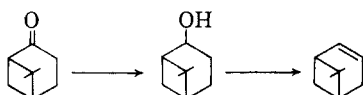


Study in the Terpene Series. XXXI.¹ Synthesis of Apopinene by Catalytic Decarbonylation of Myrtenal

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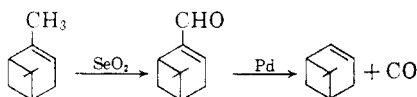
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The synthesis of apopinene, 7,7-dimethylbicyclo[3.1.1]hept-2-ene, reported in the literature³ consisted in the hydrogenation of nopinone to nopinol followed by dehydration with potassium acid sulfate:



The nopinone was prepared by a two step process: (a) oxidation of β -pinene with potassium permanganate to nopinic acid and (b) oxidation of the sodium salt of the nopinic acid to nopinone.^{4,5} Nopinone was also synthesized in about 40% yield by the ozonolysis of β -pinene.⁶⁻⁸

The present paper describes a two-step procedure for the preparation of apopinene from the readily available α -pinene. The first step consists in oxidizing α -pinene to myrtenal and the second step in the catalytic decarbonylation of the aldehyde:



The yield of apopinene produced based on α -pinene used was 55%.

The myrtenal was prepared in 75% yield³ by oxidizing freshly distilled α -pinene with selenium dioxide, according to the general procedure described by Stalleup and Hawkins.⁹ The palladium on barium sulfate catalyst used for the decarbonylation of myrtenal was prepared according to the method described previously.¹⁰

The myrtenal distilled at 84–85° at 6 mm., $\alpha_D^{20} +8^\circ$; its 2,4-dinitrophenylhydrazone melted at 222°. The procedure used for the decarbonylation

was about the same as described previously.¹¹ One hundred thirty five grams of the myrtenal and 2.5 g. of freshly prepared 5% palladium hydroxide on barium sulfate were placed in a 1-l. flask provided with a 5 ml. Dean-Stark distillation trap to which was attached a reflux condenser. The top of the latter was connected by means of a rubber tubing to a gas collecting bottle.

Upon heating the catalyst turned black and a strong evolution of carbon monoxide took place. The temperature in the flask dropped after 4 hr. of refluxing from a maximum of 195° to 155°, while the gas evolution dropped from 200 cc. to about 15–20 cc. per min. At this point the distillation trap was opened and 70 g. of apopinene was collected. The remainder in the flask was refluxed for an additional 10 hr. yielding 10 more grams of apopinene and leaving about 15 g. of residue. The total amount of carbon monoxide evolved amounted to 85% of the theoretical.

The apopinene thus obtained was almost pure and distilled at 47–48° at 30 mm., 140.5 at 760 mm., n_D^{20} 1.4678, d_4^{20} 0.8710. The literature³ reports: b.p. 139.5–140.5, n_D^{20} 1.4670–1.4675, d_4^{20} 0.870.

On hydrogenation the apopinene yielded nopinane (7,7-dimethylbicyclo[3.1.1]heptane) which was identical according to physical constants and infrared spectra with nopinane synthesized previously.⁸ The hydrogenation was carried out by dissolving 12.5 g. of the apopinene in 28 ml. of *n*-pentane and hydrogenating it in a 120-ml. capacity rotating autoclave in the presence of 3 g. of nickel-kieselguhr catalyst. The hydrogenation was carried out at 68–80° in the presence of 100 atm. of initial hydrogen pressure. The nopinane distilled at 149°, n_D^{20} 1.4616.

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Preparation of 2-Isobutyl-2-methyl-4-trimethylacetoxymethyl-1,3-dioxolane and Its Reaction with Phosphoric Acid

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The addition of aldehydes to poly(vinyl phosphates) was discussed in a recent article.¹ Acetal formation was shown to proceed either by displacement of phosphate by aldehyde or by reaction of aldehyde with the glycol obtained on hydrolysis

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