

Procedure.—The procedure described here for the preparation of 2-butylheptanoic acid is typical of the method used for all the acids mentioned in Table I.

2-Butylheptanoic Acid.—Anhydrous THF (35 ml) and diisopropylamine (4.9 g, 0.049 mol) was added to a dry, nitrogen-flushed flask under an atmosphere of nitrogen. *n*-Butyllithium in hexane (30 ml of 1.6 *M*, 0.048 mol) was added to the magnetically stirred solution at such a rate as to maintain the temperature below 0°. *n*-Heptanoic acid (2.95 g, 0.0227 mol) was then added to the cold basic solution and again the temperature was kept below 0°. After 15 min, HMPA (9 ml, 0.050 mol) was added to the milky white solution, which became transparent and light yellow after 5 min of stirring at 5°. The solution was stirred for an additional 15 min at 5°, and *n*-butyl bromide (3.3 g, 0.024 mol) was added at once at 0°. The reaction temperature immediately rose to 18°. After 2 hr of additional stirring at room temperature, the reaction was worked up in the following manner. Dilute hydrochloric acid (10%) was added at 0° until the mixture became acidic. The aqueous layer was separated and extracted with petroleum ether (bp 30–60°). The combined organic layers were washed five times with 100-ml portions of dilute hydrochloric acid, H₂O, and saturated sodium chloride solutions. The organic layer was then dried and the solvent was stripped off. The residue was distilled through a 5-in. Vigreux column to give 4.06 g (96%) of a colorless oil, bp 175–177° (30 mm). Examination of this oil on a gas chromatographic column (0.25 in. × 6 ft, 25% DEGA, phosphoric acid treated 60–80 Chromosorb A) at 180° showed this product to be 96.5% 2-butylheptanoic acid and 3.5% *n*-heptanoic acid.

Registry No.—HMPA, 680-31-9; 2-butylheptanoic acid, 22058-70-4.

An Improved Synthesis of 2,4,6-Octatriene

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The title compound has been prepared previously *via* a coupling reaction followed by a dehydration.¹ The yields are low (20–40%) and the product is often contaminated with its isomers.^{1c,d,h} Recently, 1,3,6- and 1,3,7-octatriene (I and II, respectively) have become available in high yield by the metal-catalyzed dimerization of the butadiene.² Attempts at converting I and II to 2,4,6-octatriene (III) have shown that the bases studied which are strong enough to isomerize II will catalyze a cyclization of the octatrienyl anion, forming a mixture of methylcycloheptadienes.^{3,4}

We wish now to report that some hydroxide bases in dimethyl sulfoxide (DMSO) are specific for the isomerization of I and II, giving 70–85% yields of III with little or no accompanying cyclization. Triton B and

tetramethylammonium hydroxide catalyze the reaction smoothly, and <5% cyclic products are obtained even with prolonged reaction times. Cyclization is obtained with KOH; however, the reaction time may be controlled to give an 84% yield of 95% pure 2,4,6-octatriene. Other alkali metal hydroxides give a less clear-cut reaction.

Thus, 2,4,6-octatriene may be obtained as a mixture of stereoisomers³ in 70% overall yield from butadiene.

Experimental Section

All boiling points are uncorrected. Analyses by gas-liquid partition chromatography (glpc) were performed on an F & M Model 720 chromatograph using a 20-ft column packed with 20% tris(cyanoethoxy)propane on 35/80 mesh Chromosorb P. The octatrienes were prepared by the dimerization of butadiene in the presence of a zero-valent nickel complex and a hydroxylic solvent,^{2c} and consisted of a 1:3 mixture of 1,3,6-octatriene and 1,3,7-octatriene contaminated with *ca.* 6% of 4-vinylcyclohexene and 1–2% of other unidentified materials.

Preparative Isomerization of the Octatriene Mixture. A. With Triton B in DMSO at 90°.—The octatriene mixture (0.82 g) and DMSO (10.0 ml) were sealed under N₂ in a glass-walled pressure vessel equipped with a septum through which liquids could be injected. After the mixture had equilibrated at 90°, 0.25 ml of Triton B (40% benzyltrimethylammonium hydroxide in methanol, K & K Laboratories) was added. The reaction mixture was stirred for 10 min, cooled briefly, and quenched in 20 ml of ice-water. Following work-up, 0.67 g (81.8%) of material was distilled at 58° (30 mm). Glpc analysis showed the presence of 2,4,6-octatriene (85.3%), methylcycloheptadienes (3.6%), 4-vinylcyclohexene (5.8%), 1,3,7-octatriene (1.3%), and unidentified materials (4.0%). Fractional distillation may be employed to give III in >95% purity.

B. With KOH in DMSO at 80°.—Potassium hydroxide pellets (5.0 g) and DMSO (30 ml) were sealed in a pressure vessel. When equilibrium was established, 2.28 g of octatrienes was added *via* a syringe and stirring was continued for 2 hr at 80°. The reaction vessel was allowed to cool at room temperature for 30 min, at which time the contents were quenched in 150 ml of ice-water. After work-up, 1.91 g (84%) of 95% pure 2,4,6-octatriene was distilled at 66° (44 mm). In a separate experiment the reaction temperature and time were extended to 105° and 4 days, respectively, and a 53% yield of methylcycloheptadienes³ (96% pure) was obtained.

Registry No.—III, 764-75-0.

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The Meerwein-Ponndorf-Verley Reduction of 1,2-Cyclopentanedione. Stereochemical Evidence for Dual Reductive Paths

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Reduction of 1,2-cyclohexanedione¹ with aluminum isopropoxide in toluene has been shown to produce *cis*- and *trans*-1,2-cyclohexanediols in a stoichiometrically

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(1) Although both 1,2-cyclohexanedione and 1,2-cyclopentanedione have been shown to exist largely as the tautomeric enolones (footnote 14, ref 2), the dione nomenclature will be used here because both compounds behave as diones in this study.