Vigreux column, a still-head containing a cold-finger reflux condenser, a dry ice trap and a liquid nitrogen trap. The system was first purged with helium and a slow stream of helium was maintained during the reaction. The reaction flask was heated so as to maintain a slow reflux at the base of the Vigreux column but the temperature in the still-head did not exceed 30°. The temperature of the reaction mixture in the runs with diethoxybutane was initially 120° and rose to 140° during the course of the reaction. The temperature of the runs with diisopropoxybutane was about 10° higher. After 4 to 5 hr. of heating the reaction flask was allowed to cool and the flow of helium was increased to ensure the complete transfer of volatile products to the traps. At the conclusion of a run the contents of the liquid nitrogen trap were transferred to an evacuated 1-l. flask and brought to atmospheric pressure with helium. The gaseous products were analyzed with a mass spectrometer. The dry ice trap was connected to an evacuated flask and allowed to come to room temperature. The contents were thus separated into a gaseous and a liquid fraction. The gaseous fraction which was analyzed by means of gas chromatography and the mass spectrometer was at least 98% acetaldehyde. The reaction mixture was distilled at atmospheric pressure through a 12-inch Vigreux column until the temperature reached the boiling point of the acetal. The distillate was combined with the liquid fraction of the dry ice trap and analyzed by means of a Perkin-Elmer "Fractometer" using their column "A" which is supplied with the instrument. Helium was used as the carrier gas. The temperature was 50° and the pressure was 25 p.s.i. The chromatogram from the run with the ethyl acetal contained a number of well-separated bands which were identified as acetaldehyde, acetone, ethanol, *t*-butyl alcohol, *n*-butyraldehyde, ethyl *n*-butyl ether, *t*-butyl peroxide, ethyl butyrate, and the acetal in that order. The ethyl alcohol was not a reaction product but was an impurity of the acetal. The products were identified by trapping each fraction from the gas chromatography apparatus in a Dry Ice trap and transferring the condensate to an infrared cell and obtaining the infrared spectrum. The identification of each fraction was confirmed by showing that the retention time in the gas chromatogram of the known material was identical with the unknown in the reaction mixture. For quantitative analysis of the reaction mixture, a synthetic mixture was made which contained equal molecular amounts of the different substances which were found to be present. This mixture was run on the fractometer and the peak heights measured. It was found that the relative peak heights were independent of the sample size. Dividing each relative peak height of the chromatogram of the unknown mixture by the corresponding relative peak height of the known mixture gave the relative amounts of each constituent of the reaction mixture. To convert these relative amounts to absolute concentrations it was necessary to determine the concentration of any one of the constituents. For this purpose the concentration of *t*-butyl peroxide was determined from the intensity of its infrared band at 11.4 microns using a calibration curve that had previously been prepared using solutions of *t*-butyl peroxide in carbon tetrachloride in a 0.1-mm. cell. This band was chosen because there was no interference from the other constituents. The residue from the distillation of the reaction mixture was further distilled at reduced pressure. The unreacted acetal distilled at 55° to 60° at 40 mm. and a high boiling product (0.8 gram) was obtained, b.p. 72–76° at 2 mm. Its infrared curve showed no bands due to hydroxyl or carbonyl groups.

Anal. Calcd. for $C_{12}H_{26}O_2$: C, 71.29; H, 12.87; mol. wt. 202. Found: C, 71.12; H, 12.75; mol. wt. 196.

In a similar manner the decomposition of the diisopropyl acetal yielded 0.6 gram of a product, b.p. 75–80° at 2 mm.

Anal. Calcd. for $C_{14}H_{30}O_2$: C, 73.04; H, 13.04; mol. wt. 230. Found: C, 72.88; H, 12.70; mol. wt. 224.

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[CONTRIBUTION NO. 243 FROM THE DEPARTMENT OF CHEMISTRY, TUFTS UNIVERSITY]

Conversion of 4-Bromo-2-heptene to Conjugated Diene[1]

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4-Bromo-2-heptene has been converted to a mixture of 1,3- and 2,4-heptadiene by dehydrobromination with *s*-collidine and by the Hofmann exhaustive methylation procedure. The mixtures obtained by the two procedures differed both in the ratio of structural isomers and in the distribution of geometrical isomers.

For another study a straight-chain, unsymmetrical, conjugated diene without terminal unsaturation was desired. Not many such dienes are recorded in the literature, and of those that have been reported the usual method of preparation (dehydration of an allylic alcohol prepared from a Grignard reagent and an α,β-unsaturated aldehyde) leaves the structure assignment somewhat doubtful. For instance, 2,4-heptadiene has been reported at least ten times. The boiling point reported for this diene has varied from 103° to 109.7°, and agreement of literature values for the refractive index is no better. Dumoulin[3] carried out a permanganate oxidation on his 2,4-heptadiene, and the acids obtained led him to conclude that the diene contained some of the 1,3-isomer. He appears to be the only worker to have indicated that the 2,4-heptadiene might contain some of the 1,3-diene. Owens[4] did some work on the dehydration of *n*-butylvinylcarbinol which indicated that a mixture of structural isomers was obtained. The distillation curve of the dehydration product

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[1] Presented before the Division of Organic Chemistry, ACS, Atlantic City Meeting, September, 1956.

[2] From the master's thesis of J.A.S. and work of F.L.G.

[3] J. Dumoulin, *Compt. rend.*, **182**, 974 (1926).

[4] G. R. Owens, Ph.D. thesis, Ohio State University, 1937.

showed two plateaus. On the basis of the differences in the values of the exaltation of the molar refractivity the lower boiling material (b.p. 100.0–100.5°) was assigned the 1,3-heptadiene structure and the higher boiling material (b.p. 103.8–108.3°) was designated as 2,4-heptadiene.

In their original paper on allylic bromination Ziegler *et al.*[5] advocated the reaction of an alkene with *N*-bromosuccinimide followed by dehydrobromination as a method for the preparation of conjugated dienes. A branched-chain heptadiene, and straight-chain nonadiene and dodecadiene were reported as having been prepared in fairly good yield. No experimental work on the structures of these dienes was reported; the only evidence offered for the nature of the products were diene numbers[6] which were about 95% of the theoretical values. These high diene numbers are surprising in light of later work[7] on the reaction of maleic anhydride with conjugated dienes, where it has been shown that the high yield of adduct is obtained only when the carbon-carbon double bonds of the diene are of the *trans*-configuration. It is not likely that the dienes obtained by Ziegler *et al.* were of high steric purity, and the high diene numbers can be explained by the long reflux time employed, during which the maleic anhydride was involved in a polymerization reaction.[8]

In the years since 1942 the procedure suggested by Ziegler *et al.* has been highly successful and widely used for the introduction of a conjugated diene system into cyclic compounds, but the method has seen little application in open-chain compounds. The open-chain compounds that have been used[9] have been of high molecular weight, and the conversion to conjugated diene has been only moderately successful.

Heptadiene was chosen as the final product, for ultraviolet and infrared absorption should enable one to establish the diene as the 1,3- or 2,4-isomer. Hurd and Ensor[10] reported that 4-bromo-2-pentene was dehydrobrominated by trimethylamine at a low temperature. On the basis of this report it was hoped that 4-bromo-2-heptene could be converted to 2,4-heptadiene under these mild conditions. The bromoheptene was treated with various amines under a variety of reaction conditions; but to obtain a bromine-free product it was necessary to keep the reaction mixture at a rather high temperature for a fairly long period of time. The procedure finally adopted was to drop the bromoheptene into hot (165°) *s*-collidine which was stirred. The diene distilled from the reaction flask through a small, helix-filled column. After washing, the crude distillate was distilled through a spinning-band column. This distillation gave fractions amounting to a 78% yield of diene. The distillation curve exhibited two plateaus, one at b.p. 101.9–103° (22% yield of diene) and the other at b.p. 108.2–109.1° (26% yield of diene.)

In establishing the identity of the two principal products, the diene number of each material was determined. The lower boiling compound gave a diene number (220) which was 83% of the theoretical value (264), whereas the higher boiling material had a diene number (165) which was but 62% of theory. These data may be explained by the steric requirements[7] of the diene reaction. Both of these materials had an ultraviolet absorption maximum at 226 mμ with $\epsilon_{\text{max.}}$ 24,800 and 25,700, respectively. These $\epsilon_{\text{max.}}$ values would indicate that both materials are essentially pure conjugated diene.[11]

Maleic anhydride adducts of the low - and high-boiling materials were prepared. The amounts of crystalline adducts isolated correlated well with the values for diene number. The two adducts had identical melting points, but differences in crystal form and marked depression in a mixed melting point determination showed the adducts to be different compounds. Elemental analyses of the hydrocarbons and of the maleic anhydride adducts agreed with the theoretical values for heptadiene and for the maleic anhydride adduct of heptadiene.

The infrared curve of the lower boiling material had a doublet at 10.00 and 11.16μ which is associated with terminal unsaturation.[12] A strong band at 10.53μ indicated a *trans*-configuration of the carbon-carbon double bond.[13] Medium bands at 6.03 and 6.22μ also supported a highly unsymmetrical conjugated diene structure.[13] These data were consistent with a 1,3-diene structure for the lower boiling material, and in conjunction with the diene number the data indicated the material to be predominantly the *trans*-1,3-heptadiene.

The doublet at approximately 10 and 11μ was missing from the infrared curve of the higher boiling material. Very weak bands at 6.05 and 6.23μ indicated a fairly symmetrical conjugated diene.[13] These data indicated the absence of terminal unsaturation, and since the ultraviolet

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absorption showed this material to be conjugated diene, the higher boiling material must be the 2,4-heptadiene.

Another method for converting an alkyl halide to an alkene is the Hofmann exhaustive methylation procedure. Some years ago we carried 4-bromo-2-heptene through this procedure. The infrared absorption of the final product showed the presence of terminal unsaturation, indicating that rearrangement had occurred during the transformations. Since that time Young *et al.*[14] have shown that the conversion of an allylic halide to the quaternary salt was accompanied by considerable rearrangement.

4-Bromo-2-heptene was subjected to the Hofmann procedure, and distillation of the final product gave fractions amounting to an 84% yield (based on the quaternary salt) of diene. The distillation curve had two plateaus, one at b.p. 68.1–68.5°/230 mm. (47% yield of diene) and the other at b.p. 75.3–76.0°/230 mm. (20% yield of diene). The lower boiling material proved to be identical with the 1,3-heptadiene and the higher boiling material identical with the 2,4-heptadiene obtained by the collidine dehydrobromination procedure. Differences in diene numbers and slight differences in infrared curves showed the geometric isomer composition of the various materials to be different.

EXPERIMENTAL

Chemicals. 4-Bromo-2-heptene was prepared as described previously.[15] The material used had b.p. 70–71°/32 mm., n_D^{25} 1.4710.

Trimethylamine (anhydrous) was purchased from Distillation Products, Rochester, N. Y., and used as received.

Triethylamine, 2,6-lutidine, s-collidine, quinoline, and *lepidine* were the best grades available from Distillation Products. The materials were distilled just before use, and the higher boiling ones were vacuum distilled.

Maleic anhydride (Distillation Products) was recrystallized three times from chloroform and stored in a desiccator over calcium chloride.

Dioxane was the best grade available from Distillation Products. The material was refluxed with sodium and distilled in a nitrogen atmosphere.

Preliminary experiments. To establish desirable experimental conditions for the dehydrobromination, 0.028 mole of 4-bromo-2-heptene was heated with 0.056 mole of an amine in a nitrogen atmosphere for varying periods of time. Precipitates formed in all cases except with quinoline, where a lower, dark, liquid layer was formed. To the reaction mixture ligroin (b.p. 30–60°) was added, and this mixture extracted successively with 5% acetic acid, 10% sodium bicarbonate, and water. The organic layer was dried and distilled through a column (14 × 140 mm.) which was packed with helices. A bromine-free distillate could be obtained only if a temperature of at least 140° and 2 hr. reaction time were used. The following procedure was used for the larger scale experiments.

Dehydrobromination of 4-bromo-2-heptene with s-collidine. In a 250 ml. flask fitted with a dropping funnel, Hershberg stirrer, and helix-filled column (packed portion, 14 × 170 mm.) was placed 93.2 g. (0.77 mole) of *s*-collidine (b.p. 63.5°/16 mm.). The apparatus was flushed with nitrogen and the reaction system protected from air during the course of the reaction. The reaction flask was placed in a metal bath, the temperature of which was maintained at 165–170° during the reaction. 4-Bromo-2-heptene (54.5 g., 0.31 mole) was added dropwise to the reaction flask over a period of 2 hr. When the rate of distillation decreased, the temperature of the metal bath was raised until the boiling point of the distillate suddenly rose, indicating collidine was coming into the distillate. The reaction was discontinued at this point. The distillate (30.3 g.) came over at 102–106°. A portion of the distillate gave a negative test for bromine.

The residue in the reaction flask was filtered, the precipitate washed with ligroin (b.p. 30–60°) and dried. This precipitate was collidine hydrobromide (58.7 g.; 95% yield).

The distillate was washed into a separatory funnel with 400 ml. of ligroin (b.p. 30–60°). This solution was extracted with three 130-ml. portions of 5% acetic acid, once with 100 ml. of 10% sodium bicarbonate, and finally with 100 ml. of water. Hydroquinone was added to the organic layer and it was then dried with freshly heated sodium sulfate overnight.

The ligroin solution was filtered from the sodium sulfate, the drying agent washed three times with ligroin, and the washings added to the main solution. Some hydroquinone was added to the solution and the ligroin distilled from the solution through a Fenske column (18 plates) under a nitrogen atmosphere. The distillation was discontinued when the temperature of the distilling liquid reached 85°. The residue was transferred to a smaller flask, some hydroquinone was added, and the liquid was distilled under nitrogen through a Nester spinning-band column (7 mm. I.D. × 600 mm.). After removal of solvent 27 fractions were collected which were combined to give the following: Forerun, 0.98 g., b.p. 96–102°/752 mm., n_D^{25} 1.4321–1.4425; Liquid I, 6.49 g., 22% yield of diene, b.p. 101.9–103°/752 mm., n_D^{25} 1.4438–1.4445, d^{25} 0.722; Intermediate Fraction, 8.11 g., 27% yield of diene, b.p. 103–108°/755 mm., n_D^{25} 1.4452–1.4529, d^{25} 0.726; Liquid II, 7.66 g., 26% yield of diene, b.p. 108.2–109.1°/755 mm., n_D^{25} 1.4542–1.4549, d^{25} 0.737. The total weight of distillate (23.24 g.) corresponded to a 78% yield of diene from the bromoheptene. Vacuum distillation of the product in another preparation gave essentially the same results.

Liquid I was identified as a mixture of *cis*- and *trans*-1,3-heptadiene. In the ultraviolet the material had $\lambda_{\max.}^{\text{EtOH}}$ 226 mμ, ϵ 24,800. The infrared curve had the following peaks (microns): 3.24(m), 3.34(sh), 3.41(vs), 3.47(vs), 5.56(w), 6.03(ms), 6.22(ms), 6.85(s), 7.24(m), 7.68(w), 10.00(vs), 10.53(s), 11.16(vs), 13.14(m). The curve indicated terminal unsaturation, conjugated diene and *cis*- and *trans*-configurations with a preponderance of the *trans*-isomer.

Anal. Calcd. for C_7H_{12}: C, 87.4; H, 12.6; diene number, 264. Found[16]: C, 87.4; H, 12.5; diene number[6] (1 hr. reflux), 220.

A maleic anhydride adduct of the material was prepared by refluxing a benzene solution of the reactants for 2 hr.; 1.01 g. of diene gave 1.80 g. of solid, m.p. 58–65°. Considerable waxy material was present in the solid. One crystallization from ligroin (b.p. 60–90°) gave 1.28 g. of plates, m.p. 67.6–68.3°. Two more crystallizations gave material of m.p. 68.8–69.5°.

Anal. Calcd. for $C_{11}H_{14}O_3$: C, 68.0; H, 7.3. Found: C, 67.6; H, 6.9.

Liquid II was identified as a mixture of geometric isomers of 2,4-heptadiene. In the ultraviolet the material had $\lambda_{\max.}^{\text{EtOH}}$ 227 mμ, ϵ 25,700. The infrared curve had the following peaks (microns): 3.34(s), 3.41(vs), 3.48(sh), 5.59(vw),

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(16) Elemental analyses by Dr. Carol Fitz, Needham Heights, Mass.

6.05(w), 6.23(vw), 6.90(s), 7.27(m), 7.67(w), 9.35(w), 10.18(vs), 10.58(vs), 10.78(m), 11.15(vw), 11.53(vw), 12.18(m). The curve indicated a fairly symmetrical conjugated diene,[13] absence of terminal unsaturation and *cis*- and *trans*-configurations.

Anal. Calcd. for C_7H_{12}: C, 87.4; H, 12.6; diene number, 264. Found: C, 87.5; H, 12.6; diene number, 165.

The diene (1.08 g.) gave 1.58 g. of waxy maleic anhydride adduct, m.p. 61.8–67°. One crystallization from ligroin (b.p. 60–90°) gave 0.83 g. of needles, m.p. 67.9–69.0°. Two more crystallizations gave material of m.p. 68.8–69.5°. Mixed m.p. with adduct of Liquid I, 35.6–42.8°.

Anal. Calcd. for $C_{11}H_{14}O_3$: C, 68.0; H, 7.3. Found: C, 67.8; H, 7.0.

The Intermediate Fraction must be a mixture of 1,3- and 2,4-heptadiene. The material had an ultraviolet absorption maximum at 226 mμ, $\epsilon_{max.}$ 25,900. The material (1.02 g.) gave 1.46 g. of gummy maleic anhydride adduct. Fractional crystallization of the adduct gave 0.51 g. of plates, m.p. 68–69°. This material gave no depression in a mixed melting point determination with the adduct of Liquid I. This proves the presence of the 1,3-diene in this fraction. Attempts to isolate the adduct of the 2,4-diene from the Intermediate Fraction adduct were unsuccessful.

Reaction of 4-bromo-2-heptene with trimethylamine. A pressure bottle containing 100 ml. of dioxane was placed in an ice bath. To this flask was added 10.1 g. (0.171 mole) of trimethylamine which was passed through a drying tube containing potassium hydroxide pellets before entering the dioxane. The reaction flask was kept cold during the dropwise addition of 15.0 g. (0.0847 mole) of 4-bromo-2-heptene. Three reaction mixtures were prepared as above, and the bottles placed in the refrigerator overnight. The bottles were then placed in a water bath (75–80°) for 8 hr. The white solid which was initially present melted to a colorless, lower layer on warming. The reaction flasks were shaken occasionally during the 8 hr. heating period. The bottles were cooled, and the reaction mixtures were combined in a 500 ml. wide-mouth Erlenmeyer flask.

The liquid was removed from the reaction mixture with a filter stick, and the residue washed twice with dry ether. The ether was also removed with the filter stick. The quaternary salt was extremely hygroscopic and had to be protected from moisture at all times. We were unsuccessful in finding a suitable solvent for crystallization of the salt. The flask containing the quaternary salt was kept in a vacuum desiccator over phosphorus pentoxide until it came to a constant weight. Yield, 58.1 g., 97%.

Anal. Calcd. for $C_{10}H_{22}BrN$: Br, 33.8. Found: Br, 34.6.

The quaternary salt was surely a mixture of normal and rearranged product.[14] The bromine analysis showed that the reaction product was predominantly the desired quaternary salt and did not contain much trimethylamine hydrobromide which would have resulted from a dehydrobromination reaction.

Conversion of quaternary salt to heptadiene. Into a 2-l. flask fitted with a Hershberg stirrer and dropping funnel were placed 250 ml. of water and silver oxide which had been freshly prepared from 249.1 g. (1.466 moles) of silver nitrate and 58.6 g. (1.466 moles) of sodium hydroxide. Into the dropping funnel was placed a solution of 172.1 g. (0.729 mole) of the quaternary salt in 250 ml. of water. This solution was added dropwise to the reaction flask over a period of 40 min. The reaction mixture was allowed to stir overnight. The reaction mixture was filtered, the residue washed twice with water, and the washings and filtrate were combined to give 1 l. of water-white solution.

A 500 ml. Claisen flask was fitted with a dropping funnel, downward condenser, and receiver which was immersed in an ice bath. The apparatus was flushed with nitrogen and protected from air during the course of the reaction. The reaction flask was immersed in a metal bath which was maintained at 170–180° during the pyrolysis. The solution of the quaternary base was added at such a rate that the decomposition flask was essentially dry during the pyrolysis. The addition of the base solution required 7.5 hours. Acetic acid (50.0 g., 0.833 mole) was added to the distillate, and the organic layer was separated. The aqueous layer was extracted with 2 100-ml. portions of ligroin (b.p. 30–60°), and the extracts combined with the organic layer. The organic layer was extracted with 100 ml. of 5% sodium bicarbonate and with 50 ml. of water. The organic layer was placed in a flask containing some hydroquinone and some freshly heated sodium sulfate.

The drying agent was removed by filtration and washed three times with ligroin. The combined washings and filtrate were placed in a flask with some hydroquinone, and the solvent removed through a Fenske column (18 plates) under a nitrogen atmosphere. The distillation was discontinued when the temperature of the distilling liquid reached 95° The residue was transferred to a smaller flask, hydroquinone added, and the liquid distilled *in vacuo* through the Nester spinning-band column. After removal of a small amount of solvent 37 fractions were collected which were combined to give the following: Forerun, 1.42 g., b.p. 64.0–68.1°/230 mm., n_D^{25} 1.4391; Liquid III, 33.04 g., 47% yield of diene, b.p. 68.1–68.5°/230 mm., n_D^{25} 1.4427–1.4443; Intermediate Fraction, 10.69 g., 15% yield of diene, b.p. 68.5–75.3°/230 mm., n_D^{25} 1.4448–1.4538; Liquid IV, 14.04 g., 20% yield of diene, b.p. 75.3–76.0°/230 mm., n_D^{25} 1.4543–1.4552. The total weight of distillate (59.19 g.) represented an 84.4% yield of diene.

Liquid III proved to be 1,3-heptadiene. The material had an infrared absorption nearly identical with that of Liquid I. In the ultraviolet this material had $\lambda_{max.}^{EtOH}$ 225.5 mμ, ε 23,600. Liquid III gave a maleic anhydride adduct of m.p. 68.7–69.2°, undepressed when mixed with the Liquid I adduct. The diene number (137.4) of Liquid III was 52% of the calculated value, which indicated this 1,3-diene to contain less of the *trans*-isomer than Liquid I.

Liquid IV was 2,4-heptadiene. Its infrared curve was almost identical with that of Liquid II. In the ultraviolet this 2,4-diene had $\lambda_{max.}^{EtOH}$ 229.5 mμ, ε 24,900. Liquid IV gave a maleic anhydride adduct of m.p. 68.8–69.2°, which gave no depression of melting point when mixed with the Liquid II adduct. Liquid IV had a diene number (60.6) which was 23% of the calculated value. This would indicate that Liquid IV contained much less of the *trans,trans*-isomer than did Liquid II.

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