Dimerization of Conjugated Dienes

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In previous papers, the dimerization of isoprene[1] and 1, 3-cyclooctadiene[2] by the action of lithium naphthalene was reported. The present paper will deal with the preparation of linear dimers from butadiene (I), piperylene (IV), 2, 3-dimethyl-1, 3-butadiene (XI), and myrcene (XIII) by means of lithium naphthalene.

Experimental

Dimerization of Butadiene (I). All the experiments were carried out in a dry apparatus under nitrogen. To a mixture of 27 g (0.25 mol) of naphthalene and 150 m*l* of tetrahydrofuran, 3.5 g (0.5 mol) of metallic lithium cuts were added. After 3 hr, 27 g (0.5 mol) of I were passed through gradually for two hours, and then the whole was stirred for an additional two hours at 30°C. The reaction mixture was decomposed with methanol, and the insoluble matter was dissolved in water. The product was extracted with ether, washed with water, dried over anhydrous sodium sulfate, and distilled to give 11.5 g (bp 52°C/80 mmHg—72°C/50 mmHg) of a crude dimer. The fractional redistillation of the product gave the dimer mixture (II), bp 39°C/37 mmHg; d_4^{17} 0.7608; n_D^{15} 1.4540; yield 7.5 g. Since the original dimer (II) was absorbed by the column of a molecular sieve 5A (length, 10 cm), it was confirmed that II was a mixture of aliphatic olefins. (Found: C, 87.12; H, 12.79%. Calcd for C_8H_{14}: C, 87.19; H, 12.81%). Upon the hydrogenation of 2.2 g of II in methanol using a Pd-C catalyst, 855 cc of hydrogen (theoretical for C_8H_{14}, F_2, 896 cc) were absorbed to give *n*-octane quantitatively.

Gas chromatography with a 7 m column of polyphenyl ether (20%) on Chromosorb W (60—80 mesh) at a temperature of 120°C, using helium as the carrier gas (40 m*l*/min), showed five peaks. 2, 6-Octadiene (II_A) and 1, 6-octadiene (II_B) were separated by gas chromatographic trapping. II_A showed the following spectral data: IR: 965 cm^{-1}, 700 cm^{-1}; NMR: 8.45τ ($C\underline{H}_3\text{–}\overset{|}{C}=$, 6H), 8.0τ ($\text{–}C\underline{H}_2\text{–}CH=$, 4H), 4.65τ ($\text{–}C\underline{H}=C\underline{H}\text{–}$, 4H). The IR spectra of II_B showed the absorptions 700, 910, 965, and 990 cm^{-1}.

The oxidation of II_A with potassium permanganate in the usual fashion gave succinic acid and acetic acid. Similarly, II_B was oxidized to give acetic acid and glutaric acid.

Dimerization of Piperylene (IV). To a tetrahydrofuran solution of 3.0 g (0.435 mol) of metallic lithium cuts and 3.0 g (0.023 mol) of naphthalene, 25 g (0.368 mol) of piperylene (IV) were added gradually; treatment similar to that in the case of I gave 7.5 g of a crude dimer (bp 65—80°C/55 mmHg). The redistillation of the crude product (15 g) with a Widmer column (30 cm in length) gave the following fractions: (a) 2.5 g, bp 60°C/30 mmHg, (b) 3.0 g, bp 60—70°C/32 mmHg, (c) 2 g, bp 70—80°C/32 mmHg, (d) 3 g, 80—105°C/7 mmHg. The quantitative hydrogenation of the original dimer (3.0 g) in methanol, using a Pd-C catalyst, required 940 cc of hydrogen (theoretical

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1) K. Suga and S. Watanabe, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **69**, 354 (1966).

2) K. Suga and S. Watanabe, *Tetrahedron Letters*, **1966**, 2527.

value for $C_{10}H_{18}F_2$, 971 cc). This product (bp 70—71°C/30 mmHg) consisted of 59% 4-methylnonane (VIII), 35% 4, 5-dimethyloctane (IX), and 6% *n*-decane (X), as determined by gas liquid chromatography.

The liquid chromatography of 2 g of the above-mentioned fraction (a) with a silica gel (50 g), using *n*-hexane, gave 500 mg of 4, 5-dimethyl-2, 6-octadiene (VI), bp 167—168°C, n_D^{15} 1.4510; IR; 965, 725 cm^{-1}; NMR: 9.1τ ($C\underline{H}_3$–, 6H), 8.4τ ($C\underline{H}_3$–$\overset{|}{C}$=, 6H), 4.7τ (–$C\underline{H}$=$C\underline{H}$–, 4H); (Found: C, 86.82; H, 13.08%. Calcd for $C_{10}H_{18}$: C, 86.90; H, 13.10%). The liquid chromatography of 3 g of the fraction (c) gave 500 mg of 4-methyl-2, 6-nonadiene (V), bp 175—176° C; IR: 965 cm^{-1}; NMR: 9.1τ ($C\underline{H}_3$–, 6H), 8.4τ ($C\underline{H}_3$–$\overset{|}{C}$=, 3H), 8.05τ ($C\underline{H}_3$–CH=, 4H), 4.75τ (–$C\underline{H}$=$C\underline{H}$–, 4H). (Found: C, 86.71; H, 13.04. Calcd for $C_{10}H_{18}$: C, 86.90; H, 13.10%.)

Dimerization of 2,3-Dimethyl-1, 3-butadiene (XI). From 0.3 g (0.043 mol) of metallic lithium cuts, 1.4 g (0.0109 mol) of napthalene, and 3.0 g (0.038 mol) of XI, 0.5 g of a crude dimer (bp 100°C/30 mmHg) was obtained. Chromatographic purification with activated silica gel (20 g) gave 0.3 g of 2, 3, 6, 7-tetramethyl-2, 6-octadiene (XII), obtained from the elute with *n*-hexane. NMR: 8.2τ ($C\underline{H}_3$–$\overset{|}{C}$=, 18H), 8.02τ (=C–$\overset{|}{C}\underline{H}_2$–, 4H). (Found: C, 86.3; H, 13.1%. Calcd for $C_{12}H_{22}$: C, 86.65; H, 13.35%.) The oxidation of XII with potassium permanganate gave acetone.

Dimerization of Myrcene (XIII). From 0.7 g (0.1 mol) of lithium cuts, 6.4 g (0.05 mol) of naphthalene, and 13.6 g (0.1 mol) of XIII, 7.0 g of a crude dimer (bp 165—167°C/6 mmHg) were obtained. The redistillation of this fraction (7.0 g) gave 3.0 g of the dimer (XIV), bp 149—151°C/4 mmHg; n_D^{20} 1.4910; d_4^{20} 0.8544; IR: 825 cm^{-1}; NMR: 8.4τ ($C\underline{H}_3$–$\overset{|}{C}$=, 18H), 8.0τ (=$\overset{|}{C}$–$C\underline{H}_2$–, 12H), 4.9τ (–$\overset{|}{C}$=$C\underline{H}$–, 4H). Gas liquid chromatography showed two peaks (Rt 21 min and 24 min). (Column: Reoplex 400 (20%) on Celite 545 (60—80 mesh) 2m×3.5 mmϕ; temperature, 190°C; carrier gas, He 40 m*l*/min). (Found: C, 86.9; H, 11.6%. Calcd for $C_{20}H_{34}$: C, 87.50; H, 12.50%.) One gram of XIV was hydrogenated over a Pd-C catalyst in a methanol solution; it absorbed 310 cc of hydrogen (the theoretical amount for $C_{20}H_{34}$, F_4, 327 cc). Bp 147°C/8 mmHg, IR: 1380 cm^{-1} (doublet); NMR: 9.05τ ($C\underline{H}_3$–, 18H), 8.72τ (–$C\underline{H}_2$–, 20H), 8.25τ (–$C\underline{H}$–, 4H).

Results and Discussion

The structure of the butadiene dimer (II) was determined to be as follows. On the basis of the gas chromatography, it may be said that II is a mixture of various isomers. The hydrogenation of II absorbed two equivalents of hydrogen, giving *n*-octane (III). II was separated into two components, II_A and II_B, by gas-liquid-chromatographic trapping. The oxidation of II_A with potassium permanganate gave acetic acid and succinic acid. From these results and from the spectral evidence, II_A may be considered to be a mixture of *trans-trans*, *trans-cis*, and *cis-cis* isomers of 2, 6-octadiene. Similarly, the structure of II_B, 1, 6-octadiene, was determined by a study of the IR spectra and by oxidation with potassium permanganate.

A similar dimerization of piperylene (IV) leads to the formation of many isomers of the piperylene dimer. The hydrogenated products of the original dimer mixture were identified as 4-methylnonane (VIII) (59%), 4, 5-dimethyloctane (IX) (35%), and *n*-decane (X) (6%) by a comparison of their IR and GC retention times with those of authentic samples. 4-Methylnonadiene (V) and 4, 5-dimethyloctadiene (VI) could be separated by means of column chromatography. The structure of V was identified as 4-methyl-2, 6-nonadiene on the basis of the spectral evidence of IR and NMR. Similarly, from the results of IR and NMR, 4, 5-dimethyl-2, 6-octadiene is a reasonable assignment for the hydrocarbon (VI).

Similarly, from the dimerization of 2, 3-dimethyl-1, 3-butadiene (XI), 2, 3, 6, 7-tetramethyl-2, 6-octadiene (XII) was obtained in a poor yield. The structural assignment was further supported by the IR spectra, the NMR spectra and the results of oxidation with potassium permanganate.

The product mixture from myrcene (XIII) contained a mixture of two isomers (XIV). An attempted direct separation of this mixture into its two isomeric components by means of fractional distillation and gas chromatographic trapping was unsuccessful. From the spectral evidence and by comparison with a similar case recently reported,1) this may be considered to be a mixture of 2,6, 11, 15-tetramethyl-2, 6, 10, 14-hexadecatetraene (XIV_A) and 2, 6, 14-trimethyl-10-ethyliden-2, 6, 13-pentadecatriene (XIV_B).

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