

aldehydes from the corresponding halides except for the difficulty of obtaining the ethyl *N*-phenylformimidate, a reagent which is now easily available.

Experimental

Materials.—Ethyl orthoformate, Eastman Kodak Co., redistilled, b. p. 142–144°; *N,N'*-diphenylformamidine (m. p. 138.5–139.5°, cor.), *N,N'*-di-*p*-tolylformamidine (m. p. 141.4–142.8°, cor.), prepared from the amines and ethyl orthoformate⁷; aniline hydrochloride, *p*-toluidine hydrochloride, prepared from the amines and concentrated hydrochloric acid, dried in a vacuum desiccator.

***N,N'*-Diphenylformamidine and Ethyl Orthoformate.**
A. Aniline Hydrochloride as Catalyst.—In a 200-ml. flask was placed 19.6 g. (0.10 mole) of *N,N'*-diphenylformamidine, 29.6 g. (0.20 mole) of ethyl orthoformate and 1.0 g. (0.008 mole) of dry aniline hydrochloride. An efficient 40-cm. distilling column having a total reflux partial take-off type head was attached and the reaction mixture was heated. Ethanol began to reflux immediately. After one hour of reflux the ethanol was distilled; 6.7 ml. was collected in about fifteen minutes. Anhydrous potassium carbonate (2.0 g.) was added and the mixture was shaken and allowed to stand two hours. The reaction mixture was then distilled through the same column under reduced pressure. Excess ethyl orthoformate was first recovered, 12.3 g., b. p. 83–85° (93 mm.). The pressure was then lowered to 40 mm. and colorless ethyl *N*-phenylformimidate distilled constantly at 117° (40 mm.); 28.7 g. or 96% of the theoretical amount was obtained.

The difference in the conditions under which the two steps of the reaction take place is illustrated by the following experiment. A mixture of 0.40 mole of aniline and 0.60 mole of ethyl orthoformate was heated in a flask to which was attached a 40-cm. distilling column. During one and one-quarter hours 36 ml. of ethanol distilled and then the distillation practically stopped. Aniline hydrochloride (1.30 g., 0.01 mole) was added to the reaction mixture and heating was resumed; distillation of ethanol now took place again at a rapid rate and 11.5 ml. was collected in thirty minutes, then the evolution practically stopped again. Anhydrous potassium carbonate (2.60 g.) was added and the mixture was distilled under reduced pressure. The excess ethyl orthoformate (27.2 g.) was removed first, b. p. 83° (90 mm.), then the product was distilled at 10-mm. pressure; 53.2 g. (89% of the amount calculated from aniline was obtained, b. p. 87–88° (10 mm.), n_D^{25} 1.5275 (lit., 1.52787⁸).

B. Sulfuric Acid as Catalyst.—Aniline (1 mole), ethyl orthoformate (1.5 moles) and sulfuric acid (10 drops, ca. 0.04 mole) were heated under reflux thirty minutes and then 117 ml. of ethanol was distilled through a short column. The catalyst was neutralized with 3.5 g. of dry sodium *t*-butoxide and the mixture was distilled under reduced pressure. After the excess ethyl orthoformate was recovered, 121.6 g. (82% of the theoretical amount) of ethyl *N*-phenylformimidate was obtained, b. p. 117–119° (40 mm.).

C. Acetic Acid as Catalyst.—*N,N'*-Diphenylformamidine (0.10 mole), ethyl orthoformate (0.20 mole) and glacial acetic acid (0.6 ml., 0.01 mole) were heated under reflux for one hour, then 4.5 g. of distillate, b. p. 76–80°, was collected during forty minutes; the distillation temperature then began to rise sharply. Ethyl orthoformate (ca. 17 g.) was recovered at 82–83° (90 mm.), and 14.6 g. (55% of the theoretical amount calculated from 0.09 mole of *N,N'*-diphenylformamidine) of ethyl *N*-phenylformimidate was obtained, b. p. 117–118° (40 mm.).

***N,N'*-Di-*p*-tolylformamidine and Ethyl Orthoformate; *p*-Toluenesulfonic Acid as Catalyst.**—*N,N'*-Di-*p*-tolylformamidine (0.10 mole), ethyl orthoformate (0.20 mole) and *p*-toluenesulfonic acid (0.001 mole) were heated in a 100-ml. flask to which was attached a 15-cm. Vigreux col-

umn with a total reflux partial take-off head. After one hour of reflux 5.8 ml. of ethanol, b. p. 75–79°, was removed. Calcium carbonate was added and the mixture was stirred overnight. Distillation of the filtered reaction mixture gave ca. 12 ml. of ethyl orthoformate, b. p. 83° (93 mm.), and 24.0 g. of ethyl *N*-*p*-tolylformimidate,⁴ b. p. 133.5–134° (40 mm.). This was 74% of the calculated amount of product.

Treatment of *p*-toluidine or *N,N'*-di-*p*-tolylformamidine with ethyl orthoformate in the presence of *p*-toluidine hydrochloride or sulfuric acid as described above gave similar results—yields of 74–76% of ethyl *N*-*p*-tolylformimidate.

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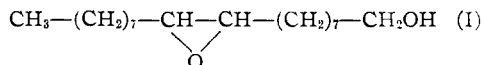
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Chemistry of Epoxy Compounds. X.¹ Polymerization of the Isomeric 9,10-Epoxyoctadecanols

BY DANIEL SWERN AND GERALDINE N. BILLEN

The thermal polymerization of the isomeric 9,10-epoxystearic acids was recently reported.² The present note reports the results of the thermal polymerization of the isomeric 9,10-epoxyoctadecanols (I), m. p. 54 and 48°, respectively, in



the presence of naphthalene-2-sulfonic acid as catalyst.

Starting Materials.—The isomeric 9,10-epoxyoctadecanols, m. p. 54 and 48°, were prepared from oleyl³ and elaidyl⁴ alcohols, respectively, by epoxidation with peracetic⁵ or perbenzoic acid.⁶ Calcd. for $\text{C}_{18}\text{H}_{34}\text{O}_2$, oxirane oxygen,⁷ 5.62%; found, 5.62%.

Polymerization Procedures.—9,10-Epoxyoctadecanol (either isomer) and the required quantity of naphthalene-2-sulfonic acid were mixed and then ground until the catalyst was uniformly distributed. Approximately 5-g. portions of the mixture were then weighed into a series of test-tubes which had been flushed with nitrogen or carbon dioxide. After being filled, the tubes were again flushed with inert gas, stoppered tightly, and then immersed in a constant-temperature oil-bath which maintained the desired temperature to $\pm 0.2^\circ$. Fifteen minutes was allowed for the establishment of temperature equilibrium before the polymerization time was counted. During the equilibration period, the tubes were shaken occasionally to ensure homogeneity. At selected time intervals, a tube was removed from the oil-bath, cooled rapidly to room temperature, and then analyzed within twenty-four hours.

(1) For the previous paper in this series, see *THIS JOURNAL*, **71**, 2219 (1949).

(2) Swern, Billen and Eddy, *THIS JOURNAL*, **70**, 1228 (1948).

(3) Swern, Knight and Findley, *Oil and Soap*, **21**, 133 (1944).

(4) Swern, Jordan and Knight, *THIS JOURNAL*, **68**, 1673 (1946).

(5) Swern, Findley and Scanlan, *ibid.*, **66**, 1925 (1944).

(6) Findley, Swern and Scanlan, *ibid.*, **67**, 412 (1945).

(7) Swern, Findley, Billen and Scanlan, *Anal. Chem.*, **19**, 414 (1947); Nicolet and Poulter, *THIS JOURNAL*, **52**, 1186 (1930).

(7) Roberts, *J. Org. Chem.*, **14**, 277 (1949).

(8) Schmidt, *Z. physik. Chem.*, **58**, 523 (1907).

Analytical Procedures.—Analyses were carried out as previously reported.² Carbonyl oxygen was determined by the procedure reported by Knight and Swern.⁸

Discussion

Figure 1 shows the course of the catalyzed polymerization of 9,10-epoxyoctadecanol (ol), m. p. 54°, at 60, 80, 90 and 100°. Figure 2

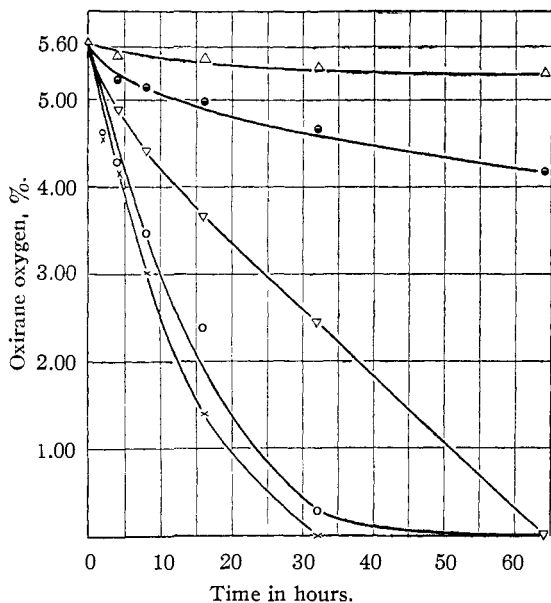


Fig. 1.—Thermal polymerization of 9,10-epoxyoctadecanol(ol), m. p. 54°, with naphthalene-2-sulfonic acid as catalyst: O, 90°, 2% catalyst; Δ, 60°, 0.75% catalyst; ×, 100°, 2% catalyst; ●, 80°, 0.75% catalyst; ▽, 100°, 0.75% catalyst.

shows the course of the catalyzed polymerization of 9,10-epoxyoctadecanol (el), m. p. 48°, at 80, 90, 100, 120 and 140°. These data may be briefly summarized as follows: (a) under identical conditions, the high-melting epoxyoctadecanol (ol) polymerizes at a more rapid rate than does the low-melting isomer (el); (b) both isomers can be converted to viscous liquids if the polymerization is permitted to proceed far enough; (c) when the oxirane oxygen value is substantially zero, the molecular weight is about 900, or approximately that of a trimer; (d) in all the polymerizations except the one at 60°, about 20 to 30% of the reduction in oxirane oxygen can be accounted for by isomerization to the carbonyl group; (e)

in two cases in which the comparison has been made, molecular weights determined ebullioscopically in benzene differ from those calculated from the oxirane oxygen analyses by only 7 to 15%; (f) the isomerization of the oxirane group to the carbonyl group is a function of both the temperature and the percentage of catalyst, although there appears to be no simple relationship involved; and (g) the refractive index of the polymers levels off at 1.462 to 1.464 (60°).

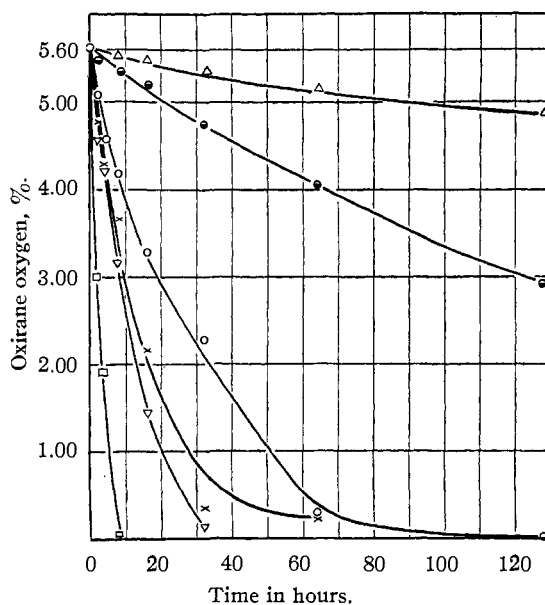
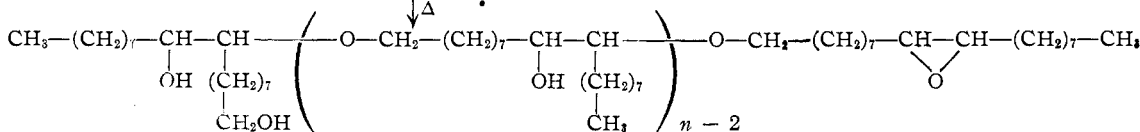


Fig. 2.—Thermal polymerization of 9,10-epoxyoctadecanol(el), m. p. 48°, with naphthalene-2-sulfonic acid as catalyst: O, 90°, 2% catalyst; Δ, 80°, 0.75% catalyst; ▽, 120°, 0.75% catalyst; ×, 100°, 2% catalyst; ●, 100°, 0.75% catalyst; □, 140°, 0.75% catalyst.

On the basis of the data reported here and the known reactions of oxirane groups, it can be concluded that the main reactions which occur during the thermal polymerization of the 9,10-epoxyoctadecanols are (a) a condensation reaction between the oxirane and primary hydroxyl groups, yielding a polyether, as shown in Equation 1, and (b) isomerization of the oxirane group to the carbonyl group. All the polymers are readily soluble in the common organic solvents, with the exception of petroleum naphtha, thus indicating that cross-linking reactions occur only to a limited extent, if at all.



(8) Knight and Swern, *J. Am. Oil Chem. Soc.*, **26**, 366 (1949).

No information is available on the occurrence

of other possible acid-catalyzed condensation and addition reactions, such as dioxane or polyethylene oxide formation.²

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(9) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Note not copyrighted.

NEW COMPOUNDS

2-Methyl-4,6-Dichlorophenoxyacetic Acid

2-Methyl-4,6-dichlorophenoxyacetic Acid.—4,6-Dichloro-*o*-cresol¹ (3.82 g.) dissolved in 10 ml. of aq. 20% sodium hydroxide was added hot in 1-ml. portions to a hot solution of 4.75 g. of chloroacetic acid in 10 ml. of 20% sodium hydroxide, and the mixture refluxed for four hours. The solution was then made acid and the precipitate removed by filtration. It was dissolved in dilute sodium carbonate and the excess phenol extracted with ether. The product was precipitated from the carbonate solution with acid and crystallized from alcohol-water; yield 3.3 g., m. p. 187–187.5°.

Anal. Calcd. for C₉H₈O₃Cl₂: C, 45.95; H, 3.40. Found: C, 45.87; H, 3.54.

This compound was checked for plant growth activity using the Avena test. The work was done by Dr. Robert Muir, Dept. of Botany, University of Iowa. The compound was found to be inactive. Complete results of these tests will be published elsewhere.

(1) Claus and Riemann, *Ber.*, **16**, 1598 (1883).

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Some Derivatives of Benzylvanillin and Benzylvanillic Acid

The benzyl ethers of the monochloro and monobromo derivatives of vanillin and benzyl-2-nitrovanillin were prepared by the alkylation of the appropriate vanillin derivative and benzyl chloride in the presence of sodium hydroxide.¹

Benzyl Ethers of Derivatives of Vanillic Acid.—Five grams of the benzyl ether of the requisite vanillin derivative was dissolved in 50 cc. of pyridine and the solution heated

(1) Späth, Orechhoff and Kufner, *Ber.*, **67B**, 1214-1217 (1934).

to 60–70°. A hot (90–100°), concentrated aqueous solution of 5 g. of potassium permanganate was added in small portions. A vigorous reaction ensued with the immediate precipitation of manganese dioxide. The mixture was cooled and filtered. The residue was washed with a little pyridine and the filtrate and washing were combined. The manganese dioxide in the residue was dissolved in sodium bisulfite solution and dilute hydrochloric acid. A white precipitate remained which was extracted with ethyl ether. The pyridine was removed from the filtrate by steam distillation and the residue was extracted with the ether previously used. The ether layer was repeatedly extracted with sodium hydroxide solution until acidification gave no precipitate. The aqueous extracts were combined, acidified and the resultant precipitate filtered, washed with water and dried. It was then recrystallized from the appropriate solvent (either aqueous ethanol or aqueous acetic acid). The properties of some benzyl ethers of derivatives of vanillin and vanillic acid are listed in the accompanying table. The ethers crystallized as colorless needles except where otherwise noted.

BENZYL ETHERS OF DERIVATIVES OF VANILLIN AND OF VANILIC ACID

Substituent	Yield, %	M. p., °C.	Halogen, % Calcd.	% Found
Vanillin Derivatives				
2-Bromo-	48	99–99.5	24.88	24.61
5-Bromo-	52	49–50	24.88	24.80
6-Bromo-	71	96–97	24.88	24.83
2-Chloro-	73	94	12.81	12.79
5-Chloro-	54	43–44	12.81	12.80
6-Chloro-	58	101–102 ^a	12.81	12.92
2-Nitro-	41	106–107 ^b		
Vanillic Acid Derivatives				
2-Bromo-	74	162–163 ^c	23.70	23.73
5-Bromo-	83	157–157.2	23.70	23.77
6-Bromo-	76	173–174	23.70	23.64
2-Chloro-	74	149–150	12.11	11.94
5-Chloro-	81	154	12.11	12.01
6-Chloro-	60	164–165	12.11	12.09
2-Nitro-	78	183–184 ^d	4.62 ^e	5.08 ^e

^a Pale orange prisms. ^b Brown needles. ^c Light yellow needles. ^d White plates. ^e % Nitrogen.

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