$H_{22}O_7N_4$: C, 48.64; H, 5.99; N, 15.13. Found: C, 48.32; H, 5.93; N, 14.95. N-Methylcyclooöctylamine gave an oily sulfonamide which could not be crystallized.

N-Methylgranatanine.—A mixture of N-methylcyclooctylamine (7.75 g.) in purified petroleum ether (30–38°) (50 ml.), ice (20 g.) and 12% sodium hydroxide (100 ml.) was treated in a pressure bottle with chlorine gas under 30 mm. of pressure until no more fuming was noticed. During the addition the bottle was cooled in an ice-bath. The petroleum ether solution of the chloroamine was separated and the aqueous layer extracted with two 20-ml. portions of cold petroleum ether. The extracts were combined, washed with 12% sodium hydroxide (50 ml.) and dried for one hour over anhydrous sodium carbonate in a flask immersed in an ice-bath. The solution was then analyzed for chloroamine by adding a cold sample (20 ml.) to a solution of potassium iodide (3 g.) in a mixture of acetic acid (10 ml.), distilled water (20 ml.) and acetone (20 ml.). The liberated iodine was titrated with standard 0.100 *N* sodium thiosulfate using the disappearance of iodine as an end-point. The cold petroleum ether solution containing 0.054 mole of chloroamine was extracted with two 30-ml. portions of cold 84% sulfuric acid (80 ml. of concentrated sulfuric acid, 20 ml. of water) and then analyzed for completeness of extraction of chloroamine. If this was incomplete a third extraction with cold 84% sulfuric acid (40 ml.) was made and the extract combined with the other two. If the extraction was complete, the two extracts were combined and added to 40 ml. of cold 84% sulfuric acid. The combined solutions were treated in various ways listed in Table I. At the end of the reaction the sulfuric acid solution was poured onto 400 g. of ice, diluted with water to 1000 ml. and extracted with 100 ml. of ligroin. The ligroin was tested for the presence of unreacted chloroamine.

The aqueous acid solution of the amine was placed in a 5-liter flask fitted for steam distillation and equipped with an addition funnel through which 300 ml. of 50% sodium hydroxide was added to make the solution basic. Steam distillation into dilute hydrochloric acid was continued until about 3–4 liters of distillate were obtained or until the distillate came over neutral to nitrazine paper. Evaporation of the distillate to dryness under reduced pressure (30–50 mm.) gave the amine hydrochloride. This salt was dissolved in water (100 ml.) in a Pyrex flask with a glass stopper, benzenesulfonyl chloride (20 g.) and 50% sodium hydroxide (30 ml.) were added and the resulting mixture shaken for thirty minutes. After cooling the mixture was made acid with concentrated hydrochloric acid and the N-benzenesulfonyl-N-methylcyclooöctylamine which forms as a viscous oil was extracted with three portions each of 50 ml. of ether. The ether solution upon drying and removal of the solvent gave 8.7 g. of the sulfonyl derivative which is equivalent to 55.6% of the unchanged amine. The remaining aqueous acidic solution was made alkaline with 50% sodium hydroxide and extracted with three 50-ml. portions of ether. The ether solution after drying over potassium hydroxide was treated with a saturated ethanol solution of picric acid and gave 4.4 g. of N-methylgranatanine picrate. After one recrystallization from ethanol the picrate melted at 295–300°. Piccinini[9] reports a sample softening at 270° and melting at 300°. A mixture with a sample prepared from pseudopelletierene[5] melted without any lowering.

N-Methylgranatanine Chloroplatinate.—N-Methylgranatanine picrate (2.0 g.) was treated with excess sodium hydroxide and the liberated free amine was extracted with ether. The ether solution was extracted with 5 ml. of 6 *N* hydrochloric acid and the resulting acid solution of the amine was treated with the calculated amount of platinic chloride. The chloroplatinate precipitated immediately and was filtered. Recrystallization from water gave a product melting at 220–221°. Willstätter and Veraguth[10] report 220–221°. A mixture with a sample prepared from pseudopelletierene[5] melted with no lowering.

Acknowledgment.—The authors wish to thank Dr. A. C. Cope and Dr. C. G. Overberger of Massachusetts Institute of Technology for a sample of pseudopelletierine.

Summary

N-Methylgranatanine has been prepared by the irradiation with ultraviolet light of N-chloro-N-methylcyclooöctylamine in sulfuric acid.

A mechanism has been proposed for the cyclization of N-haloamines in sulfuric acid.

[9] Piccinini, *Gazz. chim. ital.*, **32**, I, 260 (1902).

[10] Willstätter and Veraguth, *Ber.*, **38**, 1984 (1905).

IOWA CITY, IOWA RECEIVED NOVEMBER 28, 1949

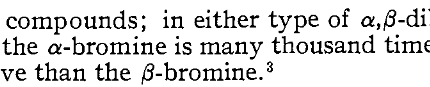
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

The Synthesis of Some 4-Alken-1-ols[1]

BY RICHARD C. BRANDON,[2] JOHN M. DERFER AND CECIL E. BOORD

The β-bromoether synthesis has been highly developed as a method for preparing olefins.[3] The present paper describes a modification of this synthesis whereby unsaturated carbinols containing more than five carbon atoms can be prepared in acceptable yield from the commercially available 3,4-dihydro-1,2-pyran.

Paul[4] found that with bromine 3,4-dihydro-1,2-pyran formed a very active addition product which condensed readily with ethyl and phenyl Grignard reagents according to the following equations. These reactions with a cyclic ether are analogous to those which take place with the open



chain compounds; in either type of α,β-dibromoether the α-bromine is many thousand times more reactive than the β-bromine.[3]

In the present work a series of 2-alkyl-3-

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[1] This paper was abstracted from a dissertation presented by R. C. Brandon to the Graduate School of The Ohio State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

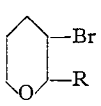
[2] Present address: Standard Oil Development Company, Elizabeth, New Jersey.

[3] (a) Swallen and Boord, THIS JOURNAL, **52**, 651 (1930); (b) Dykstra, Lewis and Boord, *ibid.*, **52**, 3396 (1930); (c) Shoemaker and Boord, *ibid.*, **53**, 1505 (1931); (d) Schmitt and Boord, *ibid.*, **54**, 751 (1932); (e) Soday and Boord, *ibid.*, **55**, 3293 (1933); (f) Schurman and Boord, *ibid.*, **55**, 4930 (1933).

[4] Paul, *Compt. rend.*, **198**, 1246 (1934); *Bull. soc. chim.*, [5] **2**, 311 (1935).

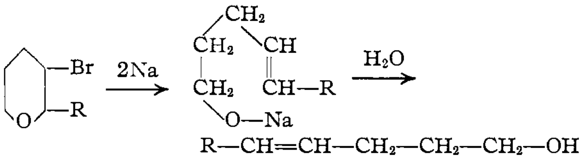
TABLE I

2-ALKYL-3-BROMOTETRAHYDROPYRANS



R group	B. p. °C.	B. p. Mm.	d^{20}_4	$n^{20}D$	Yield, %	Bromine, % Calcd.	Bromine, % Found
Methyl	60–61	17	1.3660	1.4834	65	44.63	44.81
Ethyl	70.5–71.5	14	1.3143	1.4822	55	41.39	41.26
n-Propyl	89–90	14	1.2663	1.4807	50	38.59	37.95
n-Butyl	98–99	13	1.2169	1.4785	43	36.16	35.97
n-Amyl	111.0–111.7	11	1.1841	1.4768	37	34.00	33.17
Isopropyl	71.5–72.5	13	1.2766	1.4818	25	38.59	38.29
Isobutyl	72.2–72.4	6	1.2085	1.4748	32	36.16	35.83
Isoamyl	96.0–96.5	7	1.1854	1.4768	35	34.00	33.24

bromotetrahydropyrans was prepared according to the scheme shown above. It was originally believed that treatment of these bromopyrans with zinc (as in the β-bromoether synthesis), followed by hydrolysis, would yield unsaturated alcohols. Zinc, however, proved unsatisfactory: even the powdered metal activated by a deposit of copper was without action on the bromopyrans. Likewise powdered magnesium had no effect, although magnesium amalgam showed some activity. On the other hand, sodium metal proved quite satisfactory and decomposed the bromopyrans at the reflux temperature of diisopropyl ether to produce the sodium salts of 4-alken-1-ols, which on hydrolysis gave the corresponding unsaturated carbinols.



$R—CH=CH—CH_2—CH_2—CH_2—OH$

The method was successfully applied to the preparation of 4-alken-1-ols where the R-group was methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *n*-amyl and isoamyl. The success of the synthesis depends largely on the success of the Grignard reaction. Good yields (see Table I) were obtained with the primary Grignard reagents; isopropylmagnesium bromide gave a fair yield (25%), but the reaction with *s*-butylmagnesium bromide (not listed) was unsatisfactory. *t*-Butylmagnesium bromide showed practically no reaction. The yields with isobutyl and isoamyl Grignard reagents were acceptable.

The relationship between the physical properties and molecular structure of olefins has been developed by Boord.[3,5] To some extent the generalizations given apply to the unsaturated alcohols whose preparation has just been discussed. The boiling points are about the same as those of the saturated carbinols, as would be expected, while the densities and refractive indices are greater for the unsaturated alcohols. Introduction of an "iso" group corresponding to a methyl group on the second carbon atom of the chain causes the expected lowering of the boiling point, density and refractive index.

The over-all yields in the four-step synthesis of the unsaturated carbinols (with the exception of the isopropyl derivative) ranged from 16 to 30%.

Experimental

3,4-Dihydro-1,2-pyran.—This compound is available from the Quaker Oats Company and E. I. du Pont de Nemours and Company, Inc. It can be prepared synthetically from tetrahydrofurfuryl alcohol by the procedure of Paul[6] or Sawyer and Andrus.[7] In the present work the procedure of Paul[6] was used; the purified pyran boiled at 83 to 86° at atmospheric pressure. A portion of the product was purified by three fractionations through a 60 × 1.2 cm. column packed with glass rings, and the following physical properties were determined: b. p. 85.4 to 85.6° (760 mm.), d^{20}_4 0.9261, $n^{20}D$ 1.4420.

2,3-Dibromotetrahydropyran.—In a typical run an amount of 84 g. (1.0 mole) of 3,4-dihydro-1,2-pyran was dissolved in 200 ml. of anhydrous ether in a 500-ml. three-neck flask fitted with reflux condenser, separatory funnel and mercury-sealed stirrer; all outlets were properly protected against atmospheric moisture. The solution was cooled to and maintained at 0°, while a quantity of 160 g. (1.0 mole) of bromine was added dropwise with vigorous stirring. If the reaction mixture became colored by excess bromine, sufficient 3,4-dihydro-1,2-pyran was added to reduce the color to a straw-yellow.

No effort was made to purify the dibromide as it was unstable, even at room temperature, and very sensitive to traces of moisture, giving off large quantities of hydrobromic acid when exposed to the atmosphere. The crude product was added to the previously prepared Grignard reagent, as soon as the last of the bromine had been added.

2-Alkyl-3-bromotetrahydropyrans.—The Grignard reagents (in 20 to 25% excess) were prepared in the usual manner.[3] The solution was then cooled to 0° and maintained at this temperature while the crude 2,3-dibromotetrahydropyran was added dropwise, after which the reaction mixture was held at 0° for thirty-six to seventy-two hours. The ether solutions were then hydrolyzed, and the ether was removed by distillation. The residual oils were steam distilled, dried and fractionated under reduced pressure through a 50 × 2 cm. column packed with glass rings. The physical properties given in Table I were determined immediately after distillation since the products were slightly unstable.

4-Alken-1-ols.—In a three-neck flask, equipped with stirrer, dropping funnel and reflux condenser, was placed an amount of 2 moles of finely cut sodium covered with 800 to 1000 ml. of dry di-isopropyl ether. One mole of

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(5) Boord, Chapter in the "Science of Petroleum," Vol. II, Oxford University Press, London, 1938, p. 1349.

(6) Paul, *Compt. rend.*, **196**, 1409 (1933).

(7) Sawyer and Andrus, "Organic Syntheses," **23**, 25 (1943).

Table II

4-Alken-1-ols, R—CH=CH—CH_2—CH_2—CH_2OH

R group	B. p., °C. (760 mm.)	d^{20}_4	n^{20}_D	Yield,[a] %	Over-all[b] yield, %	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Methyl	159.0–159.4	0.8513	1.4407	45	30	71.95	71.28	12.07	12.01
Ethyl	176.0–176.4	.8452	1.4433	29	16	73.64	73.22	12.35	12.30
n-Propyl	194.1–194.6	.8452	1.4460	36	18	74.94	74.36	12.57	12.58
n-Butyl	211.9–212.2	.8454	1.4478	60	26	75.99	75.83	12.76	12.78
n-Amyl	228.0–228.5	.8433	1.4499	60	22	76.86	77.04	12.90	12.77
Isopropyl	185.8–186.3	.8365	1.4419	20	5	74.94	74.40	12.57	12.56
Isobutyl	203.5–204.0	.8426	1.4454	59	19	75.99	75.65	12.76	12.61
Isoamyl	220.0–221.0	.8445	1.4492	67	23	76.86	76.72	12.90	12.69

[a] From 2-alkyl-3-bromotetrahydropyrans. [b] From 3,4-dihydro-1,2-pyran.

the β-bromoether was added at such a rate as to maintain gentle reflux; in some cases the reaction mixture became very viscous and it was necessary to add more di-isopropyl ether in order to maintain stirring. The reaction mixtures were allowed to stand at room temperature for two days, after which they were hydrolyzed with small portions of cold water (caution). The ether layers were thoroughly washed, dried over lime and fractionated through the same column as were the 2-alkyl-3-bromotetrahydropyrans; the higher boiling alkenols were distilled under reduced pressure. Each of the alkenols was redistilled before the physical properties and yields listed in Table II were determined. The products were colorless liquids having characteristic odors, those of the lower boiling members being stronger and less pleasant.

Proof of Structure.—Since all of the alkenols were prepared by the same procedure, two, 4-hexen-1-ol and 4-octen-1-ol, were picked as representative products, and their carbon skeletons were demonstrated by hydrogenation to the corresponding saturated alcohols which are well known.

The procedure followed in hydrogenating 4-hexen-1-ol and 4-octen-1-ol over platinic oxide catalyst has been described in the literature.[8] Absolute alcohol was used as the solvent, and in each case approximately the theoretical amount of hydrogen was absorbed. The hydrogenates were distilled through a 20-cm. Vigreux column to obtain a 78% yield of 1-hexanol (b. p. 155 to 156° (744 mm.)) and an 85% yield of 1-octanol (b. p. 191 to 192° (742 mm.)). The compounds were identified by the melting points of their phenyl urethans and dinitrobenzoates.

To fix the position of the double bond, a sample of 4-hexen-1-ol was treated in the cold with a slight excess of aqueous potassium permanganate. (A similar reaction with this alcohol had been described previously,[9] but no physical properties were given.) The manganese dioxide was removed by filtration and the acidified (sulfuric acid) solution was distilled rapidly. The distillate was neutralized with dilute sodium hydroxide and evaporated to dryness. Gray crystals remained and when treated with concd. sulfuric acid, gave a distinct odor of acetic acid; addition of alcohol to the acidified portion gave the characteristic odor of ethyl acetate. The crystals were identified as sodium acetate by conversion to the corresponding *p*-bromophenacyl ester which melted at 83 to 84° (literature,[10] 85°). Identification of the acetate radical showed that the double bond was, as expected, in the 4-position.

Summary

A method has been devised whereby unsaturated primary alcohols of more than five carbon atoms can be prepared from the commercially available 3,4-dihydro-1,2-pyran by a new modification of the β-bromoether synthesis of olefins.

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(8)(a) Adams and Vorhees, *Organic Syntheses*, **8**, 10 (1928); (b) Adams, Vorhees and Shriner, *ibid.*, **8**, 92 (1928).

(9) Fischer and Wiedemann, *Ann.*, **522**, 1 (1936).

(10) Judefind and Reid, This Journal, **42**, 1048 (1920).

Columbus, Ohio Received November 23, 1949

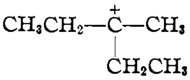
[Contribution No. 270 from the Chemical Department, Experimental Station, E. I. du Pont de Nemours & Company]

Synthesis of Ethyl α-Ethyl-α-methylbutyrate from Ethylene and Carbon Monoxide

By J. R. Roland, J. D. C. Wilson, II, and W. E. Hanford[1]

In an exploration of carbon monoxide reactions, ethyl α-ethyl-α-methylbutyrate was the principal and unexpected product obtained from ethylene and carbon monoxide with boron fluoride hydrate catalyst at 115° and 1,000 atmospheres total pressure. This unusual reaction can be explained as proceeding through carbonium ions, and the present paper offers evidence in support of such a mechanism.

From a consideration of the various mechanisms by which this highly branched ester might have been formed, it seemed likely that the precursor of the ester was a carbonium ion that on carboxylation and esterification gave ethyl α-ethyl-α-methylbutyrate. The carbonium ion VI



$$CH_3CH_2-\overset{+}{C}(CH_2CH_3)-CH_3 \quad \text{VI}$$

may arise from the conversion of ethylene to ethyl carbonium ion by addition of a proton[2] from the boron fluoride hydrate, followed by a sequence of additions to ethylene as represented in equations 1, 2 and 3.

$$(1)\quad C_2H_4 + H^+ \rightleftarrows CH_3CH_2^+ \qquad \text{I}$$

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[1] Present address: M. W. Kellogg Company, 225 Broadway, New York 7, N. Y.

[2] Whitmore, *Chem. Eng. News*, **26**, 668 (1948).