

The linear equations given here predict the midpoints of the boiling point ranges with a maximum error of 1.8%.

An interesting empirical relationship between the density and refractive index was developed and may be of some utility in enabling one to predict fairly accurately the density of an alkyl tetralin by measurement of the refractive index. The following least square linear equation between d^{20}_4 and n^{20}_D was found and proven to be significant

$$d^{20}_4 = -2.2483 + 2.0900n^{20}_{D_{obs.}}$$

Substitution of $n^{20}_{D_{obs.}}$ in this equation in the case of twenty-six alkyl tetralins of diverse types gave a maximum error in estimating the value of d^{20}_4 of less than one per cent. Exact determination of the density, would, of course, require experimental measurement.

Ultraviolet and infrared spectra of the compounds have been determined by the Bureau of Mines, Petroleum Experiment Station at Bartlesville, Oklahoma, and will be published in a catalog of such spectra issued by the American Petroleum Institute Research Project 44 at the National Bureau of Standards.

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The authors also wish to express their gratitude to Mr. Sutton Monro of the Department of Mathematical Statistics, University of North Carolina, for his aid in developing the statistical relationships reported in this paper.

Summary

1. Twenty new 6-alkyl and 6,7-dialkyl tetralins have been synthesized and their physical constants determined.

2. Values for the specific refraction, the observed molar refraction, the theoretical molar refraction, and the specific exaltation have been calculated for these tetralins.

3. There is a well-defined linear relationship between the boiling points and the number of carbon atoms when the data are segregated into groups according to molecular types.

4. An empirical relationship between the density and refractive index of the alkyl tetralins is reported.

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The Reaction of Propylene Oxide with Methanol¹

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The base catalyzed reaction of propylene oxide with methanol and ethanol has been shown recently by Petrov³ and Chitwood and Freure⁴ to give a product consisting almost entirely of one isomer, 1-alkoxypropanol-2. A mixture of 1-alkoxypropanol-2 and 2-alkoxypropanol-1 is obtained when an acid catalyst is employed.^{3,4} A mixture of isomers is also obtained when no catalyst is used.^{3,4} In the case of the ethoxypropanols, the evidence for the assigned structures is based on the cleavage of the ethoxy group by a small amount of sulfuric acid in acetic anhydride in one isomer (assigned the secondary ether structure) and not in the other.⁴ The methoxypropanols were assigned their structures on the basis of oxidation products isolated in 10–15% yields.³ Subsequent to our work, infrared absorption data have been reported.⁵ The work of earlier investigators is reviewed by Petrov,³ Chitwood and Freure,⁴ and Kadesch.⁶ No un-

equivocal syntheses of any of the isomeric alkoxypropanols have been reported, nor have crystalline derivatives of these compounds been prepared. Most of the published physical data on the products obtained by acid catalysis are questionable because of the difficulty of separating the mixture of isomers formed.

The object of the present work was to develop unequivocal syntheses for 2-methoxypropanol-1 and 1-methoxypropanol-2, to prepare suitable derivatives of these, and to compare these compounds with the products obtained by the reaction of methanol with propylene oxide.

2-Methoxypropanol-1 was prepared by the copper chromite catalyzed hydrogenolysis of ethyl α -methoxypropionate. The reduction of the ester proceeded normally and no by-products were detected. In view of its successful use in this case, this method holds promise of being generally applicable in the syntheses of pure 2-alkoxy-substituted primary alcohols. This reduction of α -alkoxy esters using the usual small amounts of catalyst does not appear to have been previously employed.

1-Methoxypropanol-2 was prepared by the reduction of methoxyacetone with hydrogen over Raney nickel catalyst. The methoxyacetone was prepared from methoxyacetonitrile and methylmagnesium bromide.

(1) Presented before the Division of Organic Chemistry at the Chicago Meeting of the American Chemical Society, April, 1948.

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(3) Petrov, *J. Gen. Chem. (U. S. S. R.)*, **14**, 1038 (1944); **16**, 1206 (1946).

(4) Chitwood and Freure, *THIS JOURNAL*, **68**, 680 (1946).

(5) Sexton and Britton, *ibid.*, **70**, 3606 (1948). This paper was submitted after our results had been presented at the 1948 Chicago meeting. No description is given of the isomers used.

(6) Kadesch, *ibid.*, **68**, 41 (1946).

TABLE I
PHYSICAL PROPERTIES OF THE METHOXYPROPANOLS AND THEIR DERIVATIVES

B. p. { °C. Mm.	1-Methoxypropanol-2 from			2-Methoxypropanol from	
	Methoxyacetone	Propylene oxide, basic catalysis ^b	Propylene oxide, acid catalysis ^{c, d}	Ethyl α -methoxypropionate	Propylene oxide, acid catalysis ^{c, e}
	118	118.5-119	118.3	130-130.2	130-130.5
	750	765	750	758	758
n_{20}^D	1.4038	1.4034	1.4034	1.4070	1.4076
n_{25}^D	1.4020	1.4017	1.4017	1.4048	1.4055
d_{20}^4	0.923 ^a	0.922	0.920	0.938	0.938
d_{25}^4	0.920 ^a	0.919	0.917	0.934	0.934
M. p. 3,5-dinitrobenzoate, ^f °C.	84-85	84-85	83.5-84.5	96.5-97	95.5
M. p. α -naphthyl urethan, ^g °C.	71-73	72-73	72-73	60-60.5	60-60.5

^a Determined with a small pycnometer. ^b Previously reported values: Petrov³ b. p. 118-118.5°, n_{20}^D 1.4040, d_{20}^4 0.9213 (incorrectly given as 0.9312 in *C. A.*, 40, 7153 (1946)). ^c Previously reported values: Petrov³ (isomer incompletely purified by partial acetylation) b. p. 119-123°, n_{20}^D 1.4046, d_{20}^4 0.9260. ^d Previously reported values: Dewael⁸ (assigned 1-methoxypropanol-2 structure but actually mixture of isomers) b. p. 126-127°, n_{20}^D 1.4070, d_{20}^4 0.9260. ^e Previously reported values: Petrov³ (isomer incompletely purified by partial acetylation) b. p. 122-127°, n_{20}^D 1.4062, d_{20}^4 0.9315. ^f Melting points of the three dinitrobenzoates, m. p.s 83.5-85° were not depressed on mixing; m. p.s of the two dinitrobenzoates, m. p.s 95.5-96.5°, were not depressed on mixing; m. p. of mixture of isomers, 74-82°. ^g Melting points of the three urethans, m. p.s 71-73°, were not depressed on mixing; m. p.s of the two urethans, m. p. 60-60.5° were not depressed on mixing; m. p. of mixture of isomers, 55-64°.

From the sodium methoxide catalyzed reaction of methanol and propylene oxide by Petrov's³ procedure, 1-methoxypropanol-2 was obtained in 63% yield, and had physical properties which agreed in all respects with the material prepared by the reduction of methoxyacetone. Careful fractionation of 80 ml. of the sodium methoxide catalyzed reaction mixture through a 50-cm. helices-packed column has failed to indicate the presence of any of the other isomer, but this does not eliminate the possibility that traces are present in the material held up in the column. This work indicates the preferred procedure for preparing 1-methoxypropanol-2 is by the sodium methoxide catalyzed reaction of methanol and propylene oxide.

The sulfuric acid catalyzed reaction of methanol and propylene oxide by Chitwood and Freure's⁴ procedure gave a 15% yield of 1-methoxypropanol-2, 6% 2-methoxypropanol-1, and an additional estimated 25% of the mixed isomers in the form of low boiling and intermediate fractions. It was difficult to obtain either isomer in a reasonably pure state except by fractionation through a 30 plate Oldershaw⁷ column. Even after such careful fractionation, the methoxypropanols had an unpleasant odor, and the 2-methoxypropanol-1 fraction was contaminated with traces of aldehydes. Because of the difficulty of separating the isomeric methoxypropanols, the low yields, and the presence of residual impurities, it is more practical to obtain pure 2-methoxypropanol-1 by the reduction of ethyl α -methoxypropionate than from propylene oxide.

The physical properties of the methoxypropanols and the melting points of their derivatives are given in Table I.

The physical constants given in Table I show clearly that the low boiling isomer is 1-methoxypropanol-2 and the high boiling isomer 2-methoxy-

propanol-1. The physical constants for the 1-methoxypropanol-2 are in agreement with those previously reported by Petrov.³ Dewael⁸ and Petrov³ have studied the acid-catalyzed reaction of methanol and propylene oxide, and Dewael assigned the 1-methoxypropanol-2 structure to the product obtained. A comparison of the physical constants given in Table I with those of his product shows he actually had a mixture of isomers. Petrov was the first to demonstrate that the acid catalyzed reaction of propylene oxide with aliphatic alcohols gave a mixture of isomers. He tried to obtain 2-methoxypropanol-1 in a pure state by acetylating the reaction mixture with insufficient acetic anhydride, separating the acetate and unreacted 1-methoxypropanol-2, and hydrolyzing the acetate. However, the physical properties of his product show it was still contaminated with large amounts of the 1-methoxypropanol-2.

Petrov,³ Kadesch,⁶ and Chitwood and Freure⁴ have given a logical electronic explanation of the course of the acid and base catalyzed reaction of alcohols with epoxides.

Experimental

All melting points are uncorrected. Analyses are by Miss Eleanor Werble and Mrs. Mary Aldridge of this Laboratory.

Refractive indices were determined with a Spencer Abbe Refractometer. Both of the methoxypropanols slowly absorb water from air of approximately 50% relative humidity; this possible error in the determination of physical constants was minimized as much as possible.

Materials.—Commercial propylene oxide and alcohols were used without further purification.

1-Methoxypropanol-2 from Methoxyacetone

Methoxyacetone was prepared in 20% yield by treating methoxyacetone nitrile⁹ with methylmagnesium bromide as described by Gauthier,¹⁰ b. p. 114.5-115.5°. The *p*-nitrophenylhydrazone was recrystallized from water, m. p.

(8) Dewael, *Bull. soc. chim. Belg.*, **39**, 395 (1930).

(9) Scarrow and Allen, "Organic Syntheses," Coll. Vol. II, 387 (1944).

(10) Gauthier, *Ann. chim. phys.*, [8] **16**, 318 (1909).

(7) Oldershaw, *Ind. Eng. Chem., Anal. Ed.*, **13**, 265 (1941).

108–109°; literature,¹¹ m. p. 110–111°. *Anal.* Calcd. for $C_{10}H_{12}N_2O_8$: C, 53.81; H, 5.84; N, 18.83. Found: C, 53.72; H, 5.91; N (Dumas), 19.05. The 2,4-dinitrophenylhydrazone was recrystallized from 95% ethanol, m. p. 157–159°. *Anal.* Calcd. for $C_{10}H_{12}N_4O_8$: C, 44.78; H, 4.51; N, 20.88. Found: C, 44.93; H, 4.58; N (Dumas), 20.65.

1-Methoxypropanol-2.—Five and one-half grams of methoxyacetone dissolved in 45 ml. of ether was reduced with hydrogen under 5800 lb. (400 atm.) pressure at 140° over approximately 2 g. of Raney nickel catalyst.¹² After two fractionations through a Vigreux column, a yield of 3 g. was obtained, b. p. 118° at 750 mm. The 3,5-dinitrobenzoate was crystallized from 60–80° petroleum ether and from methanol. *Anal.* Calcd. for $C_{11}H_{12}N_2O_7$: C, 46.46; H, 4.23. Found: C, 46.60; H, 4.35. The α -naphthyl urethan was recrystallized from 60–80° petroleum ether, and the mixed melting point with the α -naphthylurethan of the product obtained from the alkali catalyzed condensation gave no depression.

2-Methoxypropanol-1 from Ethyl α -Methoxypropionate

α -Methoxypropionic acid was prepared by the procedure described for ethoxyacetic acid.¹³ It distilled at 103–106° at 25 mm. Reported¹⁴ b. p. (a) 95–96° at 12 mm., (b) 108–110 at 30 mm. (for levorotatory material).

Ethyl α -methoxypropionate was prepared in 54% yield by the procedure¹⁵ described for ethyl α -ethoxyacetate. The fraction distilling at 140–142° at 760 mm. was collected, refluxed over Raney nickel, and redistilled before use; reported b. p.¹⁶ 135.5° at 760 mm.

2-Methoxypropanol-1.—Eighty grams of ethyl α -methoxypropionate in 50 ml. of dioxane (purified by refluxing over sodium) was hydrogenated under 6000 lb. (400 atm.) pressure at 250° over 10 g. of copper chromite catalyst.¹⁷ The reduction was complete in two hours. Distillation of the product through a 45-cm. column packed with glass helices yielded 25 g. of alcohol, b. p. 129.5 to 130.5°. The low yield, 40%, was due to the hold-up of the column. The alcohol was redistilled and the fraction distilling at 130–130.2° at 758 mm. taken for analysis. *Anal.* Calcd. for $C_4H_{10}O_2$: C, 53.33; H, 11.11. Found: C, 53.40; H, 11.15. The 3,5-dinitrobenzoate was recrystallized from 60–80° petroleum ether. *Anal.* Calcd. for $C_{11}H_{12}N_2O_7$: C, 46.46; H, 4.23; N, 9.85. Found: C, 46.58; H, 4.46; N (Dumas), 10.02. The α -naphthyl urethan was recrystallized from 30–60° petroleum ether. *Anal.* Calcd. for $C_{15}H_{17}NO_3$: C, 69.50; H, 6.56; Found: C, 69.64; H, 6.77.

Alkaline Catalyzed Propylene Oxide Condensation

1-Methoxypropanol-2 was made by the sodium methoxide catalyzed condensation of propylene oxide and methanol according to Petrov³: 48 ml. of propylene oxide and 35 ml. methanol, in which 1.7 g. of sodium had been dissolved, reacted in a steel reaction vessel with shaking at 100° for four hours, and then was fractionated through a 50-cm. helices-packed column; yield 40 g. (63%), b. p. 118.5–119° at 765 mm. There was no evidence of the presence of 2-methoxypropanol-1. The 3,5-dinitrobenzoate was recrystallized from 60–80° petroleum ether and then from methanol. *Anal.* Calcd. for $C_{11}H_{12}N_2O_7$: C, 46.46; H, 4.23; N, 9.85. Found: C, 46.62; H, 4.22; N (Dumas), 10.00. The α -naphthylurethan was recrystallized from 30–60° petroleum ether. *Anal.* Calcd. for

$C_{15}H_{17}NO_3$: C, 69.50; H, 6.56. Found: C, 69.52; H, 6.90.

Acid Catalyzed Propylene Oxide Condensation.—One thousand sixty-eight grams (34.4 moles) of dry methanol, 15.6 g. (8.5 ml.) of concentrated sulfuric acid, and 387 g. (6.7 moles) of propylene oxide reacted according to the directions of Chitwood and Freure.⁴

The reaction mixture was neutralized with 10% sodium hydroxide, the sodium sulfate removed by filtration, and the filtrate distilled through an Oldershaw column⁷ after some plain distillations and dryings of various fractions over anhydrous potassium carbonate. There was finally obtained: Fraction I, b. p. 62–97.5°, 58 ml.; Fract. II, b. p. 97.5–100°, 28 ml.; Fract. III, b. p. 100–120°, 130 ml.; Fract. IV, b. p. 120–120.5°, 99 ml.; Fract. V, b. p. 120.5–131°, 48 ml.; Fract. VI, b. p. 131–132°, 36 ml.; and Fract. VII, residue, 85 ml. Fractions IV and VI, consisting predominately of the isomeric methoxypropanols, represent yields of 15 and 6% of 1-methoxypropanol-2 and 2-methoxypropanol-1, respectively. The low-boiling and intermediate fractions are estimated to contain 155 g. of the isomeric methoxypropanols corresponding to an additional 25% of the theoretical yield.

Fraction IV, 1-methoxypropanol-2, was redistilled through a 40-cm. glass helices-packed column, and the center portion, b. p. 118.3°, used for physical constants and derivatives. This material still has a slight unpleasant odor. 1-Methoxypropanol-2 was found to form an azeotrope with water, b. p. 97.2–98.0°. When this azeotrope was saturated with potassium carbonate, the decrease in volume was such as to indicate the azeotrope contained approximately 65% of the alcohol.

Fraction VI, 2-methoxypropanol-1, was redistilled through a 60-cm. Widmer column and a middle fraction used for physical constants and derivatives. This material still had an unpleasant odor and gave a positive Schiff test and a positive test with a saturated 2 *N* hydrochloric acid solution of 2,4-dinitrophenylhydrazine. 2-Methoxypropanol-1 also formed an azeotrope boiling at 98°, and on treatment with potassium carbonate the decrease in volume indicated the azeotrope contained approximately 33% of the alcohol.

Fraction VII was redistilled through a glass helices packed column and gave a series of fractions distilling over the range 130–190°. The 130–140° fraction (25 ml.) gave a 0.1% yield of the 2,4-dinitrophenylhydrazone of pyruvic aldehyde, insoluble in alcohol and toluene, m. p. 298° with decomp. after recrystallization from nitrobenzene.¹⁸ From the 140–180° fraction (12 ml.), the 2,4-dinitrophenylhydrazone of propionaldehyde was isolated in about 1% yield. The 183–190° fraction (10 ml.) consisted of propylene glycol, identified by its p-nitrobenzoate ester and by an alkoxyl determination as mentioned by Pregl for glycerol.

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Summary

1. The structures of 1-methoxypropanol-2 and 2-methoxypropanol-1, previously obtained only from propylene oxide and methanol, have been established by independent syntheses.

2. 1-Methoxypropanol-2 is the only isomer detected in the sodium methoxide catalyzed reaction of propylene oxide and methanol.

3. The acid catalyzed condensation of propylene oxide and methanol gives a mixture of both isomers from which 2-methoxypropanol-1 can be separated in poor yield.

4. 2-Methoxypropanol-1 is obtained in a pure state by the copper chromite catalyzed hydrogenolysis of ethyl α -methoxypropionate.

(18) Ingold, Pritchard and Smith, *J. Chem. Soc.*, 83 (1934).

(11) Leonard, *Gazz. chim. ital.*, **33**, I, 322 (1903); Beilstein, 4th ed., Vol. **15**, 475 (1932).

(12) Pavlic and Adkins, *THIS JOURNAL*, **68**, 1471 (1946).

(13) Fuson and Wojcik, "Organic Syntheses," Coll. Vol. II, 260 (1944).

(14) (a) Brown, Anton and Weisbach, *Ber.*, **63B**, 2860 (1930); (b) Purdie and Irvin, *J. Chem. Soc.*, **75**, 486 (1899).

(15) Ref. 13, p. 261.

(16) Schreiner, *Ann.*, **197**, 13 (1879).

(17) Prepared by a method similar to that described by Adkins in "Organic Syntheses," Coll. Vol. II, 144, note 11 (1944).

5. The isomeric methoxypropanols can be characterized by their 3,5-dinitrobenzoates and α -naphthyl urethans.

6. Each of the isomeric methoxypropanols forms an azeotrope with water.

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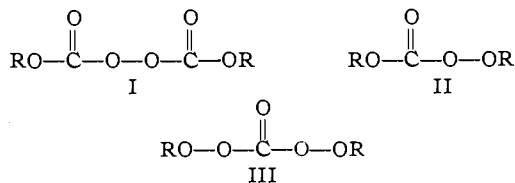
Esters of Peroxycarbonic Acids

BY F. STRAIN, W. E. BISSINGER, W. R. DIAL, H. RUDOFF,¹ B. J. DEWITT, H. C. STEVENS AND J. H. LANGSTON²

Diethyl peroxydicarbonate (I, R = C₂H₅), obtained in impure form by Wieland, vom Hove and Borner, is described³ as an explosive oil of extreme instability, decomposing at moderate temperatures, and possessing the sharp ozone-like odor of volatile acyl peroxides. The preparative method consisted of the reaction of ethyl chloroformate in chloroform solution with powdered sodium peroxide, promoted by a drop or two of water added to the dry reagents. Control of the reaction was difficult. The instability of the compound, under the conditions of preparation and attempted purification by distillation, probably accounted for their failure to obtain a product of greater than 88% purity.

Our preliminary experiments confirmed this description, and further demonstrated that the diethyl and other esters of peroxydicarbonic acid could be prepared readily by the careful reaction of chloroformates with aqueous sodium peroxide solutions, and that the products were effective polymerization catalysts for several ethenoid monomers. A series of the esters was therefore prepared for further observation of their properties.

While the present paper is concerned chiefly with the aforementioned esters of peroxydicarbonic acid (Type I), illustrative preparations of the related esters of monoperoxydicarbonic acid (Type II) and of diperoxydicarbonic acid (Type III), derived from the reactions of a chloroformate



and phosgene, respectively, with *t*-butyl hydroperoxide in the presence of acid acceptors are also included. Although the identity of some of the inorganic salts of peroxydicarbonic acids has been disputed,⁴ structures corresponding to formulas

of Types I, II and III have been assigned.⁵ Preparation of esters of these three types tends to support further the plausibility of the assigned structures of these salts.

Esters of Type I.—The ready availability of many chloroformates from the alcohols and phosgene affords access to a variety of the dialkyl and substituted dialkyl peroxydicarbonates. Some of the chloroformates used were prepared by the common procedure of passing phosgene into the cooled alcohol,^{6a,b} but a number were obtained by an improved method in which the alcohol was added to an established pool of the chloroformate containing some phosgene, which refluxed and served to cool the reaction mixture. The latter method enabled maintenance of an excess of phosgene throughout the reaction without the necessity for handling large quantities^{7a,b} of liquid phosgene. This improved procedure also gave increased yields, and often a chloroformate of higher purity than the simpler method. Chloroformates employed in this investigation included a number previously unreported. These are listed in Table I, along with hitherto unreported characterizing data upon the isopropyl and allyl compounds.

The preparative procedure for the esters of Type I consisted of careful addition of cold aqueous sodium peroxide solutions (or slurries) to the cooled chloroformate⁸ with efficient mixing. Due to the high degree of thermal instability and danger of violent decomposition observed for a number of the esters at temperatures only slightly above the temperature (0–10°) of preparation, special care was required in temperature control in all of the operations of preparation and purification. The chief impurity present in the crude esters was the alcohol formed by hydrolysis of the chloroformate. Since this impurity was easily removed from the crude lower alkyl esters by washing with cold water to give a product of high

(5) F. Ephraim, "Inorganic Chemistry," Fourth Edition revised, Nordeman Publishing Co., Inc., New York, N. Y., 1943, p. 842.

(6) (a) See Dyson, *Chem. Revs.*, **4**, 149–150 (1927), for a review of early literature references to the preparation of chloroformates from alcohols and phosgene; (b) see Huntress, "Organic Chlorine Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, index pp. 1420–1421, and text indicated for references and reported properties on many of the chloroformates used.

(7) (a) Ashburn, Collett and Lazzell, *THIS JOURNAL*, **60**, 2933 (1938); (b) Slimowicz and Degering, *ibid.*, **71**, 1043 (1949).

(8) F. Strain, U. S. Patent 2,370,588, Feb. 27, 1945.

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(3) Wieland, vom Hove and Borner, *Ann.*, **446**, 46 (1925).

(4) Tanatar, *Ber.*, **32**, 1544 (1899); Wolfenstein and Peltner, *ibid.*, **41**, 280–297 (1908); Le Blanc and Zellerman, *Z. Elektrochem.*, **29**, 179, 192 (1923); Kamtikar and Husain, *J. Osmania Univ. Coll.*, **2**, 39 (1934).