

propylamine was withdrawn from the stillhead. The kettle contents were fractionated at reduced pressure yielding 75 g. of 1,3-bis-(1-piperidyl)-propene, b.p. 96–100° (0.5 mm.); equiv. wt. 101, calcd. $C_{15}H_{24}N_2$ 104; lit.¹ b.p. 150–152°, 12 mm.) and 11 g. of higher boiling amines. Hydrogenation of the propenediamine gave 1,3-bis-(1-piperidyl)-propane, b.p. 116–118° (4 mm.), equiv. wt., 105, calcd. $C_{15}H_{26}N_2$ 105; lit.¹ b.p. 135–137° (12 mm.).

Preparation of N-Phenyl-N',N',N'-diethyl-1,3-propenediamine.—A mixture of 159 g. of N,N,N',N'-tetraethyl-1,3-

propene diamine (prepared from acrolein and diethylamine) and 186 g. of aniline was refluxed for 1.5 hours under a fractionating column at 15 mm. pressure and a kettle temperature of 105°. Diethylamine was collected in a Dry Ice trap and 60 g. of aniline was slowly distilled from the mixture. Fractionation of the kettle contents gave 69 g. of N-phenyl-N',N'-diethyl-1,3-propenediamine and 64 g. of higher boiling amines. Properties of the propenediamine are listed in Table I.

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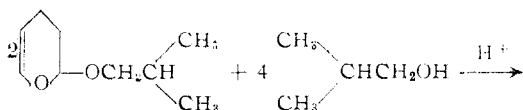
Reactions of Acrolein and Related Compounds. VII. Reactions of 2-Alkoxydihydropyrans

BY CURTIS W. SMITH, DOUGLAS G. NORTON AND SEAVER A. BALLARD

Recently a new class of compounds, the 2-alkoxy-3,4-dihydro-2H-pyrans have been made readily available by thermal addition of vinyl ethers to conjugately unsaturated carbonylic compounds. Reaction of these agents with alcohols, capric acid, phenol and hydrogen cyanide are reported. Reaction with ammonia leads to pyridine and other nitrogen bases. Thermal cleavage gives the isomeric 5-alkoxy-4-pentenals.

2-Alkoxy-3,4-dihydro-2H-pyrans, a new class of compounds, have been prepared¹⁻⁴ by heating conjugated carbonylic compounds, such as acrolein, with vinyl ethers. Reactions of the 2-alkoxy-3,4-dihydro-2H-pyrans may be related to the presence of a vinyl ether and an acetal linkage sharing a single oxygen atom. Hydrolysis leads to glutaraldehyde and substituted glutaraldehydes.^{2,5} An interesting by-product isolated for the first time from hydrolysis of 2-methoxy-3,4-dihydro-2H-pyran is 2-(6-methoxytetrahydropyranyl) ether. Hydrogenation^{3,4} leads to the 2-alkoxytetrahydropyrans which have been converted to 2-hydroxytetrahydropyran by hydrolysis. Hydrogenation in aqueous solution with catalytic amounts of acetic acid leads to 1,5-pentanedols.⁶ Other novel reactions of the 2-alkoxydihydropyrans are presented in the following sections.

Reactions with Alcohols.—In acidic solution, with alcohols, the 2-alkoxydihydropyrans enter into a fairly complex equilibrium involving 2,6-dialkoxytetrahydropyrans (by addition to the vinyl ether) and glutaraldehyde tetraalkyl acetals (by alcoholysis of the vinyl ether and acetal). If the alkoxy group of the entering alcohol is different from that attached to the dihydropyran, then either mixed products are formed or the alkoxy group originally present may be displaced completely under controlled conditions:



(1) C. W. Smith, D. G. Norton and S. A. Ballard, U. S. Patent 2,514,168, 1950.

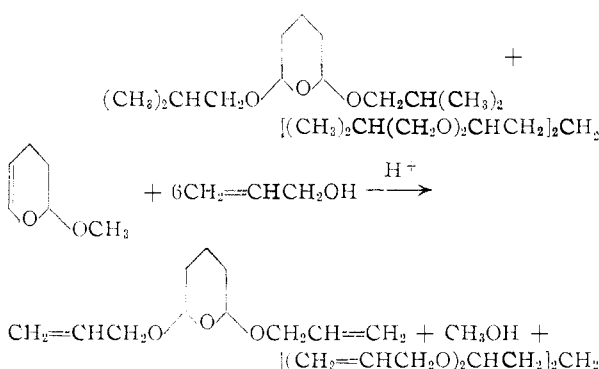
(2) R. I. Longley and W. S. Emerson, THIS JOURNAL, **72**, 3079 (1951).

(3) C. W. Smith, D. G. Norton and S. A. Ballard, *ibid.*, **73**, 5267 (1951).

(4) W. E. Parham and H. E. Holmquist, *ibid.*, **73**, 913 (1951).

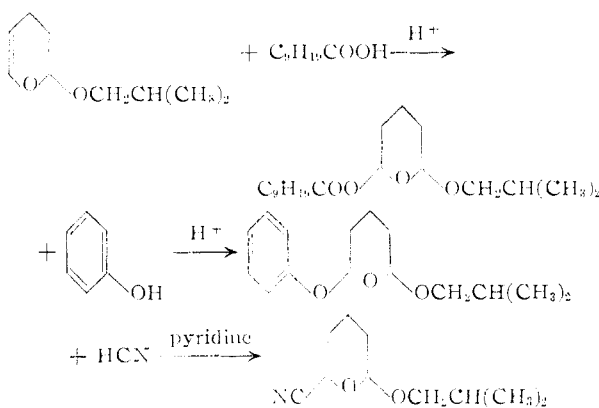
(5) C. W. Smith and S. A. Ballard, U. S. Patent 2,546,018 (1951).

(6) C. W. Smith, U. S. Patent 2,546,019 (1951).



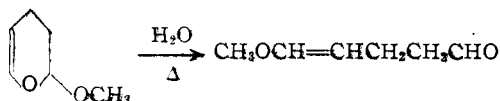
Thus the acid-catalyzed reaction of isobutyl alcohol with 2-isobutoxydihydropyran has given 2,6-diisobutoxytetrahydropyran and glutaraldehyde tetraisobutyl acetal; and the reaction of 2-methoxydihydropyran with excess allyl alcohol has given 2,6-diallyloxytetrahydropyran and glutaraldehyde tetraallyl acetal.

Addition of Acidic Agents.—From the addition of capric acid to 2-isobutoxydihydropyran with a trace of hydrochloric acid as catalyst, an 87% yield of the caprate of 2-isobutoxy-6-hydroxytetrahydropyran was obtained.



Similar addition of phenol gave 2-isobutoxy-6-phenoxytetrahydropyran. The addition of hydrogen cyanide in the presence of pyridine has given 2-isobutoxy-6-cyanotetrahydropyran. Without the pyridine, hydrogen cyanide causes dimerization to give 2,6-diisobutoxytetrahydropyran as the only product identified. Analogous additions of organic acids, phenol and hydrogen cyanide to vinyl ethers have been reported by others.⁷

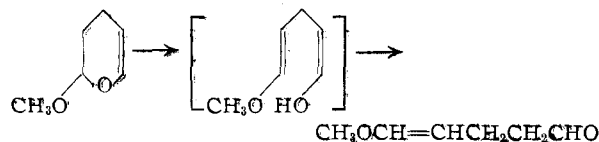
Isomerization with Cleavage.—A rather interesting reaction is the cleavage of 2-methoxy- and 2-isobutoxydihydropyran to the isomeric 5-alkoxy-4-pentenals.



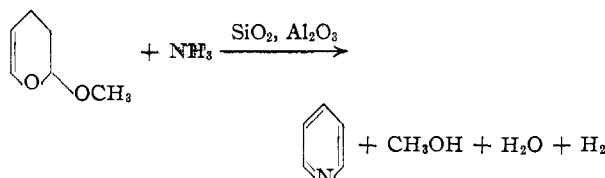
The identity of the isomeric structures was established as follows: (1) The infrared absorption spectra of the isomers indicated the presence of an unconjugated ethylenic linkage and an aldehyde group; (2) the isomers gave the bis-2,4-dinitrophenylhydrazone of glutaraldehyde (establishing the functional groups at the ends of the chain). (3) In the case of the isobutoxy derivative, hydrogenation without added water gave the saturated alcohol, 5-isobutoxy-1-pentanol.

The greatest cleavage to isomer (12%) was obtained by passing 2-methoxydihydropyran over a silica-alumina catalyst at 250° and at atmospheric pressure. Apparently water catalyzes the isomerization. Heating acrolein which contained 2% water with isobutyl vinyl ether at 180° for one hour gave a 6.6% conversion to 5-isobutoxy-4-pentenal in addition to the 2-isobutoxydihydropyran. When the reagents were anhydrous or when anhydrous 2-isobutoxydihydropyran was heated at 180° in a sealed tube, no indication of isomer was observed.

The mechanism of the reaction is not established. However, a reaction which bears some similarity is catalytic pyrolysis of acetals⁸ to give alcohols and vinyl ethers. According to this scheme cleavage of the acetal linkage of 2-alkoxydihydropyrans might lead to a vinyl ether and a vinyl alcohol linkage, the latter of which would rearrange to an aldehyde.



Synthesis of Pyridine.—Passing 2-methoxydihydropyran and ammonia in vapor phase over an alumina catalyst at 400° has given a 29% conversion to pyridine along with other higher boiling nitrogen bases.



(7) C. E. Schildknecht, A. O. Zoss and C. McKinley, *Ind. Eng. Chem.*, **39**, 180 (1947).

(8) F. Sigmund and R. Vchann, *Monatsh.*, **51**, 234 (1929).

This reaction obviously involves dehydrogenation. No attempt has been made to achieve maximum conversion or yield in this reaction.

Polymerization.—Like vinyl ethers the 2-alkoxydihydropyrans are polymerized by Friedel-Crafts type catalysts and by iodine but are little affected by peroxides. 2-Methoxydihydropyran with boron trifluoride etherate gave a light-yellow, brittle, non-tacky solid.

Acknowledgment.—The authors are grateful to Messrs. Harry de V. Finch and Kenneth E. Furman for carrying out the vapor-phase reactions.

Experimental

2-(6-Methoxytetrahydropyranyl) Ether.—Reaction of 114 g. (1 mole) of 2-methoxydihydropyran, 10 g. (0.55 mole) of water and 0.2 ml. of concd. hydrochloric acid gave a 21% recovery of 2-methoxydihydropyran, a 45% conversion to glutaraldehyde and a 3% conversion to 2-(6-methoxytetrahydropyranyl) ether, 4 g., b.p. 114–116° (1 mm.), which gave the bis-2,4-dinitrophenylhydrazone of glutaraldehyde.

Anal. Calcd. for C₁₂H₂₂O₄: C, 58.52; H, 9.00. Found: C, 58.85; H, 8.95.

Addition of Isobutanol to 2-Isobutoxy-3,4-dihydro-2H-pyran.—A mixture of 78 g. (0.5 mole) of 2-isobutoxy-3,4-dihydro-2H-pyran and 74 g. (1 mole) of isobutyl alcohol with 0.1 ml. of concd. hydrochloric acid was allowed to react spontaneously, using a cooling-bath to keep the temperature below 50°. Distillation of the product gave the following fractions: A, 23 g. of isobutyl alcohol (b.p. 43–58° (100 mm.)); B, 86 g. (75%) of 2,6-diisobutoxytetrahydropyran, b.p. 63° (0.07 mm.), *n*_D²⁰ 1.4322, sp. gr.₄ 0.9177.

Anal. Calcd. for C₁₃H₂₆O₃: C, 67.78; H, 11.38. Found: C, 67.64; H, 11.35.

C, 33 g. (19%) of glutaraldehyde tetraisobutyl acetal, b.p. 134° (0.04 mm.).

Anal. Calcd. for C₂₁H₄₄O₆: C, 69.95; H, 12.30; acetal value, 0.555 equiv./100 g. Found: C, 69.90, 69.85; H, 12.24, 12.25; acetal value, 0.559, 0.556 equiv./100 g.

The acetal value was determined by an extension of the method of Bryant and Smith⁹ in which the acetal was heated at reflux with the hydroxylamine hydrochloride.

Reaction of 2-Methoxy-3,4-dihydro-2H-pyran with Allyl Alcohol.—On mixing 85.5 g. (0.75 mole) of 2-methoxydihydropyran, 232 g. (4 moles) of allyl alcohol and 0.1 ml. of concd. hydrochloric acid a mildly exothermic reaction occurred and the temperature rose to 55°. After the initial reaction had subsided, the mixture was refluxed under a fractionating column and 22 g. (0.69 mole) of methanol was removed. Distillation of the residue gave: A, 114 g. (1.97 moles) of allyl alcohol; B, 80 g. (54%) of 2,6-diallyloxytetrahydropyran, b.p. 78–80° (3.3 mm.), *n*_D²⁰ 1.4575; sp. gr.₄ 0.9898, 0.9899; C, 72 g. (32%) of glutaraldehyde tetraallyl acetal, b.p. 130–134° (1 mm.), *n*_D²⁰ 1.4582, sp. gr.₄ 0.9506, 0.9508.

Anal. of B. Calcd. for C₁₇H₂₈O₃: C, 66.64; H, 9.15; bromine no., 161 g. Br/100 g. Found: C, 66.22; H, 9.14; bromine no., 162 g. Br/100 g. *Anal.* of C. Calcd. for C₁₇H₂₂O₄: C, 68.80; H, 9.52; bromine no., 216 g. Br/100 g. Found: C, 68.80, 68.97; H, 9.55, 9.57; bromine no., 220 g. Br/100 g.

Addition of Capric Acid to 2-Isobutoxy-3,4-dihydro-2H-pyran.—A mixture of 160 g. of capric acid (Armour's Neofat No. 15), 156 g. of 2-isobutoxy-3,4-dihydro-2H-pyran and 0.4 ml. of concd. hydrochloric acid was warmed to 39° and allowed to stand at room temperature for two days. Following the addition of 1.5 g. of sodium acetate, the product was distilled from a Claisen flask. There was obtained: A, 23.5 g. of 2-isobutoxydihydropyran (b.p. 45–70° (0.5 mm.), *n*_D²⁰ 1.4387); B, 87.5 g. of capric acid (b.p. 88–132° (0.5 mm.)); and C, 191.0 g. of crude caprate (b.p. 140–145° (0.5 mm.)). This represents a 76% yield based on unrecovered 2-isobutoxydihydropyran. Redistillation of the above product gave 87.5% of 2-isobutoxy-6-tetrahydropy-

(9) W. M. D. Bryant and D. M. Smith, *THIS JOURNAL*, **57**, 57 (1935).

ranol caprate which boiled at 130° (0.05 mm.), n_D^{20} 1.4448, sp. gr.²⁰, 0.9389, 0.9388.

Anal. Calcd. for $C_{19}H_{36}O_4$: C, 69.47; H, 11.05; acetal value, 0.609 eq./100 g. Found: C, 69.10, 69.22; H, 11.02, 11.03; acetal value, 0.560, 0.557.

The infrared absorption spectrum showed a strong band at 5.75 μ (ester).

Addition of Phenol to 2-Isobutoxy-3,4-dihydro-2H-pyran.—A mixture of 80 g. (0.513 mole) of 2-isobutoxydihydropyran, 48 g. (0.511 mole) of phenol and 0.1 ml. of concd. hydrochloric acid warmed spontaneously to 55°. After the mixture had stood overnight, it was distilled to give 35 g. of a mixture of 2-isobutoxydihydropyran and phenol and 65 g. (52%) of product, b.p. 110–115° (1 mm.). On redistillation 2-isobutoxy-6-phenoxytetrahydropyran boiled at 104° (0.5 mm.), n_D^{20} 1.4398; sp. gr.²⁰, 1.0221.

Anal. Calcd. for $C_{15}H_{22}O_3$: C, 71.96; H, 8.86. Found: C, 71.67; H, 8.85.

This material gave the bis-2,4-dinitrophenylhydrazone of glutaraldehyde which caused no depression in mixture with an authentic sample.

Reaction of Hydrogen Cyanide with 2-Isobutoxy-3,4-dihydro-2H-pyran.—A mixture of 156 g. (1 mole) of 2-isobutoxy-3,4-dihydro-2H-pyran, 27 g. (1 mole) of hydrogen cyanide and 4 ml. of pyridine (2%) was heated in a glass tube at 150° for three hours. Distillation gave 150 g. (82%) of 2-isobutoxy-6-cyanotetrahydropyran, b.p. 73° (0.07 mm.), n_D^{20} 1.4422, sp. gr.²⁰, 0.9790.

Anal. Calcd. for $C_{10}H_{17}NO_2$: C, 65.54; H, 9.36; N, 7.64. Found: C, 65.76, 65.72; H, 9.51, 9.44; N, 7.08, 7.02.

In the absence of pyridine a mixture of 59 g. (0.38 mole) of 2-isobutoxydihydropyran and 21 g. (0.78 mole) of hydrogen cyanide reacted in a mildly exothermic manner. The mixture was allowed to stand at room temperature for approximately 60 hours and then gave the following fractions on distillation from a Claisen flask: A, 3 g. hydrogen cyanide; B, 30 g. isobutyl alcohol; C, 15.5 g. of 2,6-diisobutoxytetrahydropyran, b.p. 59–70° (0.3 mm.), n_D^{20} 1.4330, and 28.5 g. of tarry residue. The boiling point and refractive index of fraction C are in agreement with those of 2,6-diisobutoxytetrahydropyran prepared by addition of isobutyl alcohol to 2-isobutoxydihydropyran.

Anal. Calcd. for $C_{14}H_{26}O_3$: C, 67.78; H, 11.38. Found: C, 67.54, 67.47; H, 11.22, 11.23.

Isomerization of 2-Methoxy-3,4-dihydro-2H-pyran by Thermal Cleavage.—The isomerization of 2-methoxy-3,4-dihydro-2H-pyran was carried out by passing the liquid over about 100 ml. of catalyst in a steel tube at 250°. Flow rate was 180 g. per hour. With an alumina-silica catalyst a 12% conversion to crude 5-methoxy-4-pentalen and a 76% recovery of 2-methoxydihydropyran were obtained. With alumina (Alorco F-11) the conversion and recovery figures were 8 and 86%, respectively. J. T. Baker silica gel gave a 4% conversion to isomer and 92% recovery of 2-methoxydihydropyran. The crude 5-methoxy-4-pentalen, b.p. 65–70° (20 mm.), was washed with water to remove any glutaraldehyde which might have been present. Distillation of the residue after drying gave a heart cut (90% of crude) of 5-methoxy-4-pentalen which boiled at 68–69° (20 mm.), n_D^{20} 1.4442, sp. gr.²⁰, 0.9746.

Anal. Calcd. for $C_8H_{10}O_2$: C, 63.09; H, 8.86; carbonyl value, 0.88 equiv./100 g.; bromine no., 140 g. Br/100 g. Found: C, 62.57; H, 8.87; carbonyl value, 0.88 equiv./100 g.; bromine no., 152 g. Br/100 g.

5-Methoxy-4-pentalen gave the bis-2,4-dinitrophenylhydrazone of glutaraldehyde as shown by melting point and mixed melting point, 193.7–194.7°.

Isomerization of 2-Isobutoxy-3,4-dihydro-1,2-pyran by Thermal Cleavage.—2-Isobutoxydihydropyran, 179 g., was passed over a catalyst of 25% alumina-on-silica gel at 250°

with a liquid hourly space velocity of 1.05. There was recovered 156 g. of which 7.5 g. was a water layer. Most of the loss (23 g.) was accounted for by increase in weight of the catalyst (22 g.). The oil was separated and dried over sodium sulfate. Distillation of the oil gave the following fractions: A, 9 g. unidentified, b.p. below 105°; B, 5.5 g. isobutyl alcohol, b.p. 105–110°, n_D^{20} 1.3970; C, 106.5 g. (59% recovery) 2-isobutoxydihydropyran, b.p. 88–92° (50 mm.); D, 14 g. (8% conversion to isomer) of 5-isobutoxy-4-pentalen, b.p. 83–84° (10 mm.), n_D^{20} 1.4407; sp. gr.²⁰, 0.9016.

Anal. Calcd. for $C_9H_{16}O_2$: C, 69.19; H, 10.32; carbonyl value, 1.022 equiv./100 g.; bromine no., 102 g. Br/100 g. Found: C, 68.92; H, 10.28; carbonyl value, 1.022 equiv./100 g.; bromine no., 98 g. Br/100 g.

The infrared absorption spectrum of this material had bands at 3.65 μ and 5.79 μ indicative of an aldehyde grouping and a strong band at 6.01 μ indicative of an olefinic linkage. As a derivative, this material gave the bis-2,4-dinitrophenylhydrazone of glutaraldehyde, m.p. 193–194°.

Formation of 5-Isobutoxy-4-pentalen during Addition of Isobutyl Vinyl Ether to Wet Acrolein.—A mixture of 472 g. of acrolein (95% pure, 2% water) and 800 g. of isobutyl vinyl ether was heated in a steel vessel at 180° for one hour. Distillation of the product gave the following fractions: A, 32 g. (7% recovery) of acrolein, b.p. 50–71°; B, 53 g. (6.6% recovery) of isobutyl vinyl ether; C, 91 g. unidentified, b.p. 95–174°; D, 893 g. (72% conversion to product) of 2-isobutoxydihydropyran, b.p. 174–177°, n_D^{20} 1.4380; E, 84 g. (6.6% conversion to isomer) of 5-isobutoxy-4-pentalen, b.p. 80–90° (10 mm.), n_D^{20} 1.4408; F, residue, 72 g.

Hydrogenation of 5-Isobutoxy-4-pentalen.—A mixture of 20 g. of 5-isobutoxy-4-pentalen, 20 g. of absolute ethanol and 3 g. of Raney nickel was treated with hydrogen at 1500 p.s.i.g. at room temperature for three hours during which time the theoretical two molar equivalents of hydrogen had been absorbed. The catalyst was removed by filtration and the filtrate was distilled. After removal of alcohol, there was collected 18 g. of 5-isobutoxy-1-pentalen which boiled constantly at 94° (5 mm.) (90%), n_D^{20} 1.4319; sp. gr.²⁰, 0.8813.

Anal. Calcd. for $C_8H_{12}O_2$: C, 67.45; H, 12.59; hydroxyl value, 0.624 equiv./100 g. Found: C, 67.42; H, 12.59; hydroxyl value, 0.619, 0.611 equiv./100 g.

Preparation of Pyridine from 2-Methoxy-3,4-dihydro-2H-pyran.—A mixture of 158 g. (1.38 moles) of 2-methoxydihydropyran and 57 g. (3.35 moles) of dry ammonia was passed over Alorco F-11 Alumina at 400° and at the rate of 60 ml. per hour. The product recovered weighed 173 g. with an additional 32 g. of material, chiefly ammonia, collected in a cold trap. During the reaction there was a "hot spot" in the catalyst of about 420°. At the end of the run, the catalyst showed only slight carbonization. The product consisted of two layers, an upper, light yellow layer and a lower, dark layer. The upper layer, 70 g., was separated and distilled to give the following fractions: A, 8 g. unidentified, b.p. 40–86°; B, 33 g. of an azeotrope of pyridine and water, b.p. 86–96°; residue, 23 g. Cut B was dried over sodium hydroxide and the oil which separated boiled on a flat at 112–113°, n_D^{20} 1.5034, in agreement with pyridine (b.p. 115°, n_D^{20} 1.509). This oil, 15 g., gave a picrate, m.p. 165–166°, which caused no depression in melting point with the picrate of authentic pyridine.

The residue from the above distillation was combined with the original lower layer and the combination was dried over sodium hydroxide and distilled. The loss on drying was 13 g. The following fractions were collected: C, 9 g., b.p. 69–100°; D, 17 g. of pyridine, b.p. 110–120°; E, 40 g., b.p. 120 (atm.)–108° (0.5 mm.). Cut D gave the picrate of pyridine. Cuts B, 15 g., and D, 17 g., represent a 29% conversion to pyridine. Cut E smelled of nitrogen bases but was not further investigated.

EMERYVILLE, CALIF.

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