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

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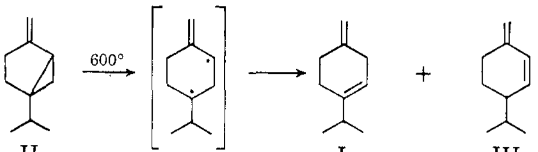
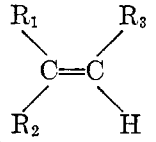
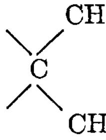
The only reported synthesis of β-terpinene (I)[1] is that of Wallach[2] in five steps from sabinene (II). β-Phellandrene (III) has not been unequivocally synthesized, but is found in nature.[3]

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.

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[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

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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.

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

The separation of 2-butanol and methyl-*t*-butylcarbinol from *d*-isoborneol was accomplished by first distilling through a six-inch Vigreux column and subsequently fractioning through a 23-plate spinning band column. Both alcohols were found to be optically inactive. It is possible that in the procedure employed by Bothner-By,[1] separation of 2-butanol and methyl-*t*-butylcarbinol from small quantities of optically active material was incomplete and consequently caused the observed positive rotation.[2]

In a recent communication, Eliel[3] has presented evidence for a possible disporportionation step in the reduction of 3,3,5-trimethylcyclohexanone with lithium aluminum hydride. If this is of general consequence in the reduction of ketones to secondary alcohols, perhaps the production of racemic alcohols from ketones with lithium aluminum hydride–*d*-camphor is indicative of attack by AlH_4^- rather than $Al(OR)_2H_2^-$. Thus during the reduction of two equivalents of *d*-camphor by one equivalent of lithium aluminum hydride, the initially formed $Al(OR)H_3^-$ can conceivably be transformed to AlH_4^- *via* a disproportionation step.[3] Since $Al(OR)H_3^-$ is not as effective as reducing agent,[4] AlH_4^- could act as the reducing species even in the presence of a substantial quantity of alkoxyhydride anion.

Experimental

Reduction of 2-Butanone.—A solution of 30 g. (0.2 mole) of *d*-camphor in 50 ml. of ether was dropped with stirring over a 0.5-hr. period into a solution of 3.8 g. (0.2 mole) of lithium aluminum hydride in 300 ml. of ether. This was followed by a 0.5-hr. addition of 15 ml. (0.2 mole) of 2-butanone in 50 ml. of ether. To the above mixture there was added 100 ml. of 17% hydrochloric acid followed by several grams of sodium chloride so as to facilitate separation of the ether layer. The organic phase was dried over calcium chloride and subsequently with calcium hydride. The ether was distilled from a mixture on a steam bath and 15 ml. of xylene added to the residue. Distillation through a 6-in. Vigreux column followed by two fractionations through a 23-plate spinning band column afforded 5 ml. of 2-butanol; b.p. 99° (750 mm.), $n^{25°}$ 1.3952, $[\alpha]^{25}D$ 0°.

Reduction of Pinacolone.—Pinacolone, 20 g. (0.2 mole), was reduced in a manner identical to that of 2-butanone. After treatment with 100 ml. of 17% hydrochloric acid the ether solution was dried over calcium chloride and the solvent removed by distillation. To the residue was added 15 ml. of decalin and the methyl-*t*-butylcarbinol distilled through a 6-in. Vigreux column. Two subsequent fractionations through a 23-plate spinning band column gave 7 ml. of methyl-*t*-butylcarbinol; b.p. 119–119.5 (748 mm.), n^{25} 1.4127, $[\alpha]^{25}D$ 0°.

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[2] In a recent private communication, Dr. Bothner-By has expressed his agreement with us concerning the absence of asymmetric induction in the *d*-camphor–lithium aluminum hydride reduction of 2-butanone and pinacolone.

[3] E. L. Eliel and H. Haubenstock, Abstracts of papers presented at 141st National Meeting, American Chemical Society, p. 11-O.

[4] H. C. Brown and R. F. McFarlin, *J. Am. Chem. Soc.*, **80**, 5372 (1958).

Acidity of Hydrocarbons. VI. Metalation of Norbornadiene with Butyllithium[1]

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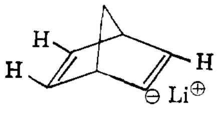
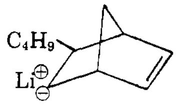
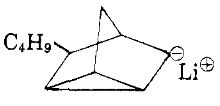
Wittig and Hahn[3] have reported that the reaction of norbornadiene with equimolar butyllithium gives products expected from the ion-pairs, I, II, and III. We have performed similar experiments in order to obtain evidence relating to the relative acidities of the various hydrogens in norbornadiene. Of particular interest is the relative mobility of the 7-hydrogens (bridge) because simple MO calculations predict no delocalization energy for the anion IV.



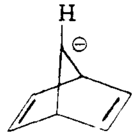
I



II



III



Norbornadiene was allowed to react with excess butyllithium in refluxing ether–heptane. After quenching with deuterium oxide, the recovered norbornadiene was studied by infrared and n.m.r. No evidence was obtained for significant abstraction of a 7-hydrogen, in qualitative agreement with the molecular orbital prediction.

The reaction mixture had typically a magenta color (λ_{max} 560 mμ). The product mixture as analyzed by gas chromatography contained norbornadiene and high-boiling materials, presumably the butylated products reported by Wittig and Hahn.[3] Norbornadiene as separated by gas chromatography showed vinyl deuterium in amounts depending on the duration of the reaction (Table I). In the product of the ten-hour reaction the

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[1] Paper V, A. Streitwieser, Jr., D. E. Van Sickle, and L. Reif, *J. Am. Chem. Soc.*, **84**, 258 (1962). This research was supported in part by an Air Force Grant, AFOSR-62-175.

[2] Alfred P. Sloan Fellow, 1958–1962.

[3] G. Wittig and E. Hahn, *Angew. Chem.*, **72**, 781 (1960).