[Contribution from the Chemical Laboratory of the
University of California]

BRANCHED-CHAIN FATTY ACIDS. VII. SIMPLIFIED METHODS FOR PREPARING PURE BRANCHED-CHAIN ALCOHOLS AND HALIDES

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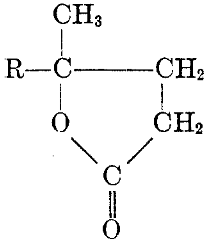
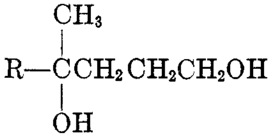
In a previous paper (1) of this series, there was pointed out the undesirability of using secondary alkyl halides for preparation of pure branched-chain fatty acids. The threat of impurities arising from isomeric secondary halides is always present. A method was developed for obtaining branched-chain compounds from straight-chain starting materials involving the following steps: (a) preparation of a γ-alkyl-γ-valerolactone from a Grignard reagent and ethyl levulinate; (b) opening the lactone ring with thionyl chloride and converting the reaction product to an unsaturated ester; (c) hydrogenation to the saturated ester and, if desired, reduction to the alcohol. This method gave satisfactory yields of compounds of the desired purity; however, step (b) is rather laborious, so a study has been made of other methods of opening the lactone ring.

Although there have been several reports (2) of the Bouveault-Blanc reduction of lactones to glycols, none of the lactones reduced contained tertiary oxygen. This method of reduction has been found to proceed normally when applied to γ-*n*-butyl-γ-valerolactone (I) or γ-*n*-amyl-γ-valerolactone (II); however, the corresponding glycols, III and IV, were isolated in poor yield when the usual ratio of reagents (3) was used. By increasing the ratio of sodium to lactone by seventy-five per cent, the yield of glycol was raised to about 74%. Treatment of the diol with phosphorus tribromide leads to no recognizable products, and conversion of the diol to a branched-chain primary mono-alcohol was complicated by the fact that dehydration under mild conditions leads to a mixture of unsaturated alcohol and tetrahydrofuran (V or VI). The unsaturated alcohol may be converted readily into the saturated primary alcohol; however, conversion of the tetrahydrofuran to the primary alcohol proved rather tedious. Wilson (4) has recently made a study of the ring-opening of tetrahydrofurans and obtained relatively clean-cut results with hydrogen bromide in acetic acid or acetic anhydride in the presence of catalytic amounts of zinc chloride. A study of the opening of our 2,2-dialkyltetrahydrofurans indicates that acetyl

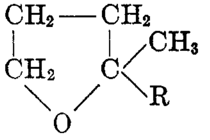


I. R = n-C_4H_9
II. R = n-C_5H_{11}



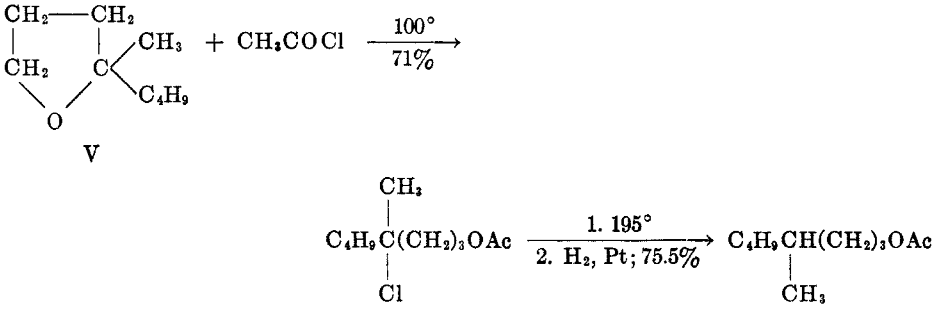
$R-\overset{CH_3}{\underset{OH}{C}}CH_2CH_2CH_2OH$

III. R = n-C_4H_9
IV. R = n-C_5H_{11}



V. R = n-C_4H_9
VI. R = n-C_5H_{11}

chloride with zinc chloride as catalyst (5) gives more clean-cut results than do the reagents studied by Wilson. The chief product from the tetrahydrofuran V is 1-acetoxy-4-chloro-4-methyloctane (VII).



V VII VIII

$$C_4H_9\underset{\displaystyle Cl}{\overset{\displaystyle CH_3}{C}}(CH_2)_3OAc \xrightarrow[\text{2. } H_2,\ Pt;\ 75.5\%]{\text{1. } 195^\circ} C_4H_9\underset{\displaystyle CH_3}{CH}(CH_2)_3OAc$$

Pyrolysis of the chloro ester, VII, at about 195° converts it to the unsaturated ester, which may be readily hydrogenated to the saturated ester, VIII. Saponification of VIII gave 4-methyl-1-octanol, identical with the sample obtained below by unequivocal procedures. The unsaturated ester was also obtained as one of the products of the reaction of acetic anhydride with V, and hydrogenation gave the saturated ester, VIII.

Although the above combination of reactions may be used to convert a lactone to the desired branched-chain primary alcohol, it is more laborious and less efficient than the previously-used method employing thionyl chloride; therefore, our investigation of the opening of lactone rings was continued by studying the catalytic hydrogenation of lactones I and II. Adkins and Folkers (6) hydrogenated γ-valerolactone over copper chromite catalyst at 250°, and obtained 78% yield of 1,4-pentanediol and 8% yield of *n*-amyl alcohol. When this procedure was applied to the tertiary lactones, I and II, there were obtained directly yields of 80–84% of the saturated mono-alcohols, 4-methyl-1-octanol and 4-methyl-1-nonanol. Since this represents the easiest and most efficient method yet discovered for converting a tertiary lactone to a primary mono-alcohol, its generality was further investigated by hydrogenating γ-ethyl-γ-valerolactone to 4-methyl-1-hexanol in 79–83% yield, and γ-*n*-hexyl-γ-valerolactone to 4-methyl-1-decanol in 82–88% yield. In order to obtain rapid hydrogenation and high yield, it is desirable to use a relatively high ratio of catalyst, for a mole equivalent of water is formed during the hydrogenation. A very small amount of the corresponding tetrahydrofuran was always obtained as a by-product.

γ-*n*-Butyl-γ-valerolactone was hydrogenated at lower temperatures in order to learn whether a better yield could be so obtained. Although the best yields of mono-alcohol were obtained at 250°, the results at lower temperatures are of considerable interest in connection with the mechanism of the hydrogenation and other products which may be obtained. In Table I are listed data concerning this reduction. In all runs there were used 20 g. of compound to be hydrogenated and 6 g. of copper chromite (7) catalyst, or else the same ratio in a smaller run. The initial pressure at 23° was always in the range 2800–3000 lbs. per sq. in., and the final pressure was in the range 3600–4000 lbs.

Examination of the data in this table shows that at 250° the rate of hydrogenation of the lactone falls off sharply after hydrogenation is about 80% complete, indicating the possibility of two routes of hydrogenation. At 200° considerable glycol is obtained, in addition to mono-alcohol, and in the slow reaction at 150° the principal product obtained is glycol. Since the glycol is hardly attacked at 200°, and hydrogenated much more slowly than the lactone at 250°, it would seem that part of the mono-alcohol may be formed *via* the glycol (slow hydrogenation at end), but that the major portion must be formed at this temperature by some other route. The most obvious intermediate would appear to be the tetrahydrofuran, but this is eliminated by its exceedingly slow hydrogenation to give a poor yield of mono-alcohol. On the basis of the evidence available concerning the nature of the intermediates in the rapid hydrogenation of the lactone at 250°, the route indicated in the accompanying equation seems reasonable.

TABLE I

HYDROGENATION DATA

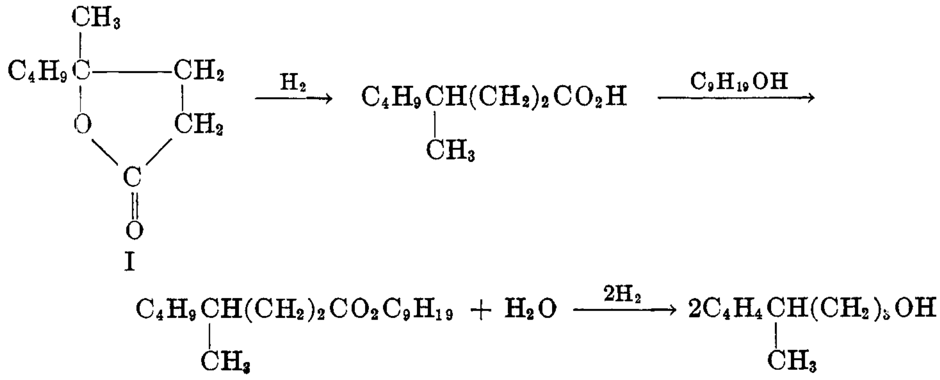
COMPOUND HYDROGENATED	TIME[a], HOURS	TEMP., °C	PRODUCTS AND YIELDS, %		
			4-Methyl-1-octanol	Glycol, III	Tetrahydrofuran, V
Lactone, I	2.8[b]	250	80.7	—	few
Lactone, I	7.5	200	39	28	few
Lactone, I	50	150	few	56.5	trace
Glycol, III	8	250	82.5	—	—
Glycol, III	3[c]	200	5	68	trace
Tetrahydrofuran, V	20	250	27.3[d]	—	17.6[d]
4-Methyloctyl 4-methyloctanoate	2.2	250	88.6	—	—

[a] Time required, after heater and shaker were started, for maximum hydrogenation, as indicated by no further pressure drop. About seventy minutes were required for the temperature to reach 250°.

[b] Hydrogenation was 80% complete after 1.6 hour.

[c] Pressure drop was small.

[d] Nothing else was recovered.



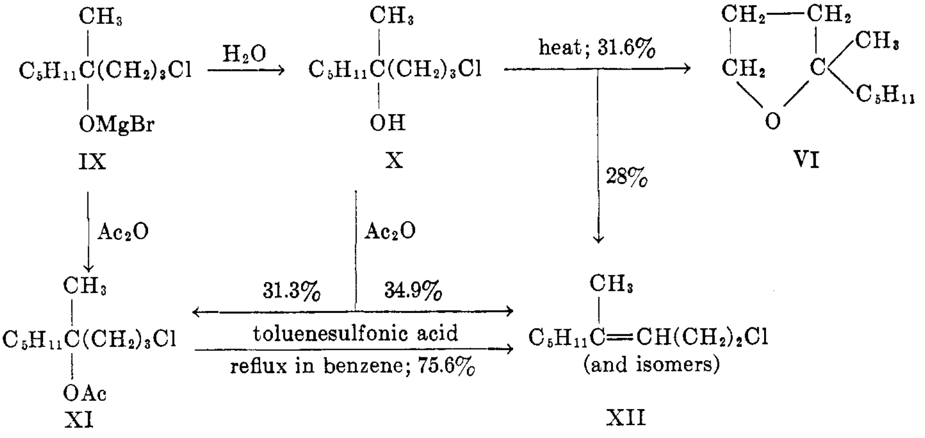
I

$$\xrightarrow{H_2} C_4H_9\underset{\underset{CH_3}{|}}{C}H(CH_2)_2CO_2H \xrightarrow{C_9H_{19}OH}$$

$$C_4H_9\underset{\underset{CH_3}{|}}{C}H(CH_2)_2CO_2C_9H_{19} + H_2O \xrightarrow{2H_2} 2C_4H_4\underset{\underset{CH_3}{|}}{C}H(CH_2)_3OH$$

Formation of the acid might occur by direct hydrogenolysis or by hydrogenation of unsaturated acid in equilibrium with the lactone. Alcohol for conversion of acid to ester could be initially supplied by hydrogenation *via* the glycol, and would accumulate as hydrogenation progressed. In a hydrogenation of lactone I, at 250°, in which a poor grade of catalyst was used, the major product obtained was the ester, 4-methyloctyl 4-methyloctanoate. Hydrogenation[1] of this ester at 250°, with Adkins catalyst, proceeded more rapidly (*cf.* Table I) than hydrogenation of the lactone. This is reasonable, since the lactone is hydrogenated partly by the slower route involving the glycol. Since water is formed in hydrogenation of the lactone by any route, the rate would be expected to fall off rapidly at lower temperature where more time is available for deactivation of the catalyst by water. Also, the data indicate that rate of hydrogenolysis to glycol falls off much less rapidly with decreasing temperature and deactivation of catalyst than does the rate of hydrogenolysis by the route which gives ester. The failure to attain good material balance in all of these hydrogenations is attributed to chain cleavage to products of too low boiling point to be normally recovered.

Although the above methods make pure branched-chain alcohols readily available by a two-step procedure, it would seem possible to obtain the corresponding alkyl chloride still more readily by way of a Grignard reaction on the commercially available 5-chloro-2-pentanone. The initial reaction product expected from such a reaction, using *n*-amylmagnesium bromide, is represented by formula IX. Such a product appears to be obtained, and may be converted to the unsaturated chloride, XII, in a variety of ways, as shown in the chart.



All yields indicated in this chart are over-all yields based on 5-chloro-2-pentanone. The unsaturated chloride may be converted to 1-chloro-4-methylnonane in 75–80% yield by hydrogenation with platinum catalyst at low pressure and room temperature.

The chlorohydrin, X, may be obtained by decomposing the Grignard reagent

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[1] We are indebted to Dr. F. B. Zienty for suggesting this interesting experiment.

with saturated ammonium chloride, but distillation of this substance without decomposition was not accomplished. Since pyrolysis gave a mixture of products and conversion of VI to desired compounds had been found difficult, dehydration with acetic anhydride was attempted but, surprisingly enough, about equal amounts of acetoxy chloride, XI, and unsaturated chloride, XII, were obtained. In the course of identification of the acetoxy chloride it was discovered that it may be converted in high yield to the unsaturated chloride by the procedure of Baumgarten and Hauser (8). Further, if the Grignard complex, IX, is decomposed with acetic anhydride, the acetoxy chloride is the principal product, and this may be converted directly, without isolation, to the unsaturated chloride. Thus, 1-chloro-4-methylnonane may be obtained from 5-chloro-2-pentanone in an over-all yield of 61%.

The synthesis of branched-chain acids from the alcohols and chloride described in this paper will be reported later.

EXPERIMENTAL

All boiling points are uncorrected. All distillations, unless otherwise specified, were carried out in a half-meter column containing a tantalum wire spiral of the Podbielniak type, and equipped with a heated jacket and partial reflux head. Microanalyses by C. W. Koch and V. H. Tashinian.

γ-Alkyl-γ-valerolactones were prepared according to the procedure (1) described for γ-*n*-propyl-γ-valerolactone, and the data on these compounds are found in Table II. The ethyl levulinate and alkyl bromides used as starting materials were distilled through the column and collected over ranges of about one degree.

4-Methyl-1,4-octanediol (III) was prepared by reduction of 52 g. (0.33 mole) of lactone I with 1 liter of anhydrous *n*-butyl alcohol and 60 g. (2.6 atoms) of sodium, according to the procedure of Reid *et al.* (3). After all the sodium had dissolved, 350 ml. of water was added and the mixture heated under reflux for thirty minutes to ensure saponification of any ester which may have been formed by trans-esterification of the lactone. The butanol layer was separated and the water layer extracted with 75 ml. of butanol. The residue obtained after distillation of the butanol was distilled at 4 mm. pressure. After a small fore-run, the colorless, viscous diol was collected at 125–126°, n_D^{27} 1.4540, wt. 32.3 g. (60.6%) [literature (9), b.p. 119° (3.5 mm.), n_D^{20} 1.4587].

There was about 20 g. of very viscous distillation residue which set to a glass on cooling. This proved to consist largely of the sodium salt of γ-hydroxy-γ-methylcaprylic acid. By solution in water, acidification, extraction with ether and distillation of the residue obtained from the extract, the lactone was recovered from this salt. When more sodium was used in the reduction, as described for the homolog below, there was very little of this residue.

4-Methyl-1,4-nonanediol (IV) was prepared as described for its homolog, III, except that the amount of sodium was increased to 2.93 atoms for 0.33 mole of lactone. This increased the yield of diol to 73.7%. After a small fore-run it was collected at 131–132° (5 mm.), n_D^{27} 1.4553.

Anal. Calc'd for $C_{10}H_{22}O_2$: C, 68.91; H, 12.73.
Found: C, 68.19; H, 12.65.

Dehydration of 4-methyl-1,4-octanediol. A mixture of 44.8 g. of the diol (III) and a few crystals of iodine was heated under the column in an oil-bath kept at 155–165°. Water was smoothly evolved and was removed by keeping the jacket temperature of the column at about 90°. If water is allowed to run back there is much sputtering and frothing. After water evolution had ceased (thirty to forty-five minutes), the organic layer was separated from the small two-phase distillate and returned to the distillation flask. Distillation at 24 mm. pressure gave two main fractions: (a) b.p. 68–68.5°, n_D^{30} 1.4260, wt. 18.5 g.; (b) b.p. 109–110°, wt. 11.3 g.

Fraction a is *2-n-butyl-2-methyltetrahydrofuran* (V), and has a characteristic penetrating odor.

Anal. Calc'd for $C_9H_{18}O$: C, 76.00; H, 12.75.
Found: C, 75.54; H, 12.92.

Fraction b is *4-methyl-1-octenol,* and it was hydrogenated immediately at low pressure and room temperature in 125 ml. of 95% ethyl alcohol, using 0.25 g. of platinum oxide catalyst. Distillation yielded 9.2 g. of *4-methyl-1-octanol*, b.p. 104–105° (19 mm.), n_D^{31} 1.4309. [Literature (10, 11), b.p. 106° (17 mm.), n_D^{25} 1.4335.]

In another, smaller run, there was obtained 14.4 g. of tetrahydrofuran and 14.0 g. of unsaturated alcohol.

Dehydration of 4-methyl-1,4-nonanediol (21 g.) as described above gave 5.7 g. of *2-n-amyl-2-methyltetrahydrofuran* (VI), b.p. 75–77° (16 mm.), n_D^{25} 1.4314, and 5.7 g. of *4-methyl-1-nonenol*, b.p. 113–114° (16 mm.). A center cut of VI was used for analysis.

Anal. Calc'd for $C_{10}H_{20}O$: C, 76.86; H, 12.90.
Found: C, 76.80: H, 13.10.

TABLE II

γ-ALKYL-γ-VALEROLACTONES

γ-VALEROLACTONE	B. P., °C	MM. HG	YIELD, %	n_D^{27}
γ-Ethyl-[a]	117–117.5	25	64	1.4380
γ-*n*-Butyl-	125–126[b]	15	76	1.4410
γ-*n*-Amyl-[c]	130–132	9	71	1.4446
γ-*n*-Hexyl-	136–137[d]	7.5	76	1.4470[d]

[a] This lactone boils only 11° above ethyl levulinate and was separated from this ester by distillation through a 1-meter packed column.

[b] Wilson (ref. 11) gives b.p. 120–123° (15 mm.).

[c] *Anal.* Calc'd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66.
Found: C, 70.56; H, 10.62.

[d] Frank, Arvan, Richter, and Vanneman, *J. Am. Chem. Soc.*, **66**, 6 (1944), give b.p. 120–125° (4–5 mm.), n_D^{20} 1.4487.

The unsaturated alcohol was hydrogenated like its homolog in 150 ml. of 95% ethyl alcohol, using 0.1 g. of platinum oxide catalyst. Hydrogenation was complete in twenty minutes, and distillation of the product gave a 78% yield of *4-methyl-1-nonanol*, b.p. 111–112° (14 mm.), n_D^{30} 1.4333. [Literature (10), b.p. 120° (17 mm.), n_D^{25} 1.4364.] No solid derivative of this alcohol could be obtained, although the phenylurethan, α-naphthylurethan, and *p*-phenylbenzoate were prepared.

Reaction of 2-n-butyl-2-methyltetrahydrofuran with acetic anhydride. A mixture of 10 g. of V, 25 g. of acetic anhydride, and 0.2 g. of anhydrous zinc chloride was heated under reflux for twenty-four hours. After addition of five volumes of water the mixture was extracted with benzene three times. The extracts were washed with water, sodium bicarbonate solution, and water, then dried. The residue remaining after distillation of the solvent was distilled at 12 mm. pressure to give: (a) 5.45 g., b.p. 103°; (b) 1.06 g., b.p. 103–148°; (c) 3.17 g., b.p. 148°, n_D^{28} 1.4530. Fraction (a), which is *4-methyloctenyl acetate* was hydrogenated immediately at low pressure and room temperature with platinum oxide catalyst to yield 4.6 g. of *1-acetoxy-4-methyloctane*, b.p. 101° (12.5 mm.), n_D^{28} 1.4215. A center cut was used for analysis.

Anal. Calc'd for $C_{11}H_{22}O_2$: C, 70.91: H, 11.91.
Found: C, 70.69: H, 11.90.

This substance was shown to be the primary acetate, rather than the tertiary acetate, by its failure to lose acetic acid on heating in benzene with toluenesulfonic acid (8). The material recovered had the b.p. 102–103° (13.5 mm.) and n_D^{29} 1.422.

Fraction (c), above, has about the right boiling point for the diacetate of the diol, III; however, it failed to react with toluenesulfonic acid in boiling benzene (8), and the analytical values (C, 69.43, 69.51; H, 9.81, 9.80) are in disagreement with those calculated for the diacetate (C, 63.91; H, 9.90). The analytical values found give the improbable empirical formula, $C_9H_{16}O_2$, and this fraction may be an azeotrope.

Reaction of 2-n-amyl-2-methyltetrahydrofuran with hydrogen bromide in acetic acid. To 25 ml. of a 35.5% solution of anhydrous hydrogen bromide in glacial acetic acid was added 10 g. of VI, the addition causing no appreciable evolution of heat. After the mixture had been kept at room temperature for twenty-two hours it was diluted with four volumes of water and extracted with two portions of benzene. On attempted distillation of the residue from this extract, hydrogen bromide was lost; so the material was heated for one hour at 185–195°, and then distilled at 10 mm. pressure. This gave a principal fraction boiling at 90–93° and weighing 8.2 g. Hydrogenation at low pressure and room temperature in 75 ml. of 95% ethyl alcohol with 0.1 g. of platinum oxide catalyst resulted in absorption of one equivalent of hydrogen in about twelve minutes, and distillation of the product gave only 4.8 g. of material boiling at 75–103° (19 mm.). Redistillation gave 2.0 g. of material of b.p. 102.5–103.5°, n_D^{27} 1.4313. This substance is probably *1-acetoxy-4-methylnonane.*

Anal. Calc'd for $C_{12}H_{24}O_2$: C, 71.94: H, 12.08.
Found: C, 72.41: H, 12.29.

The behavior of these reaction products during the work-up suggests a mixture of compounds resulting from different combinations of bromine and acetoxy on the primary and tertiary carbons, and since the reaction is so unpromising it was not further investigated.

Reaction of 2-n-butyl-2-methyltetrahydrofuran with acetyl chloride. A mixture was prepared of 11.7 g. (0.08 mole) of the tetrahydrofuran, V, about 0.1 g. of fused zinc chloride, and 0.1 mole of freshly distilled acetyl chloride. After a brief induction period the reaction became vigorously exothermic and cooling was necessary to keep it under control. After heat evolution had ceased (about five minutes) the dark red-brown mixture was heated under reflux on the steam-bath for one hour. After dilution of the cooled reaction mixture with water it was extracted with benzene, and the extract was washed with water, sodium bicarbonate solution, and water. After drying, the solvent was distilled and the residue distilled at 1.6 mm. pressure. After a fore-run of 0.9 g. the *chloro ester*, VII, was collected at 96–101°, wt. 12.9 g. (70.9%), n_D^{28} 1.4443. In order to avoid loss of hydrogen chloride from this compound, the bath temperature must not exceed about 130°. A center cut was used for analysis.

Anal. Calc'd for $C_{11}H_{21}ClO_2$: eq. wt., 110.4.
Found: eq.wt., 113.5, 113.0.

In order to prove the structure of VII, 10.4 g. (0.05 mole) was pyrolyzed at 190–200° for seventy-five minutes, the gas evolved giving a precipitate of silver chloride when absorbed in aqueous silver nitrate. On distillation of the pyrolysis product there was obtained 7.0 g. (80.5%) of unsaturated ester, b.p. 106.5–108.5° (25 mm.). This was hydrogenated immediately at low pressure and room temperature in 75 ml. of glacial acetic acid in the presence of 0.1 g. of platinum oxide catalyst, the theoretical quantity of hydrogen being consumed in ten minutes. Distillation at 19 mm. pressure gave 6.6 g. (93.5%) of *1-acetoxy-4-methyloctane* (VIII), b.p. 110–111.5°, n_D^{28} 1.4209.

Anal. Calc'd for $C_{11}H_{22}O_2$: eq. wt., 186.3.
Found: eq. wt., 190.7, 191.2.

Saponification of this ester with alcoholic potassium hydroxide gave a 72% yield of 4-methyl-1-octanol, b.p. 111–111.5°, (24 mm.) n_D^{27} 1.4318.

Reaction of 2-n-amyl-2-methyltetrahydrofuran with acetyl chloride was carried out as described above for the lower homolog. From 9.0 g. (0.06 mole) of the tetrahydrofuran, VI, there was obtained 1.1 g. of the starting material (b.p. 48–49° at 1.5 mm. n_D^{27} 1.4299), 1.3 g. of intermediate fraction and 11.2 g. (82.0%) of *1-acetoxy-4-chloro-4-methylnonane*, b.p. 101–105° (1.5 mm.) n_D^{28} 1.4452. A center cut was used for analysis.

Anal. Calc'd for $C_{12}H_{23}ClO_2$: Cl, 15.10; eq. wt., 117.4.
Found: Cl, 14.43, eq. wt., 120.3.

Hydrogenation of γ-alkyl-γ-valerolactones at 250°. In all hydrogenations, a steel bomb was charged with lactone and copper chromite (7) catalyst in the ratio of 20 g. of lactone to 6 g. of catalyst. The initial pressure at room temperature was in the range 2700–3100 lbs. per sq. in. Shaking and heating were started simultaneously, and hydrogen was absorbed rapidly above 200° so that the maximum pressure never exceeded about 4800 lbs. Shaking was continued until the pressure became constant, which occurred after 2.5–3.5 hours from the time heating was started. The pressure drop corresponded to 3.0–3.1 moles of hydrogen per mole of lactone. The product was washed out with acetone and distilled. Data on the products are given in Table III.

In one run with γ-*n*-hexyl-γ-valerolactone, only one-third as much catalyst was used as specified above. The time of hydrogenation was about 5.5 hours, but the yield of 4-methyl-1-decanol, b.p. 92–94° (3 mm.), was 82.5%, almost as high as obtained with the higher ratio of catalyst.

In all successful runs, catalyst prepared according to Adkins (7) was used. When Harshaw copper chromite catalyst (Cu-186-powder) was used, the hydrogenation did not go to completion. In a run in which 30 g. of lactone I was reduced, the total recovery of products boiling above 44° (8 mm.) was as follows: (a) 6.6 g. of 4-methyl-1-octanol, b.p. 85.5–87.5° (6 mm.), n_D^{27} 1.4347; (b) 11.5 g. of *4-methyloctyl 4-methyloctanoate*, b.p. 151–153.5° (4 mm.), n_D^{27} 1.4404, saponification equivalent, 276 (calc'd 284).

TABLE III

PREPARATION OF 4-METHYL-1-ALKANOLS BY LACTONE HYDROGENATION

ALCOHOL	B. P., °C	MM. HG	n_D^{27}	YIELD %
4-Methyl-1-hexanol	83–84	23.5	1.4223	79–83
4-Methyl-1-octanol	104–105	18	1.4320	77–81
4-Methyl-1-nonanol	115–116.5	17	1.4350	84
4-Methyl-1-decanol[a]	105–107	5	1.4375	82–88

[a] *Anal.* Calc'd for $C_{11}H_{24}O$: C, 76.69; H, 14.04.
Found: C, 76.62; H, 14.00.

Data on hydrogenation of 4-methyloctyl 4-methyloctanoate are included in Table I. Properties of the resultant 4-methyl-1-octanol were, b.p. 110.5–111.5° (24 mm.), n_D^{22} 1.4340.

In all hydrogenations, the product contained 2–4% of material boiling below the alcohol and consisting largely of the tetrahydrofuran. In the case of the hexyl lactone, this fore-run was redistilled, and yielded *2-n-hexyl-2-methyltetrahydrofuran*, b.p. 67° (5 mm.) n_D^{27} 1.4340.

Anal. Calc'd for $C_{11}H_{22}O$: C, 77.59; H, 12.98.
Found: C, 77.70; H, 13.08.

The fore-run from 4-methyl-1-nonanol consisted of 2-*n*-amyl-2-methyltetrahydrofuran, b.p. 77–80° (17 mm.), n_D^{26} 1.4307, these properties being in agreement with those of the sample obtained by dehydration of diol IV.

Hydrogenations carried out at 150° and 200° followed the same general procedure as those at 250°, and results are found in Table I.

Reaction of n-amylmagnesium bromide with 5-chloro-2-pentanone. (A) *Preparation of 1-chloro-4-methylnonene* (XII). A Grignard reagent was prepared in an atmosphere of nitrogen from 37.8 g. (0.25 mole) of purified *n*-amyl bromide and 5.34 g. (0.22 mole) of magnesium in 115 ml. of ether. As this stirred solution was cooled in an ice-salt bath there was added

24.1 g. (0.2 mole) of freshly-distilled 5-chloro-2-pentanone in 50 ml. of ether at as fast a rate (10–15 minutes) as consistent with keeping the temperature at 0° or less. After addition was complete stirring was continued at 0° for one hour, then there was added to the cold mixture, during about ten minutes, 61.2 g. (0.6 mole) of acetic anhydride. After this addition the cooling bath was removed and stirring continued for forty-five minutes as the mixture warmed up to room temperature (a precipitate separated during this period). After decomposition of the organometallic complex with ice and water, the ether layer was separated and dried, then solvent and acetic acid were distilled, the last traces *in vacuo*. The residue was heated under reflux for two hours with 1 g. of *p*-toluenesulfonic acid monohydrate and 100 ml. of dry benzene. The resultant solution was washed with enough sodium bicarbonate solution to remove acetic and *p*-toluenesulfonic acids, washed with water, and filtered through a layer of sodium sulfate. Distillation at 18 mm. pressure of the residue obtained from this solution gave 2.2 g. of fore-run, b.p. 55–98°, and 26.4 g. (75.6%) of 1-chloro-4-methylnonene, b.p. 98–100°, n_D^{25} 1.4524.

In several runs in which the Grignard solution was added to the chloro ketone solution, the yield was considerably lower than in the above-described procedure, and a large distillation residue was obtained. In one run, the Grignard reagent was decomposed with concentrated aqueous hydrochloric acid, in hopes of obtaining the 1,4-dichloride, which could be pyrolyzed to the desired product; however, the behavior on pyrolysis indicated that the tertiary hydroxyl had not been converted to chloride.

(B) *2-n-Amyl-2-methyltetrahydrofuran* (VI) *and 1-chloro-4-methylnonene* (XII). The Grignard reaction between *n*-amylmagnesium bromide and the chloro ketone was run as above, and the complex was decomposed with 32 ml. of saturated ammonium chloride solution. The ether solution was decanted from the precipitated salts, and the salts washed with several portions of ether. The residue remaining after removal of solvent was pyrolyzed at 160–180° for three hours, then distilled. After a fore-run of 1.8 g., there was obtained 10.0 g. (31.6%) of 2-*n*-amyl-2-methyltetrahydrofuran, b.p. 87.5–89.5° (28 mm.). After an intermediate fraction of 2.5 g. the unsaturated chloride was colleted at 98–100° (20 mm.), wt. 10.0 g. (28%).

(C) *4-Acetoxy-1-chloro-4-methylnonane* (XI) *and 1-chloro-4-methylnonene* (XII). The Grignard reaction was carried out and the complex decomposed with ammonium chloride as described under (B). After the ether solution had been dried overnight with calcium sulfate, 50 ml. of acetic anhydride was added, and solvent was distilled until the bath temperature reached 125°. After heating at this temperature had been continued for three hours, low-boiling material was removed *in vacuo* and the residue distilled to give two principal fractions: (a) 12.2 g. (34.9%) of unsaturated chloride, b.p. 97.5–101.5° (17 mm.); (b) 14.7 g. (31.3%) of 4-acetoxy-1-chloro-4-methylnonane, b.p. 141–143° (17 mm.). A center cut of the acetoxy chloride, b.p. 141.5–141.7° (18 mm.) n_D^{23} 1.4442, was used for analysis.

Anal. Calc'd for $C_{12}H_{23}ClO_2$: C, 61.39; H, 9.87: Cl, 15.10.
Found: C, 61.54: H, 9.86: Cl, 15.55.

When the acetoxy chloride was treated with *p*-toluenesulfonic acid as described under (A), it was converted in 86% yield to the unsaturated chloride, b.p. 97–100° (17 mm.).

1-Chloro-4-methylnonane. In a typical run, 15.1 g. of freshly distilled unsaturated chloride was hydrogenated at low pressure and room temperature in 150 ml. of 95% ethyl alcohol with 0.1 g. of platinum oxide. Hydrogenation was complete in fifteen minutes, and distillation of the product gave 12.3 g. (80.7%) of the saturated chloride, b.p. 103–104.5° (21 mm.), n_D^{26} 1.4362.

Anal. Calc'd for $C_{10}H_{21}Cl$: C, 67.96: H, 11.97: Cl, 20.06.
Found: C, 68.00: H, 12.00: Cl, 19.87.

SUMMARY

Several γ-alkyl-γ-valerolactones have been prepared and it has been shown that they may be converted to 4-alkyl-1-alkanols in yields of 80–88% by high pressure hydrogenation over copper chromite catalyst.

1,4-Glycols may be obtained by reduction of such lactones with sodium and alcohol; however, conversion of the glycols to unsaturated mono-alcohols is difficult on account of tendency toward tetrahydrofuran formation.

Ring opening of 2-alkyl-2-methyltetrahydrofurans with acetic anhydride, acetyl chloride, and hydrogen bromide in acetic acid has been studied. Acetyl chloride was the most satisfactory reagent as regards better yield of a single product.

The reaction between *n*-amylmagnesium bromide and 5-chloro-2-pentanone has been studied and a method developed for obtaining 1-chloro-4-methylnonene in good yield. Under other conditions there may be obtained products consisting in part of 4-acetoxy-1-chloro-4-methylnonane or 2-*n*-amyl-2-methyltetrahydrofuran.

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