237. The 'Aldol Condensation' of Citral and Related Reactions

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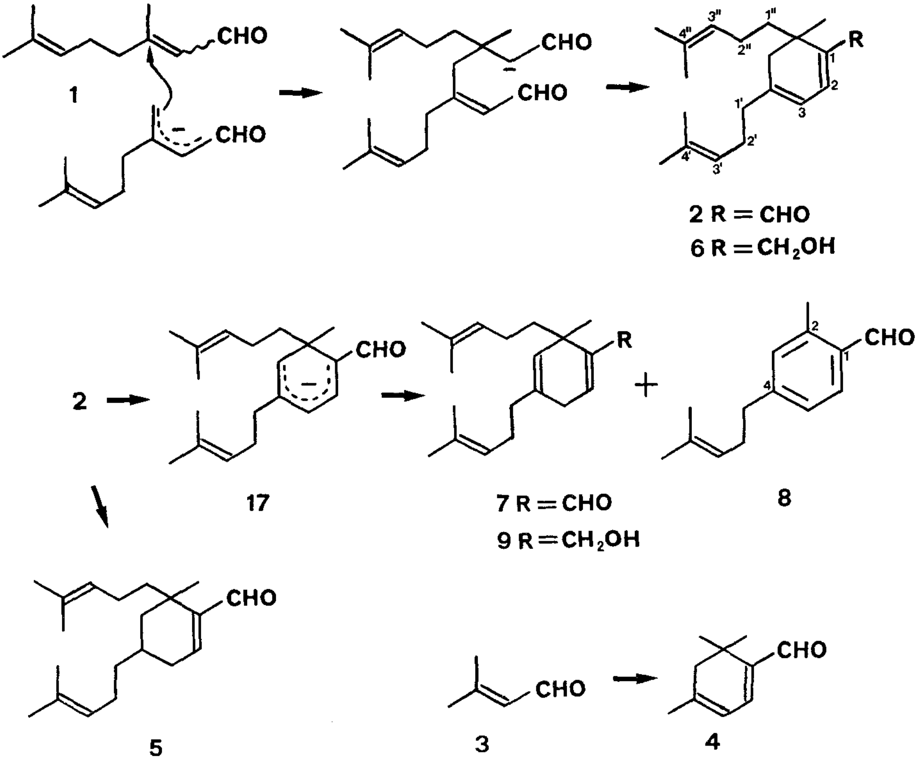
Summary. The reaction of citral with anhydrous base leads initially to a cyclohexa-1,3-diene-carbaldehyde. Stronger base and longer reaction times result in deconjugation to a cyclohexa-1,4-diene-carbaldehyde, together with oxidative loss of six carbon atoms to yield 2-methyl-4-(4-methylpent-3-enyl)benzaldehyde. A mixed aldol reaction between citral and 3-methyl-2-butenal (= senecia aldehyde) is described.

It has been known for a long time that citral[1] (**1**) 'polymerizes' in the presence of alcoholic potassium hydroxide; it was soon suspected that the major product was a single substance [2], and in 1932 a probable structure (**2**) was ascribed to what was

Scheme



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[1] This paper employs the term 'citral' to mean the commercial mixture of (*E*) and (*Z*) isomers. The early history of citral is given by *Tiemann* [1].

presumably the same substance (obtained this time with sodium amide in ether) by analogy with a similar reaction using 3-methyl-2-butenal (**3**) and which yielded substance **4** [3]. We now provide evidence supporting structure **2**, and describe further reactions of the same type.

In the presence of anhydrous potassium hydroxide in toluene, citral (**1**) dimerizes with loss of water to give 60% isolated yield of a single substance (by thin-layer (TLC.) and gas chromatography (GC.)), 4,6-bis-(4-methylpent-3-en-1-yl)-6-methylcyclohexa-1,3-diene-carbaldehyde (**2**). The cyclohexadiene-carbaldehyde structure is demonstrated by the UV. spectrum. Catalytic reduction of **2** with absorption of one equivalent of hydrogen gave an α,β-unsaturated aldehyde (**5**, by UV. spectrum), lithium aluminium hydride reduction yielding a 1,3-cyclohexadienylmethanol (**6**, by UV. and NMR. spectra).

When **2** was stirred with potassium *t*-butoxide in toluene, it slowly disappeared, quenching of the mixture ultimately yielding a number of products, the two main ones being the cyclohexa-1,4-diene-carbaldehyde **7**, and a substituted benzaldehyde **8**. The UV. spectrum of **7** indicated the presence of an α,β-unsaturated aldehyde, but after lithium aluminium hydride reduction, the UV. spectrum of the alcohol **9** showed no evidence of double bond conjugation. A signal at 2.88 ppm in the ^{1}H–NMR. spectrum of the aldehyde **7**, and at 2.58 ppm in the spectrum of the alcohol **9**, corresponds to the presence of a methylene group between two double bonds, and the changes in the ^{13}C–NMR. spectrum after conversion of **2** to **7** support the structures ascribed. In particular, the highest field triplet in the off-resonance spectrum of **2** is at 41.9 ppm, consistent with the methylene group $H_2C(5)$ of the cyclohexadiene ring adjacent to the quaternary atom C(6), and a doublet at 118.0 ppm corresponds to C(3). In the rearranged dienal **7**, there is no triplet at higher field than 39.4 ppm, and the doublet for the unsaturated carbon (now C(5)) is at 130.9 ppm, the high field again being associated with the adjacent quaternary centre.

Formation of the benzaldehyde **8** corresponds to an oxidation, and in order to investigate this more thoroughly, we repeated the reactions described above with dihydrocitral (**10**) [4]. The fact that all the products are exactly paralleled indicates that the double bonds of the side chains play no part in the double bond rearrrangement of **2** with strong base; an additional advantage of working with dihydrocitral is that the gas chromatographic separation of the products is less tedious than in the case of citral. From the reaction of what we can safely take to be **11** (the spectra are as expected, based on those of the analog **2**) with potassium *t*-butoxide in toluene, we isolated, in addition to the aldehydes **12**, and **13** (corresponding to **7** and **8**), a less unsaturated aldehyde to which we ascribe the structure **14** based on the following considerations. The double bond is not conjugated with the carbonyl group (UV. spectrum) and carries only one proton. The ^{1}H–NMR. spectrum shows the signal for this proton at 5.38 ppm, and its width at half height ($w_{1/2}$) is 8 Hz, similar to the values found in the model compound 4,6,6-trimethylcyclohex-3-ene-carbaldehyde (**15**), the preparation of which is described below, and not like the one of the known [5] 2,2,4-trimethylcyclohex-3-ene-carbaldehyde (**16**) which has a signal at 5.11 ppm with $w_{1/2}$ = 4 Hz²).

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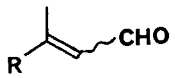
²) We are grateful to Mr. *R. Chappaz* for the NMR. spectrum of this substance.



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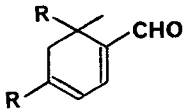

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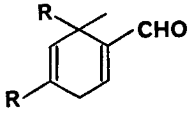

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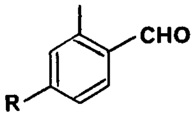

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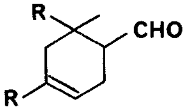

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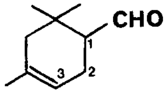

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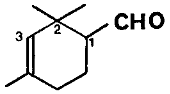

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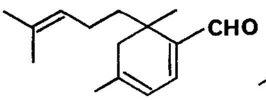
R= $(CH_2)_3CH(CH_3)_2$

The position of the substituents in the benzaldehyde derivative **13**, was confirmed by the fact that the displacement of the signals caused by addition of the shift agent Eu(fod)$_3$ was greater for the methyl group attached to the aromatic ring than for the methylene group $H_2C(1')$ of the side chain. By analogy, this confirms the positions accorded to the substituents in **8**.

The mechanism for the formation of the aldehydes **2** and **7**, respectively, is presumably as shown in the *Scheme*. Anions of the type **17** are known to be protonated at C(3) [6], and oxygen addition also takes place at this position [7]. In the oxygenation reaction of the anion derived from an ester similar to **11** (R=CH_3) loss of a methyl group leading to an aromatic compound was reported [7]. In our case, formation of the benzaldehydes **8** and **13** in the absence of oxygen could occur with excess **2** serving as hydrogen acceptor, evidence being provided by the isolation of **14** in the case of the dihydrocitral reaction.

As expected, we isolated from the reaction of a mixture of excess citral (**1**) and 3-methyl-2-butenal (**3**) with anhydrous potassium hydroxide a mixture of the two possible 'mixed' condensation products **18** and **19**, besides the citral 'dimer' **2**. The aldehyde with the shorter retention time (GC.) on Apiezon columns was readily identified as **18** by the facile loss of a C_6 fragment (substituent in allylic position and at a quaternary centre) in its mass spectrum.



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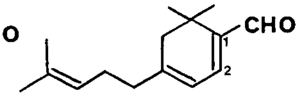

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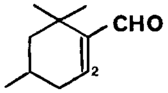

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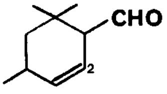

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The model compound **15** was prepared by reduction of the 'dimer' **4** of 3-methyl-2-butenal with sodium in liquid ammonia. The presence of oxygen during the reaction tends to produce small amounts of by-products with an oxygen function at C(3), but in its absence, the principal products of the reaction were the desired compound **15** and the α,β-unsaturated aldehyde **20**, the latter possibly arising from 1,4-addition of hydrogen across the diene system of **4** yielding **21**, followed by rearrangement of the double bond to the conjugated isomer **20** during work up. Under the conditions used the double bond isomer **16** was not detected.

Experimental Part

^{1}H-NMR. spectra were recorded in $CDCl_3$ either on a *Hitachi-Perkin Elmer* R-20B instrument, or on a *Bruker* HX-90, ^{13}C-NMR. spectra being recorded on the latter. Chemical shifts δ are given in ppm, coupling constants J in Hz. Mass spectra were measured on an *Atlas* CH 4 mass spectrometer, using an inlet temperature of about 150° and electrons of 70 eV. Results are quoted as m/e (% most important fragment), and generally, the ten most important fragments are given. UV. spectra were measured on a *Unicam* SP 700A spectrometer in ethanol (λ_{max} (ε) in nm.) For gas chromatography of the C_{14} and C_{20} compounds, a column (2 m × 4 mm, or 1 m × 4 mm) of purified Apiezon, 10% an Chromosorb W, was used. The Apiezon was purified by chromatography in pentane on a column of silica gel; it was eluted with the solvent as a colorless thick oil, the brown impurities being retained on the column. Thus purified, the Apiezon can be heated to 230° in the GC. oven without appreciable elution.

4,6-bis(4-Methylpent-3-en-1-yl)-6-methylcyclohexa-1,3-diene-carbaldehyde (**2**). A suspension of 28 g of anhydr. potassium hydroxide in 500 ml of abs. toluene was stirred at –5° while 50 g of citral were added over 5 min. The mixture was stirred at room temp. for 6 h, then about 300 ml of ether were added, and the organic phase washed to neutrality with water, concentrated, and distilled. A fraction of b.p. 140–150°/0.1 Torr, weighing 28 g (60%), that was practically pure was obtained. For analysis, this was purified by GC., or by chromatography on silica gel. – ^{1}H-NMR.: 1.19 (*s*, 3H, H_3C—C(6)); 1.55 to 1.75 (12H, 2H_3C—C(4′) and 2H_3C—C(4″)); 2.05 to 2.35 (6H, 2H—C(5), 2H—C(2′) and 2H—C(2″)); 1.85 (br.*d*, 2H, 2H—C(1′)); 5.12 (br.*s*, 2H, H—C(3′) and H—C(3″)); 5.95 (br.*d*, J = 6, 1H, H—C(3)); 6.67 (sharp *d*, J = 6, 1H, H—C(2)); 9.47 (*s*, 1H, C*HO*). – ^{13}C-NMR.: 17.5 (*q*), 17.7 (*q*) and 25.6 (2*q*) (2*C*H_3—C(4′) and 2*C*H_3—C(4″)); 25.2 (*q*, H_3*C*—C(6)); 36.2 (*s*, C(6)); 41.9 (*t*, C(5)); 118.0 (*d*, C(3)); 123.4, 124.9 (2*d*), 130.9 and 132.2 (2*s*) (C(4′), C(4″), C(3′) and C(3″)); 141.5 (*s*, C(4)); 145.7 (*d*, C(2)); 150.7 (*s*, C(1)); 193.0 (C*HO*). – MS.: 41 (100), 203 (82), 69 and 105 (68), 55 (46), 91 (32), 199 (30), 43 (28), 83 (27), 134 (23) ... 268 ($M^{\dot{+}} - 18$, 9), 253 ($M - 33^+$, 8), 286 ($M^{\dot{+}}$, 4). – UV.: 319 (11300).

$C_{20}H_{30}O$ (286.44) Calc. C 83.86 H 10.56% Found C 83.76 H 10.70%

Semicarbazone, m.p. 102° (methanol).

$C_{21}H_{33}N_3O$ (343.49) Calc. C 73.42 H 9.68 N 12.23% Found C 73.50 H 9.71 N 12.27%

4,6-Diisohexyl-6-methylcyclohexa-1,3-diene-carbaldehyde (**11**). From 0.1 g of dry potassium hydroxide and 2.7 g of dihydrocitral [4] in 20 ml of toluene were obtained after 3.5 h in the same way as in the preceding experiment, 0.7 g of **11**, b.p. 135°/0.001 Torr. – NMR.: 0.83 and 0.88 (2*d*, J = 6, 12H, 2H_3C—C(4′) and 2H_3C—C(4″)); 1.18 (*s*, 3H, H_3C—C(6)); 5.88 (*d*, 1H); 6.62 (*d*, J = 6, 1H); 9.38 (*s*, 1H) (attributions similar to those of **2**). – MS.: 43 (100), 85 (73), 41 (24), 177 (22), 57 (21), 105 (14), 91 (11) ... 205 (9), 204 (8), 261 (1), 290 ($M^{\dot{+}}$, 2.5).

$C_{20}H_{34}O$ (290.47) Calc. C 82.69 H 11.80% Found C 81.48 H 11.50%

4,6-bis(4-Methylpent-3-en-1-yl)-6-methylcyclohex-6-ene-carbaldehyde (**5**). A solution of 10 g of the aldehyde **2** in 100 ml of ethanol was shaken in a hydrogen atmosphere with 10% Pd/C. After 40 min, 870 ml of H_2 were used (theor. 860 ml/mol), the catalyst filtered and the solvent removed to yield, after distillation at 135°/0.001 Torr, 8.9 g of a compound which was *ca.* 90% pure **5.** The latter was purified by GC. for analysis. – ^{1}H-NMR.: 1.18 (*s*, 3H, H_3C–C(6)); 1.5 to 1.8 (12H, 2H_3C–C(4′) and 2H_3C–C(4″)); 5.14 (approx. *t*, *J* = 6, 2H, H–C(3′) and H–C(3″)); 6.77 (*d*×*d*, 1H, H–C(2)); 9.42 (*s*, 1H, C*H*O). – MS.: 43 (100), 41 (80), 55 and 69 (70), 29 and 99 (44) ... 270 ($M - 18^{+\cdot}$, 14); 288 ($M^{+\cdot}$, 1). – UV.: 232 (12000).

$C_{20}H_{32}O$ (288.45) Calc. C 83.27 H 11.18% Found C 82.72 H 11.14%

4,6-bis(4-Methylpent-3-en-1-yl)-6-methylcyclohexa-1,4-diene-carbaldehyde (**7**). A suspension of 208 g of potassium *t*-butoxide in 2800 ml of dry toluene was stirred at –5° while 280 g of citral were introduced over 1 h. The reaction was followed by GC. (the samples were quenched in water and the solvent was concentrated). After less than 1 h the aldehyde **2** was formed, together with **8** of much shorter retention time. After several hours, **2** had almost disappeared, and **7** of intermediate retention time had appeared. After stirring for a total of 12 h, during which time the mixture was allowed to come to room temp., 1000 ml of ether were added, and after washing to neutrality, the solvents were removed, and the residue distilled. The fraction (88 g) of b.p. 95–145°/0.01 Torr was redistilled, yielding a) 19 g of material with b.p. 96–103°/0.001 Torr (see below), b) 31 g of 90% pure **7**, b.p. 110–130°/0.001 Torr. Redistillation was always accompanied by polymerisation, and for further analytical purification GC. was used. – ^{1}H-NMR.: 1.22 (*s*, 3H), 1.50 to 1.75 (12H), 2.0 to 2.2 (6H), attributions as for the isomer **2** (above); 2.88 (*d*, *J* = 3, 2H, ^{2}H–C(3)); 4.9 to 5.2 (*m*, 3H, H–C(5), H–C(3′) and H–C(3″)); 6.73 (*t*, *J* = 3, 1H, H–C(2)); 9.39 (*s*, 1H, C*H*O). – ^{13}C-NMR.: 17.5, 25.6 and 26.2 (3*q*, 3CH_3); 36.5 (*t*, C(5)); 38.6 (*s*, C(2)); 124.0, 124.9 (2*d*); 130.8 and 131.7 (2*s*); C(3″), C(4″), C(3′), C(4′); 130.7 (*s*, C(4)); 130.9 (*d*, C(3)); 144.6 (*s*, C(1)); 150.4 (*d*, C(6)); 193.7 (*d*, *C*HO). – MS.: 69 (100), 41 (87), 134 (69), 55 (29), 83 (24), 29 (20), 43 (17), 91 and 133 (15) ... 199 (8), 203 (10), 253 (4), 268 (2), 286 ($M^{+\cdot}$, 1). $\lambda_{\max}^{\text{EtOH}}$ 230 shoulder (*ca.* 9000).

$C_{20}H_{30}O$ (286.44) Calc. C 83.86 H 10.56% Found C 83.87 H 10.58%

The semicarbazone could not be crystallized.

2-Methyl-4-(4-methylpent-3-en-1-yl)benzaldehyde (**8**) was obtained almost pure from fraction a) of the distillation described in the foregoing experiment; it was further purified by either redistilling or GC. – ^{1}H-NMR.: 1.54 and 1.58 (2*s*, each 3H, isopropylidene group); 2.62 (*s*, 3H, H_3C–C(2)); 5.12 (*d*×*t*, *J* = 1.5 and 6, 1H, H–C(3′)); 7.03 (*s*, 1H), 7.13 (*d*, *J* = 7, 1H), 7.66 (*d*, *J* = 7, 1H) (arom. protons); 10.17 (*s*, 1H, C*H*O). – MS.: 69 (100), 134 (82), 41 (68), 105 (48), 43 (23, 91 and 119 (16), 29 and 55 (13) ... 201 (6), 202 ($M^{+\cdot}$, 5). $\lambda_{\max}^{\text{EtOH}}$ 263 nm, $\varepsilon_{\max}$ 16000.

$C_{14}H_{18}O$ (202.28) Calc. C 83.10 H 8.97% Found C 83.20 H 8.92%

Semicarbazone, m.p. 190–192° (ethanol).

$C_{15}H_{21}N_3O$ (259.35) Calc. C 69.46 H 8.16 N 16.21% Found C 69.62 H 8.18 N 16.07%

4,6-Diisohexyl-6-methylcyclohexa-1,3-diene-carbaldehyde (**12**). This was prepared in the same way as **7** (above) from 10 g of dihydrocitral and 7.35 g of potassium *t*-butoxide in 100 ml of toluene. After 5 h, the product was distilled (75–127°/0.001 Torr) giving 3.5 g of a mixture with three main components, **12**, **13**, and **14**, in proportions of *ca.* 55:35:10, respectively. **12** had the following data. – ^{1}H-NMR.: 0.79 and 0.85 (2*d*, *J* = 6, 12H); 1.22 (*s*, 3H, H_3C–C(2)); 2.84 (*d*, *J* = 4, 2H, 2H–C(3)); 5.00 (*d*, *J* = 1, 1H, H–C(5)); 6.72 (*t*, *J* = 4, 1H, H–C(2)); 9.35 (*s*, 1H, CHO). – ^{13}C-NMR.: 36.6 (*t*, C(5)); 38,6 (*s*, C(2)); 130.6 (*s*, C(4)); 130.9 (*d*, C(3)); 144.9 (*s*, C(1)); 150.7 (*d*, C(6)); 194.1 (CHO). – MS.: 43 (100), 85 (61), 105 (40), 204 (35), 41 (31), 134 (28), 106 and 177 (26), 91 (19) ... 290 ($M^{+\cdot}$, 1). $\lambda_{\max}^{\text{EtOH}}$ 225 nm, $\varepsilon_{\max}$ 8600.

$C_{20}H_{34}O$ (290.47) Calc. C 82.69 H 11.80% Found C 83.10 H 11.50%

2-Methyl-4-isohexylbenzaldehyde (**13**) was purified by GC. for analysis. – ^{1}H-NMR.: 0.86 (*d*, *J* = 6, 6H, 2H_3C–C(4′)); 1.0 to 1.8 (*m*, 5H); 2.62 (*s*, 3H, H_3C–C(2), superimposed on 2H, H_2C–C(4)); 7.05 (*s*, 1H, superimposed on 7.14, *d*, 1H, coupled with 7.67, *d*, *J* = 8; arom. protons);

10.19 (*s*, 1H, CHO). Addition of Eu(fod)$_3$: 2.62 (H$_3$C—C(2)) → 3.95 and signal of 2H—C(1′) → 2.95 (*t*). – MS.: 105 (100), 204 (M^{+}, 84), 134 (71), 43 (51), 91 and 121 (40), 133 (37), 41 (30), 203 (22).

$C_{14}H_{20}O$ (204.34) Calc. C 82.30 H 9.86% Found C 82.34 H 9.92%

4,6-Diisohexyl-6-methylcyclohex-3-ene-carbaldehyde (**14**) was also purified by GC. for analysis. – ^{1}H-NMR.: 0.87 (*d*, *J* = 6.5, 12H); 0.98 and 1.04 (2*s*, together 3H, H$_3$C—C(2), two isomers); 2.0–2.3 (*m*, 4H, 2H—C(2) and 2H—C(5)); 5.38 (br.*s*, 1H, H—C(3)); 9.77 (*d*, *J* = 3, 1H, CHO). – MS.: 43 (100), 85 (60), 177 and 41 (53), 69 (45), 95 (44), 55, 81 and 207 (38) ... 292 (M^{+}, 2). – UV.: only end absorption.

Reductions with Lithium Aluminium Hydride. They were carried out by adding the substance drop by drop to a slurry of excess reagent in dry ether, stirring for 5 min, then decomposing the excess hydride with careful addition of wet ether and water. The products were isolated by filtration and concentration. Generally, the C$_{20}$ alcohols were not easily purified by GC., but were chromatographed on silica gel, after which they exhibited a single spot on TLC. They were dried in high vacuum over P_2O_5.

4,6-bis(4-Methylpent-3-en-1-yl)-6-methylcyclohexa-1,3-dienyl-methanol (**6**). Prepared from **2** as described above. – ^{1}H-NMR.: 1.02 (*s*, 3H, H$_3$C—C(6)); 1.55–1.75 (12H, two isopropylidene groups); 1.95–2.25 (6H, 2H—C(1′), 2H—C(2′) and 2H—C(2″)); 4.16 (*s*, 2H, CH$_2$OH); 4.9–5.3 (*m*, 2H, H—C(3′) and H—C(3″)); 5.60 (*d*, *J* = 5, 1H, H—C(3)); 5.86 (*d*, *J* = 5, 1H, H—C(2)). – MS.: 41 (100), 119 (86), 69 (85), 55 (66), 132 (56), 83 (45), 105 (41), 145 and 201 (39), 91 (37) ... 270 ($M-18^{+}$, 8), 288 (M^{+}, trace). $\lambda_{\max}^{\text{EtOH}}$ 270 nm, $\varepsilon_{\max}$ 8300.

$C_{20}H_{32}O$ (288.45) Calc. C 83.27 H 11.18% Found C 83.17 H 10.99%

4,6-bis(4-Methylpent-3-en-1-yl)-6-methylcyclohexa-1,4-dienyl-methanol (**9**). Prepared from **7** as described above. – ^{1}H-NMR.: 1.08 (*s*, 3H); 1.45–1.75 (12H); 1.95–2.15 (6H); 2.58 (*d*, *J* = 2.5, 2H, 2H—C(3)); 4.10 (*d*, *J* = 1, 2H, C*H*$_2$OH); 4.85–5.20 (*m*, 3H, H—C(5), H—C(3′) and H—C(3″)); 5.80 (*t*, *J* = 2.5, 1H, H—C(2)). – MS.: 105 (100), 41 (57), 69 (41), 55 and 119 (31), 135 and 175 (23), 83 (19), 91 and 131 (16) ... 255 (1), 270 ($M-18^{+}$, trace).

$C_{20}H_{32}O$ (288.45) Calc. C 83.27 H 11.18% Found C 83.20 H 11.44%

2-Methyl-4-(4-methylpent-3-en-1-yl)benzyl alcohol. Prepared from **8** as described above. – ^{1}H-NMR.: 1.57 and 1.68 (2*s*, each 3H); 2.29 (*s*, 3H, H$_3$C—C(2)); 4.54 (*s*, 2H, C*H*$_2$OH); 5.15 (*t*, *J* = 6, 1H, H—C(3′)); 6.8–7.3 (*m*, 3H, arom. protons). – MS.: 135 (100), 69 (84), 41 (62), 107 (52), 118 (38), 91 (33), 134 and 119 (25), 105 (21), 204 (M^{+}, 17).

$C_{14}H_{20}O$ (204.34) Calc. C 82.30 H 9.87% Found C 82.52 H 9.81%

Reaction between Citral and 2-Methyl-2-butenal. A suspension of 5.6 g (0.5 mol) of potassium *t*-butoxide in 350 ml of dry toluene was stirred vigorously at 0–4° while a mixture of 30.4 g (2 mol) of citral and 8.4 g (1 mol) of 2-methyl-2-butenal was added during 15 min. The temp. was allowed to rise to 20° and the mixture was stirred for 4 h, then 150 ml of ether were added, and the mixture washed to neutrality, dried, and concentrated. Distillation yielded a fraction (12.5 g) that contained largely C$_{15}$ compounds. On redistillation at 82–84°/0.001 Torr it gave 6.6 g of a mixture of two substances (GC.) in equal amounts.

$C_{15}H_{22}O$ (218.33) Calc. C 82.51 H 10.16% Found (on mixture) C 81.53 H 10.21%

The two substances were separated by GC. (Apiezon); the one with shorter retention time was *4,6-dimethyl-6-(4-methylpent-3-en-1-yl)cyclohexa-1,3-diene-carbaldehyde* (**18**). – ^{1}H-NMR.: 1.20 (*s*, 3H, H$_3$C—C(6)); 1.55, 1.65 and 1.90 (3*s*, each 3H, H$_3$C—C(4) and isopropylidene group); 5.05 (*m*, 1H, H—C(3′)); 5.90 (*d*×*q*, *J* = 6 and 1, 1H, H—C(3)); 6.62 (*d*, *J* = 6, 1H, H—C(2)); 9.38 (1H, CHO). – MS.: 135 ($M-C_6H_{11}^{+}$, 100), 107 (88), 41 (71), 91 (61), 55 (51), 121 and 43 (50), 105 (38) ... 185 and 200 (6), 203 (4), 218 (M^{+}, 4).

The aldehyde of longer retention time was *4-(4-methylpent-3-en-1-yl)-6,6-dimethylcyclohexa-1,3-diene-carbaldehyde* (**19**). – ^{1}H-NMR.: 1.20 (6H); 1.61 and 1.69 (each 3H); 2.1–2.25 (4H, 2H—C(1′) and 2H—C(2′)); 5.10 (1H); 5.94 (br.*d*, *J* = 6, 1H); 6.61 (*d*, *J* = 6, 1H); 9.38 (*s*, 1H);

all attributions as before. – MS.: 69 (100), 41 (82), 43 (58), 29 (48), 105 (31), 150 and 39 (24), 135 and 91 (20) ... 203 (2), 218 (M^{+}, 1).

4,6,6-Trimethylcyclohexa-1,3-diene-carbaldehyde (**4**, *cf.* [3]). A suspension of 5.6 g of potassium hydroxide in 500 ml of dry ether was stirred at 0–5° while 86 g of 2-methyl-2-butenal (**3**) were introduced fairly rapidly (15 min). The mixture was stirred for 2.75 h, then washed with water to neutrality. The residue after removal of the ether was distilled at 64–72°/10 Torr to yield 52.2 g of a nearly pure product, which was purified by redistillation. – ^{1}H-NMR.: 1.21 (*s*, 6H, 2H_3C—C(6)); 1.93 (*m*, J = *ca.* 1, 3H, H_3C—C(4)); 2.14 (*s*, 2H, 2H—C(5)); 5.98 (*d*, J = 6+long range, 1H, H—C(3)); 6.63 (*d*, J = 6, H—C(2)): 9.41 (*s*, 1H, CHO). – MS.: 107 (100), 91 (82), 121 (63), 150 (M^{+}, 57), 105 (45), 79 (26), 77 and 39 (23), 65 and 41 (15).

Semicarbazone, m.p. 210–211° (methanol).

Sodium/Ammonia reduction of 4,6,6-Trimethylcyclohexa-1,3-diene-carbaldehyde (**4**). About 15 ml of ammonia were condensed in a 4-necked flask provided with a current of dry nitrogen. Sodium (0.25 g) was added, followed by 1.5 g of the aldehyde **4**, added at such a rate that the blue color was maintained throughout. After 1 h 40 ml of dry ether were added, and the ammonia allowed to evaporate. The ether solution was washed to neutrality, dried and concentrated. The residue yielded on distillation 1.1 g of material of b.p. below 80°/10 Torr, which was purified by GC. on a 4 m Apiezon column. In order of elution there were obtained: **15**, **20** and **4**.

4,6,6-Trimethylcyclohex-3-ene-carbaldehyde (**15**). – ^{1}H-NMR.: 0.98 and 1.17 (2*s*, each 3H, 2H_3C—C(6)); 1.65 (br.*s*, 3H, CH_3—C(4)); 5.37 (br.*s*, 1H, $w_{1/2}$ *ca.* 8 Hz, H—C(3)); 9.77 (*d*, J = 2, 1H, CHO). – MS.: 107 (100), 121 and 41 (89), 81 (81), 67 (77), 39 (55), 109 and 43 (54), 44 (53), 68 (44) ... 152 (M^{+}, 30).

4,6,6-Trimethylcyclohex-1-ene-carbaldehyde (**20**). – ^{1}H-NMR.: 1.00 (*d*, J = 6, 3H, H_3C—C(4)); 1.18 and 1.25 (2*s*, each 3H, 2H_3C—C(6)); 6.68 (*d*×*d*, J = 6 and 2.5, 1H, H—C(2)); 9.36 (*s*, 1H, CHO). – This substance was very readily oxidized, and mass spectral measurement was obtained by direct coupling of a UCON capillary column with the mass spectrometer: 123 (100), 109 (78), 41 (74), 81 (70), 67 (68), 152 (M^{+}, 66), 137 (61), 39 (52), 95 (45), 43 (43).

2,2,4-Trimethycyclohex-3-ene-carbaldehyde (**16**) [5]. – ^{1}H-NMR.: 0.98 and 1.17 (2*s*, each 3H); 1.65 (3H); 5.11 (*s*, $w_{1/2}$ *ca.* 4 Hz, 1H); 9.77 (*d*, J = 2.5, 1H, CHO).

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