Reductive Dimerization of Isoprene

Kyoichi SUGA and Shoji WATANABE

Department of Applied Chemistry, Faculty of Engineering, Chiba University, Yayoicho, Chiba

(Received April 23, 1966)

Recently, some dimers of isoprene have been produced with transition metal complexes.[1,2] This paper will deal with the preparation of a linear terpenic hydrocarbon from isoprene (I) using lithium naphthalene. The dimerization of butadiene with excess sodium dispersion and aromatic hydrocarbon, and the preparation of dibasic acids have been reported.[3] The polymerization of I by means of a lithium naphthalene complex produces a polyisoprene comparable to natural rubber.[4,5] These studies have not, however, confirmed the production of a linear mono terpene or sesquiterpene. The authors suspected that a linear isoprene dimer would be prepared in the presence of excess initiators for I. We have found that a catalyst of lithium naphthalene is active in the reductive linear dimerization of I.

Experimental

Reagents. A commercial tetrahydrofuran was purified by drying it with metallic sodium and then distilling it over metallic sodium under nitrogen. Naphthalene was recrystallized from benzene several times. I was distilled under nitrogen, bp 34—35°C. All the experiments were carried out in a dry apparatus under nitrogen, which had been dried by passing it through columns of calcium chloride and silica gel.

Reductive Dimerization of I with Lithium Naphthalene. To a mixture of 40 g (0.312 mol) of naphthalene and 150 m*l* of tetrahydrofuran, 4.5 g (0.65 mol) of lithium cuts were added; the contents were then agitated at room temperature. After 3 hr, 40 g (0.59 mol) of I were added, and then the mixture was stirred for 3 hr at 30°C. The reaction mixture was decomposed with methanol, and the unsoluble compounds were dissolved with water. The organic layer was isolated with ether, washed with water, dried over sodium sulfate, and distilled to give 18 g (bp 60—110°C/40 mmHg) of a crude isoprene dimer. By gas chromatographic analysis it was determined that the fraction consisted of an isoprene dimer (II) (95%) and a trimer of I (5%). The redistilled product of II had

---

[1] L. I. Zakharkin, G. G. Zhigareva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1964**, 168.

[2] A. Misono, Y. Uchida, M. Hidai, Y. Ohsawa, The 18th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1965.

[3] M. Hiraoka, T. Takase, A. Misono, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **66**, 1080 (1963).

[4] H. E. Dien, H. Tucker, C. F. Gibbs, paper presented to the Division of Rubber Chemistry, 132nd Meeting, American Chemical Society, New York, September, 1957.

[5] K. Ziegler, *Ann.*, **511**, 1344 (1934); **542**, 90 (1939).

the following properties; bp 79—81°C/85 mmHg; d_4^{20} 0.7777; n_D^{20} 1.4496; molecular refraction, 47.77 (Calcd for $C_{10}H_{18}$, F$_2$, 47.44), molecular weight (Rast method) 145 (Calcd for $C_{10}H_{18}$, 138). IR: 835 cm^{-1} ($-\overset{|}{C}=CH-$); NMR; 4.87 τ (2H, $-\overset{|}{C}=C\underline{H}-$), 8.11 τ (triplet, 4H, $-C\underline{H_2}-$), 8.4 τ (12H, three methyl groups).

Found: C, 86.6; H, 13.07%. Calcd for $C_{10}H_{18}$: C, 86.9; H, 13.3%.

Gas Liquid Chromatography. II$_A$ and II$_B$ could not be completely separated. Column: Polyphenylether (20%) on Chromosorb W (60—80 mesh), 4 m×4 mmϕ; temperature 80°C; carrier gas He 40 m*l*/min.

The molecular distillation of the residue gave 2.5 g of a viscous oil (bp 110°−180°C/10^{-3} mmHg), the structure of which was not determined.

Catalytic Hydrogenation of II. The quantitative hydrogenation of II in methanol using a Pd-C catalyst required two molar equivalents of hydrogen, bp 153—154°C; n_D^{20} 1.4110. The hydrogenated product was separated to 2, 6-dimethyloctane (III) and 2, 7-dimethyloctane (IV) by gas-liquid chromatographic trapping. Column: Polyphenylether (20%) on Chromosorb W (60—80 mesh) 7 m×4 mmϕ; temperature 128°C; carrier gas He 40 m*l*/min. The IR and NMR spectra and the gas-liquid chromatograms of III and IV agreed with those of their respective authentic samples.

The Oxidation of the Dimer (II) with Potassium Permanganate. A mixture of 2 g of potassium permanganate, 0.1 g of concentrated sulfuric acid, and 10 cc of water was added to 2 g of II, and the mixture was agitated for 3 hr. After the mixture had been left alone overnight, the precipitated part was filtered off. After the reaction mixture had been alkalined with potassium hydroxide, it was extracted with ether (the ether solution A). The aqueous solution was concentrated by evaporation. The concentrated solution was then acidified with sulfuric acid and extracted with ether (the ether solution B). After the ether had been evaporated, the residue was analyzed by gas liquid chromatography; acetone (from A) and acetic acid (from B) were recognized by comparing them with authentic samples.

2, 6-Dimethyloctane (III). 2, 6-Dimethyloctane (III) was prepared by the hydrogenation of an authentic myrcene. Bp 102°C/128 mmHg, bp 82—84°C/57 mmHg.

2, 7-Dimethyloctane (IV). 2, 7-Dimethyloctane (IV) was prepared by the action of metallic sodium on isoamylbromide in dry ether. Bp 155°C.

Reductive Dimerization of I with Sodium Dispersion. From a mixture of 20 g of I, 8 g of a sodium dispersion, and 2 g of naphthalene, 10 g of a viscous oil were obtained. The molecular distillation of the product with a pot still gave the following fractions: (a) 1.6 g, bath temperature 130—140°C/10^{-3} mmHg, n_D^{15} 1.4941, molecular weight 270, IR: 885, 835 and 740 cm^{-1}. (b) 3.2 g, bath temperature 170—200°C/10^{-3} mmHg, n_D^{15} 1.5018, molecular weight 330, IR: 885, 835 and 740 cm^{-1}.

Results and Discussion

The structure of the dimer (II) was determined as follows. On the basis of the results of elemental analysis, the molecular weight determination, and the catalytic hydrogenation, II may be said to be $C_{10}H_{18}$, F$_2$, which has two isolated double bonds. This shows that a dimer of I is reduced with methanol and lithium at the termination of the reaction. The hydrogenated product of II was separated into two components (III (50%) and IV (50%)) by gas-liquid chromatographic trapping. 2, 6-Dimethyloctane (III) and 2, 7-dimethyloctane (IV) were proved to be identical by gas-liquid chromatography, and by comparing their infrared absorption spectra and nuclear magnetic resonance spectra with those of authentic III and IV respectively. The original dimer (II) consisted of three isomeric components, but their direct separation with gas-liquid chromatographic trapping was unsuccessful. In the IR of II, the absorption of the trisubstituted double bond (835 cm^{-1}) was observed. The NMR indicated the signal of the two protons of the trisubstituted double bond at 4.87 τ. The signal at 8.1 τ was presumably due to protons of the methylene groups ($-C=C-C\underline{H_2}-$), while the signal at 8.4 τ was presumably due to the twelve protons of the four methyl groups. The ratio of these peak areas was 2 : 4 : 12. The oxidation of II with potassium permanganate gave acetone and acetic acid. Judging from these results, II may be considered to be a mixture of 2, 6-dimethyl-2, 6-octadiene (II$_A$) (a mixture of cis and trans isomers) and 2, 7-dimethyl-2, 6-octadiene (II$_B$).

The effects of reaction variables on the yields of II have also been examined; the results are shown in Figs. 1, 2 and 3. From these results, it can be

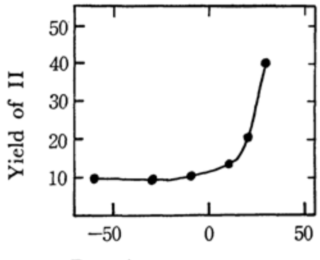


Fig. 1. Effect of temperature.

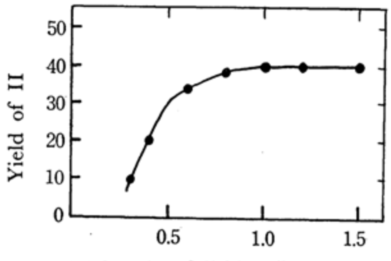


Fig. 2. Effect of lithium.

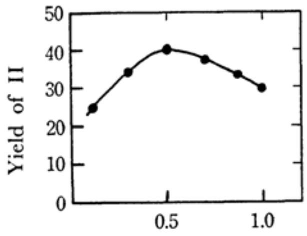
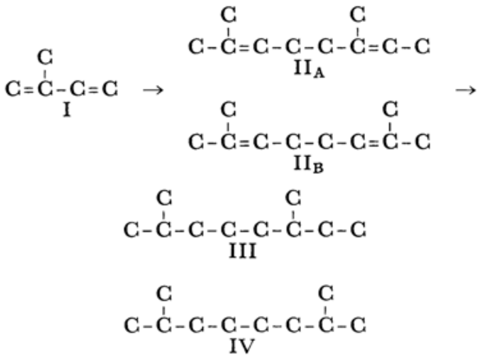


Fig. 3. Effect of naphthalene.

said that the use of 1 mol of metallic lithium and 0.5 mol of naphthalene per mole of I at +30°C give the best results. As an aromatic hydrocarbon, naphthalene was better than diphenyl, anthracene, or *o*-diphenyl-benzene. Metallic sodium and metallic potassium did not give a linear dimer, but a liquid polyisoprene containing a small amount of a tetramer of I.



The reductive dimerization of various conjugated dienes using this method is now in progress at our laboratory.

The authors are indebted to Dr. Sanae Tanaka of the Mitsubishi Petrochemical Co., Ltd., for his cordial guidance throughout this work and for his measurements of the NMR spectra.