acid (20 g.) was stirred and heated at 140–150° for 1 hr. after which the viscous mass was treated with 20% hydrochloric acid to form the sparingly soluble hydrochloride of the quinoline which was then warmed with 10% sodium hydroxide, filtered from very small quantities of the 4-phenyl-2-hydroxyquinoline; the filtrate was treated with charcoal and then acidified with acetic acid. The 2-phenyl-4-hydroxyquinolines were deposited in 35–40% yields. However, by increasing the amount of ester to 0.1 mole the yields of the quinolines increased to 50–70%.

The following quinolines were obtained by this procedure: 2-phenyl-4-hydroxyquinoline, 2-phenyl-4-hydroxy-6-methylquinoline, 2-phenyl-4-hydroxy-8-methylquinoline, 2-phenyl-4-hydroxy-6-methoxyquinoline, 2-phenyl-4-hydroxy-6-chloroquinoline.

2-Phenyl-4-hydroxy-6-nitroquinoline. A mixture of *p*-nitroaniline (4.0 g.), ethyl benzoylacetate (6 g.), and polyphosphoric acid (10 g.) was stirred and heated at 160° for 20 min. The product was extracted with hot, dilute acetic acid (to remove unchanged amine), the residue warmed wth 10% sodium hydroxide, and the alkaline solution filtered off from a dark tarry product and acidified with acetic acid to yield 0.42 g. of a compound which, after purification by dissolvind in dilute sodium hydroxide, treatment with charcoal, ang reprecipitating with acetic acid, gave a pale-yellow amorphous powder, m.p. 328–330°.

Anal. Calcd. for $C_{15}H_{10}N_2O_3$: C, 67.67; H, 3.76. Found: C, 67.96; H, 3.89.

On treatment with a mixture of phosphorus oxychloride and phosphorus pentachloride the hydroxyquinoline gave 2-phenyl-4-chloro-6-nitroquinoline, pale yellow needles, m.p. 168–169°.

Anal. Calcd. for $C_{15}H_9N_2O_2Cl$: 63.26; H, 3.16. Found: C, 63.48; H, 3.09.

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JOHANNESBURG, SOUTH AFRICA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

Pyrolysis of Esters. XIX. Synthesis of Racemic and Optically Active 3-Methyl-1-pentene[1-3]

WILLIAM J. BAILEY AND EDWIN T. YATES[4]

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Racemic 3-methyl-1-pentene was synthesized in three steps from *sec*-butyl bromide in an over-all yield of 12%, with the pyrolysis of a butyrate as the final step. Optically active *d*-3-methyl-1-pentene, the simplest optically active olefin, with $[\alpha]^{25}_{D}$ +33.49°, was prepared in four steps in an over-all yield of 20% from active amyl alcohol, with the pyrolysis of the butyrate as the final step.

In an over-all program to determine the correlation between the chemical structure and physical properties of polymers, the effect of asymmetry in the side chain of an isotactic polyolefin has been of interest.[5] For this study racemic and optically active 3-methyl-1-pentene, the simplest optically active olefin, was desired. Although Schmitt and Boord[6] had previously prepared *d,l*-3-methyl-1-pentene in five steps from *sec*-butyl bromide and acetaldehyde in an over-all yield of 18%, it was thought that a three-step synthesis involving the pyrolysis of an ester would be more convenient. For this reason the Grignard reagent from racemic *sec*-butyl bromide was treated with ethylene oxide to give a 28% yield of *d,l*-3-methyl-*n*-amyl alcohol. When this alcohol was esterified with acetyl chloride and pyridine, an 80% yield of *d,l*-3-methyl-*n*-amyl acetate was obtained. However, vapor phase chromatography revealed that a very careful and tedious fractionation was required to remove the unchanged alcohol from the ester, since their boiling points are very close. For this reason the preparation of a higher boiling ester was found to be considerably more convenient. Thus, when the *d,l*-3-methyl-*n*-amyl alcohol was esterified with a mixture of butyric anhydride and sodium butyrate, a 78% yield of the corresponding butyrate was obtained in a relatively pure state by a simple distillation.

Pyrolyses of the esters were carried out under conditions that had been demonstrated not to cause rearrangement of double bonds in the preparation of isomers of aromatic hydrocarbons.[7] Thus, at 530° the *d,l*-3-methyl-*n*-amyl acetate gave a 72% yield of the racemic 3-methyl-1-pentene, while the corresponding *n*-butyrate gave a 54% yield. As this olefin was intended for use in polymerization, the emphasis throughout the synthesis was on purity of the product, which was conveniently followed with gas-phase chromatography. With the butyrate it was much easier to obtain a pure product.

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[1] Previous paper in this series, *J. Am. Chem. Soc.*, **81**, 5397 (1959).

[2] Presented in part before the Division of Polymer Chemistry at the 137th Meeting of the American Chemical Society, Cleveland, Ohio, April 1960.

[3] This work was supported in part by a grant from the National Science Foundation.

[4] Office of Naval Research Fellow, 1955–1957; Goodyear Tire and Rubber Fellow, 1957; and Dunlop Research Fellow, 1957–1958.

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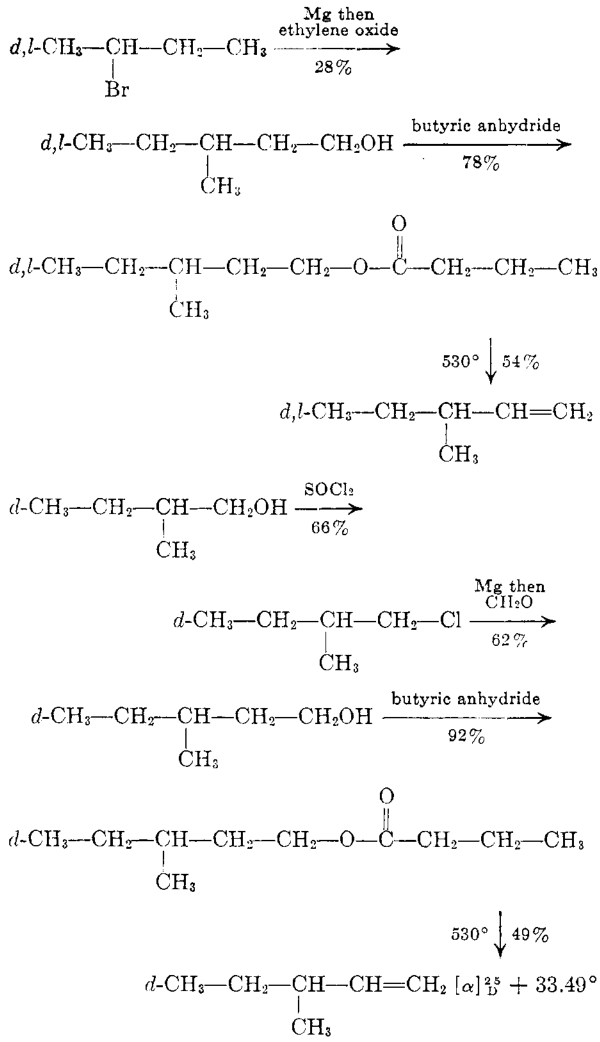

$$d,l\text{-}CH_3\text{—}\underset{\displaystyle Br}{CH}\text{—}CH_2\text{—}CH_3 \xrightarrow[28\%]{\text{Mg then ethylene oxide}}$$

$$d,l\text{-}CH_3\text{—}CH_2\text{—}\underset{\displaystyle CH_3}{CH}\text{—}CH_2\text{—}CH_2OH \xrightarrow[78\%]{\text{butyric anhydride}}$$

$$d,l\text{-}CH_3\text{—}CH_2\text{—}\underset{\displaystyle CH_3}{CH}\text{—}CH_2\text{—}CH_2\text{—}O\text{—}\overset{\displaystyle O}{\overset{\|}{C}}\text{—}CH_2\text{—}CH_2\text{—}CH_3$$

$$\downarrow 530^\circ \quad 54\%$$

$$d,l\text{-}CH_3\text{—}CH_2\text{—}\underset{\displaystyle CH_3}{CH}\text{—}CH{=}CH_2$$

$$d\text{-}CH_3\text{—}CH_2\text{—}\underset{\displaystyle CH_3}{CH}\text{—}CH_2OH \xrightarrow[66\%]{SOCl_2}$$

$$d\text{-}CH_3\text{—}CH_2\text{—}\underset{\displaystyle CH_3}{CH}\text{—}CH_2\text{—}Cl \xrightarrow[62\%]{\text{Mg then } CH_2O}$$

$$d\text{-}CH_3\text{—}CH_2\text{—}\underset{\displaystyle CH_3}{CH}\text{—}CH_2\text{—}CH_2OH \xrightarrow[92\%]{\text{butyric anhydride}}$$

$$d\text{-}CH_3\text{—}CH_2\text{—}\underset{\displaystyle CH_3}{CH}\text{—}CH_2\text{—}CH_2\text{—}O\text{—}\overset{\displaystyle O}{\overset{\|}{C}}\text{—}CH_2\text{—}CH_2\text{—}CH_3$$

$$\downarrow 530^\circ \quad 49\%$$

$$d\text{-}CH_3\text{—}CH_2\text{—}\underset{\displaystyle CH_3}{CH}\text{—}CH{=}CH_2 \quad [\alpha]^{25}_{D} + 33.49^\circ$$

For the synthesis of the optically active 3-methyl-1-pentene a slightly different synthetic route starting from active amyl alcohol was used. This change was dictated by the fact that the synthesis from the optically active amyl alcohol appeared to be more convenient than the resolution to obtain the optically active 3-methyl-*n*-amyl alcohol. Since this work was completed, Pino, Lardicci, and Centoni[8] have reported a similar synthesis of this olefin, (+)(S)-3-methyl-1-pentene, by the pyrolysis of the corresponding acetate. We, of course, preferred the butyrate because of the greater ease of separation from any unchanged alcohol. Their synthesis of the *d*-3-methyl-*n*-amyl alcohol was the same as that reported here but with a lower over-all yield (36%) for the conversion of the optically active chloride to the Grignard and subsequent treatment with formaldehyde. Their conditions for the pyrolysis of the active ester apparently were more vigorous than ours, as they report a 70% conversion to the optically active olefin and the formation of lower boiling, highly refractive compounds. They estimated from regeneration of the starting alcohol from the olefin that up to 8.55% racemization occurred during esterification and pyrolysis. For this reason they concluded that their sample of 3-methyl-1-pentene probably contained 91.7% of (+)(S)-3-methyl-1-pentene, 5.7% of (−)(R)-3-methyl-1-pentene and 2.6% of 4-methyl-1-pentene.

In a pilot study, which is reported separately,[5] a mixture containing 60% *d*-amyl alcohol and 40% isoamyl alcohol was converted in four steps to a mixture of *d*-3-methyl-1-pentene and 4-methyl-1-pentene. The conditions that gave maximum yields in the pilot study were then used for the synthesis of the optically active olefin. Fusel oil (which contained approximately 10% *d*-(−)-amyl alcohol and 90% isoamyl alcohol) was carefully fractionated to give a sample of *d*-amyl alcohol, which, on the basis of reported rotational values,[9] was assumed to be approximately 96% pure. Vapor phase chromatography indicated that the major impurity was isoamyl alcohol. The reported methods for purification of the active amyl alcohol through solid derivatives proved impractical for large scale preparations. In any case, vapor phase chromatographic studies showed that derivatives related to the isoamyl alcohol greatly diminished in concentration during the subsequent steps of the synthesis. By the method of McKenzie and Clough,[10] the *d*-(−)-amyl alcohol was converted to *d*-(+)-2-methyl-*n*-butyl chloride. Treatment of the optically active chloride with magnesium produced the corresponding Grignard reagent, which was treated with gaseous formaldehyde plus solid paraformaldehyde to give a 62% yield of *d*-(+)-3-methyl-*n*-amyl alcohol. Treatment of this alcohol with a mixture of butyric anhydride and sodium butyrate gave a 92% yield of *d*-(+)-3-methyl-*n*-amyl *n*-butyrate. Pyrolysis of the optically active butyrate was carried out at 530° under conditions that would minimize any racemization or rearrangement.[7] Under these fairly mild conditions, a 33% conversion to *d*-(+)-3-methyl-1-pentene [L-(+)-3-methyl-1-pentene or (+)(S)-3-methyl-1-pentene] was realized. Vapor phase chromatographic studies indicated very little 4-methyl-1-pentene in our sample of optically active olefin, and the milder pyrolysis conditions may have caused less racemization. Nevertheless, the properties of their olefin[8] agree fairly well with those of our sample; for example, they report $[\alpha]^{17}_{D}$ + 32.86° compared to our $[\alpha]^{25}_{D}$ + 33.49. The present work does have the advantage that the purity of every intermediate in the synthesis was checked by vapor phase chromatography. The corresponding racemic materials, as well as a mixture[5] containing

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[8] P. Pino, L. Lardicci, and L. Centoni, *J. Org. Chem.*, **24,** 1399 (1959).

[9] W. Marckwald and A. McKenzie, *Ber.*, **34**, 485 (1901).

[10] A. McKenzie and D. W. Clough, *J. Chem. Soc.*, **103,** 699 (1913).

those derived from isoamyl alcohol, were available as reference materials. Of course, the vapor phase chromatograms gave no indication of the optical purity of these materials.

One must conclude that the pyrolysis of esters is well suited for the synthesis of optically active olefins. The relatively high specific activity obtained for *d*-(+)-3-methyl-1-pentene suggests that many of the optically active olefins reported in the literature are not of high optical purity. For example, dehydration of optically active 4-methyl-2-hexanol over alumina[11] gave a mixture of olefins with $[\alpha]^{26}_{D}$ + 13.7°

EXPERIMENTAL[12]

d,l-3-Methyl-n-amyl alcohol. In a modification of the general procedure of Huston and Agett,[13] a few drops of methyl iodide, 240 ml. of dry ether and a few milliliters of a solution of 766.9 g. (5.6 moles) of *d,l-sec*-butyl bromide dissolved in 1500 ml. of anhydrous ether were added to a 5-l., three-necked flask. After the ether solution of bromide had been added at a rate such as to maintain gentle reflux, the mixture was heated under reflux on the steam bath for an additional 3 hr. A solution of 400 g. (9.1 moles) of ethylene oxide (dried over soda lime) in 650 ml. of anhydrous ether was kept cool in ice and small portions were added to the stirred Grignard reaction mixture which was kept below 10° by immersion in an ice bath. After all the ethylene oxide was added, the reaction mixture was allowed to warm until gentle refluxing began. It was then heated under reflux on the steam bath for 2 hr. and finally stirred for 1 day at room temperature. After about 1 l. of ether was removed by distillation, 1 l. of dry benzene was added to the reaction flask. The distillation was continued with stirring until the temperature of the vapor reached 65°. After the mixture was allowed to stand overnight at room temperature, it was decomposed with 2.5 l. of ice and water. A viscous tar, which was not decomposed by the ice water, was hydrolyzed by a concd. hydrochloric acid-ice mixture. Enough of the hydrochloric acid-ice mixture was added to the reaction mixture to dissolve the magnesium hydroxide. The benzene layer was separated, and the aqueous phase was extracted with six 200-ml. portions of ether. After the combined extracts were dried over anhydrous magnesium sulfate, the solvents were removed by distillation through a 6-inch, helix-packed column. Distillation of the residue through the same column yielded 159 g. (28%) of crude *d,l-3*-methyl-*n*-amyl alcohol, b.p. 64–85° (30–32 mm.) [reported[14] b.p. 153.7–154.1° (760 mm.)].

d,l-3-Methyl-n-amyl acetate. To a cooled solution of 106.1 g. (1.04 moles) of *d,l*-3-methyl-*n*-amyl alcohol and 500 ml. of pyridine was slowly added, with stirring, 89.5 g. (1.1 moles) of acetyl chloride. The mixture was heated on the steam bath for 2.5 hr. and was then allowed to stand overnight at room temperature. When the reaction mixture was poured into 1 l. of dilute hydrochloric acid containing ice, the acetate separated as an oil. The aqueous phase was extracted with seven 200-ml. portions of ether, and the ethereal extracts, combined with the previously separated organic layer, were washed with dilute hydrochloric acid to remove any dissolved pyridine. After the ether solution was dried with anhydrous magnesium sulfate, the ether was removed by distillation through a 6-inch, helix-packed column. The residue was distilled twice through the same column under reduced pressure to yield 115.8 g. (80%) of *d,l*-3-methyl-*n*-amyl acetate, b.p. 65–73° (20 mm.), n^{25}_{D} 1.4106. A vapor-phase chromatogram of this material over didecyl phthalate on Chromosorb showed the presence of a single symmetrical peak.

Anal. Calcd. for $C_8H_{16}O_2$: C, 66.62; H, 11.18. Found: C, 66.63; H, 11.05.

Pyrolysis of d,l-3-methyl-n-amyl acetate. The pyrolysis apparatus was essentially the same as that described[15] previously. At a rate of 30 drops per min., 150 g. (1.04 moles) of *d,l*-3-methyl-*n*-amyl acetate was added from a dropping funnel to a Vycor tube heated at 510–530°. The pyrolysate was collected in a receiver cooled in a Dry Ice–Methyl Cellosolve bath. After the pyrolysate was dissolved in *n*-butyl ether, the resulting solution was extracted with ice water until the extracts were neutral. Distillation of the *n*-butyl ether solution through a 6-inch, helix-packed column yielded 54.3 g. (62%) of *d,l*-3-methyl-1-pentene, b.p. 50–53°, n^{24}_{D} 1.3819-1.3831 (reported[6] b.p. 53.6–54°, n^{20}_{D} 1.3835), and 21.3 g. (14% recovery) of unchanged starting ester. The yield of *d,l*-3-methyl-1-pentene, based on unrecovered acetate, was 72%. A vapor-phase chromatogram over silicone grease on Chromosorb showed a single symmetrical peak.

d,l-3-Methyl-n-amyl n-butyrate. After a mixture of 81.6 g. (0.80 mole) of *d,l*-3-methyl-*n*-amyl alcohol, 150.8 g. (0.95 mole) of butyric anhydride and 8.8 g. (0.08 mole) of sodium butyrate was heated under reflux for 20 hr., it was allowed to stand overnight at room temperature. Agitation with 300 ml. of warm water hydrolyzed the excess butyric anhydride and dissolved most of the acid. The aqueous phase was extracted with four 50-ml. portions of ether, and the ethereal extracts were added to an ether solution of the butyrate. Extraction of the combined ether solutions with six 50-ml. portions of water and eight 50-ml. portions of dilute sodium bicarbonate solution rendered the extracts neutral to litmus. After the solution had been dried over anhydrous magnesium sulfate, the ether was removed by distillation through a 6-inch, helix-packed column. Fractionation of the residue through the same column yielded 107.7 g. (78%) of *d,l*-3-methyl-*n*-amyl *n*-butyrate, b.p. 92.5–94.4° (20 mm.), n^{26}_{D} 1.4163–1.4166.

Anal. Calcd. for $C_{10}H_{20}O_2$: C, 69.74; H, 11.70. Found: C, 69.81; H, 11.77.

Pyrolysis of d,l-3-methyl-n-amyl n-butyrate. To the Vycor tube heated at 530° was added 105.8 g. (0.61 mole) of *d,l*-3-methyl-*n*-amyl *n*-butyrate from a dropping funnel at the rate of 0.4 g. per min. The pyrolysis was conducted in a nitrogen atmosphere, and a receiver cooled in a Dry Ice–Methyl Cellosolve bath was used to collect the pyrolysate. A solution of the pyrolysate in 150 ml. of *n*-butyl ether was washed with ice water and then dilute sodium hydroxide until the extracts were neutral to litmus. Distillation of the ether solution yielded 18.8 g. (36%) of *d,l*-3-methyl-1-pentene, b.p. 52–53°, n^{25}_{D} 1.3828–1.3830, and 35.9 g. (34% recovery) of unchanged starting material. The yield of olefin, based on unrecovered butyrate, was 54%.

d-2-Methyl-n-butyl chloride. Approximately 3 gallons of fuel oil (about 10% *d*-amyl alcohol and 90% isoamyl alcohol) was distilled through a 5-foot Podbielniak column equipped with an automatic fraction cutter[16] to yield 845 g. of 96% *d*-amyl alcohol, $[\alpha]^{25}_{D}$ − 5.64° (reported[9] $[\alpha]_{D}$ − 5.90°).

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(12) The authors are grateful to Mrs. Kathryn Gerdeman Baylouny and Miss Jane Swan for the microanalyses. Vapor phase chromatograms were determined on a special apparatus described previously [W. J. Bailey and W. H. Hale, *J. Am. Chem. Soc.*, **81**, 647 (1959)].

(13) R. C. Huston and A. H. Agett, *J. Org. Chem.*, **6**, 123 (1941).

(14) J. F. Norris and F. Cortese, *J. Am. Chem. Soc.*, **49**, 2640 (1927).

(15) W. J. Bailey and C. King, *J. Am. Chem. Soc.*, **77**, 75 (1955).

(16) The authors are grateful to J. G. O'Rear and P. Sniegoski of the Naval Research Laboratories, Washington, D. C., for making available this column which was essential for the purification of the *d*-amyl alcohol.

A portion of the *d*-amyl alcohol was converted to the 3,5-dinitrobenzoate and recrystallized from 80% ethanol-20% benzene to give *d*-amyl 3,5-dinitrobenzoate, m.p. 84–86°, $[\alpha]^{25}_{D}$ + 4.47° (reported[17] m.p. 83–84°, $[\alpha]^{25}_{D}$ + 4.9°). Saponification of the ester resulted in recovery of *d*-amyl alcohol, $[\alpha]^{25}_{D}$ − 5.83°.

The procedure for the preparation of the chloride was esentially that used by McKenzie and Clough.[10] Treatment of 636.8 g. (7.24 moles) of the *d*-amyl alcohol, 800 ml. of anhydrous ether, and 6 ml. of pyridine with 868.6 g. (7.30 moles) of thionyl chloride yielded 507.9 g. (66%) of *d*-2-methyl-*n*-butyl chloride, b.p. 98–100°, n^{24}_{D} 1.4111–1.4115, α^{24}_{D} + 1.44° (1:1.0) [reported[10] b.p. 98–99°, α^{15}_{D} + 0.75° (1:0.5)]. A vapor-phase chromatogram over didecyl phthalate on Celite gave essentially a single symmetrical peak with a very small shoulder.

d-3-Methyl-n-amyl alcohol. The general procedure of Wood and Scarf[18] for the reaction of gaseous formaldehyde on a Grignard reagent to yield an alcohol was adapted to this synthesis. To a 5-l., three-necked flask, fitted with a stirrer, a reflux condenser, and a dropping funnel, was added 114.2 g. (4.7 moles) of magnesium turnings, followed by a small amount of anhydrous ether, a few milliliters of a solution of 494.9 g. (4.6 moles) of *d*-2-methyl-*n*-butyl chloride in 1 l. of anhydrous ether and a few drops of methyl iodide. After the mixture had been heated on the steam bath to initiate the reaction, the ether solution of the chloride was added at a rate such as to maintain gentle reflux. After the alkyl chloride was added, the mixture was heated under reflux on the steam bath for 1 hr. In a 500-ml., round-bottomed flask was placed 165 g. (equivalent to 5.5 moles of formaldehyde) of paraformaldehyde which has been dried in a vacuum desiccator over Drierite. The paraformaldehyde was decomposed at 160–190° and the gaseous formaldehyde was conducted through a tube heated by resistance wire to just above the surface of the stirred Grignard reagent. An additional 20 g. of solid paraformaldehyde and 1.5 l. of anhydrous ether were added to the reaction mixture which was heated under reflux on the steam bath for 6 hr. and then allowed to stand for 17 hr. at room temperature. Crushed ice was added to the reaction mixture, followed by the addition of a slight excess of dilute hydrochloric acid. The ether layer was separated, and the aqueous phase was extracted with twelve 200-ml. portions of ether. The combined ether solutions were washed with a 5% potassium carbonate solution and the aqueous washings were, in turn, extracted with two 200-ml. portions of ether which were added to the original ether solution. After the solution was dried with two successive charges of anhydrous potassium carbonate, the ether was removed by distillation through a 10-inch, helix-packed column. Distillation of the residue yielded 294.5 g. (62%) of *d*-3-methyl-*n*-amyl alcohol, b.p. 151.5°, n^{25}_{D} 1.4186, d^{25}_{4} 0.829, $[\alpha]^{25}_{D}$ + 8.36° (reported b.p. 151–152°,[19] n^{25}_{D} 1.4182,[19] $d^{20.5}_{4}$ 0.8262,[19] $[\alpha]^{20.5}_{D}$ + 8.77,°[19] $[\alpha]^{19}_{D}$ + 7.890[10]). A vapor-phase chromatogram with a Polyglycol E1000 on Chromosorb column gave essentially a single symmetrical peak.

d-3-Methyl-n-amyl n-butyrate. In a procedure similar to that employed for the synthesis of the corresponding racemic butyrate, 282.4 g. (2.77 moles) of *d*-3-methyl-*n*-amyl alcohol was treated with 475.0 g. (3.10 moles) of butyric anhydride and 11.9 g. (0.11 mole) of sodium butyrate. Fractionation of the reaction product through a 10-inch, helix-packed column yielded 437.0 g. (92%) of *d*-3-methyl-*n*-amyl *n*-butyrate, b.p. 93–94° (20 mm.), n^{25}_{D} 1.4170, d^{25}_{4} 0.877, $[\alpha]^{24}_{D}$ + 7.61°.

Anal. Calcd. for $C_{10}H_{20}O_2$: C, 69.74; H, 11.70. Found: C, 69.71; H, 11.57.

Pyrolysis of d-3-methyl-n-amyl n-butyrate. The pyrolysis procedure was the same as that used for the *d,l*-butyrate. To a Vycor tube heated at 530° was added 103.5 g. (0.60 mole) of *d*-3-methyl-*n*-amyl *n*-butyrate at a drop rate of 0.4 g. per min. Distillation of a butyl ether solution of the pyrolysate through a 6-inch, helix-packed column yielded 17.0 g. (33%) of *d*-3-methyl-1-pentene, b.p. 53°, n^{25}_{D} 1.3830, d^{25}_{4} 0.668, $[\alpha]^{25}_{D}$ + 33.49° [reported[8] b.p. 54–54.3° (765 mm.), n^{20}_{D} 1.3840–1.3842, $[\alpha]^{17}_{D}$ + 32.86°], and 33.4 g. (32% recovery) of unchanged starting material. The yield of olefin, based on unrecovered butyrate, was 49%.

Anal. Calcd. for C_6H_{12}: C, 85.62; H, 14.38. Found: C, 85.48; H, 14.54.

Vapor-phase chromatograms on silicone grease, didecyl phthalate, Tide, and silver nitrate on tetraethylene glycol all showed a single symmetrical peak.

COLLEGE PARK, MD.

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