Studies on Isoprenoide. XIII. Transformation of Pinene by the Action of Boron Trifluoride

By Kimiko NAGAI

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The transformation in the reaction of various reagents upon pinenes have been investigated[1-4] in detail, and the existence of camphene has been observed in the conversion products of pinene in almost all cases. The author has been engaged in a series of experiments on the reaction of boron trifluoride, an electrophilic agent, upon terpenes. It has been reported[5] that the reaction of boron trifluoride upon terpenes produces mainly polymerized products; my experiments seen to verify this.

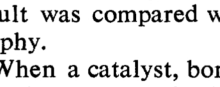
According to another paper[6] stating that isoborneol was produced by the reaction of glacial acetic acid upon camphene with a catalyst of boron trifluoride, the author has obtained bornyl acetate in a considerable yield in the reaction of glacial and anhydrous acetic acids upon α-pinene with a catalyst of boron trifluoride, as has been formerly communicated[7].

Because in this reaction α-pinene is isomerized to camphene by boron trifluoride ethyl ether complex and further is esterified[6], the isomerization of α-pinene to camphene in the absence of glacial and anhydrous acetic acids was attempted. Namely, solutions of boron trifluoride ethyl ether complex in various solvents were prepared, α-pinene was subjected to a reaction at room temperature with various amounts of catalyst and various reaction times, and the transformation of α-pinene and the production of camphene were investigated, taking advantage of the infrared absorption spectrum and gas chromatography.

The determination of α-pinene and camphene based on the infrared absorption spectrum has already been investigated by Kitajima, Takeshita et al.[8], who adopted 772 cm^{-1} for α-pinene and 667 cm^{-1} for camphene as a characteristic absorption in the practice of estimation. The author adopted 1130 cm^{-1} for α-pinene and 1115 cm^{-1} for camphene, made a calibration curve using α-pinene purified by distillation, and diluted solutions of camphene 10~80 per cent, for which determination was carried out on the amount of α-pinene and camphene in the reaction products catalyzed by boron trifluoride ethyl ether complex; at the same time, this result was compared with that of gas chromatography.

When a catalyst, boron trifluoride ethyl ether complex, was used with a solvent of ligroin or benzene, and also when it was directly applied to α-pinene without the use of any solvents, violent heat generation and polymerization occurred, and the degree of heat generation and polymerization descending from ligroin through benzene to an absence of solvents.

When ethyl ether was used as a solvent, the generation of heat was hardly observed, and it was noted from the infrared absorption spectrum that by the action of boron trifluoride ethyl ether complex, α-pinene is converted to camphene through the Wagner-Meerwein rearrangement and that the greater the extent of isomerization to camphene the larger the amount of boron trifluoride ethyl ether complex used and the longer the reaction time.

As the infrared absorption spectrum show peaks at 817 and 827 cm^{-1}, the existence of a group  $\begin{matrix}R\\R'\end{matrix}\!>\!C=C\!<\!\begin{matrix}R''\\H\end{matrix}$ is presumed, and hence the formation of polymers of α-pinene is conceivable.

Reaction products in the solvent of benzene or ligroin for which no heat generation and polymerization appeared showed such infrared absorption spectra that, while the characteristic absorption (at 1130 cm^{-1}) was not observed, that for camphene was observed faintly at 1115 cm^{-1} and those for end-methylene and *gem*-dimethyl radical were observed at 877 and 1660 cm^{-1}, and at 1363 and 1384 cm^{-1} respectively. Gas chromatography of these reaction products showed a small peak corresponding to camphene; also in the case of solvents of benzene or ligroin, the formation of camphene was found, though in an extremely small amount.

In this reaction, the isomerization of α-pinene into camphene by the action of boron

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3) E. Schwent and K. Schmidt, D. R. Pat. 578569 (1934).
4) P. A. Mulany, C., II, 430 (1931).
5) M. Berthelot, *Ann. chim. phys.*, (3) 38, 38 (1853).
6) I. G. Farbenindustrie, D. R. Pat. 589779 (1933).
7) K. Nagai, *Bull. Pharm. Kinki Univ.*, 3, 11 (1960).
8) M. Kitajima and T. Takeshita, *Report of the Central Research Institute, The Monopoly Corporation*, 95, 95 (1956).

trifluoride ethyl ether complex through the Wagner-Meerwein rearrangement was confirmed, and in the case of a violent reaction, although it almost polymerizes, the formation of a small amount of camphene was detected.

Experimental

Sample. — α-Pinene and camphene purified by repeated distillation on metallic sodium were used. The physical constants of the samples are as follows: α-pinene b. p. 154.5~156°C, d_4^{25} 0.8550, n_D^{25} 1.4641; camphene b. p. 154~155°C, m. p. 47.0~47.5°C.

The Calibration Curve of α-Pinene and Camphene.—Camphene was diluted with α-pinene 10~80 per cent, and the characteristic absorption at 1130 and 1115 cm^{-1} was selected for the infrared absorption spectra of α-pinene and camphene respectively; from the ratio of the above two absorptions, a calibration curve as seen in Fig. 1 was obtained.

TABLE I. RATIO OF ABSORPTION AT 1130 AND 1115 cm^{-1}

α-Pinene % I_1	Camphene % I_2	log I_1/I_2
100	—	0.5090
90	10	0.6256
80	20	0.7238
70	30	0.8443
60	40	1.0164
50	50	1.222
40	60	1.411
30	70	1.644
20	80	1.905

I_1: The height of the mininum point on the absorption band of α-pinene

I_2: The height of the minimum point on the absorption band of camphene

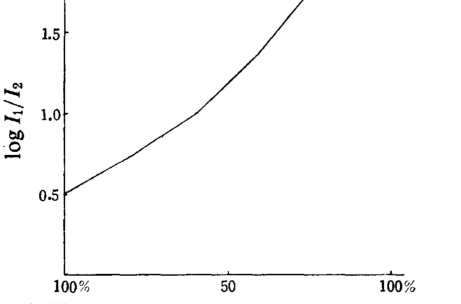

Fig. 1. Calibration curve of camphene and α-pinene.

Reaction in the Solvent of Ethyl Ether. — A mixture of α-pinene 10 ml. and ethyl ether 15 ml. was added to each 0.8, 1.5, 2.0 and 3.0 ml. of boron trifluoride ethyl ether complex and was allowed to react for 72 hr. at room temperature; after washing with 10% sodium carbonate and water, followed by drying, the reaction product was examined with the aid of the infrared absorption spectrum and gas chromatography. Figure 2 is the infrared absorption spectrum of the product obtained when α-pinene, camphene and 3.0 ml. of a catalyst were used. As shown from the calibration curve in Fig. 1, the yield of camphene is maximum, about 50 per cent, when 3.0 ml. of boron trifluoride ethyl ether complex was used, whereas in the reaction with 0.8 ml., the α-pinene remained almost unchanged.

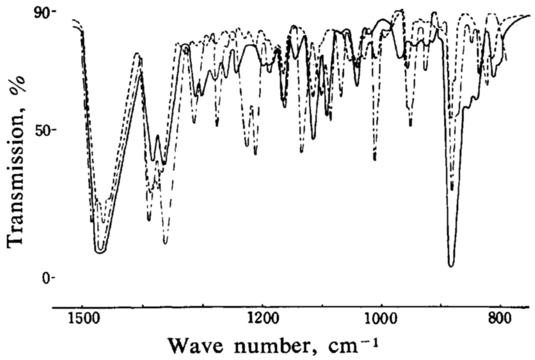

Fig. 2. Infrared absorption spectrum obtained by using α-pinene, camphene and 3.0 ml. catalyst.

——— Camphene ----- 3.0 ml. Catalyst
—·—· α-Pinene

TABLE II. ESTIMATION OF CAMPHENE ON THE BASIS OF INFRARED ABSORPTION SPECTRA OF REACTION PRODUCTS IN ETHYL ETHER

Boron trifloride, ml.	Camphene %	Absorption coefficient
0.8	10.0	0.529
1.5	41.0	1.029
2.0	46.2	1.127
3.0	50.0	1.214

ESTIMATION OF α-PINENE AND CAMPHENE BASED ON GAS CHROMATOGRAPHY

Boron trifluoride, ml.	Camphene %	α-Pinene %
0.8	12.1	80.9
1.5	44.2	29.7
2.0	44.0	16.9
3.0	52.9	10.6

P. E. G. 6000 (20 ml./min. 180°C, 0.25 kg./cm^2, 16 mV. 150 mA. 5 mm./min. He)

Moreover, the relation between the yield of camphene and the reaction time in the case of 3.0 ml. of boron trifluoride ethyl ether complex was investigated; the result is shown in Table III, from which it can be observed that a large amount of

TABLE III. RLATION BETWEEN THE YIELD OF CAMPHENE AND REACTION TIME

Infrared absorption spectrum	Reaction time, hr.	24	48	72
	Camphene %	49.5	49.9	50.5
	Absorption coefficient	1.210	1.213	1.225
Gas chromato-graphy	Reaction time, hr.	24	48	72
	Camphene %	50.9	51.2	51.5
	α-pinene, %	12.8	12.4	10.6

camphene is formed in the case of an hour-long reaction.

Reaction in the Solvent of Benzene and Ligroin.—To 10 ml. of a sample, 15 ml. of both benzene and ligroin were added, and boron trifluoride ethyl ether complex was added to the benzene solution in amounts of 0.3, 0.5 and 1.0 ml. and to the ligroin solution in amounts of 1.5, 2.0 and 3.0 ml., and after reaction ceased, treatment similar to that described above was performed. In the case of these reactions, heat generation and polymerization occurred violently; when the amount of catalyst was small, the existence of camphene was observed, but α-pinene was not, as shown from the data of the infrared absorption spectra and gas chromatography, although the estimation of the camphene formed was nevertheless difficult.

Reaction Without Solvents.—This reaction shows a remarkable heat generation and polymerization, yielding reddish-brown, viscous, oily substances; because the existence of α-pinene was still observed only on the basis of the infrared absorption spectrum and gas chromatography, the estimation was not successful.

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Pharmaceutical Faculty
Kinki University
Fuse-shi, Osaka