Thermal condensation of formaldehyde with 3-*p*-menthene, 1-*p*-menthene, and cyclooctene

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When a mixture of 3-*p*-menthene, paraformaldehyde, and acetic anhydride was heated at 200 °C in an autoclave, an acetate was obtained. By saponification of the acetate with alcoholic potassium hydroxide, 3-hydroxylmethyl-4-*p*-menthene was obtained. Similarly, 2-hydroxymethyl-6-*p*-menthene was produced from 1-*p*-menthene, and 1-hydroxylmethyl-2-cyclooctene was produced from cyclooctene.

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The addition reaction of formaldehyde with olefins is known as the Prins thermal reaction. The condensation product is mainly the primary alcohol or its acetate, in which the double bond is located at a position adjacent to its original site in the starting olefin (1, 2). This note describes the chemical structures of the Prins alcohols obtained from 3-*p*-menthene (**1**), 1-*p*-menthene (**4**), and cyclooctene (**6**).

From the condensation of 3-*p*-menthene (**1**) with *para*formaldehyde in the presence of acetic anhydride (at 200 °C), an acetate was obtained as the main product. The saponification of the acetate gave an unsaturated alcohol (**2**). The infrared (i.r.) absorption spectrum showed an absorption band at 810 cm^{-1}, indicating the presence of a trisubstituted ethylenic bond. Reduction of the alcohol gave 3-hydroxylmethyl-*p*-menthane (**3**). Therefore, **2** must be 3-hydroxylmethyl-4-*p*-menthene. The structural assignment was further supported by the nuclear magnetic resonance (n.m.r.) spectrum, as will be shown in the Experimental section.

Saponification of the condensation product from 1-*p*-menthene (**4**) with paraformaldehyde gave the corresponding alcohol, 2-hydroxylmethyl-6-*p*-menthene (**5**), as the main product. The structural assignment was supported by i.r. and n.m.r. spectra and also by the catalytic hydrogenation to the corresponding dihydro compound.

From the condensation product of cyclooctene (**6**), an unsaturated alcohol, $C_9H_{16}O$ (**7**), was obtained in ca. 23% yield. The infrared absorption spectrum showed a primary hydroxyl absorption band at 1040 cm^{-1}, and a characteristic band of a *cis* type double bond at 755 cm^{-1}. The dihydro compound obtained by the hydrogenation of **7** was hydroxylmethyl cyclooctane. Therefore, 1-hydroxylmethyl-2-cyclooctene (**7**) is a reasonable assignment for the alcohol.

Experimental

Materials

3-*p*-Menthene (**1**) was prepared as reported previously (3). It was repeatedly distilled until 90% pure. The boiling point at 100 Torr was 102 °C; n_D^{20}, 1.4518.

1-*p*-Menthene (**4**) was prepared by the hydrogenation of *d*-limonene over palladium on carbon: b.p. 68–70 °C at 41 Torr; d_4^{20}, 0.8401; n_D^{20}, 1.4730, infrared: 1360–1380 cm^{-1} (doublet), 800 cm^{-1}.

Commercial cyclooctene (**6**) was fractionally distilled until 95% pure (as shown by gas–liquid chromatographic analysis), b.p. 32 °C at 10 Torr; d_4^{25}, 0.8451; n_D^{25}, 1.4732; infrared: 750 cm^{-1}.

Condensation of 3-p-Menthene (1) with Formaldehyde

A mixture of 180 g of **1**, 60 g of *para*formaldehyde and 75 g of acetic anhydride was heated at 180–220 °C in a stainless steel autoclave for several hours. The reaction mixture was extracted with ether. The ethereal solution was then washed with water and dried over anhydrous sodium sulfate. Fractional distillation gave 102 g of **1** and 60 g of a crude acetate (b.p. 90–110 °C at 5 Torr). Saponification of the product gave 25 g of **2**. This was fractionally distilled until a pure product was obtained, b.p. 100–104 °C at 5 Torr; n_D^{30}, 1.4815; d_4^{30}, 0.9160; hydroxyl group, 10.81% (calcd. for monohydric alcohol, 10.11%); infrared (i.r.): 1050 cm^{-1}, 810 cm^{-1}; nuclear magnetic resonance (n.m.r.): δ 0.97 (two CH_3), δ 1.08 (CH_3), δ 1.72 (two —CH_2), δ 3.60 (—CH_2OH), δ 5.45 (—CH=C—).

Anal. Calcd. for $C_{11}H_{20}O$: C, 78.49; H, 11.98. Found: C, 78.31; H, 11.64.

The 3,5-dinitrobenzoate derivative of **2** was prepared in the usual manner and recrystallized from methanol, m.p. 81 °C.

Anal. Calcd. for $C_{18}H_{22}O_6N_2$: N, 7.73. Found: N, 7.88.

Compound **2** was hydrogenated over a Raney nickel catalyst in methanol solution at 100 °C. An initial hydrogen pressure of 50 kg/cm^2 was used to give 3-hydroxylmethyl-*p*-menthane (**3**), b.p. 91–94 °C at 5 Torr; n_D^{20}, 1.4738; n.m.r.: δ 0.93 (two CH_3), δ 1.02 (CH_3—), δ 1.46 (—CH_2—), δ 2.46 (OH), and δ 3.55 (—CH_2OH).

Anal. Calcd. for $C_{11}H_{22}O$: C, 77.59; H, 13.03. Found: C, 77.12; H, 12.87.

Condensation of 1-p-Menthene (4) with Formaldehyde

From a mixture of 38 g of **4**, 8.5 g of *para*formaldehyde and 14 g of acetic anhydride, 15 g of a crude acetate was obtained. Saponification of this acetate gave 2-hydroxylmethyl-6-*p*-menthene, b.p. 92 °C at 3 Torr; d_4^{20}, 0.9378; n_D^{20}, 1.4850; molecular refraction 52.10 (calcd. for $C_{11}H_{20}O$, $F_1 = 51.85$); i.r.: 1385 and 1365 cm^{-1} (doublet), 1030 cm^{-1}, 800 cm^{-1}; n.m.r.: δ 0.9 (two CH_3), δ 1.4 (CH_3—C(—)=), δ 1.65 (CH_2—), δ 1.8 (—CH_2—C(—)=), δ 2.2 (O*H*), δ 3.68 (—CH_2OH), δ 5.6 (—C*H*—C(—)=).

Anal. Calcd. for $C_{11}H_{20}O$: C, 78.49; H, 11.98. Found: C, 78.12; H, 11.36.

The 3,5-dinitrobenzoate derivative of **5** was prepared and recrystallized from methanol, m.p. 138–139 °C.

Anal. Calcd. for $C_{17}H_{22}O_6N_2$: N, 7.73. Found: N, 7.70.

The compound **5** absorbed one equivalent of hydrogen by catalytic hydrogenation to give 2-hydroxylmethyl-*p*-menthane, b.p. 88 °C at 3 Torr.

Anal. Calcd. for $C_{11}H_{22}O$: C, 77.59; H, 13.03. Found: C, 77.36; H, 12.99.

Condensation of Cyclooctene (6) with Formaldehyde

From a mixture of 45 g of **6**, 14.5 g of *para*formaldehyde, and 20.5 g of acetic anhydride, 21 g of a crude acetate was obtained. Saponification of this acetate gave 1-hydroxylmethyl-2-cyclooctene (**7**), b.p. 74–76 °C at 2 Torr; d_4^{20}, 0.9778; n_D^{20}, 1.4950; molecular refraction 41.92 (calcd. for $C_9H_{16}O$, $F_1 = 42.15$); i.r.: 1040 cm^{-1}, 755 cm^{-1}; n.m.r.: δ 1.6 (—CH_2—), δ 2.2 (—CH_2—C(—)=), δ 3.37 (—CH_2OH), δ 3.4 (O*H*), δ 5.6 (—C*H*=C*H*—).

Anal. Calcd. for $C_9H_{16}O$: C, 77.10; H, 11.51. Found: C, 77.01; H, 11.12.

The 3,5-dinitrobenzoate derivative from **7** was prepared in the usual manner, m.p. 72–73 °C.

Anal. Calcd. for $C_{16}H_{18}O_6N_2$: N, 18.17. Found: N, 18.30.

The compound **7** was hydrogenated over palladium on carbon in a methanol solution, under an initial hydrogen pressure of 20 kg/cm² to give hydroxylmethylcyclooctane (**8**), b.p. 125 °C at 40 Torr; i.r.: 1040 cm^{-1}, 1450 cm^{-1}; n.m.r.: δ 1.45 (—CH_2—), δ 1.7 (—C*H*—), δ 3.48 (—CH_2OH), δ 1.95 (O*H*).

Anal. Calcd. for $C_9H_{18}O$: C, 76.02; H, 12.76. Found: C, 75.98; H, 12.41.

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Deuterated 4-hydroxycoumarin derivatives[1]

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4-Hydroxycoumarin exchanges rapidly with heavy water, resulting in deuterium replacing both the 3- and the 4-hydroxy proton. Preparation of the following deuterated coumarin derivatives is described: 4-chlorocoumarin-3-d_1, 4-piperidylcoumarin-3-d_1, and 4-anilinocoumarin-3-d_1.

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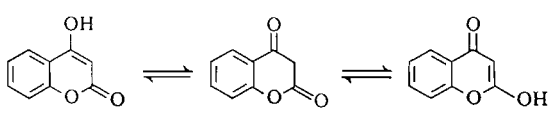
A number of authors (1–4) have discussed the structure and the tautomers of 4-hydroxycoumarin (**1**) shown below, and suggest that in solution, **1** is the predominant structure. If such tautomerization occurs readily, the 3-proton would be expected to exchange rapidly in protonic solvents, and in D_2O an equilibrium with both the 4-hydroxy proton and the 3-proton would be established. This would then provide a facile method to synthesize coumarin derivatives labelled in the 3-position.



1 **2** **3**

In our investigation of coumarin condensation reactions, we have prepared coumarin derivatives deuterated in the 3-position by reacting 4-hydroxycoumarin (**1**) with D_2O in acetone to

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