The residue (130 mg.) was chromatographed over 3.5 g. of alumina. The eluates obtained with 10-cc. portions of 3:7, 2:8 and 1:9 petroleum ether-ether, with 10 cc. of ether and with 10 cc. of 9:1 ether-chloroform were combined and gave 69 mg. of amorphous Δ^{17}-pregnene-21-ol-3,11-dione acetate. This was dissolved in 3.5 cc. of methanol and treated with a solution of 2 cc. of water containing 60 mg. of potassium carbonate and 60 mg. of potassium bicarbonate. After two hours at room temperature, the solution was acidified with 2 drops of acetic acid and concentrated to a small volume *in vacuo*. The oily precipitate was dissolved in chloroform, washed and the solution concentrated to dryness. The residue (54 mg.) was chromatographed over 2 g. of alumina. The fraction eluted with 1:1 ether-chloroform and mixtures with an increasing proportion of chloroform could be crystallized from a small volume of ether. The combined crystals weighed 30 mg. and melted at 127.5–128°. Recrystallization from ether raised the melting point to 128–128.5°.

Anal. Calcd. for $C_{21}H_{30}O_3$: C, 76.33; H, 9.15. Found: C, 76.63; H, 9.38.

A 5-mg. sample was permitted to stand at room temperature with acetic anhydride-pyridine for two hours. The product was an oil, from which the original alcohol could be obtained by saponification.

Δ^{17}-Pregnene-21-ol-3,11-dione from Δ^{17}-Pregnene-3(α),21-diol-11-one 21-Hemisuccinate.—A sample of 159 mg. of the 21-hemisuccinate of Δ^{17}-pregnene-3(α),21-diol-11-one was oxidized and then saponified as previously described[8]. Crystallization of the product gave 70 mg. of Δ^{17}-pregnene-21-ol-3,11-dione, m. p. 128°. It did not depress the melting point of XV.

Pregnene-17(α),20,21-triol-3,11-dione Diacetate from XV.—A sample (82 mg.) of Δ^{17}-pregnene-21-ol-3,11-dione, (XV), m. p. 128°, was treated with osmium tetroxide, hydrolyzed and acetylated as previously described.[8] The crystalline diacetate weighed 72 mg., melted at 212–213°, and had $[\alpha]^{25}D$ +95°. A mixed melting point with the original sample showed no depression.

Acknowledgment.—For valuable suggestions concerning this work the author is indebted to Dr. K. Folkers and Dr. R. T. Major of these laboratories, and to Dr. E. S. Wallis of Princeton University. For the microanalyses reported herein acknowledgment is made to Messrs. R. Boos, W. H. Humphrey, E. Thornton, J. McGregor and R. Funk.

Summary

The application of the *p*-toluenesulfonate-tertiary amine reaction to certain 20-hydroxypregnenes is described. In the case of pregnane-20(β),21-diol-3,11-dione 21-acetate 20-tosylate, Δ^{17}-pregnene-21-ol-3,11-dione was obtained.

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(8) Sarett, *J. Biol. Chem.*, **162**, 601 (1946).

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Preparation of 2-Alkylbutadienes[1]

BY C. S. MARVEL, R. L. MYERS[2] AND J. H. SAUNDERS[3]

The observation[4] that emulsion copolymers of isoprene with styrene contain more diene units joined in the 1,4-manner than do the corresponding butadiene-styrene copolymers suggested the importance of investigating other 2-alkylbutadienes. The literature on the synthesis of this class of dienes is very limited. 2-Ethyl-1,3-butadiene has been reported as a product of dehydrohalogenation of 3-methyl-3,4-dibromopentane,[5] but no evidence of structure was presented. 2-Isopropyl-1,3-butadiene has been prepared by von Braun and Keller[6] by the Hofmann degradation of 2-isopropyl-1,4-diaminobutane. While this method gave a well-characterized product, the starting materials needed for the synthesis are not readily available. This communication describes the synthesis of 2-isopropyl-1,3-butadiene[7] by various routes, one of which appears to be a good general method for making 2-alkylbutadienes.

2-Isopropylbutadiene was first obtained by dehydration of 2-isopropyl-1,4-butanediol through acetylation and pyrolysis. The diol was synthesized by the method of Adkins and Wojcik.[8] The final yield of diene based on diethyl isopropylidenesuccinate was about 4%. An attempt to find an improved preparation of diethyl isopropylsuccinate through the addition of isopropyl-metal halides to diethyl maleate or fumarate did give the ester in 30% yields but the over-all reaction was still not a satisfactory one for preparative work.

A second series of reactions was then investigated. The starting material was isovaleraldehyde (I). It was converted either to isopropylacrolein (III) or to 2-isopropyl-3-hydroxypropionaldehyde (II) and then by the Grignard reaction and subsequent dehydration to the desired diene. Different sequences of reactions were tried and these are indicated in the chart.

The final choice of steps is that indicated by the heavy arrows. The Mannich intermediate[9] (VI) was not isolated but was converted directly to isopropylacrolein (VII). The unsaturated carbinol

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(2) Present address: General Electric Company, Schenectady, New York.

(3) Present address: Monsanto Chemical Company, Anniston, Alabama.

(4) I. M. Kolthoff, T. S. Lee and Mary Anne Mairs, *J. Polymer Sci.*, **2**, 220 (1947).

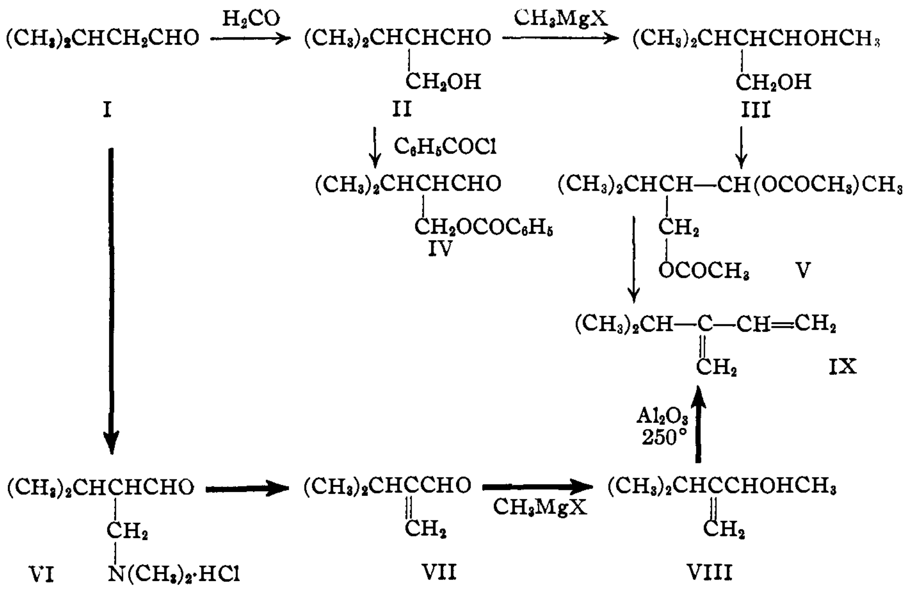
(5) Pariselle and Simon, *Compt. rend.*, **173**, 86 (1921).

(6) von Braun and Keller, *Ber.*, **64**, 2617 (1931).

(7) The desirability of synthesizing this diene was first brought to our attention by Drs. W. E. Messer and V. C. Neklutin of the United States Rubber Company.

(8) Adkins and Wojcik, THIS JOURNAL, **55**, 4939 (1933); **56**, 2424 (1934).

(9) Mannich, Lesser and Silten, *Ber.*, **65**, 378 (1932).



(VIII) was also dehydrated by converting to the acetate and pyrolyzing this ester. This method may be useful in large scale work to effect dehydration. The over-all yield of diene from isovaleraldehyde is about 11%. The reactions are relatively simple to carry out in the laboratory on a fairly large scale.

By use of the preferred scheme outlined above *n*-butyraldehyde was converted to 2-ethylbutadiene and *n*-heptaldehyde was converted to 2-*n*-amylbutadiene.

Experimental

Diethyl Isopropylidenesuccinate.—Diethyl isopropylidenesuccinate was prepared according to the procedure of Adkins and Wojcik[8] with slight modifications. Sodium ethoxide was prepared in ether suspension by the method of Brühl[10] and used without isolation. The reaction was run for four hours at 0° after the addition of the acetone and diethyl succinate mixture to the sodium ethoxide suspension. The reaction mixture was then permitted to warm to room temperature and stand for sixteen hours prior to hydrolysis. Longer reaction times did not increase the yield. From 136 g. (2.0 moles) of sodium ethoxide in 1500 ml. of ether, 217.5 g. (1.25 moles) of diethyl succinate, and 116 g. (2.0 moles) of acetone there was obtained 120 g. (45%) of diethyl isopropylidenesuccinate, b. p. 91-96° (1 mm.), $n^{20}D$ 1.4521. When 2.0 moles of sodium ethoxide, 1.5 moles of ester, and 2.4 moles of acetone were used the yield was 53%. Other variations in the concentrations of reactants did not increase the yield.

The product was redistilled through a 12-in., helix-packed column to obtain pure diethyl isopropylidenesuccinate which boiled at 100–102° (2 mm.), $n^{20}D$ 1.4550, d^{20}_4 1.0304.

Adkins and Wojcik[8] reported the b. p. 115–122° (7 mm.).

Diethyl Isopropylsuccinate by Reduction of Diethyl Isopropylidenesuccinate.—A total of 815 g. (3.81 moles) of diethyl isopropylidenesuccinate was reduced over Raney nickel in a high pressure bomb without solvent. With an initial pressure of 1700 p. s. i. at 25° only one-third of the theoretical amount of hydrogen was taken up. The pressure was raised to 2150 p. s. i., the temperature to 100°, and the reduction was completed. The nickel was removed by filtration and the diethyl isopropylsuccinate was reduced to the glycol without purification.

Diethyl Isopropylsuccinate from Diethyl Fumarate and Isopropylmagnesium Bromide.—In a 1-liter, three-necked, round-bottomed flask equipped with a reflux condenser and a dropping funnel with calcium chloride tubes, and a Hershberg stirrer were placed 50 g. (0.3 mole) of diethyl fumarate and 250 ml. of dry ether. A Grignard reagent prepared in the usual manner from 7.07 g. (0.3 mole) of magnesium, 35.8 g. (0.3 mole) of isopropyl bromide and 300 ml. of ether was added dropwise to the reaction flask with vigorous stirring. The reaction mixture was stirred for an additional fifteen minutes after all of the Grignard reagent had been added.

The reaction mixture was worked up in the usual manner and the residual oil was distilled through a 12-in., helix-packed column. The yield of diethyl isopropylsuccinate was 18.8 g. (29.8%), b. p. 65° (0.5 mm.) or 82° (1 mm.), $n^{20}D$ 1.4261. A sample which was redistilled for analysis boiled at 123–125° (20 mm.), $n^{20}D$ 1.4284, d^{20}_4 0.9925.

Anal.[11] Calcd. for $C_{11}H_{20}O_4$: C, 61.09; H, 9.32. Found: C, 60.82; H, 9.10.

Adkins and Wojcik[8] who prepared this compound by the reduction of diethyl isopropylidenesuccinate reported the b. p. 110–112° (8 mm.). Neklutin[12] who prepared this compound in a manner similar to that of Adkins and Wojcik,[8] reported b. p. 71–78° (0.8 mm.), $n^{20}D$ 1.4288.

The use of 50% mole excess of diethyl fumarate did not increase the yield. When diethyl maleate was substituted for diethyl fumarate, the results were essentially the same (30.2% yield).

Five grams of diethyl isopropylsuccinate was hydrolyzed by refluxing for six hours with 40 ml. of 25% sodium hydroxide solution. The solution was cooled, extracted with ether and acidified. The white solid thus obtained was recrystallized from acetone and water, m. p. 115.5–116.5°. Roser[13] reported a melting point of 114° for *dl*-isopropylsuccinic acid. Henry and Paget[14] reported a melting point of 117° for this compound.

Diethyl Isopropylsuccinate from Diethyl Maleate and Isopropyl-cadmium Halide.—A Grignard reagent was prepared in the usual way, using 28.6 g. (1.18 moles) of magnesium, 143 g. (1.16 moles) of isopropyl bromide,

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[10] Brühl, *Ber.*, **35**, 3510 (1902); **37**, 2066 (1904).

[11] We are indebted to Mr. H. S. Clark, Illinois State Geological Survey, for all microanalyses reported in this communication.

[12] Neklutin, private communication.

[13] Roser, *Ann.*, **220**, 271 (1883).

[14] Henry and Paget, *J. Chem. Soc.*, 70 (1928).

and 1000 ml. of dry ether in a 3-liter, three-necked, round-bottomed flask. The reaction mixture was stirred for fifteen minutes after the addition of the halide had been completed, and then was cooled to 0° by means of an ice-salt bath and was maintained at that temperature. During one and one-quarter hours 212 g. (1.16 moles) of anhydrous cadmium chloride was added in small portions to the reaction flask. The suspension was stirred for three-quarters of an hour and a solution of 200 g. (1.16 moles) of diethyl maleate in 500 ml. of ether was added dropwise to the reaction mixture during a period of three and one-half hours. During the addition of the ester the reaction mixture became very gnmmy and hard to stir. A less vigorous glass stirring shaft was substituted for the Hershberg stirrer and the reaction was continued. Stirring at 0° was continued for five hours.

The reaction mixture was worked up in the usual way and the residual oil was distilled through a 6-in., helix-packed column. The recovery of diethyl maleate was 69.5 g. (34.8%). The yield of diethyl isopropylsuccinate was 48 g. (29.3%), b. p. 118–126° (20 mm.), $n^{20}\text{D}$ 1.4311.

A similar experiment which involved longer reaction times between the isopropyl bromide and magnesium and between the isopropylmagnesium bromide and cadmium chloride did not give an increased yield.

2-Isopropyl-1,4-butanediol.—The diethyl isopropylsuccinate obtained from the reduction of the diethyl isopropylidenesuccinate was reduced over copper chromite at 260°, with an initial pressure of 6000 p. s. i.[8] Only about two-thirds of the theoretical amount of hydrogen was taken up.

The reduction mixture was filtered through a fluted filter paper to remove most of the catalyst, and the filtrate was distilled through a 12-in., helix-packed column. The recovery of diethyl isopropylsuccinate was 76.5 g. (9.4%). The yield of 2-isopropyl-1,4-butanediol was 72.5 g. (15.8%), b. p. 145–146° (18 mm.), $n^{20}\text{D}$ 1.4535, d^{20}_{4} 0.9672.

Adkins and Wojcik reported b. p. 119–122° (3 mm.), $n^{25}\text{D}$ 1.4535.

Diacetate of 2-Isopropyl-1,4-butanediol.—In a 200-ml., round-bottomed flask were placed 22 g. (0.167 mole) of 2-isopropyl-1,4-butanediol, 75 g. (0.73 mole) of acetic anhydride, and 1 g. of pyridine. The flask and its contents were set aside for three days. At the end of that time the acetic acid was removed by distillation through a 12-in., helix-packed column at atmospheric pressure, and the acetic anhydride was distilled at 100 mm. The residue was carefully fractionated. The yield of diacetate was 28.7 g. (80%), b. p. 105° (3 mm.), $n^{20}\text{D}$ 1.4346. A sample was redistilled for analysis, b. p. 96° (1.5 mm.), $n^{20}\text{D}$ 1.4349, d^{20}_{4} 1.0055.

Anal. Calcd. for $C_{11}H_{20}O_4$: C, 61.09; H, 9.32. Found: C, 61.32; H, 9.19.

2-Isopropyl-1,3-butadiene.—A 20-mm. Pyrex tube was packed for a distance of 12 in. with glass beads and heated in a furnace to 575 ± 10°. Twenty-eight grams (0.13 mole) of the diacetate of 2-isopropyl-1,4-butanediol was dropped through the hot tube at a rate of one drop every second. The pyrolysate was dissolved in 25 ml. of ether and washed twice with 50 ml. of water. The washings were combined and extracted with two 20-ml. portions of ether. All three ether solutions were combined and dried over 1 g. of anhydrous magnesium sulfate. The drying agent was removed and the ether solution was fractionated through a 4-in., helix-packed column. The fraction boiling at 82–84° was collected, $n^{20}\text{D}$ 1.4280. Since this fraction contained a trace of acetic acid it was dried over 0.25 g. of anhydrous potassium carbonate. The yield of 2-isopropylbutadiene thus obtained was 4 g. (32%), $n^{20}\text{D}$ 1.4339. von Braun and Keller[6] reported b. p. 86–87°, $n^{23}\text{D}$ 1.4321, $d^{24.5}_{4}$ 0.7276.

Maleic Anhydride Adduct of 2-Isopropylbutadiene.—In a 2-oz., screw-cap bottle were placed 5 ml. of dry benzene, 1 ml. (0.73 g., 0.0076 mole) of 2-isopropylbutadiene and 0.49 g. (0.005 mole) of maleic anhydride. The bottle was capped and rotated in a water-bath at 50° for twenty-two hours. The adduct was precipitated from the benzene solution by the addition of 5 ml. of low petroleum ether. After recrystallization from benzene and low petroleum ether the adduct melted at 86–86.5°.

The various maleic anhydride adducts obtained from 2-isopropylbutadiene produced by the different methods described in this paper had the same melting points, and mixed melting points showed no depression. A sample of this adduct was submitted for analysis.

Anal. Calcd. for $C_{11}H_{14}O_3$: C, 68.02; H, 7.26. Found: C, 68.21; H, 7.21.

α-Isopropylacrolein by the Mannich Method.—In a 5-liter, three-necked, round-bottomed flask fitted with a reflux condenser, a mechanical stirrer, and a thermometer were placed 975 g. (12.0 moles) of dimethylamine hydrochloride, 900 g. (12 moles) of a 40% solution of formalin, and 860 g. (10 moles) of isovaleraldehyde. The flask was heated by an oil-bath maintained electrically at 70° and stirred for twenty-four hours. The flask was then fitted for steam distillation, and the contents steam-distilled until organic material no longer separated from the distillate. The water layer was removed, and the organic material was dried over anhydrous magnesium sulfate. Distillation through an 18-in., electrically heated, helix-packed column yielded 113.5 g. of recovered isovaleraldehyde (13.1%), b. p. 92–95°, an intermediate fraction, 117 g., b. p. 95–105°, $n^{20}\text{D}$ 1.4115–1.4170, and 453 g. of α-isopropylacrolein, b. p. 105–108°, $n^{20}\text{D}$ 1.4223, d^{20}_{4} 0.8389, a yield of 52.6% (based on unrecovered isovaleraldehyde). Because of the unstable nature of the compound a good analysis was difficult to obtain, but a sample which was freshly distilled gave fair results.

Anal. Calcd. for $C_6H_{10}O$: C, 73.43; H, 10.27; *MR*, 29.79. Found: C, 72.92; H, 10.15; *MR*, 29.74.

A 2,4-dinitrophenylhydrazone, prepared according to a standard procedure,[15] melted at 164.5–165°.

Anal. Calcd. for $C_{12}H_{14}O_4N_4$: C, 51.79; H, 5.07. Found: C, 51.92; H, 5.10.

2-Isopropyl-3-hydroxypropionaldehyde.—In a 5-liter, three-necked, round-bottomed flask fitted with a mechanical stirrer, a dropping funnel, and condenser were placed 430 g. (5 moles) of isovaleraldehyde, 1200 g. (16 moles) of a 40% solution of formalin, and 1000 ml. of ethyl ether. Stirring was begun, and 1 liter of a 10% solution of potassium carbonate was added dropwise. After the addition of the alkali (four hours) stirring was continued an additional twenty-hours at room temperature. The organic layer was then separated and the aqueous layer was extracted three times with 300-ml. portions of ethyl ether. The extracts were combined with the original organic layer and the solution dried over anhydrous magnesium sulfate. After removal of the drying agent by filtration and flash distillation of the ether, the residual liquid was distilled through a 6-in., helix-packed column. There was obtained 215 g. of unreacted isovaleraldehyde, and 150 g. (52%) of 2-isopropyl-3-hydroxypropionaldehyde, b. p. 83.5° (9.5 mm.), $n^{20}\text{D}$ 1.4603, d^{20}_{4} 1.0517. A sample of the material was redistilled for analysis.

Anal. Calcd. for $C_6H_{12}O_2$: C, 62.04; H, 10.42; *MR*, 30.45. Found: C, 61.48; H, 10.60; *MR*, 30.05.

An attempt to prepare a 2,4-dinitrophenylhydrazone[15] resulted in yellow plates, m. p. 123–126°, which on recrystallization from ethanol turned red and melted at 158–159°. This melting point is almost that of the derivative for α-isopropylacrolein and a mixture of this product with that known derivative melted at 161–164°. The lack of depression indicated that the present compound had dehydrated on recrystallization.

Benzoate of 2-Isopropyl-3-hydroxypropionaldehyde.—In a 3-liter, three-necked, round-bottomed flask fitted with a mechanical stirrer, a dropping funnel and reflux condenser were placed 214 g. (1.85 moles) of 2-isopropyl-

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[15] Shriner and Fuson, "The Systematic Identification of Organic Compounds," 2nd ed., J. Wiley and Sons, Inc., New York, N. Y., 1940, p. 143.

3-hydroxypropionaldehyde and 584 g. (4 moles) of benzoyl chloride. The flask was cooled by means of an ice-bath. To the stirred and cooled mixture was added 1000 ml. of a 10% solution of sodium hydroxide at a rate such that the temperature of the reaction did not exceed 35°. Following the addition of the alkali, stirring was continued for one-half hour. The semi-solid reaction mixture was dissolved in 600 ml. of benzene, and the solution was washed with 10% sodium carbonate solution until the washings were alkaline. The benzene was removed, and the residue was distilled through a 6-in., helix-packed column. The yield of the benzoate was 55 g. (13.5%), b. p. 103° (0.3 mm.), $n^{20}\mathrm{D}$ 1.4820. A 2,4-dinitrophenylhydrazone of the material was prepared,[16] m. p. 130.5°.

Anal. Calcd. for $C_{19}H_{20}O_6N_4$: C, 56.99; H, 5.03. Found: C, 56.87; H, 5.06.

α-Isopropylacrolein by Pyrolysis of the Benzoate.—Fifty-five grams (0.25 mole) of the benzoate of 2-isopropyl-3-hydroxypropionaldehyde was passed dropwise through a 19-mm. outside diameter Pyrex tube packed for a distance of 12 in. with 4-mm. glass beads and heated to 575° by means of a combustion furnace. Distillation of the pyrolysate yielded 12 g. (50%) of α-isopropylacrolein, b. p. 108.5°, $n^{20}\mathrm{D}$ 1.4223.

α-Isopropylacrolein by Dehydration of the Aldol.—After several preliminary attempts resulted in only polymeric material, a solution of 29 g. (0.25 mole) of 2-isopropyl-3-hydroxypropionaldehyde in 40 ml. of benzene was refluxed with 1.0 g. of iodine. Distillation of the material yielded 4.5 g. of α-isopropylacrolein, b. p. 108.5°, $n^{20}\mathrm{D}$ 1.4230 (18%). Attempts to dehydrate the aldol by passing over activated alumina at 350° in a Pyrex tube, and by dropping on fused potassium acid sulfate at 225° produced only polymeric material.

2-Isopropyl-3-hydroxy-1-butene.—In a 5-liter, three-necked, round-bottomed flask fitted with a dropping funnel, a reflux condenser (both connected to calcium chloride drying towers) and a mechanical stirrer were placed 116.5 g. (4.84 moles) of magnesium turnings and 500 ml. of dry ether. A solution of 675 g. (4.84 moles) of methyl iodide in 1200 ml. of absolute ether was added with stirring as rapidly as control of the reaction would permit. After formation of the Grignard complex, a solution of 379 g. (3.87 moles) of α-isopropylacrolein in 1000 ml. of dry ether was added dropwise. After completion of the reaction the mixture was poured onto about 3 kg. of crushed ice. The complex was decomposed with dilute hydrochloric acid, and the ether layer was separated. The aqueous layer was extracted three times with 300-ml. portions of ethyl ether and combined with the original ether layer. After drying the ether solution over anhydrous magnesium sulfate, the drying agent was removed, and the ether was removed by distillation through a 6-in., helix-packed column. Distillation of the residual material through an 18-in., helix-packed column yielded 330.9 g. (75%) of 2-isopropyl-3-hydroxy-1-butene, b. p. 84° (75 mm.), $n^{20}\mathrm{D}$ 1.4361, d^{20}_4 0.8473.

Anal. Calcd. for $C_7H_{14}O$: C, 73.63; H, 12.36; *MR*, 35.59. Found: C, 73.60; H, 12.27; *MR*, 34.82.

2-Isopropyl-1,3-butadiene by the Alumina Dehydration of 2-Isopropyl-3-hydroxy-1-butene.—One hundred grams of 2-isopropyl-3-hydroxy-1-butene was passed dropwise through an 18-mm. outside diameter Pyrex tube packed for a distance of 18 in. with 6–8 mesh activated alumina and heated to 250° by means of an electrically heated jacket. The pyrolysate was collected in a 500-ml. suction flask cooled in a Dry Ice–ethanol bath. The product was dried and distilled to yield 25.8 g. (30.4%) of 2-isopropyl-1,3-butadiene, b. p. 85–86°, $n^{20}\mathrm{D}$ 1.4340, d^{23}_4 0.723. von Braun and Keller[6] reported b. p. 86–87°, $n^{23}\mathrm{D}$ 1.4321, $d^{24.5}_4$ 0.7276. A higher-boiling fraction was also obtained, b. p. 75° (90 mm.), $n^{20}\mathrm{D}$ 1.4130. This material is presumably 3,4-dimethylpentanone-2, b. p. 136–138°, which van Romburgh[16] reported b. p. 135–136°, d^{20}_4 0.815.

An analogous rearrangement was observed with the corresponding ethyl derivative reported later.

2-Isopropyl-3-acetoxy-1-butene.—In a 125-ml. Erlenmeyer flask was placed a mixture of 28.8 g. (0.25 mole) of 2-isopropyl-3-hydroxy-1-butene, 36 g. (0.35 mole) of acetic anhydride and a few drops of pyridine. The mixture was allowed to stand overnight, washed with three 25-ml. portions of distilled water and distilled through a 6-in., helix-packed column to yield 31.1 g. (0.196 mole) of 2-isopropyl-3-acetoxy-1-butene, b. p. 89° (66 mm.), $n^{20}\mathrm{D}$ 1.4256, d^{20}_4 0.8857, a yield of 79%. A sample of this material was redistilled for analysis.

Anal. Calcd. for $C_9H_{16}O_2$: C, 69.19; H, 10.32; *MR*, 44.96. Found: C, 69.09; H, 10.31; *MR*, 45.20.

2-Isopropyl-1,3-butadiene from the Pyrolysis of 2-Isopropyl-3-acetoxy-1-butene.—Pyrolysis of 82.7 g. (0.53 mole) of 2-isopropyl-3-acetoxy-1-butene was accomplished by passing the material dropwise through a 19-mm. Pyrex tube packed for a distance of 12 in. with 4-mm. glass beads and heated to 500° by means of a combustion furnace. Distillation of the washed and dried pyrolysate yielded 11.7 g. (23%) of 2-isopropyl-1,3-butadiene, b. p. 85–87°, $n^{20}\mathrm{D}$ 1.4345.

2-Isopropyl-1,3-butanediol.—By the usual Grignard procedure, a solution of methylmagnesium iodide was prepared from 59 g. (0.42 mole) of methyl iodide, 10.0 g. (0.42 atom) of magnesium turnings and 200 ml. of anhydrous ethyl ether. To this solution was added 24 g. (0.21 mole) of 2-isopropyl-3-hydroxypropionaldehyde in 200 ml. of dry ethyl ether. The reaction was fairly violent, presumably because of the consumption of one-half of the Grignard reagent by the hydroxyl group. The complex was decomposed by pouring over ice and acidifying with dilute hydrochloric acid. After extraction of the aqueous layer with three 75-ml. portions of ethyl ether the combined ether extracts were dried over anhydrous magnesium sulfate, the ether was removed and the residue distilled through a 12-in., helix-packed column. There was obtained 20.0 g. (0.151 mole) of 2-isopropyl-1,3-butanediol, b. p. 106° (4 mm.), $n^{20}\mathrm{D}$ 1.4528, a yield of 72%. A sample of the diol was redistilled for analysis.

Anal. Calcd. for $C_7H_{16}O_2$: C, 63.59; H, 12.20. Found: C, 63.34; H, 12.37.

2-Isopropyl-1,3-diacetoxybutane.—A mixture of 20.0 g. (0.15 mole) of 2-isopropyl-1,3-butanediol, 45 g. (0.45 mole) of acetic anhydride, and a few drops of pyridine was placed in a 125-ml. Erlenmeyer flask and allowed to stand overnight. The resulting solution was washed with three 10-ml. portions of distilled water, separated and the organic solution was distilled through a 6-in., helix-packed column. There was obtained 25.0 g. (0.116 mole) of 2-isopropyl-1,3-diacetoxybutane, b. p. 127° (24 mm.), $n^{20}\mathrm{D}$ 1.4330, d^{20}_4 1.0026, a yield of 77%. A sample of the material was redistilled for analysis.

Anal. Calcd. for $C_{11}H_{20}O_4$: C, 61.08; H, 9.32; *MR*, 56.51. Found: C, 61.21; H, 9.24; *MR*, 56.06.

Pyrolysis of this material in a manner described above for the 2-isopropyl-3-acetoxy-1-butene yielded only 0.5 g. (4.5%) of 2-isopropyl-1,3-butadiene in addition to some higher boiling materials that were not characterized.

α-Ethylacrolein.—In a 5-liter, three-necked, round-bottomed flask fitted with an efficient stirrer, a reflux condenser, and a thermometer were placed 405 g. (5.0 moles) of dimethylamine hydrochloride, 324 g. (4.5 moles) of *n*-butyraldehyde, and 375 g. (5 moles) of 40% formalin. The flask and its contents were heated to 60°, maintained by an electrically heated oil-bath, and stirred for six hours. The condenser was arranged for distillation and the mixture was subjected to steam distillation until organic material no longer separated in the distillate. The organic layer was separated, dried and distilled through an 18-in., helix-packed column. Distillation yielded 280 g. of α-ethylacrolein, b. p. 91–92°, $n^{20}\mathrm{D}$ 1.4205, a yield of 73.5%. α-Ethylacrolein has been previously

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(16) van Romburgh, *Rec. trav. chim.*, **5**, 228 (1886).

prepared by Sommelet[17] who heated over oxalic acid the 1,3-diethyl ether of 2-ethylglycerol. It has also been prepared by passing 2-ethylallyl alcohol over zinc oxide at 350°, but again no physical constants were given.[18] A semicarbazone of the material was prepared, m. p. 185.5–186°. Sommelet reported[17] 192.5°. A 2,4-dinitrophenylhydrazone was prepared according to the method of Shriner and Fuson,[15] m. p. 166.5–167°.

Anal. Calcd. for $C_{11}H_{12}O_4N_4$: C, 50.00; H, 4.58. Found: C, 50.06; H, 4.41.

2-Ethyl-3-hydroxy-1-butene.—In a 5-liter, round-bottomed, three-necked flask fitted with a dropping funnel, a reflux condenser (protected from the atmosphere by calcium chloride towers) and a mechanical stirrer, was placed 1000 ml. of a 4 molar solution of methylmagnesium bromide in ether (Arapahoe Chemicals Company). To this was added with stirring a solution of 280 g. (3.3 moles) of α-ethylacrolein in 1500 ml. of absolute ether. An ice collar around the top of the flask permitted relatively rapid addition of the ether solution. The reaction was stirred an additional hour and then poured onto crushed ice. The Grignard complex was decomposed by adding dilute hydrochloric acid until complete solution had been effected. The ether layer was separated and the aqueous layer extracted with two 300-ml. portions of ether. The ether extracts were combined with the original organic layer and dried over anhydrous magnesium sulfate. After removal of the drying agent by filtration, the ether was removed through a 6-in., helix-packed column and the residual liquid distilled through an 18-in., helix-packed, electrically heated column equipped with a total reflux partial take-off head. A total of 282 g. of 2-ethyl-3-hydroxy-1-butene was collected, b. p. 83° (100 mm.), n^{20}_D 1.4350, d^{20}_4 0.8491, a yield of 85.5%.

Anal. Calcd. for $C_6H_{12}O$: C, 71.92; H, 12.08; *MR*, 30.97. Found: C, 72.04; H, 11.99; *MR*, 30.77.

2-Ethyl-1,3-butadiene.—Dehydration of 2-ethyl-3-hydroxy-1-butene was accomplished by passing 50.0 g. (0.5 mole) dropwise through a 19-mm. outside diameter Pyrex tube packed for a distance of 18 in. with crystalline potassium acid sulfate and heated to 190–200° by means of an electrically heated jacket. The pyrolysate was collected in a 500-ml. filter flask immersed in a Dry Ice–methanol bath. The product was washed with water, and dried over anhydrous magnesium sulfate and distilled. Distillation yielded 17.5 g. of 2-ethyl-1,3-butadiene, b. p. 72–74°, n^{20}_D 1.4488, d^{20}_4 0.7173, a yield of 42.8%.

Anal. Calcd. for C_6H_{10}: C, 87.73; H, 12.27. Found: C, 87.87; H, 12.27.

There was also obtained an 8.0 g. sample of material which did not have the physical constants of the original carbinol. A sample of this material, b. p. 60° (95 mm.), n^{20}_D 1.4012, d^{20}_4 0.8130, was redistilled for analysis.

Anal. Calcd. for $C_6H_{12}O$: C, 71.92; H, 12.08. Found: C, 71.36; H, 11.77.

This material discharged bromine in carbon tetrachloride but with much evolution of hydrogen bromide. It reduced potassium permanganate and reacted with the 2,4-dinitrophenylhydrazine reagent. This indicated that it was not the original 2-ethyl-3-hydroxy-1-butene. A 2,4-dinitrophenylhydrazone derivative prepared according to the directions of Shriner and Fuson[15] had a constant melting point of 70–71° after three recrystallizations from 95% ethanol. This corresponds to the 71.2° reported by Drake and Veitch[19] for the derivative of methyl *s*-butyl ketone. A comparison of the physical properties of the unknown with those of this ketone further confirms their identity.

	Unknown	Methyl *s*-butyl ketone
B. p.	60° (95 mm.)	117° (760 mm.)
n^{20}_D	1.4012	n^{18}_D 1.4002
d^{20}_4	0.8130	0.815

***α-n*-Amylacrolein.**—In a 5-liter, three-necked, round-bottomed flask fitted with a mechanical stirrer, a thermometer, and a reflux condenser were placed 800 g. (9.9 moles) of dimethylamine hydrochloride, 740 g. (9.9 moles) of 40% formalin, and 855 g. (7.5 moles) of *n*-heptaldehyde. The flask and its contents were heated to 70° and maintained at that temperature by means of an electrically heated oil-bath. Stirring was continued for eighteen hours. The flask was then equipped for steam distillation and the contents were steam-distilled until organic material no longer separated from the distillate. The organic material was separated from the water layer and distilled through an 18-in., helix-packed, electrically heated column. There was obtained 650.5 g. of α-*n*-amylacrolein, b. p. 72° (30 mm.), n^{20}_D 1.4373, a yield of 69%. A sample of the material was redistilled for analysis.

Anal. Calcd. for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.15; H, 10.90.

A 2,4-dinitrophenylhydrazone prepared according to the directions of Shriner and Fuson[15] had a constant melting point of 134–134.5° after three recrystallizations from 95% ethanol.

Anal. Calcd. for $C_{14}H_{20}O_4N_4$: C, 54.89; H, 5.92. Found: C, 55.20; H, 6.43.

2-*n*-Amyl-3-hydroxy-1-butene.—In a 3-liter, three-necked, round-bottomed flask fitted with a mechanical stirrer, a reflux condenser and a dropping funnel both fitted with calcium chloride towers to exclude moisture, was placed 53 g. (2.2 atoms) of magnesium turnings, and 300 ml. of dry ether. To this was added with stirring a solution of 312 g. (2.2 moles) of methyl iodide in 750 ml. of dry ether. An ice collar around the top of the flask permitted very rapid addition of the methyl iodide solution. The mixture was permitted to stir an additional half-hour after the methyl iodide had been added. To this was then added a solution of 252.4 g. (2.0 moles) of α-*n*-amylacrolein in 700 ml. of dry ether. The mixture was allowed to stir an additional half-hour and was then poured onto about 2 kg. of crushed ice. The complex was decomposed with dilute hydrochloric acid, the ether layer separated, and the aqueous layer extracted three times with 300-ml. portions of ether. The ether extracts were combined with the original ether layer and dried over anhydrous magnesium sulfate. The drying agent was removed by filtration and the ether was removed by distillation through a 12-in., helix-packed column and the residual liquid distilled through an 18-in., helix-packed, electrically heated column. A total of 203.0 g. (71.5%) of 2-*n*-amyl-3-hydroxy-1-butene was collected, b. p. 68° (3 mm.), n^{20}_D 1.4448. A sample of the material was redistilled for analysis.

Anal. Calcd. for $C_9H_{18}O$: C, 76.00; H, 12.75. Found: C, 76.14; H, 12.25.

2-*n*-Amyl-1,3-butadiene.—Dehydration of 536.6 g. (3.78 moles) of 2-*n*-amyl-3-hydroxy-1-butene was accomplished by passing the material dropwise over activated alumina in a 19-mm. outside diameter Pyrex tube packed for a distance of 18 in. and heated to 240–250° by means of an electrically heated jacket. The dehydration products were collected in a 500-ml. suction flask cooled in a Dry Ice–methanol-bath. The water layer was separated and the organic material distilled through an 18-in., helix packed column. There was obtained 103 g. (22%) of 2-*n*-amyl-1,3-butadiene, b. p. 148–149°, n^{20}_D 1.4510, d^{20}_4 0.7578.

Anal. Calcd. for C_9H_{16}: C, 87.02; H, 12.98. Found: C, 86.94; H, 13.04.

A higher-boiling fraction was obtained which was believed to be 3-methyloctanone-2, by analogy to the reaction that produced methyl *s*-butyl ketone from 2-ethyl-3-hydroxy-1-butene. This compound has been prepared by Powell, Murray and Baldwin[20] who reported b. p. 64–65° (18 mm.), n^{27}_D 1.424, d^{27}_4 0.832. The frac-

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(17) Sommelet, *Ann. chim.*, [8] **9**, 562 (1906).

(18) French Patent 777,032, July 16, 1934, *Chem. Zentr.*, **106**, II, 757 (1935).

(19) Drake and Veitch, This Journal, **57**, 2623 (1935).

(20) Powell, Murray and Baldwin, *ibid.*, **55**, 1153 (1933).

tion obtained in this work had the constants, b. p. 109° (65 mm.), $n^{20}D$ 1.4269. A 2,4-dinitrophenylhydrazone was prepared which had a constant melting point of 111–112° after two recrystallizations from ethanol.

Anal. Calcd. for $C_{16}H_{22}O_4N_4$: C, 55.88; H, 6.88. Found: C, 55.80; H, 6.90.

Summary

2-Ethyl-, 2-isopropyl- and 2-*n*-amyl-1,3-butadiene have been prepared by a general procedure which can presumably be applied to other 2-alkylbutadienes.

Experiments covering alternate routes to various of the intermediates and final products have been recorded.

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[Contribution from the Department of Biochemistry, College of Agriculture, University of Wisconsin]

The Synthesis of Unsaturated Fatty Acids[1]

By Kamalludin Ahmad and F. M. Strong

Despite the large number of unsaturated fatty acids which occur in the most diverse types of living organisms and their great technical and biological importance, only a very few have been synthesized to date by methods which could be expected to lead to pure products of unequivocal structure.[2] Recent improvements in methods for selectively hydrogenating acetylenes to olefins[3,4,5] and the ease of building up relatively long aliphatic chains by condensing alkyl halides with acetylene or alkyl acetylenes[6] suggested the possibility of obtaining unsaturated fatty acids from acetylenic alkyl halides *via* the nitrile or Grignard reagent:

$$R-C\equiv C-(CH_2)_nX \longrightarrow R-C\equiv C(CH_2)_n-COOH \longrightarrow R-CH=CH-(CH_2)_n-COOH$$

It was expected that acetylenic halides of the required type would be formed by reaction of alkyl acetylenes with, for example, bromo- or iodochlorides since acetylene itself readily yields analogous products.[7]

$$RC\equiv CH + I(CH_2)_n-Cl \xrightarrow{NaNH_2} RC\equiv C-(CH_2)_nCl$$

The feasibility of this method of synthesis has been tested by the preparation of 6-hendecenoic acid from 1-hexyne and 1-chloro-4-iodobutane according to the scheme

$$CH_3(CH_2)_3-C\equiv CH + I(CH_2)_4Cl \xrightarrow{NaNH_2}$$
$$CH_3(CH_2)_3C\equiv C-(CH_2)_4Cl \xrightarrow[NaOH]{NaCN}$$
$$CH_3(CH_2)_3C\equiv C-(CH_2)_4COOH \xrightarrow[Ni]{(H)}$$
$$CH_3(CH_2)_3CH=CH(CH_2)_4COOH$$

The desired product was obtained with no particular difficulty, and the olefinic bond was found by oxidative degradation to be present in the expected position.

Experimental

1-Chloro-4-iodobutane.—Sodium iodide was refluxed in acetone solution with a three-molar proportion of 1,4-dichlorobutane[8] until less than 3% of the iodine remained in the inorganic form (five to six hours). Fractional distillation gave a 71% yield (based on the sodium iodide) of 1-chloro-4-iodobutane, b. p. 93–94.5° (17 mm.), of 94% purity.

Anal. Calcd. for C_4H_8ClI: I, 58.1. Found: I, 54.4.

Since the impurity was most probably unreacted dichlorobutane, the product was used without further purification.

1-Chloro-5-decyne.—A three-liter, three-neck round-bottom flask was fitted with a stirrer, dropping funnel, gas inlet tube, and block tin condenser cooled with a chloroform–Dry Ice mixture. Fifteen-hundred ml. of liquid ammonia was placed in the flask, the stirrer was started, and 0.3 g. of ferric nitrate and 1 g. of sodium were added. Dry air was bubbled through the solution for a few minutes until the blue color was discharged, after which an additional amount of 14.6 g. (0.68 g. atom, total) of sodium was added slowly in small portions. After the reaction had been in progress for thirty minutes, 1 g. of sodium peroxide was added. After two and one-half hours the mixture assumed a dull gray color, and the conversion of the sodium to sodamide was judged to be complete.[9]

An amount of 41 g. (0.50 mole) of 1-hexyne[10] was then introduced dropwise with stirring over a period of two hours, and after an additional interval of three hours, 117 g. (0.54 mole) of 1-chloro-4-iodobutane was added during four hours. Stirring was continued four hours longer, and the mixture was then allowed to stand at room temperature until the ammonia had evaporated. About 150 ml. of water was cautiously added, the mixture filtered, and the organic layer collected in ether. The ether solution was washed free from inorganic halides with water, and fractionally distilled. The main fraction, 45.4 g. (53%), b. p. 143–145° (51 mm.), contained 2.5% of iodine. Redistillation gave 31 g. of iodine-free product, b. p. 110–112° (15 mm.); $n^{25}D$ 1.4592, d^{25}_4 0.9238, *MR* (calcd.) 51.4, *MR* (found) 51.1. The yield of pure product thus amounted to 36%.

Anal. Calcd. for $C_{10}H_{17}Cl$: Cl, 20.53. Found: Cl, 19.6, 20.6.

6-Hendecynoic Acid.—To a solution of 16 g. (0.33 mole) of sodium cyanide in 25 ml. of water were added 115 ml. of 95% ethanol and 25.7 g. (0.15 mole) of 1-chloro-5-decyne. The mixture was refluxed until the bulk of the chloride had been converted to the inorganic

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(1) Published with the approval of the Director of the Wisconsin Agricultural Experiment Station.

(2) K. S. Markley, "Fatty Acids," Interscience Publishers, Inc., New York, N. Y., 1947, p. 554.

(3) Campbell and Eby, This Journal, 63, 2683 (1941).

(4) Thompson and Shaw, *ibid.*, 64, 363 (1942).

(5) H. Adkins, private communication.

(6) Vaughn, Hennion, Vogt and Nieuwland, *J. Org. Chem.*, 2, 1 (1937).

(7) Henne and Greenlee, This Journal, 67, 484 (1945).

(8) E. I. du Pont de Nemours and Company, Electrochemical Division, generously donated this material.

(9) Vaughn, Vogt and Nieuwland, This Journal, 56, 2120 (1934).

(10) Farachan Laboratories, Cleveland, Ohio.