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THE MEERWEIN-PONNDORF-VERLEY REDUCTION OF *p*-MENTHA-1,4(8)-DIEN-3-ONE (PIPERITENONE)

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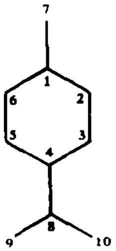
Abstract—The major products of the reduction of *p*-mentha-1,4(8)-dien-3-one with aluminium isopropoxide in isopropanol are *p*-mentha-1(7),2,4(8)-triene (28%), *p*, α-dimethylstyrene (21%), and *p*-cymen-8-ol (20%).

SEVERAL INVESTIGATORS[2,3,4] have suggested that *p*-mentha-1,4(8)-dien-3-ol (piperitenol) is an intermediate in the acid catalysed conversion of citral into *p*-cymene. As the identification of the methadienol in our studies[2] depended largely upon an *ab initio* interpretation of its mass spectrum, a procedure which when used even for relatively simple monoterpenes is fraught with ambiguities,[5] it was expedient to prepare an authentic sample.



Numbering for *para*-menthane system

In addition to its isolation from the cyclization of citral,[3] the only reported synthesis of *p*-mentha-1,4(8)-dien-3-ol is *via* allylic oxidation of *p*-mentha-1,4(8)-diene (terpinolene).[6] A more practical route appeared to be *via* the Meerwein-Ponndorf-Verley reduction[7] of the readily obtained[8] *p*-mentha-1,4(8)-dien-3-one (piperitenone). The technique is generally suitable for the synthesis of α,β-unsaturated alcohols and, although the major products of the reduction of *p*-mentha-4(8)-en-3-one (pulegone) have been reported to be *p*-mentha-2,4(8)-diene and *p*-mentha-3,8-diene,[9] the method has been successfully used in the conversion of *p*-mentha-4-en-3-one into the corresponding *p*-menthenols[10] and also for the synthesis of *p*-mentha-6,8-dien-2-ol (carveol) from *p*-mentha-6,8-dien-2-one (carvone).[11] The reaction of *p*-mentha-1,4(8)-dien-3-one with aluminium isopropoxide in isopropanol, however, gave ten products (Table) the yields of which were, in general, reproducible to *ca* 5% of the figures quoted.

Four terpenoid alcohols, with a combined yield of only *ca* 10%, were detected, whereas dehydration products[2,9] of these alcohols accounted for *ca* 45% of the

TABLE 1. PRODUCTS FROM MEERWEIN-PONNDORF-VERLEY REDUCTION OF *p*-MENTHA-1,4(8)-DIEN-3-ONE[a]

Kovats' Retention index	MW[b]	Compound	% yields	Identification[c]
1324	134	*p*-cymene	7·3	RI, IR, NMR, MS
1438	134	*p*-mentha-1,3,8-triene[d]	10·4	RI, MS, UV[e]
1480	134	*p*-mentha-1(7),2,4(8)-triene	28·2	MS, UV[e]
1498	132	*p*, α-dimethylstyrene	20·9	RI, IR, NMR, MS
1749	152[f]	*p*-mentha-1,4(8)-dien-3-ol	0·5	MS
1769	152[f]	a *p*-menthadienol	7·8	MS, IR
1796	152[f]	*p*-mentha-1,8-dien-3-ol	1·3	MS
1835	152[f]	a *p*-menthadienol	0·8	MS
1866	150	*p*-cymen-8-ol	19·9	RI, IR, NMR, MS
1990	150	thymol	2·6	RI, IR, MS

[a] Detected using a Perkin-Elmer F11 gas chromatograph with a LAC 2R-466 column at 120°. % yields were calculated from the chromatograms using a planimeter.

[b] MW's determined mass spectrometrically using an 'on-line' GLC/MS unit.

[c] RI Kovats' retention index identical with that of authentic sample. Full spectral data are available on request.

[d] Ref. 12

[e] Ref. 13

[f] Molecular ions very weak, base peaks at *m/e* 134 (M-H_2O)

overall yield. Pure samples of the *p*-menthatrienes could not be isolated due to their rapid isomerization into *p*-cymene and their identities were confirmed from mass spectral and UV absorption data[12, 13] and by comparison of their Kovats' retention indices with those of authentic menthatrienes of known structure. The high yields of *p*-cymen-8-ol and *p*, α-dimethylstyrene were somewhat unexpected. Their formation *via* an allylic oxidation route[2] or through hydrogen transfer mechanisms involving the reduction products[2] could be discounted as their relative yields were unchanged when precautions were taken to exclude oxygen from the reaction system and no *p*-menthane or *p*-menthene derivatives were detected. It is possible, however, that they were formed by a hydrogen transfer reaction involving the *p*-mentha-1,4(8)-dien-3-one. Thymol is an expected isomerization product of the ketone[14] and analysis of the products before the completion of the reaction showed the presence of the isomeric *p*-mentha-1,8-dien-3-one (isopiperitenone) as well as the unchanged 1,4(8)-dien-3-one.

EXPERIMENTAL

Reduction of p-*mentha*-1,4(8)-*dien*-3-*one*. *p*-Mentha-1,4(8)-dien-3-one[8] (7·5 g) was added to aluminium isopropoxide (10 g) in isopropanol (50 ml) and the mixture heated to produce a slow distillation of acetone at a rate of *ca* 10 drops per min. Heating was continued until the distillate gave a negative test for acetone. The excess isopropanol was removed and the residue acidified with dilute HCl to pH 5·0 and extracted with ether (3 × 25 ml). Evaporation of the dried ($MgSO_4$) extracts gave a yellow oil (6·8 g) which was analysed by gas chromatographic and spectroscopic procedures described previously.[2]

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