

Preparation of 2,2,7-Trimethyloct-6-en-3-one from Cineole

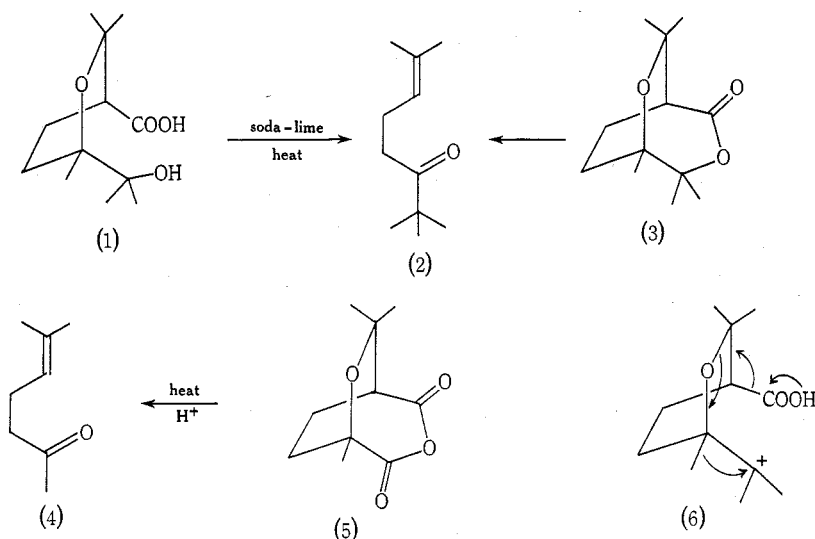
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Abstract

2,2,7-Trimethyloct-6-en-3-one is formed by decomposition of two tetrahydropyran derivatives derived from cineole. A rational synthesis of this ketone from 3,3-dimethylbutan-2-one and 1-bromo-3-methylbut-2-ene is also reported.

In continuing our study¹ of compounds derived from cineole we attempted the decarboxylation of hydroxy acid (1).² When the hydroxy acid was heated with soda-lime the major product was a ketone which we identified as 2,2,7-trimethyloct-6-en-3-one (2). In pursuing this observation we found that the lactone (3) could be distilled unchanged at room pressure but when heated with a little acid it was smoothly converted into the same C₁₁ ketone.



The decomposition product (2) showed a strong carbonyl absorption frequency at 1700 cm^{-1} in the infrared and its formula was established by microanalysis. The structure elucidation was completed from consideration of the ^1H n.m.r. spectrum where comparison with the n.m.r. spectrum of 6-methylhept-5-en-2-one was helpful.

¹ Rae, I. D., and Redwood, A. M., *Aust. J. Chem.*, 1974, 27, 1143.

² Rupe, H., and Zweidler, R., *Helv. Chim. Acta*, 1940, 23, 1025.

This latter ketone has been formed by dry distillation of cineolic acid.³ We have observed that, like the lactone (3), cineolic anhydride (5) survives simple distillation⁴ but is decomposed to (4) when heated with acid.

The identification of the ketone (2) was completed by an independent synthesis from pinacolone and dimethylallyl bromide. The mechanism of formation of ketone (2) from hydroxy acid (1) is obscure, but the route from lactone (3) seems most likely to involve cation (6) which might be decarboxylated with rearrangement as depicted by the arrows on the formula.

Experimental

The analysis was performed by the Australian Microanalytical Service, Melbourne. Infrared spectra were recorded on a Perkin-Elmer 257 grating spectrophotometer, and n.m.r. spectra on a Varian A56/60A spectrometer operating at 60 MHz. Gas chromatography was performed with a Hewlett-Packard 5750 research gas chromatograph equipped with a thermal conductivity detector and 6-ft Carbowax column.

Preparation of 2,2,7-Trimethyloct-6-en-3-one

(i) *From c-6-(2'-hydroxy-2'-methylethyl)-2,2,t-6-trimethyltetrahydropyran-r-3-carboxylic acid.*^{1,2}—The hydroxy acid (1.5 g) and crushed soda-lime (2.0 g) were mixed and heated with a small burner. Water and a yellowish oil distilled from the mixture and the oil was separated by ether extraction. The ether solution was washed with water, dried over magnesium sulphate and evaporated to give an oil which showed eight peaks when examined by gas chromatography. The oil was dissolved in hexane and chromatographed over silica gel with hexane, carbon tetrachloride and benzene as eluents. A group of middle fractions contained the major product which gave a single peak upon gas chromatography. It was a pleasant-smelling liquid whose infrared spectrum contained a strong peak at 1697 cm⁻¹.

(ii) *From 4,4,5,7,7-pentamethyl-3,6-dioxabicyclo[3,2,2]nonan-2-one.*^{1,2}—The lactone (1.5 g) and toluene-*p*-sulphonic acid (approx. 20 mg) were heated over a small burner. A colourless gas was evolved and a clear liquid distilled at approximately 160°. Gas chromatography showed it to consist almost entirely of a single product (yield 70%) which was collected for analysis. 2,2,7-Trimethyloct-6-en-3-one (Found: C, 78.6; H, 11.8. C₁₁H₂₀O requires C, 78.5; H, 12.0%) showed ν_{\max} 1700 cm⁻¹ in the infrared, and its ¹H n.m.r. spectrum (CDCl₃) showed: δ 1.12, s, 9H, (CH₃)₃C; 1.63, m, $W_{H/2}$ 6 Hz, 6H, (CH₃)₂C=; 2.0–2.7, m, 4H, CH₂CH₂; 5.05, br t (*J* c. 7 Hz), 1H, –CH=.

(iii) *From pinacolone and 1-bromo-3-methylbut-2-ene.*⁵—Sodium (2.5 g, 0.11 mol) was dissolved in liquid ammonia (100 ml) with the aid of a little ferric nitrate. The solution of sodium amide was stirred while pinacolone (10 g, 0.10 mol) in dry ether (20 ml) was added slowly. After 30 min a solution of 1-bromo-3-methylbut-2-ene (7.5 g) in dry ether (20 ml) was slowly added and the mixture was stirred for 1 h. The ammonia was evaporated overnight and the remainder was diluted with more ether and then agitated with crushed ice and hydrochloric acid (10 ml). The ether solution was washed with aqueous sodium bicarbonate and then with water and finally dried and evaporated. The resulting oil was distilled under reduced pressure to give a major fraction with b.p. 94–95°/20 mm (4.04 g, 48%) which had infrared and n.m.r. spectra identical with those of the ketone described above.

Acknowledgment

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³ Wallach, O., and Gildemeister, E., *Justus Liebigs Ann. Chem.*, 1888, **246**, 265.

⁴ Wallach, O., *Justus Liebigs Ann. Chem.*, 1890, **258**, 319.

⁵ Staudinger, H., Kreis, W., and Schilt, W., *Helv. Chim. Acta*, 1922, **5**, 743.