β-Terpinene and β-Phellandrene from the Pyrolysis of Sabinene

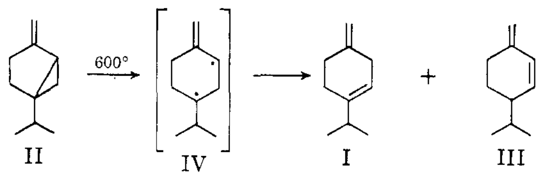
B. M. MITZNER AND E. T. THEIMER

Research Laboratories,
International Flavors & Fragrances Inc.,
Union Beach, New Jersey

Received April 5, 1962

The only reported synthesis of β-terpinene (I)[1] is that of Wallach[2] in five steps from sabinene (II). β-Phellandrene (III) has not been unequivocally synthesized, but is found in nature.[3]

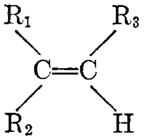
We have observed that II, when pyrolyzed at 600°, undergoes fission of the cyclopropane ring and forms I and III:



II IV I III

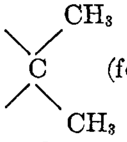
We postulate the biradical IV as an intermediate. The pyrolyzate from sabinene consists of a mixture of products including two major components, gas chromatographically eluted after the unconverted sabinene in an approximate ratio of 6:4. N.m.r. and infrared analysis confirm the structure of the first of these two peaks as β-terpinene. The n.m.r. spectrum of the β-terpinene indicated the following (in τ values, tetramethylsilane, τ = 10.00): 9.03, doublet, $J_{CH_3,H}$ 6 c.p.s., isopropyl group; 7.95, 7.87, 7.76, diffuse multiplet, allylic methylene; 7.28 multiplet, CH_2 flanked by allylic double bonds; 5.36 singlet vinylidene methylene, $>C=CH_2$; 4.70 singlet, ring olefinic proton.

The infrared spectrum of β-terpinene is characterized by a strong absorption at 883 cm.$^{-1}$ due to the $>C{=}CH_2$ group which is also found in 1,(7) *p*-menthene. A medium band is observed at 812 cm.$^{-1}$ which is due to the



$(R_1)(R_2)C{=}C(R_3)(H)$

group and is also found in 3, *p*-menthene. The split at 1375 cm.$^{-1}$ is characteristic of the "gem" dimethyl group



$>C(CH_3)_2$

(found in both 1,(7) *p*-menthene as well as 3,*p*-menthene). The second peak was identified by n.m.r. and infrared as β-phellandrene, identical with III isolated from a natural source.[4]

Experimental

Oil of savin was fractionated through a 2-ft. stainless steel protruded packed column, yielding sabinene—b.p. 45° at 10 mm. and was analyzed pure by gas chromatography. This was passed four times through a 1 ft. × $^1/_8$ in. o.d., 2/32 inch i.d., stainless steel tube heated to 600°, at a rate of 1 ml./min. A small flow of nitrogen was employed as a carrier. The pyrolyzate was then separated into its components on a preparative gas chromatograph using a 3/8 in. o.d. column packed with Reoplex 400 (20%) on 60–80 mesh silane treated Celite at 100°. In this way, β-terpinene and β-phellandrene and unconverted sabinene are easily separable. We have found that it is essential that a non-acid type of solid support be used, otherwise α- and γ-terpinene will be formed from the β-terpinene. β-Terpinene polymerizes in a matter of hours, especially when pure.

Acknowledgment.—The authors wish to acknowledge the aid given to them by Dr. S. Lemberg, of this laboratory, for his aid in the preparation and interpretation of the n.m.r. spectra.

---

[1] β-Terpinene has not been positively identified in natural materials.

[2] O. Wallach, *Ann.*, **357**, 69 (1907).

[3] J. L. Simonsen, "The Terpenes," Vol. I, Cambridge, England, University Press, 1953, p. 204.

[4] β-Phellandrene isolated from gum turpentine, and purified *via* preparative gas chromatography. The sample was graciously supplied by Mr. Ray V. Laurence, Chief, Naval Stores Laboratory; Olustee, Florida.

Absence of Asymmetric Induction in the Lithium Aluminum Hydride–*d*-Camphor Reduction of Ketones

PHILIP S. PORTOGHESE

Department of Pharmaceutical Chemistry, College of Pharmacy, University of Minnesota, Minneapolis 14, Minnesota

Received April 9, 1962

The exact mechanism of the reduction of ketones to secondary alcohols by lithium aluminum hydride is not known with certainty. In an effort to elucidate the mode of hydride transfer to an electrophilic center, we have employed the procedure of Bothner-By[1] in which he has reported the preparation of optically active secondary alcohols by reduction of the corresponding ketones. According to his procedure, one equivalent of lithium aluminum hydride is reacted with two equivalents of *d*-camphor whereupon the introduction of an unsymmetrical ketone such as 2-butanone or pinacolone supposedly affords optically active 2-butanol or methyl-*t*-butylcarbinol, respectively. In repeating his experimental procedure we have observed no evidence of asymmetric induction in the hydride reduction of 2-butanone and pinacolone.

---

[1] A. A. Bothner-By, *J. Am. Chem. Soc.*, **73**, 846 (1951).