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The Autocatalytic Oxidation of Thujopsene. A Facile Synthesis of Mayurone

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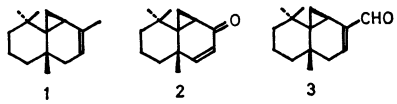
The autoxidation of cyclic terpenes, including an allyl methyl moiety, is known to give a small amount of a preferential product, accompanied by minor products. For example, the autoxidation of limonene[1] produces carveol, carvone, 8-*p*-menthene-1,2-diol, and limonene 1,2-oxide. Our interest in the autocatalytic oxidation and in the chemistry of thujopsene has led us to seek favorable catalysts for the autocatalytic oxidation of thujopsene to mayurone.

In the course of our investigations utilizing metal chelate catalysts for synthetic purposes, it has been found that the oxidation of thujopsene (**1**) with molecular oxygen in dioxane gives mayurone (**2**) and an unidentified product (**4**) in poor yields, but the oxidation was accelerated in the presence of metal chelate catalysts, as is shown in Table 1. $CoCl_2$-dioxane[2] was most effective in giving **2**, **3**, and **4**. In this system, however, the products were not obtained in good yields in the absence of the catalysts and the solvent. From this observation, it seems that the chelate complex formed from $CoCl_2$ and dioxane has a remarkably catalytic effect. Also, catalysts composed of a metallic salt, and a synthetic organic adsorbent showed a catalytic effect, affording the same products. This study promised to be of interest because of the possibility of effecting a new type of chelate-catalyzed reactions. New types of catalysts were realized. The results are summarized in Table 1.



1 2 3

The IR and NMR spectra of **2** were all consistent with those of an authentic sample, which has been prepared by the potassium permanganate and sodium perchromate oxidation[3] and the photosensitized oxidation[4] of thujopsene, and which has also been isolated from several conifers.[5,6,7] Compound **3** was identified by glpc analysis with thujopsenal which had been prepared by the selenium dioxide oxidation

Table 1. Autocatalytic oxidation of thujopsene at 70°C

Entry No.	Catalysts, g	Dioxane, ml	Distribution of products		
			Mayurone (**2**)	Thujopsenal (**3**)	Unidentified prodt. (**4**)
1	$CuCl_2$-N-GHP, 0.2	10	44	trace	5
2	$CuCl_2$-GHP, 0.2	10	23	trace	8
3	$RuCl_3$-N-GHP, 0.2	10	86	trace	16
4	$RuCl_3$-GHP, 0.2	10	67	3	19
5	$CoCl_2$-GHP, 0.2	10	31	2	6
6	$CoCl_2 \cdot 6H_2O$, 0.015	10	221	45	57
7	——	10	7	none	4
8	$CoCl_2 \cdot 6H_2O$, 0.015	—	39	2	6
9	$CoCl_2$-GHP, 0.2	—	35	4	2
10	$CoCl_2 \cdot 6H_2O$, 0.015	THF, 10 ml	153	14	23

1) E. Gildemeister und Fr. Hoffman, "Die Ätherischen Ole", Akademie-Verlag, Berlin (1960), IIIa, s 69.

2) Yu. I. Rozenberg, *Fiz. Tverd. Tela*, **1968**, 3017; M. Perrier E. Giesbrecht and G. Vicentini, *An. Ass. Brazil. Quim.*, **25**, 39 (1966).

3) S. Akiyoshi and S. Nagahama, This Bulletin, **30**, 886 (1957); S. Nagahama, H. Kobayashi, and S. Akiyoshi, *ibid.*, **35**, 1140 (1962); H. Kobayashi, S. Nagahama, and S. Akiyoshi, *ibid.*, **34**, 1123 (1961).

4) H. Takeshita, T. Sato, T. Muroi, and S. Ito, *Tetrahedron Lett.*, **1969**, 3095.

5) S. Ito, K. Endo, H. Homma, and K. Ota, *ibid.*, **1965**, 3777.

6) G. L. Chetty and S. Dev, *ibid.*, **1965**, 3773.

7) B. Tomita, Y. Hirose, and T. Nakatsuka, *ibid.*, **1968**, 843.

of thujopsene Compound **4** was not identified.

Experimental

The melting point was determined on a Büchi melting-point apparatus. The NMR spectrum was recorded on a Hitachi R-20A spectrometer at 60 MHz, using tetramethylsilane as the internal standard. The IR spectrum was determined on a Shimadzu IR-27G spectrophotometer. The UV spectrum was recorded on a Shimadzu MPS-50 spectrophotometer. Glpc analyses were performed on a Shimadzu GC-1C gas chromatograph with a 1.1-m stainless-steel column packed with 15% OV-17, at 180°C.

Materials. The thujopsene used was purified by the careful distillation of Cedar H oil (Takasago Perfumery Co., Ltd.) through a concentric column and had a boiling point of 119°C/10 mmHg, showing no trace of an impurity upon glpc analysis. The inorganic salts used for preparing the catalysts were commercial, extra-pure reagents.

Preparation of the Chelate Catalysts. Some of the catalysts shown in Table 1 were prepared according to the reported method for preparing kieselguhr using synthetic organic absorbents, GHP[8] or N-GHP[9]. For example, a 1.5-g portion of N-GHP dissolved in 6 m*l* of water was added to a solution of 0.158 g of $RuCl_3$-xH_2O in 2 m*l* of ethyl alcohol, after which the mixture was kneaded in a mortar. The slurry was washed with water and dried at 100°C.

General Procedure for Autocatalytic Oxidation. Into a stirred mixture of 3.0 g of thujopsene and 0.2 or 0.015 g of the catalyst in 10 m*l* of dioxane or without the solvent, we passed a stream of dry oxygen at a rate of 62 m*l*/min for 21 hr. The mixture was then chilled, filtered, and evaporated. The components of the reaction mixture were analyzed by means of glpc. Thier yields were accounted on the basis of the area ratio of peaks on a chromatogram, regarding the peak area of hydrocarbons in the reaction mixtures as 100. The yield of mayurone was found to be 20% by glpc, using naphthalene as the internal standard; the retention times were 18 min for mayurone (**2**), 15 min for thujopsenal (**3**), and 11 min for the unidentified product (**4**).

*Isolation of Mayurone (**2**).* Into a stirred mixture of 20.4 g (0.1 mol) of thujopsene and 1.0 g of the $RuCl_3$-N-GHP catalyst in 300 m*l* of dioxane, we passed a stream of dry oxygen at a rate of 408 m*l*/min at 70°C for 29 hr. The mixture was then chilled and filtered. After the removal of the solvent, the reaction mixture thus obtained was distilled through a concentric column to collect the distillate with a bp of 150°C/7.5 mmHg, which deposited a crystalline matter on chilling. Two recrystallizations of the crystals from petroleum ether (bp 30—40°C) gave 1.45 g of **2** as colorless crystals; mp 70.0—71.0°C; $[\alpha]_D^{27}$ +221.0 (*c* 10.0 CCl_4); MW 201.86 (benzene) (calcd 204.16); NMR (CCl_4) 0.66 (CH_3), 1.11 (CH_3), 1.30 (CH_3), 1.30 (CH_3), 5.44 (1H, J=11.9 Hz), 6.00 (1H, J=11.0 Hz); IR (CCl_4) 3010 (cyclopropyl), 1661 (conj. C=O). 1619 cm^{-1} (conj. C=C); UV $\lambda_{max}^{cyclohexane}$ 226 mμ(ε 6646).

8) M. Ito, K. Abe, T. Tsuchiya, M. Umehara, and S. Yamashiro, *Mem. Kitami Inst. Tech.*, **3**, 131 (1971).

9) M. Ito, T. Tsuchiya, and K. Abe, *ibid.*, to be published.