The Condensation of Thujopsene with Formaldehyde

By Shoji WATANABE and Kyoichi SUGA

(Received January 11, 1964)

In a previous paper,[1] the thermal condensation of thujopsene with formaldehyde was reported. The reaction of thujopsene with formaldehyde in an acetic acid solution is the subject of this paper.

In this study thujopsene (I) was added to a slurry of paraformaldehyde in glacial acetic acid at 50~60°C. The crude products were isolated by fractional distillation and liquid chromatography. A dioxane II was isolated as the major product. The minor product was an unsaturated alcohol III.

The analytical results ($C_{17}H_{28}O_2$) and the molecular weight of the major product indicated that the product was an adduct of two moles of formaldehyde to I. The infrared absorption spectrum showed characteristic absorption bands of an ethearic group (dioxane type) at 1045 cm^{-1} and 1175 cm^{-1}. It gave no positive reaction with a potassium permanganate solution and bromine water for a double bond; it was not suggested that II had a double bond.

The nuclear magnetic resonance spectrum of II is shown in Fig. 1. The four strong signals, at 8.90, 8.96, 9.45 and 8.52 τ., correspond to the four methyl groups. The quartet signal at 5.30 is presumably due to protons on the ethearic ring (AB type, $-O-CH_2-O-$). The multiplet signal at 6.0~6.7 τ is due to the ABX-type spectrum caused by two non-

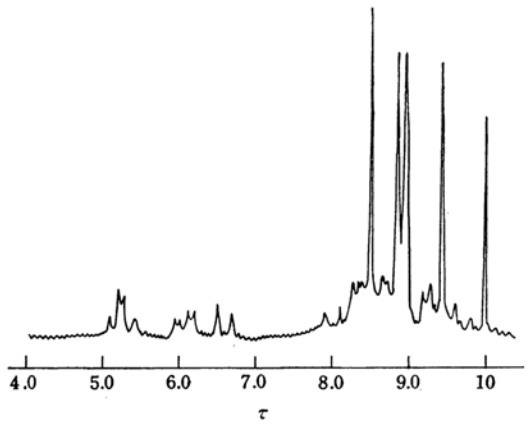
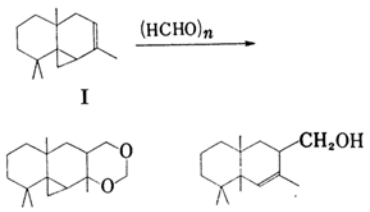


Fig. 1. The nuclear magnetic resonance spectrum of II.



I II III

equivalent protons of $-\overset{1}{C}H-CH_2-O-$.[2] The infrared spectrum exhibits the absorptions at 1000 cm^{-1} and 3050 cm^{-1} which have been reported to be characteristic of the cyclopropane ring.[3,4] The nuclear magnetic resonance spectrum shows the signal of the methylene group of the cyclopropane ring at 9.3 τ. The substance gave a pale yellow color reaction with tetranitromethane, which also indicated the presence of a cyclopropane ring.[5,6] The hydration of II gave an oily product, and the infrared absorption spectrum of this product did not indicate the absorption of the cyclopropane ring at 1000 cm^{-1} and 3050 cm^{-1}. These results indicated that the structure was 1, 3, 5, 6, 7, 8, 9, 9_a-octahydro-4_a, 5, 5, 8_a-tetramethyl-10,10_a-methano-2,4-dioxaanthracene (II).

The structure of the minor product included III. It was demonstrated as follows: the infrared absorption spectrum and gas chromatogram of the substance agreed with those of the authentic III which was prepared from the thermal condensation of I with formaldehyde.

Experimental

The Reaction of Thujopsene with Formaldehyde. —To a mixture of 60 g. of paraformaldehyde, 500 g. of glacial acetic acid and 60 g. of isopropyl ether, 300 g. of thujopsene was added at 60~70°C while the mixture was being vigorously agitated. After the completion of the addition, the mixture

1) S. Watanabe and K. Suga, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **84**, 993 (1963).

2) L. M. Jackman, "Application of NMR Spectroscopy in Organic Chemistry," Pergamon Press, London (1959), p. 90.

3) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen & Co., London (1958), pp. 17, 29.

4) G. Büchi, M. Schach v. Wittenau and D. M. White, *J. Am. Chem. Soc.*, **81**, 1968 (1959).

5) T. Norin, *Acta Chemica Scandinavica*, **15**, 1676–1694 (1961).

6) A. Zurcher, O. Jeger and L. Ruzicka, *Helv. Chim. Acta*, **37**, 2145 (1954).

was heated at 60°C while being stirred for an additional 7 hr. The reaction mixture was then dissolved in ether, and the resultant solution was washed with water. The distillation of this solution gave the following fraction : 317 g., b. p. 100～185°C/3 mmHg. The redistillation of this product (250 g.) gave 73 g. of thujopsene (b. p. 102°C/3 mmHg) and the residue (136 g.). The residue was dissolved in acetone, and 44 g. of white polymer was removed to give 92 g. of the clear oil. The liquid chromatography of this oil (15 g.) with silica gel (100 g.) gave 3 g. of viscous II from the elution of benzene ; b. p. 154°C/6 mmHg, n_D^{14} 1.5189. It did not give the positive reaction with potassium permanganate and bromine solution for a double bond. It was not hydrogenated over a nickel catalyst under high pressure (40 kg./cm^2) and at a high temperature (120°C). II gave a pale yellow color reaction with tetranitromethane.

Found : C, 77.27 ; H, 10.43. Calcd. for $C_{17}H_{28}O_2$: C, 77.22 ; H, 10.67%.

III was given from the elution of methanol. Its nature was confirmed comparing its infrared absorption spectrum and gas chromatogram with those of an authentic sample.

From the elution of benzene and methanol, an ethearic compound was obtained ; its structure has not yet, however, been determined.

The Hydration of II.—A mixture of 1 g. of II and 100 cc. of 10% sulfuric acid was agitated at 10～15°C for 10 hr. It was then extracted with ether. When the etheric solution was treated as usual, a small amount of a viscous oil was given. The infrared absorption spectrum did not show the absorptions of the cyclopropane ring at 1000 cm^{-1} and 3050 cm^{-1}.

The authors are indebted to the Takasago Perfumary Co., Ltd., for providing materials, and Dr. Sho Ito of Tohoku University and Dr. Atsuaki Arai of the Kobayashi Institute of Physical Research for the nuclear magnetic resonance spectra.

Department of Applied Chemistry
Faculty of Technology
Chiba University
Matsudo Chiba