace amounts of *p*-8-cymenol, isopiperitenol and the alcohol with retention index 1835. Under similar conditions isopiperitenol gave essentially *p*-cymene under nitrogen and, in the presence of oxygen, only *p*- α -dimethylstyrene was detected. *p*- α -Dimethylstyrene was also obtained from *p*-8-cymenol at pH 1.8 both in the presence and complete absence of oxygen.

Unfortunately it was not possible to isolate and study the effect of acid upon the *p*-menthatrienes and the menthadien-8-ols. All attempts to obtain a pure sample of the *p*-menthatriene (VIII) by standard chromatographic techniques resulted in its rapid isomerization to give *p*-cymene.¹³

EXPERIMENTAL

The IR spectra were recorded on a Perkin-Elmer 237 spectrometer using 0.025 mm AgCl microcells (RIIC), the UV spectra were measured on a Unicam SP800 spectrophotometer, and the NMR spectra were obtained at 100 MHz on a Varian HA100 spectrometer with *ca* 20% solns in CDCl₃ contained in a microtube and with TMS as an internal standard. The mass spectra were obtained using a Perkin-Elmer Hitachi RMU-6E mass spectrometer by direct insertion of the sample trapped from the GLC effluent or by direct "on-line" technique using a Perkin-Elmer F11 gas chromatograph fitted with a 4 m × $\frac{1}{8}$ in column of LAC 2R-446 on Chromosorb W (15:85 w/w) at 120° with helium as the carrier gas. Routine GLC analysis was carried out on a Perkin-Elmer F11 gas chromatograph at 120° fitted with a flame ionisation detector and a 4 m × $\frac{1}{8}$ in column containing either LAC 2R-446 on Chromosorb W (15:85 w/w) or SE30 on Chromosorb W (20:80 w/w) and with a N₂ inlet pressure of 10 psig. Preparative microscale separations were accomplished on a Varian Aerograph 90-P gas chromatograph fitted with a thermal conductivity detector and a RIIC collection unit.

Acid catalysed rearrangements. Citral (0.94 g, 10 ml) in an aqueous soln (10 ml) of known pH was vigorously stirred at 70° for a known period of time. The atmosphere above the reaction mixture was controlled by passing the gas (either "white spot" N₂, scrubbed by passage through Cr(II) soln,⁸ or O₂) through the reaction mixture at a constant rate. A mercury bubbler seal ensured a slight positive pressure of the gas in the reaction flask at all times. The reaction was quenched by rapidly cooling the mixture to 0° and the products and unreacted citral were extracted immediately with light petroleum* (15 ml, 2 × 5 ml). The combined extracts were made up to 25 ml and *n*-octanal (8 μl) was added to a sample of the extracts (2 ml) and the composition of the sample analysed with a Perkin-Elmer F11 gas chromatograph.

(a) The effect of O₂ upon the course of the reaction was investigated at pH 1.8 at 70°.

(b) The effect of the hydrogen ion concentration upon the course of the reaction was investigated using aqueous solns of known pH at 70° over a period of 6 hr.

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* Commercial light petroleum, b.p. 30–40° (May and Baker) was fractionally distilled from P₂O₅ to give a fraction having a single GLC peak on the LAC 2R-446 column.