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REARRANGEMENTS OF 3-METHYLCAR-4-EN-2-ONE

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Abstract—3-Methylcar-4-en-2-one has been shown to undergo ring opening to give 1-methyl-*p*-menthane derivatives on treatment with reagents which attack cyclopropyl ketones, e.g. dissolving metals or mineral acids. The direction of ring opening appears to be controlled by stereo-electronic factors.

THE unique relationship between the functional groups, e.g. carbonyl, double bond and cyclopropane ring, in 3-methylcar-4-en-2-one[1] (I) suggested that a study of the chemistry of this molecule might be rewarding. We have already shown that on irradiation with UV light, cleavage of the $C_{(2)}$—$C_{(3)}$ bond occurs, with redistribution of the π-electrons of the double bond and the σ-electrons of the $C_{(1)}$—$C_{(6)}$ bond, the products in nucleophilic solvents being derived from the resulting ketene,[2] cf. the photochemistry of cyclohexa-2-4-dienones.[3] This paper describes further reactions of this system.

Car-2-one (II) is known to undergo reactions which involve cleavage of the $C_{(1)}$—$C_{(7)}$ bond, with no evidence for the cleavage of the $C_{(1)}$—$C_{(6)}$ bond. On treatment with alcoholic mineral acid, car-2-one gives 8-hydroxy-*p*-menthan-2-one,[4a] presumably by protonation of the carbonyl and cleavage of the $C_{(1)}$—$C_{(7)}$ bond producing a tertiary carbonium ion. Cleavage of the $C_{(1)}$—$C_{(6)}$ bond would produce a secondary carbonium ion. Similarly, on treatment with sodium in moist ether,[4b] or lithium in liquid ammonia,[5,6] the *p*-menthane system is produced by reductive cleavage of the $C_{(1)}$—$C_{(7)}$ bond. Apart from the consideration of the relative stabilities of the carbonium ions, and radicals or carbanions, which are produced by cleavage of the $C_{(1)}$—$C_{(7)}$ or $C_{(1)}$—$C_{(6)}$ bond, examination of models of car-2-one suggests that the orbital of the $C_{(1)}$—$C_{(7)}$ bond can overlap with a p-orbital at $C_{(2)}$ (sp^2 hybridized) better than the orbital of the $C_{(1)}$—$C_{(6)}$ bond. Indeed, it has been suggested[5,6] that the reason for the preferred cleavage of the $C_{(1)}$—$C_{(7)}$ bond is stereo-electronic in nature. It was therefore of interest to see if the stereo-electronic control of the cleavage is still predominant in 3-methylcar-4-en-2-one, in which the alternative cleavage of the $C_{(1)}$—$C_{(6)}$ bond would produce an allylic ion or radical.

Reduction of 3-methylcar-4-en-2-one (I) with sodium in ethanol gave an unsaturated alcohol in 82% purity, for which the structure III is proposed on the basis of the following evidence. The new alcohol was different from the epimeric 3-methylcar-4-en-2-ols (IV), produced by LAH reduction of I, and analysis of a derivative showed that the new alcohol was two oxidation levels below the parent ketone. Oxidation gave the ketone V, which had ν_{max}^{film} 1718 cm^{-1}, characteristic of an unconjugated

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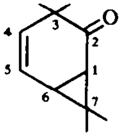
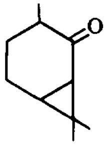


I



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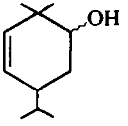

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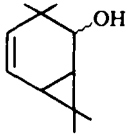

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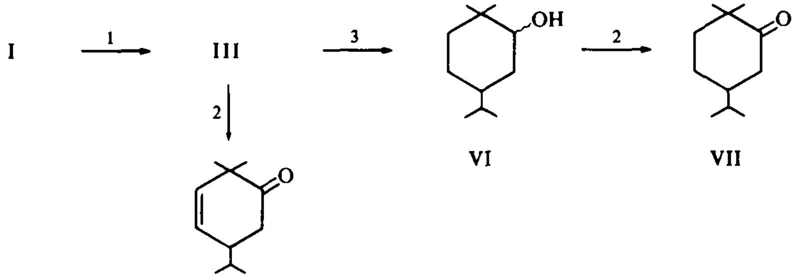
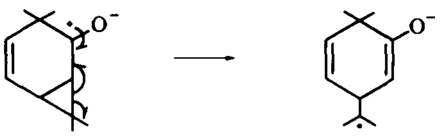
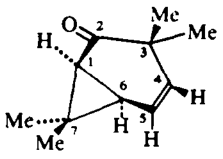


V



VIII IX



X

1, Na/EtOH; 2, CrO_3; 3, H_2/Pt.

cyclohexanone. Hydrogenation of the alcohol produced a saturated alcohol VI after the uptake of 1 mole of hydrogen. Oxidation of the saturated alcohol gave a saturated ketone (ν_{max}^{film} 1711 cm^{-1}), which could be purified *via* the sodium salt of its hydroxymethylene derivative, and which was identical with an authentic sample of 1-methyl-*p*-menthan-2-one (VII). The latter was prepared by alkylation of *p*-menthan-2-one.[7] Had the double bond in the unsaturated alcohol been between $C_{(3)}$ and $C_{(4)}$, or $C_{(4)}$ and $C_{(5)}$ (*p*-menthane numbering), a conjugated unsaturated ketone would be expected on oxidation in acid solution.

The reductive cleavage of the cyclopropane ring in 3-methylcar-4-en-2-one by a dissolving metal therefore parallels the same reaction in car-2-one. The reaction may be viewed as proceeding by the addition of one electron to the carbonyl group, followed by rearrangement of the resulting anion-radical VIII to produce the anion-radical IX. Rearrangement of the alternative form of the anion-radical,[8] e.g. two electrons on $C_{(2)}$ and the odd electron on oxygen, appears less likely since a tertiary carbanion would be formed.* The addition of a second electron to IX, followed by protonation of the dianion would give the ketone V, which would be further reduced to III. The configuration of III is thought to be that with the hydroxyl and isopropyl groups *cis*, since sodium in ethanol reduction of V would be expected to give the

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* cf. Refs 9–11.

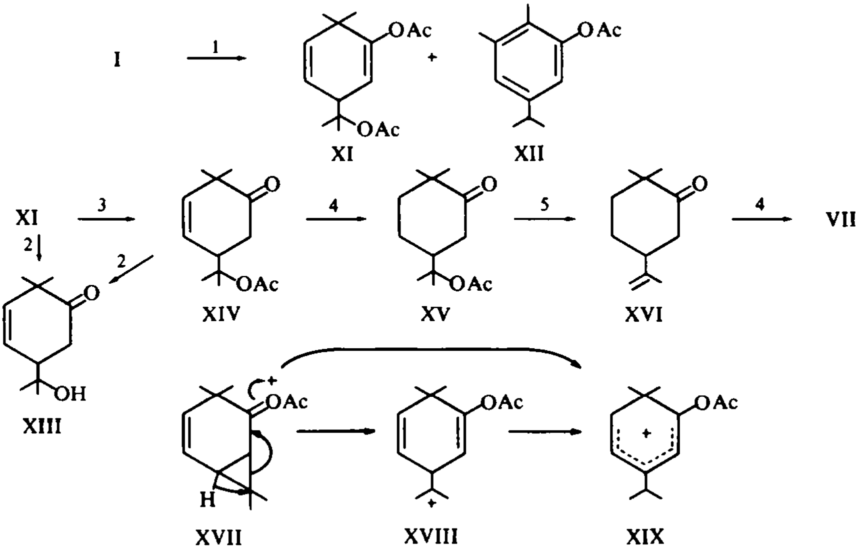
thermodynamically more stable epimer. Furthermore, reduction of V with lithium tri-t-butoxyaluminium hydride gave the same epimer.

The course of the reaction may equally well be explained in terms of the addition of two electrons to the carbonyl group followed by rearrangement,* but since the polarographic reduction of carbonyl compounds at high pH has been interpreted as the addition of one electron to the carbonyl group,[9] we prefer at present to view the reaction as a rearrangement at the anion-radical stage.

An examination of models of 3-methycar-4-en-2-one indicates that, as with car-2-one, the $C_{(1)}$—$C_{(7)}$ bond is better placed to overlap with a p-orbital of an sp^2 hybridized carbon at $C_{(2)}$ than the $C_{(1)}$—$C_{(6)}$ bond (X), considerable distortion of the molecule being necessary in the latter case. Models also suggest that further distortion would be necessary to allow the radical produced at $C_{(6)}$ to overlap with the $C_{(4)}$—$C_{(5)}$ double bond.

Thus, although *a priori* cleavage of the $C_{(1)}$—$C_{(6)}$ bond might be expected to be more energetically favourable here than in the car-2-one molecule, due to the formation of an allyl radical,† the direction of ring cleavage appears to be controlled by orbital overlap considerations of the ketone, in agreement with published work.[5,6]

A similar preference for the cleavage of the $C_{(1)}$—$C_{(7)}$ bond is observed on treating 3-methylcar-4-en-2-one with conc sulphuric acid in acetic anhydride, conditions which have been used for the rearrangement of cyclohexa-2,5-dienones,[12] and cyclohexa-2,4-dienones.[13] Two products were obtained, 2,8-diacetoxy-1-methyl-*p*-mentha-2,5-diene (66%; XI) and 5-isopropyl-2,3-dimethylphenol acetate (18%; XII).



1, H_2SO_4/Ac_2O; 2, 1% methanolic KOH; 3, 10% Na_2CO_3/H_2O–MeOH; 4, H_2/Pt; 5, 400°.

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* cf. Ref. 6.

† For the relative stabilities of allyl and tertiary radicals see: R. T. Morrison and R. N. Boyd, Organic Chemistry, Allyn and Bacon, Inc., Boston, 1966. p. 208.

The structure of the diacetate XI follows from the following evidence. Analysis indicated a formula $C_{15}H_{22}O_4$, which coupled with the IR spectrum (ν_{max}^{film} 1762, 1730, 1256, 1212 cm^{-1}) suggested the presence of two acetate groups. The compound exhibited only end absorption in the UV. Treatment with 1% methanolic potassium hydroxide hydrolysed both acetate groups, producing the hydroxy-ketone XIII (ν_{max}^{film} 3425, 1708 cm^{-1}). Again, there was only end absorption in the UV. The OH group was thought to be tertiary from the fact that it could not be oxidized. This was supported by hydrolysis of XI using sodium carbonate in aqueous methanol, which resulted in hydrolysis of the enol acetate grouping only, producing the acetoxy-ketone XIV (ν_{max}^{film} 1732, 1715, 1253 cm^{-1}). The IR bands at 1730 and 1256 cm^{-1} in XI are therefore assigned to the tertiary acetate, and bands at 1762 and 1212 cm^{-1} to the enol acetate. Treatment of XIV with 1% methanolic potassium hydroxide gave XIII.

Hydrogenation of the unsaturated acetoxy-ketone XIV produced the saturated acetoxy-ketone XV (ν_{max}^{film} 1728, 1708, 1258 cm^{-1}) with the absorption of 1 mole of hydrogen. Pyrolysis of XV at 400° over silica chips served to eliminate acetic acid from the molecule. The product, which was a mixture of two new compounds (73% and 14%), together with a small amount of unchanged XV, showed characteristic IR bands at 1705, 1645, and 890 (strong) cm^{-1}, the latter two being indicative of the $>C=CH_2$ grouping. The main component of the mixture is therefore thought to be 1-methyl-*p*-menth-8-en-2-one (XVI). Hydrogenation of the pyrolysis mixture resulted in the absorption of 0·89 mole of hydrogen. The product was again a mixture of three compounds, the main component (77%) being identified as 1-methyl-*p*-menthan-2-one (VII). The bands at 1645 and 890 cm^{-1} were absent from the IR spectrum of the hydrogenation product, confirming their assignment.

The nature and structure of the second product (18%) from the acid treatment of 3-methylcar-4-en-2-one, were determined as follows. An enolic acetate group was suggested by the IR spectrum, ν_{max}^{film} 1763, 1211 cm^{-1}. Hydrolysis with 1% methanolic potassium hydroxide gave a phenol, which had λ_{max}^{EtOH} 281 mμ (ε 1090), 275 mμ (ε 1085). 2,3,5-Trimethylphenol is reported[14] to have $\lambda_{max}^{cyclohexane}$ 282 mμ (ε 1585), 278 mμ (ε 1415), 273 mμ (ε 1415). In 5% ethanolic potassium hydroxide, the UV spectrum showed a bathochromic shift, typical of phenols.[15] The coupling constant between the two aromatic protons in the PMR spectrum of the phenol acetate was 1·5 c/s, suggesting a meta relation between them. The structure most consistent with this information, and which on mechanistic grounds is the most likely to be formed from 3-methylcar-4-en-2-one, is 5-isopropyl-2,3-dimethylphenol acetate (XII).

Acidic rearrangement of 3-methylcar-4-en-2-one leads, therefore, to products derived by cleavage of the $C_{(1)}$—$C_{(7)}$ bond. Again it appears that stereo-electronic considerations govern the route taken, attack of acetylium ion being followed by cleavage of the $C_{(1)}$—$C_{(7)}$ bond (XVII) with formation of the carbonium ion XVIII. Attack of acetic acid on the latter would give the diacetate XI directly. This reaction thus parallels the ring opening of car-2-one on treatment with acid.[4a]

The diacetate XI is found to be stable to the reaction conditions, and this is perhaps surprising since XI might be expected to reform the carbonium ion XVIII with strong acid. It is possible that the phenolic acetate XII is not obtained by way of XVIII, but that one pathway for collapse of XVII involves a hydride shift from $C_{(6)}$ to $C_{(7)}$

(carane numbering) concerted with $C_{(1)}$—$C_{(7)}$ bond cleavage, yielding the mesomeric cation XIX directly. Methyl migration followed by proton loss would then lead to the phenolic acetate XII.[12,13] Alternative routes from XVIII to XIX appear to encounter considerable non-bonded interactions between the methyl groups at $C_{(8)}$ and the olefinic protons at $C_{(3)}$ and $C_{(5)}$, and may be energetically unfavourable.

EXPERIMENTAL

Light petroleum refers to the fraction bp. 40–60°.

3-*Methylcar-4-en-2-one* (I)

This was prepared from eucarvone,[1] but NaH was used instead of $NaNH_2$. The crude product was shown by GLC to be a mixture of 3-methylcar-4-en-2-one (88%), and two other products (9%) and (3%). Fractional distillation gave 7 fractions: fraction 1 had bp. 90·5–91·5°/12 mm, λ_{max}^{EtOH} 303 mμ (ε 235), 210 mμ (ε 5400). ν_{max}^{film} 1698 (v. strong), 1655 (v. weak shoulder) cm^{-1}; fraction 3 had bp. 92°/12 mm, λ_{max}^{EtOH} 303 mμ (ε 330), λ^{EtOH} 210 mμ (ε 4890), ν_{max}^{film} 1695 (v. strong), 1655 (weak cm^{-1}; fraction 7 had bp. 94–95°/12 mm, ν_{max}^{film} 1695 (strong), 1655 (strong) cm^{-1}. GLC analysis showed a slow build up of the major side-product from fraction 1 to fraction 7, consistent with the slow build up of absorption at ν_{max} 1655 cm^{-1} and λ_{max} 303 mμ. A pure sample of 3-methylcar-4-en-2-one, prepared by the oxidation of *exo*-3-methylcar-4-en-2-ol (see below), showed no peak or inflexion around 300 mμ in the UV, and no absorption at 1655 cm^{-1} in the IR. The spectroscopic evidence suggests that the major side-product (9%) is a cyclohepta-2,4-dien-1-one, probably 2,6,6,7-tetramethylcyclohepta-2,4-dien-1-one. The early fractions from the distillation provided 3-methylcar-4-en-2-one which was sufficiently pure for the study of its chemistry. Corey and Burke[1] report λ_{max} 300 mμ (ε 780), λ 206 mμ (ε 5130), and ν_{max} 1698, 1665, 1007 cm^{-1} for 3-methylcar-4-en-2-one.

The PMR spectrum of 3-methylcar-4-en-2-one (60 Mc/s; $CDCl_3$) showed absorption at 8·99, 8·88, 8·84, 8·73 (singlets; Me groups at $C_{(3)}$ and $C_{(7)}$), 8·23 (multiplet: protons at $C_{(1)}$ and $C_{(6)}$; centre of the AB portion of an ABX system—the low intensity of the outer components of the AB portion prevented complete analysis, $J_{5,6} \simeq 3$ c/s, $J_{1,5} \simeq 1·5$ c/s), 4·44 (doublet, $J_{4,5} = 10·2$ c/s; olefinic proton at $C_{(4)}$), and 4·32 τ (2 doublets; olefinic proton at $C_{(5)}$; X portion of the ABX system, $J_{4,5} = 10·2$ c/s, $J_{5,6} \simeq 3$ c/s, $J_{1,5} \simeq 1·5$ c/s).

exo- and endo-3-*Methylcar-4-en-2-ol* (IV). Treatment of I (4·04 g) with LAH (1·97 g) in boiling ether (240 ml) during 3 hr, gave a quantitative yield of a mixture of exo-3-*methylcar-4-en-2-ol* (33%) and *endo*-3-methylcar-4-en-2-ol (67%). The alcohols were separated by chromatography on silica gel. Elution with light petroleum–ether (2:1) gave the *endo*-alcohol (1·26 g; 32%), bp. 61–93°/1·3 mm, which was pure by GLC. The 3,5-dinitrobenzoate had mp. 105–106·5° from EtOH. Unsatisfactory analyses were obtained for the *endo*-alcohol and its derivative. Elution with light petroleum–ether (3:2) gave the *exo*-alcohol (0·91 g; 23%), m.p. 83·5–85·5° (sublimed). (Found: C, 79·6; H, 10·9. $C_{11}H_{18}O$ requires: C, 79·45; H, 10·9%) which was pure by GLC. The 3,5-*dinitrobenzoate* had m.p. 126–128° from EtOH. (Found: C, 59·75; H, 5·7; N, 8·0. $C_{18}H_{20}N_2O_6$ requires: C, 60·0; H, 5·6; N, 7·75%). The alcohols could not be equilibrated using aluminium isopropoxide in isopropanol containing a trace of acetone. Both alcohols gave 3-methylcar-4-en-2-one on oxidation.

Reduction of 3-methylcar-4-en-2-one with LAH (2·6 mole equivs) in THF gave an *exo-endo* ratio of 7:43, and by using lithium tri-t-butoxyaluminium hydride (4·0 mole equivs) in THF, a ratio of 3:47 was obtained.

The structural assignments for the *exo-* and *endo-* alcohols (*exo* having the OH group and the cyclopropane ring *trans*, and *endo* having these groups *cis*) were based on the relative amounts formed when a bulky reducing agent, e.g. lithium tri-t-butoxyaluminium hydride, was used, the *endo-* alcohol being the predominant product, and on the order of elution on chromatography, the *endo*-alcohol being eluted first.

Reduction of 3-*methylcar-4-en-2-one* (I) *with sodium in ethanol*

Sodium (2·61 g) was added in small pieces to 3-methylcar-4-en-2-one (1·00 g) in dry, refluxing EtOH (20 ml). After the Na had dissolved, the soln was heated under reflux during a further 30 min. The mixture was poured into water and extraction with ether gave the liquid product (0·89 g; 88%), b.p. 63–64°/0·4 mm; ν_{max}^{film} 3400 cm^{-1}-no carbonyl absorption, which was shown by GLC to be largely III (82%). The 3,5-

dinitrobenzoate had m.p. 122·5–125·5° from EtOH. (Found: C, 59·85; H, 6·25; N, 7·4. $C_{18}H_{22}N_2O_6$ requires: C, 59·65; H, 6·1; N, 7·75%.)

1-*Methyl*-p-*menth*-5-*en*-2-*one* (V)

Compound III (0·51 g; 82% pure) in "Analar" acetone (10 ml) was oxidized with 6N chromic acid (1·02 ml). Isolation of the product gave the ketone (0·40 g; 77%), ν_{max}^{film} 1718 cm^{-1}. Reduction of the ketone with lithium tri-t-butoxyaluminium hydride in THF gave back the original alcohol.

1-*Methyl*-p-*menthan*-2-*ol* (VI)

Compound III (5·01 g) in AcOH (25 ml) was hydrogenated over Pt at atm press. The uptake of H_2 ceased after 1 mole of H_2 had been absorbed. The AcOH was neutralized with solid Na_2CO_3, water was added and the product was isolated with ether. The product (4·67 g; 93%), b.p. 68–70°/2 mm, ν_{max}^{film} 3350 cm^{-1}, was shown by GLC to consist of 1-methyl-*p*-menthan-2-ol (77%) and three other products (23%). The 3,5-*dinitrobenzoate* had m.p. 118–120° from EtOH. (Found: C, 59·25; H, 6·8; N, 7·4. $C_{18}H_{24}N_2O_6$ requires: C, 59·35; H, 6·65; N, 7·7%.)

1-*Methyl*-p-*menthan*-2-one (VII)

Compound VI (4·67 g) in "Analar" acetone (50 ml) was oxidized with 6N CrO_3 (9·20 ml). Most of the acetone was evaporated at 20°, water was added and the product was isolated with ether as a liquid (4·51 g; 97%), which was shown by GLC to be largely (89%) 1-methyl-*p*-menthan-2-one. The 2,4-*dinitrophenylhydrazone* had m.p. 100–102·5° from EtOH. (Found: C, 58·9; H, 7·05; N, 16·2. $C_{17}H_{24}N_4O_4$ requires: C, 58·6; H, 6·95; N, 16·1%). The ketone was purified through its hydroxymethylene derivative.

Impure 1-methyl-*p*-menthane-2-one (1·60 g) in dry benzene (10 ml) was added at 20° to a stirred suspension of MeONa (2·61 g) in a soln of dry HCOOEt (3·40 g) in dry benxene (40 ml). After stirring at 20° during 27 hr, the mixture was poured into ice-water and the aqueous layer separated. The benzene layer was extracted with 5% KOHaq (6 × 30 ml), the extracts were combined with the aqueous layer and washed once with ether. The aqueous soln of the Na-salt of the hydroxymethylene derivative was steam-distilled until no more ketone passed over. Extraction of the distillate with ether gave pure 1-methyl-*p*-menthan-2-one (0·58 g; 36%), bath temp ≯ 140°/1·3 mm, ν_{max}^{film} 1711 cm^{-1}. The ketone was identical with an authentic sample of 1-methyl-*p*-menthan-2-one (IR spectrum, m.p. of 2,4-dinitrophenylhydrazone, mixed GLC, PMR spectrum). The mixed m.p. of the 2,4-dinitrophenylhydrazone derivatives was however slightly depressed (mixed m.p. 90·5–101°). This is presumably due to the ketone derived from 3-methylcar-4-en-2-one being racemic, and the synthesized authentic sample, derived from (+) carvone, being optically active.

Methylation of p-*menthan*-2-*one*

p-Menthan-2-one was prepared from (+) carvone.[7]

(a) *Sodium hydride*. *p*-Menthan-2-one (1·00 g) in dry dioxan (10 ml) was added at 20° to a stirred suspension of NaH (0·25 g) in dioxan (10 ml), and the mixture was heated under reflux during 2 hr. After cooling to 20°, MeI (0·95 g) in dry dioxan (15 ml) was added with stirring and the mixture was stirred during a further 15 hr. Isolation of the product gave a mobile liquid (0·96 g) ν_{max}^{film} 1710 cm^{-1}, which was shown by GLC to be largely (83%) 1-methyl-*p*-menthan-2-one, with a trace of *p*-menthan-2-one.

(b) *Potassium t-butoxide*. A mixture of *p*-menthan-2-one (1·00 g) and MeI (2·00 g) in dry t-butanol (20 ml) was added with stirring to a soln of potassium t-butoxide in t-butanol (30 ml; from 0·73 g K), and the mixture was stirred at 20° during a further 15 hr. The product was a mobile liquid (1·13 g), ν_{max}^{film} 1710 cm^{-1}, which was shown by GLC to be largely (89%) 1-methyl-*p*-menthan-2-one.

The crude alkylation product was purified through its hydroxymethylene derivative as described above. The product was pure VII. The 2,4-dinitrophenylhydrazone had m.p. 98–99·5° from EtOH. (Found: C, 58·3; H, 7·05; N, 15·95. $C_{17}H_{24}N_4O_4$ requires: C, 58·6; H, 6·95; N, 16·1%). The PMR spectrum (40 Mc/s, CCl_4 soln) showed absorption at 9·05 [doublet, $J = 9$ c/s; $(CH_3)_2$ CH—], 9·05 [singlet; $(CH_3)_2C$ at $C_{(1)}$], 8·40 [broad singlet; protons at $C_{(4)}$, $C_{(5)}$, $C_{(6)}$ and $C_{(8)}$], and 7·80 τ [broad singlet; protons at $C_{(3)}$].

Treatment of 3-*methylcar*-4-*en*-2-*one* (I) *with acetic anhydride/conc sulphuric acid*

Conc H_2SO_4 (1·50 g) in Ac_2O (45 ml) was added at 20° to a soln of 3-methylcar-4-en-2-one (5·00 g) in Ac_2O (150 ml). The mixture was kept at 20° during 1 hr, during which time the colour of the soln changed from brown to magenta. The soln was poured into water (1000 ml) and the mixture was shaken until all the Ac_2O was hydrolysed. After making alkaline by the addition of solid Na_2CO_3, the product was isolated with ether. The liquid product (4·36 g), ν_{max}^{film} 1760, 1730, 1255, 1210 (all strong) cm^1, was shown by GLC to consist of two main products (18% and 66%). These were isolated by chromatography on silica gel. Elution with light petroleum–ether (19:1–9:1) gave XII (0·73 g; 12%), b.p. 88–89°/0·225 mm ν_{max}^{film} 1763, 1211 cm^{-1} λ_{max}^{EtOH} 305 mμ (ε 4110), λ^{EtOH} 205 mμ (ε 13,200), which was almost pure (92%). The PMR spectrum (60 Mc/s; $CDCl_3$ soln) showed absorption at 8·78 [doublet, J = 6·5 c/s; $CH_3)_2$ CH—], 7·96 [singlet; CH_3CO_2—], 7·70 [singlet, both aromatic methyl groups], 6·80–7·40 [multiplet; $(CH_3)_2$ *CH*—]. 3·25 [doublet. J = 1·5 c/s. aromatic proton]. and 3·06 τ [doublet. $J \doteq$ 1–2 c/s; aromatic proton]. Elution with light petroleum–ether (17:3–3:1) gave XI (2·86 g; 35%). (Found: C, 66·25, H, 8·4. $C_{15}H_{22}O_4$ requires: C, 67·65; H, 8·35%), b.p. 109–111°/0·25 mm, ν_{max}^{film} 1762, 1730, 1256, 1212 cm^{-1}, λ^{EtOH} 205 mμ (ε 3010).

When the reaction was followed by working up samples at intervals, it was found that the reaction was complete after 15 min; and that both products were stable under the reaction conditions during 24 hr.

5-Isopropyl-2,3-dimethylphenol

Compound XII (97 mg) in 1% methanolic KOH (10 ml) was healed under reflux during 2 hr. The soln was poured into water, the mixture acidified with dil HCl and the product was extracted with ether. Evaporation of the dried soln gave the crude phenol, which was purified by extracting into 50% NaOHaq from a soln in light petroleum, and acidifying the alkaline extract. Extraction with ether gave the purified phenol (22 mg), ν_{max}^{film} 3350 cm^{-1}, λ_{max}^{EtOH} 281 mμ (ε 1090), 275 mμ (ε 1085), λ^{EtOH} 235 mμ (ε 1390); $\lambda_{max}^{EtOH/5\% KOH}$ 294 mμ (ε, 1040). The 'neutral' fraction (60 mg) had λ_{max}^{film} 3350 cm^{-1}.

*8-Hydroxy-1-methyl-*p*-menth-5-en-2-one* (XIII)

Compound XI (0·30 g) in 1% methanolic KOH (26 ml) was heated under reflux during 1 hr. The soln was poured into brine, and the product was extracted with ether. Evaporation of the dried soln gave the hydroxy-ketone (0·21 g), bath temp ≯ 200°/0·65 mm, ν_{max}^{film} 3425, 1708 cm^{-1}, λ^{EtOH} 205 mμ (ε 1780), which was largely (97%) one compound. The 2,4-dinitrophenylhydrazone, prepared by treatment with 2,4-dinitrophenylhydrazine in pyridine, had m.p. 113–115° from light petroleum–ether. (Found: C. 56·3; H. 6·35; N, 15·25. $C_{17}H_{22}N_4O_5$ requires: C, 56·35; H, 6·1; N, 15·45%).

Attempts to oxidize the OH group using either (a) MnO_2 in light petroleum, or (b) CrO_3 in pyridine at 20°, resulted in the recovery of the hydroxy-ketone. CrO_3 in pyridine at 100° degraded the molecule.

*8-Acetoxy-1-methyl-*p*-menth-5-en-2-one* (XIV)

Compound XI (1·65 g) and 10% Na_2CO_3aq (1·35 ml) in sufficient water and MeOH to obtain a homogeneous soln, was heated under reflux during 3 hr. The soln was poured into brine, and the product was extracted with ether. The crude product (1·08 g) was purified by chromatography on silica gel. Elution with light petroleum–ether (4:1–3:1) gave the *acetoxy-ketone* (0·56 g; 40%). (Found: C, 69·75; H, 9·35. $C_{13}H_{20}O_3$ requires: C, 69·6; H, 9·0%), b.p. 111–113°/0·65 mm, ν_{max}^{film} 1732, 1715, 1253 cm^{-1}, which was pure by GLC. Treatment of the acetoxy-ketone with boiling 1% methanolic KOH gave XIII.

*8-Acetoxy-1-methyl-*p*-menthan-2-one* (XV)

Compound XIV (0·31 g) in AcOH (10 ml) was hydrogenated at atm. press. over Pt. Uptake ceased at 1 mole of H_2. The soln was neutralized with solid Na_2CO_3, water was added and the product was isolated with ether. The saturated acetoxy-ketone (0·24 g; 78%) bath temp ≯ 190°/1·5 mm, ν_{max}^{film} 1728, 1708, 1258 cm^{-1}, was largely one compound (92%). The *2,4-dinitrophenylhydrazone* had m.p. 129–132° from EtOH. (Found: C, 56·55; H, 6·25; N, 13·55. $C_{19}H_{26}N_4O_6$ requires: C, 56·15; H, 6·45; N, 13·8%.)

*Pyrolysis of 8-acetoxy-1-methyl-*p*-menthan-2-one* (XV)

8-Acetoxy-1-methyl-*p*-menthan-2-one (95 mg) was passed over silica chips heated at 400° in a stream of N_2. The product which was collected in a trap at −80°, was dissolved in ether and washed with Na_2CO_3aq to remove AcOH. Evaporation of the dried soln gave a liquid (50 mg), ν_{max}^{film} 1705, 1645, 890 (strong) cm^{-1}, which was shown by GLC to consist of XVI; (73%), XV (2%) and one other product (14%).

Hydrogenation of the pyrolysis mixture (41 mg) in AcOH (5 ml) over Pt resulted in the rapid uptake of 0·89 mole of H_2. Isolation of the product gave a liquid, ν_{max}^{film} 1705, 890 (weak) cm^{-1}, which was shown by GLC to be a mixture of three components. The major component (77%) was identified with an authentic sample of VII (IR spectrum, mixed GLC).

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