It is to be understood that an assumption basic to the present work is that the variations in rate observed are a true reflection of differences in ΔH^* (or ΔF^*) alone, and hence are solely dependent on potential energy differences. This implies that the entropies of activation for the various detriisopropylsilylations studied are essentially constant, or at least exhibit *no definite trends* as the *m*-alkyl group is made to vary from methyl to *t*-butyl. While this supposition may at first be an uncomfortable one in view of the small rate differences observed, there is definite evidence that it is valid. Thus in the mercuration of *t*-butylbenzene[15] and toluene,[16] the ΔS^* values for *m*- and *p*-substitution have been calculated and found to be constant within experimental error. This same constancy has been noted as well in recent nitration studies of ethyl benzoate.[17] In fact, wherever ΔS^* values have been determined for reactions of *m*- and *p*-substituted benzene derivatives, they provide little assurance of being anything but random.[18]

Experimental

m-Alkylbromobenzenes.—The *m*-bromotoluene used was a commercial product. *m*-Bromoethylbenzene was prepared by a Clemmensen reduction of *m*-bromoacetophenone.[19]

m-Bromoacetophenone also was used as an intermediate in the synthesis of *m*-bromocumene. Treatment of this haloketone with the methyl Grignard reagent produced *m*-bromophenyldimethylcarbinol in 71% yield. This carbinol was dehydrated (60–70%) by vacuum distillation (twice) in the presence of iodine catalyst. The resulting olefin, 2-(*m*-bromophenyl)-propylene was reduced in ethanol in a Parr hydrogenator with platinum oxide catalysis. *m*-Bromocumene was obtained in 85% yield. The physical constants of these compounds were in good agreement with those previously reported.[20]

m-Bromo-*t*-butylbenzene was obtained by a procedure already described in the literature[21].

Aryltriisopropylsilanes.—Previous directions were used to synthesize phenyltriisopropylsilane.[22]

The *m*-substituted arylsilanes were all prepared by the reaction of the appropriate aryllithium derivative with triisopropylchlorosilane.[23] The directions which follow for the preparation of *m*-*t*-butylphenyltriisopropylsilane may be considered as typical of all of these preparations.

***m*-*t*-Butylphenyltriisopropylsilane.**—To 0.84 g. (0.12 g. atom) of freshly cut lithium ribbon in 75 ml. of ether under nitrogen was added, dropwise, 11.4 g. (0.0535 mole) of *m*-bromo-*t*-butylbenzene. The refluxing which started during this addition was continued for 90 minutes, whereupon triisopropylchlorosilane (10.3 g., 0.0535 mole) was added. The refluxing was continued for 26 hours. After the mixture was poured onto ice, the organic layer was separated and dried over Drierite. Distillation through an 18-inch Vigreux column gave a low boiling fraction (b.p. 30–39° (2 mm.)) and a high boiling fraction. The latter fraction was redistilled through a glass spiral Todd column and yielded 2.4 g. (15%) of the silane (b.p. 118.5–119.5° (1 mm.), n^{21}D 1.5019).

Experimental variables for the preparation of the other *m*-substituted silanes as well as some physical constants of these compounds are summarized in Table III.

TABLE III

PREPARATION OF *m*-SUBSTITUTED ARYLTRIISOPROPYLSILANES

m-$RC_6H_4Si(i\text{-}C_3H_7)_3$

R groups	Reflux time, hr.	Boiling Pt. °C.	Mm.	n^tD	t, °C.	Yield, %
CH_3[a,d]	66	[b]		[b]		31
C_2H_5[c,e]	70.5	106.5–107.5	0.5	1.5072	24	49
i-C_3H_7[f]	26	111–112	1	1.5004	25	18
t-C_4H_9[g]	26	118.5–119.5	1	1.5019	21	15

[a] Excess triisopropylchlorosilane employed (0.104 mole to 0.073 mole of *m*-bromotoluene). [b] Solid, m.p. 53°, after recrystallization from methanol. [c] Excess triisopropylchlorosilane employed (0.104 mole to 0.068 mole of *m*-bromoethylbenzene). [d] *Anal.* Calcd. for $C_{16}H_{28}Si$: C, 77.4; H, 11.3. Found: C, 77.13; H, 11.1. [e] *Anal.* Calcd. for $C_{17}H_{30}Si$: C, 77.8; H, 11.45. Found: C, 77.54; H, 11.43. [f] *Anal.* Calcd. for $C_{18}H_{32}Si$: C, 78.3; H, 11.6. Found: C, 78.20; H, 11.91. [g] *Anal.* Calcd. for $C_{19}H_{34}Si$: C, 78.6; H, 11.7. Found: C, 78.35; H, 11.78.

The cleavage rates were measured by dilatometric techniques which were described previously.[24]

Acknowledgments.—The authors are grateful to the Monsanto Chemical Co. and the National Science Foundation for fellowship aid which made this work possible.

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[CONTRIBUTION FROM THE SHELL DEVELOPMENT CO., EMERYVILLE, CALIF.]

Chemistry of Glycidaldehyde[1]

BY PAUL H. WILLIAMS, GEORGE B. PAYNE, WILLIAM J. SULLIVAN AND PAUL R. VAN ESS

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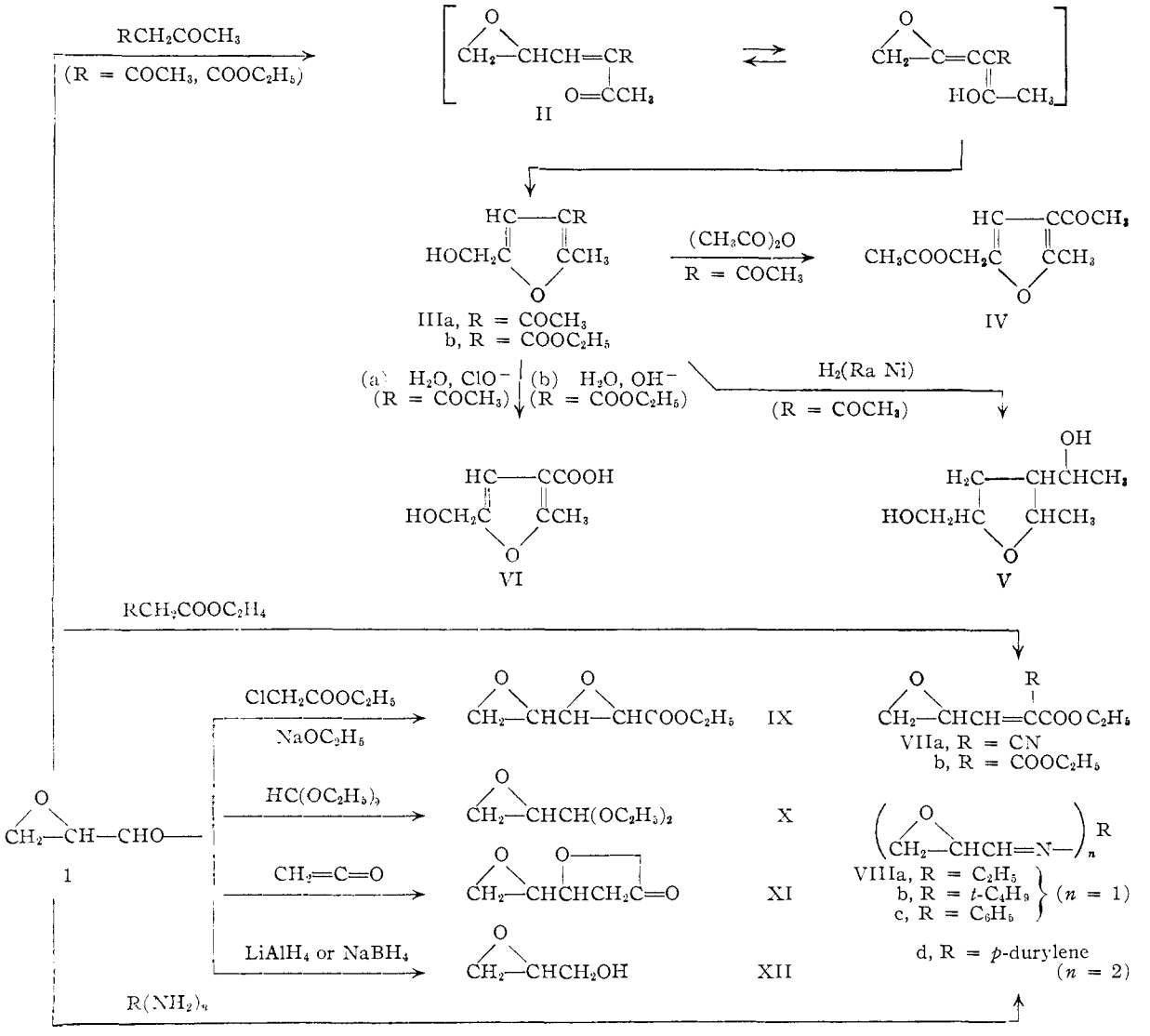
Glycidaldehyde condenses with acetylacetone and ethyl acetoacetate to form furan derivatives. It combines through its carbonyl group with cyanoacetic and malonic esters, primary amines, ethyl chloroacetate, ethyl orthoformate, ketene and hydrogen cyanide to yield products in which the oxirane ring is retained. It is reduced to glycidol with metal hydride reducing agents. The addition of active hydrogen compounds under acidic conditions yields β-substituted lactaldehydes and their derivatives.

The synthesis of glycidaldehyde (I) by the reaction of acrolein with alkaline hydrogen peroxide, and its isolation and characterization as a pure substance were reported recently.[2] Some of the carbonyl and epoxide reactions of glycidaldehyde are described in this paper.

The reactions of glycidaldehyde with reagents which attack the carbonyl group are given in the diagram. In most of these the epoxide group remains

(1) Presented in part before the Division of Organic Chemistry at the 135th National Meeting of the American Chemical Society, April, 1959.
(2) G. B. Payne, THIS JOURNAL, **80**, 6161 (1958); **81**, 1001, (1959).



intact. The reactions with acetylacetone and ethyl acetoacetate, in the presence of piperidine acetate, are believed to be novel in that furan derivatives, 4-acetyl-5-methyl-2-furfuryl alcohol (IIIa) and 4-carbethoxy-5-methyl-2-furfuryl alcohol (IIIb),[3] respectively, are formed. The initial step in each reaction is very likely a Knoevenagel-type condensation between the reagent and the glycidaldehyde carbonyl group, followed by ring closure through the enolic hydroxyl and epoxy group of the intermediate condensate II. As might be expected from its greater methylenic activity, acetylacetone condensed more readily than the acetoacetic ester and the yield of product was considerably greater.

The structure of IIIa was established by elemental and functional group analyses, positive iodoform test, and the close resemblance of its infrared absorption spectrum to that of 3-acetyl-2,5-dimethylfuran; acetylation of IIIa gave a corresponding acetate (IV), and hydrogenation afforded a product analyzing as 4-(1′-hydroxyethyl)-5-methyl-2-tetrahydrofurfuryl alcohol (V). The structure of IIIa was confirmed further and that of IIIb simultaneously established by oxidizing IIIa with potassium hypochlorite to 5-hydroxymethyl-2-methyl-3-furoic acid (VI); this acid was identical with that obtained on hydrolyzing IIIb.

Two other active methylenic compounds, ethyl cyanoacetate and diethyl malonate, yielded typical Knoevenagel condensates with glycidaldehyde, the absence of enolizable carbonyl groups in the products precluding their cyclization to furan compounds. The structures of the respective products, ethyl 2-cyano-4,5-epoxy-2-pentenoate (VIIa) and ethyl 2-carbethoxy-4,5-epoxy-2-pentenoate (VIIb), were assigned on the basis of elemental composition, oxirane oxygen content and infrared spectrum.

The reaction of primary aliphatic and aromatic amines with glycidaldehyde occurs very readily and is directed exclusively to the aldehyde group at

(3) F. G. González, R. E. Berciano, J. M. R. González and F. J. L. Aparicio, *Anales real soc. espan fis y quim. (Madrid)*, **50B**, 311 (1954); *C. A.*, **49**, 5422 (1955), report that this alcohol is the product obtained on condensing glyceraldehyde and ethyl acetoacetate in the presence of zinc chloride.

ordinary temperatures. The N-glycidylideneamines (VIIIa-c) and N,N-bis-(glycidylidene)-1,4-diaminodurene (VIIId) obtained in this manner are described in the table. Their identification was on the basis of elemental and oxirane oxygen analyses. The analogous reactions with hydroxylamine and 2,4-dinitrophenylhydrazine to form the oxime and the hydrazone of glycidaldehyde were reported previously.[2]

The product of the Darzens condensation of glycidaldehyde with ethyl chloroacetate and sodium ethoxide, ethyl 2,3,4,5-diepoxypentanoate (IX), was identified by its elemental composition and oxirane oxygen content. The latter corresponded to but one epoxy group, which is consistent with the finding that simple α,β-epoxycarboxylic esters are not reactive under the conditions of the analytical procedure used.

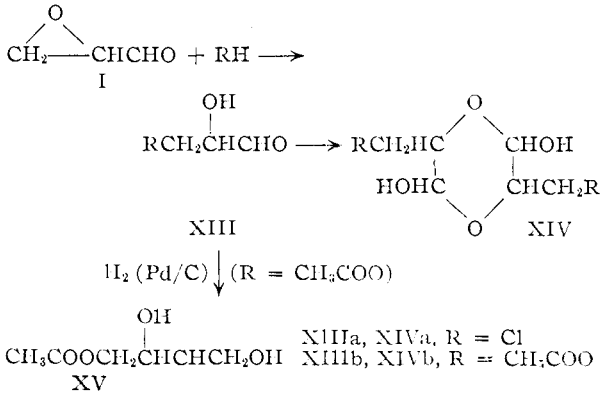
Glycidaldehyde diethyl acetal (X) is conventionally synthesized from the chlorohydrin of acrolein diethyl acetal by the action of alkalies. Its preparation from glycidaldehyde and ethyl orthoformate is convenient and efficient.

The addition of ketene to the carbonyl group of glycidaldehyde occurs readily in the presence of zinc chloride. The product, isolated in 45% yield based on aldehyde charged, was identified as the lactone of 4,5-epoxy-3-hydroxyvaleric acid (XI) by elemental and functional group analyses and by the infrared spectrum of the compound.

Glycidaldehyde readily added hydrogen cyanide in the presence of a small amount of triethylamine. Analysis of the solvent-free but undistilled product indicated it to be impure glycidaldehyde cyanohydrin. *On standing at room temperature, a sample of this product spontaneously decomposed with charring and evolution of hydrogen cyanide.*

Reduction of glycidaldehyde with potassium borohydride in aqueous ethanol and with lithium aluminum hydride in anhydrous ether in each instance, yielded glycidol (XII).

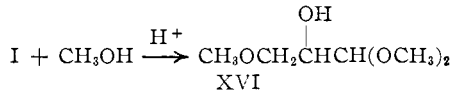
The epoxide ring of glycidaldehyde was found to open with compounds containing active hydrogens to give primarily β-substituted lactaldehydes (XIII).



Anhydrous hydrogen chloride at room temperature gave a near-quantitative yield of β-chlorolactaldehyde (XIIIa), which separated from the reaction mixture as a white crystalline solid. With acetic acid, reaction was slow even at reflux temperature; the distilled product, β-acetoxylactaldehyde (XIIIb), crystallized to a white solid on standing for several weeks.

The crystalline products of these two reactions are cyclic dimers (XIV). Their structures (and thus also the structures of their monomeric precursors) were assigned principally on the basis of composition, chemical behavior, molecular weight and infrared spectra. The latter were consistent with the cyclic hemi-acetal (1,4-dioxane) structures characteristic of dimers of α-hydroxyaldehydes such as lactaldehyde and glyceraldehyde[4]; in the case of the chloro compound XIVa the spectrum clearly excluded structures containing a free carbonyl group. The molecular weight values for the crystalline products, which corresponded approximately to the calculated values, indicate the dimeric character of the products, and together with the spectral evidence seem adequate confirmation of the proposed structures. The molecular weight of freshly distilled (liquid) XIIIb corresponded closely to the theoretical for the monomeric substance. Hydrogenation of XIIIb afforded glycerol α-acetate (XV).

The acid-catalyzed reaction of methanol in gross excess with glycidaldehyde results in a 77% yield of product XVI analyzing as the dimethyl acetal of a hydroxymethoxypropionaldehyde. Hydrolysis of XVI and analysis of the resulting product for α-glycol indicated that XVI was at least 90% β-methoxylactaldehyde dimethyl acetal; the remainder was probably the isomeric substance, α-methoxyhydracrylaldehyde dimethyl acetal.



Experimental

Glycidaldehyde was obtained by the epoxidation of acrolein with alkaline hydrogen peroxide.[2] It had b.p. 57–58° (100 mm.) and was of 98% or better purity by oxirane oxygen determination.[5]

Condensations with Active Methylene Compounds (Knoevenagel Reaction.—The procedure was a modification of that described[6] for the reductive condensation of butyraldehyde with ethyl cyanoacetate.

1. **4-Acetyl-5-methyl-2-furfuryl Alcohol.**—A solution of 50 g. (0.50 mole) of acetylacetone (Claisen-distilled, b.p. 135°) and 36 g. (0.50 mole) of glycidaldehyde in 80 ml. of acetic acid was treated with a solution of 1 ml. of piperidine in 20 ml. of acetic acid. After standing overnight at room temperature, the mixture was allowed to warm on the steam-bath for 0.5 hour. After removal of solvent at 50 mm. pressure, the product was Claisen-distilled to give 62 g. (81%) of viscous yellow liquid, b.p. 110–115° (1 mm.).

Anal. Calcd. for $C_8H_{10}O_3$: C, 62.3; H, 6.5; carbonyl value, 0.65 equiv./100 g.; hydroxyl value, 0.65 equiv./100 g.; bromine no. (one molar equiv.), 104 g./100 g. Found: C, 62.1; H, 6.6; carbonyl value,[7] 0.65 equiv./100

(4) See C. B. Kremer and L. K. Rochen, "Heterocyclic Compounds," R. C. Elderfield, Editor, Vol. 6, John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 6–10, for a brief review of these dimeric structures.

(5) By hydrogen chloride in aqueous magnesium chloride solution; see J. L. Jungnickel, E. D. Peters, A. Polgar and F. T. Weiss, "Organic Analysis," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1953, p. 134.

(6) E. R. Alexander and A. C. Cope, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 385.

(7) By Karl Fischer reagent method (see J. Mitchell, Jr., "Organic Analysis," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1953, p. 260).

TABLE I

N-GLYCIDYLIDENE AMINES FROM REACTION OF GLYCIDALDEHYDE WITH PRIMARY AMINES

Reactant	Product	B.p., °C.	Mm.	$n^{20}D$	Yield, %	Analyses, % Calculated C	H	N	Oxirane oxygen	Found C	H	N	Oxirane oxygen[a]
t-Butylamine	N-(Glycidylidene)-*t*-butylamine	40–45	8	1.4431	82	66.1	10.3	11.0	12.6	66.2	10.4	10.9	12.3
Ethylamine	N-(Glycidylidene)-ethylamine	46–47	26	1.4397	69	60.6	9.2	14.1	16.2	61.0	9.2	13.6	15.2
Aniline	N-(Glycidylidene)-aniline	58–59	0.2	1.5776	94	73.5	6.2	9.5	10.9	73.4	6.5	9.7	10.1
p-Durylenediamine	N,N′-Bis-(glycidylidene)-1,4-diaminodurene	[b]		....	54	70.6	7.4	10.3	..	70.6	7.5	10.2	

[a] By HCl–$MgCl_2$ solution (see ref. 5). [b] M.p. 155–165°.

g.; hydroxyl value ($LiAlH_4$), 0.66 equiv./100 g.; bromine no., 107 g./100 g.

The viscous liquid product was converted to solid by dissolving it in an equal volume of ether and chilling in the refrigerator. A recovery of 80% in the first crop was possible, m.p. 37–39°; recrystallized from acetone, m.p. 39–40°. It was soluble in water and benzene.

The infrared spectrum of the product was virtually identical with that of 3-acetyl-2,5-dimethylfuran (preparation below). It had maxima at 2.95 μ (hydroxyl), 5.97 (carbonyl) 6.20 (conjugated double bond), 6.37, 7.11, 8.11, 8.78, 9.45, 9.89 and 10.58 μ. The model compound, of course, had no hydroxyl absorption: it did have maxima at 5.97, 6.19, 6.36, 7.12, 8.10, 8.72, 9.45, 9.93 and 10.59 μ.

4-Acetyl-5-methyl-2-furfuryl Acetate.—A solution of 9.3 g. (0.06 mole) of 4-acetyl-5-methyl-2-furfuryl alcohol in 25 ml. of acetic anhydride was allowed to reflux for 16 hours. It was then Claisen-distilled to give 9.6 g. of fluid, pale yellow liquid, b.p. 96–98° (1 mm.), $n^{20}D$ 1.4935.

Anal. Calcd. for $C_{10}H_{14}O_5$: C, 61.2; H, 6.2; carbonyl value, 0.51 equiv./100 g.; bromine no. (for one molar equiv.), 81 g./100 g. Found: C, 61.3; H, 6.2; carbonyl value,[7] 0.52 equiv./100 g.; bromine no., 81 g./100 g.

4-(1′-Hydroxyethyl)-5-methyl-2-tetrahydrofurfuryl Alcohol.—A solution of 15.0 g. (0.097 mole) of 4-acetyl-5-methyl-2-furfuryl alcohol in 100 ml. of water was shaken in an autoclave with one teaspoon of Raney nickel and hydrogen at 500 p.s.i.g. and 35–40° temperature. After 6 hours, three molar equivalents of hydrogen had been adsorbed and uptake was then very slow. After shaking overnight the total uptake amounted to 3.3 molar equivalents; no further hydrogen absorption was noted on heating to 100°. After cooling, venting and catalyst removal, the product was Claisen-distilled to give 6.6 g. (44%) of colorless, viscous diol, b.p. 105–110° (<1 mm.). The infrared spectrum showed no carbonyl remaining, and the analysis was in substantial agreement for the expected product.

Anal. Calcd. for $C_8H_{16}O_3$: C, 60.1; H, 10.1; hydroxyl value, 1.25 equiv./100 g. Found: C, 60.1; H, 10.2; hydroxyl value ($LiAlH_4$), 1.33 equiv./100 g.

3-Acetyl-2,5-dimethylfuran.[8]—To a stirred solution of 24 g. (0.25 mole) of 2,5-dimethylfuran (redistilled, b.p. 93–94°, in 250 ml. of benzene was added 29 g. (0.28 mole) of acetic anhydride. A solution of 65 g. (0.25 mole) of stannic chloride in 50 ml. of benzene was added over 30 minutes at 15–20°. After stirring one hour longer at the same temperature, the mixture was poured onto 300 g. of ice and 100 ml. of 6 *N* hydrochloric acid was added. The benzene layer was separated and the aqueous layer was extracted with three 200-ml. portions of ether. The combined organic extract was washed with water and dried over magnesium sulfate; after concentrating to low volume on the steam-bath, the product was distilled through a 1 × 50 cm. glass spiral column to give 30 g. (87%), b.p. 65–66° (5 mm.), $n^{20}D$ 1.4881.

2. 4-Carbethoxy-5-methyl-2-furfuryl Alcohol.—A solution of 72 g. (1.0 mole) of glycidaldehyde and 140 g. (1.11 moles) of ethyl acetoacetate in 160 ml. of acetic acid was added to a solution of 2 ml. of piperidine in 40 ml. of acetic acid. The mixture was maintained at 40–50° for 8 hours. Acetic acid was then flashed off under reduced pressure; the residue was taken up in ether, washed with water, dried over magnesium sulfate and distilled through a 1 × 50 cm. glass spiral column. There was obtained 117 g. (63%) of product, b.p. 126–127° (<1 mm.), $n^{20}D$ 1.4918.

Anal. Calcd. for $C_9H_{12}O_4$: C, 58.7; H, 6.6; sapon. equiv., 184; bromine no. (for one molar equiv.), 87 g. Br/100 g. Found: C, 58.8; H, 6.6; sapon. equiv., 176; bromine no., 86 g. Br/100 g.

5-Hydroxymethyl-2-methyl-3-furoic Acid. A. By Hydrolysis of 4-Carbethoxy-5-methyl-2-furfuryl Alcohol.—This alcohol (9.2 g., 0.05 mole) and 45 ml. of 2 *N* aqueous sodium hydroxide were heated together at 95–100° for 1 hour. The resulting solution was cooled to 0° and 20 ml. of 4 *N* hydrochloric acid was added. The solid which separated was filtered, dried and recrystallized from ether-alcohol to give 7.3 g. (93.5%) of white solid, m.p. 155–155.5° (lit.[3] m.p. 153–155°).

Anal. Calcd. for $C_7H_8O_4$: C, 53.8; H, 5.1; neut. equiv., 156. Found: C, 53.2; H, 5.2; neut. equiv., 161.

B. By Oxidation of 4-Acetyl-5-methyl-2-furfuryl Alcohol.—To a 250-ml. aqueous solution containing 0.46 equivalent (6 g. titration) of potassium hypochlorite was added slowly and with stirring 15.4 g. (0.1 mole) of 4-acetyl-5-methyl-2-furfuryl alcohol, maintaining the temperature at 60–70°. The mixture was stirred an additional 30 minutes and then 50 g. of sodium bisulfite in 100 ml. of water was added. The solution was cooled in an ice-bath, acidified with dilute hydrochloric acid, saturated with ammonium sulfate and extracted with ether. The extract was dried over magnesium sulfate and then concentrated under reduced pressure to a residue of 10.2 g. This was crystallized from ether-alcohol, giving 8.4 g. (54%), m.p. 154–155°, mixed m.p. 154–155° with sample of the previously prepared (A) acid.

3. Ethyl 2-Cyano-4,5-epoxy-2-pentenoate.—A solution of 56.5 g. (0.60 mole) of ethyl cyanoacetate and 43 g. (0.60 mole) of glycidaldehyde in 80 ml. of acetic acid was treated with a solution of 2 ml. of piperidine in 20 ml. of acetic acid and allowed to stand at ambient temperature. After 1 hour the maximum temperature of 38° was reached. After standing 2 hours longer, the mixture was diluted with 200 ml. of water and extracted with three 200-ml. portions of benzene. The combined extracts were washed with 200 ml. of water and dried over magnesium sulfate. After removal of the solvent on the steam-bath, the residue was Claisen-distilled to give 66 g. (79%) of product, b.p. 80–85 (<1 mm.), $n^{20}D$ 1.4850. The product (in chloroform) absorbed at 4.49 (C≡N), 5.78 (C=O) and 6.04 μ (C=C) in the infrared.

Anal. Calcd. for $C_8H_9NO_3$: C, 57.5; H, 5.4; N, 8.4; oxirane oxygen, 9.6. Found: C, 57.4; H, 5.5; N, 8.3; oxirane oxygen,[9] 9.3.

4. Ethyl 2-Carbethoxy-4,5-epoxy-2-pentenoate.—A solution of 40 g. (0.55 mole) of glycidaldehyde and 80 g. (0.50 mole) of diethyl malonate ($n^{20}D$ 1.4134) in 150 ml. of acetic

(8) Procedure of R. A. Lutz and R. J. Rowlett, THIS JOURNAL, **70**, 1350 (1948), for acetylating the 2,5-diphenyl compound.

(9) By hydrogen chloride in dioxane (see ref. 5, p. 1350).

acid containing 5 ml. of piperidine was allowed to stand at room temperature for 4 days. The mixture then was diluted with 500 ml. of water and extracted with three 200-ml. portions of chloroform. The combined extracts were concentrated on the steam-bath and Claisen-distilled to give 50 g. of recovered diethyl malonate, b.p. 38–42° (<1 mm.), $n^{20}D$ 1.4130, and 22 g. of product, b.p. 80–85° (<1 mm.), $n^{20}D$ 1.4625. The yield was 55% based on a 37% conversion of diethyl malonate. Redistillation of the product fraction gave pure material, b.p. 107–108° (1 mm.), $n^{20}D$ 1.4667. The infrared spectrum of the product (in chloroform) showed absorption at 5.78 (C=O) and 6.04 μ (C=C).

Anal. Calcd. for $C_{10}H_{14}O_5$: C, 56.1; H, 6.6: sapon. equiv., 107; oxirane oxygen, 5.9. Found: C, 56.1; H, 6.6; sapon. equiv., 107; oxirane oxygen,[9] 6.2.

Reaction with Primary Amines.—The procedure used with *t*-butylamine was typical. Chilled solutions of 15.8 g. (0.22 mole) of glycidaldehyde and of 14.5 g. (0.20 mole) of *t*-butylamine (Rohm and Haas), each in 50 ml. of benzene, were combined and allowed to stand at room temperature for several hours. The water which separated was removed by means of magnesium sulfate. The filtered and solvent-free reaction mixture was Claisen-distilled to give 10.4 g. (82% yield based on the amine) of colorless product (see Table I for physical properties and analysis of this and the products similarly obtained with other amines). The infrared spectrum of N-(glycidylidene)-ethylamine was examined; it showed the expected absorption for the imino group (5.98 μ).

Reaction with Ethyl Chloroacetate.—To 140 g. (1.1 moles) of ethyl chloroacetate and 72 g. (1.0 mole) of glycidaldehyde at 0–10° was added 55 g. (1.01 moles) of sodium methoxide over a 4-hour period. The reaction mixture was allowed to stir an additional 2 hours while it came to room temperature. The product then was dissolved in ether and washed with cold, saturated aqueous ammonium sulfate solution. Ether was removed under reduced pressure and the crude product was distilled to give 64 g. (48% yield at 84% conversion of glycidaldehyde) of ethyl 2,3,4,5-diepoxypentanoate, b.p. 124–125° (5 mm.).

Anal. Calcd. for $C_7H_{10}O_4$: C, 53.1; H, 6.3; oxirane oxygen, 20.2. Found: C, 52.6; H, 6.4; oxirane oxygen,[9] 10.2.[10]

Glycidaldehyde Diethyl Acetal.—A mixture of 206 g. (3.0 moles) of glycidaldehyde, 540 g. (3.65 moles) of ethyl orthoformate, 2 g. of ammonium nitrate and 29 ml. of ethanol was distilled through a 10-tray Oldershaw column to remove ethyl formate as formed, b.p. 54–55°. In about one hour almost all of the ethyl formate had been removed. The residual material was flashed from the catalyst and redistilled to give 333 g. (76%) of **glycidaldehyde diethyl acetal**, b.p. 115–117° (140 mm.), $n^{20}D$ 1.4145 (lit.[11] values: b.p. 60–64° (13 mm.), $n^{25}D$ 1.4128).

Reaction with Ketene.—To 0.2 mole of ketene (freshly generated from acetone) and 0.5 g. of zinc chloride in 300 ml. of ether was added 28.8 g. (0.4 mole) of glycidaldehyde. The addition required 15 minutes, during which the reaction mixture was maintained at 0–10° by cooling and was stirred vigorously. After an additional 30 minutes the ether solution was filtered to remove the catalyst and a small amount of polymer which had formed. After removal of ether under reduced pressure, Claisen distillation of the residual material gave 9.5 g. (42%) of a colorless liquid (which immediately turned a pale yellow), b.p. 84–86° (1–2 mm.), $n^{20}D$ 1.4530; infrared absorption at 5.45 μ, characteristic of a β-lactone. Analysis of this product was in agreement for the β-lactone of **4,5-epoxy-3-hydroxyvaleric acid**.

Anal. Calcd. for $C_5H_8O_3$: C, 52.6; H, 5.3; oxirane oxygen, 14.0; sapon. equiv., 114. Found: C, 52.5; H, 5.4; oxirane oxygen,[9] 13.5; sapon. equiv., 113.

Addition of Hydrogen Cyanide.—To 0.20 mole of hydrogen cyanide, as a 4.6% wt. dioxane solution, was added 14.4 g. (0.20 mole) of glycidaldehyde and then 0.1 g. of triethylamine as catalyst. The temperature rose to 30–35° and was held there by cooling. When the reaction no longer was exothermic the mixture was allowed to stand at room temperature for 2 hours and evaporated under vacuum (20–25° at 1 mm.), leaving 18.8 g. (95%) of bottoms product which was believed to be crude **glycidaldehyde cyanohydrin.**

Anal. Calcd. for $C_4H_5NO_2$: N, 14.1; oxirane oxygen, 16.2. Found: N, 12.9; oxirane oxygen,[9] 14.1.

The product was 87% pure by oxirane oxygen analysis. It was soluble in water, methanol and warm ethanol, but less soluble in ether and benzene. On standing at room temperature for several hours, it *vigorously decomposed with evolution of hydrogen cyanide;* a sample stored in the refrigerator slowly decreased in oxirane oxygen content and became an amber-colored solid.

Reduction with Potassium Borohydride.—A solution of 5.6 g. (0.10 mole) of 97% purity potassium borohydride in 25 ml. of water was added dropwise with stirring at 20–25° over 0.5 hour to a solution of 28.8 g. (0.40 mole) of glycidaldehyde in 250 ml. of ethanol. The indicated *p*H (meter) was maintained at 9.0 ± 0.3 by simultaneous addition of 15% sulfuric acid. After completion of the borohydride addition, the mixture was allowed to stir 0.5 hour longer; titration for epoxide at that time indicated the presence of 0.38 mole (95% retention) of epoxy group. The solution was dried at room temperature and 20 mm. to remove solvent; the resulting residue was taken up in ether and filtered to remove insoluble salt. After removal of the ether at the water-pump, the residue was Claisen-distilled to give 15 g. (51%) of glycidol, b.p. 47–51° (8 mm.), $n^{20}D$ 1.4305.[12] The oxirane oxygen content[5] was 21.3 (calcd. for $C_3H_6O_2$, 21.6).

Reduction with Lithium Aluminum Hydride.—A solution of 3.8 g. (0.1 mole) of lithium aluminum hydride in 400 ml. of anhydrous ether was added over a 1-hour period to a vigorously stirred solution of 31 g. (0.44 mole) of glycidaldehyde in 400 ml. of anhydrous ether. After the reaction mixture was stirred for an additional hour, 4 ml. of water was added cautiously. The reaction mixture then was stirred for several hours, filtered and dried over magnesium sulfate. The ether was removed under reduced pressure. Analyses of the bottoms product (23.4 g., 80% conversion) by gas–liquid chromatography, using a non-polar Ucon column at 150°, showed it to contain 72% glycidol and 28% of unidentified product which was possibly 1,2-propanediol. Chemical analysis indicated only 0.006 equiv./100 g. of carbonyl[13]; oxirane oxygen content,[5] 0.95 equiv./100 g. or 70.5%; and α-glycol,[14] 0.38 equiv./100 g. or 28.8%.

Reaction with Hydrogen Chloride.—To a stirred solution of 36 g. (0.50 mole) of glycidaldehyde in 525 g. of chloroform held at 10–15° was added slowly (over 30 minutes) 135 g. (0.70 mole) of cold ethereal hydrogen chloride. On further standing at 5° there was deposited 32 g. of white solid, m.p. 136–137°, whose analysis corresponded to β-**chlorolactaldehyde** (**dimer**). The infrared spectrum of this compound (Nujol mull) showed no free carbonyl; there was absorption for hydroxyl (2.87 μ), ether oxygen (8.80 μ) and chlorine (13.3 μ).

Anal. Calcd. for $C_6H_{10}Cl_2O_4$: C, 33.2; H, 4.7; Cl, 32.7; carbonyl value (free and combined), 0.92 equiv./100 g.; mol. wt., 217. Found: C, 33.2; H, 4.7; Cl, 32.3; carbonyl[13] value (at 60° for 2 hours) 0.92 equiv./100 g.; mol. wt. (ebull., dioxane), 230.

The mother liquor from the first crop of solid was concentrated to a volume of about 100 ml. and treated with 20 ml. of 3 *N* ethereal hydrogen chloride. Chilling afforded another 22 g. of product, m.p. 135°. The 54 g. total of product thus obtained represented virtually a quantitative yield based on glycidaldehyde charged.

Reaction with Acetic Acid.—A mixture of 18 g. (0.25 mole) of glycidaldehyde and 70 g. (0.86 mole) of glacial acetic acid was refluxed for 24 hours (after 4 hours, 38.5% of epoxide remained). Excess acetic acid and unreacted glycidaldehyde were then removed by distillation at atmospheric pressure. The residue was distilled to give 14 g. (70% yield at 62% conversion) of β-acetoxylacetaldehyde, b.p. 114–115° (1 mm.).

(10) In a parallel analysis ethyl 2,3-epoxybutyrate was observed not to react with hydrochloric acid under the conditions of the oxirane oxygen determination.

(11) D. I. Weisblat, *et al.*, THIS JOURNAL, **75**, 5893 (1953), prepared this acetal from the chlorohydrin of acrolein diethyl acetal.

(12) An authentic sample, prepared by epoxidizing allyl alcohol, had b.p. 54–55° (10 mm.), $n^{20}D$ 1.4310.

(13) By hydroxylamine hydrochloride reagent (see ref. 7, p. 259).

(14) By periodic acid oxidation method (see V. C. Mehlenbacher, "Organic Analyses," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1953, p. 45.

Anal. Calcd. for $C_5H_8O_4$: carbonyl value, 0.76 equiv./100 g.; mol. wt., 132. Found: carbonyl value,[13] 0.75 equiv./100 g.; mol. wt. (ebull., benzene–water azeo.), 134.

On standing for 3 weeks, the distilled product had crystallized to the solid dimer, m.p. 115–116°; after recrystallization from acetone, m.p. 131–132° (lit.[15] m.p. 118.5°). The infrared spectrum of this product (Nujol mull) showed strong absorption for hydroxyl (2.90 μ) and either ester or aldehyde carbonyl (5.78 μ); ether-oxygen absorption was not clearly distinguishable.

Anal. Calcd. for $C_{10}H_{16}O_8$: C, 45.45; H, 6.1; carbonyl (combined) value, 0.76 equiv./100 g.; mol. wt., 268. Found: C, 45.4; H, 6.0; carbonyl[13] value (at 60° for 2 hours), 0.78 equiv./100 g.; mol. wt. (ebull., dioxane), 235.

Glycerol α-Acetate.—β-Acetoxylactaldehyde (monomeric liquid) (6.5 g.) in 200 ml. of ethanol was hydrogenated at 50 p.s.i.g. and 25° with Pd-on-carbon catalyst. After the one equivalent of hydrogen had been absorbed, the catalyst was removed by filtration and the solvent distilled under reduced pressure. Claisen-distillation of the residue gave 5.8 g. (89%) of **glycerol α-acetate**, b.p. 134–135° (4 mm.), $n^{20}D$ 1.4490 (lit.[16] b.p. 129–131° (3 mm.), $n^{20}D$ 1.4500).

Anal. Calcd. for $C_5H_{10}O_4$: C, 44.8; H, 7.5; sapon. equiv., 134; α-glycol value, 0.75 equiv./100 g. Found: C, 44.6; H, 7.6; sapon. equiv., 135; α-glycol value,[14] 0.73 equiv./100 g.

(15) H. O. L. Fischer and E. Baer, *Ber.*, **65**, 341 (1932).

(16) H. A. Schuette and J. T. Hale, THIS JOURNAL, **52**, 1978 (1930).

Reaction with Methanol.—A solution of 36 g. (0.50 mole) of glycidaldehyde in 100 ml. (2.5 moles) of methanol was added to a solution of 5 ml. of sulfuric acid in 1400 ml. of methanol. The mixture warmed by itself to 40° and was then allowed to cool to room temperature overnight. After adding barium carbonate to neutralize the acid, the mixture was filtered through filter aid and concentrated to low volume on the steam-bath. Claisen-distillation of the residue afforded 57.6 g. (77%) of product, b.p. 60–62° (2 mm.), $n^{20}D$ 1.4253, whose analysis was in agreement for **β-methoxylactaldehyde dimethyl acetal.**

Anal. Calcd. for $C_6H_{14}O_4$: C, 48.0; H, 9.4; hydroxyl value, 0.67 equiv./100 g. Found: C, 47.9; H, 9.4; hydroxyl value ($LiAlH_4$), 0.67 equiv./100 g.

The unneutralized product from a similar preparation with 9.0 g. (0.125 mole) of glycidaldehyde was freed of unreacted methanol and diluted with water to a volume of 100 ml. The solution was brought to 0.26 *N* acidity by the addition of 0.50 ml. of sulfuric acid, and allowed to stand at room temperature. Hydrolysis of the acetal was followed by a modified α-glycol procedure[17] which quantitatively determines α-hydroxyaldehydes. A constant value of 0.113 equiv./100 ml. of α-hydroxyaldehyde was reached after 9 days, indicating that the hydrolyzed product was at least 90% β-methoxylactaldehyde. On this basis, the distilled β-methoxylactaldehyde dimethylacetal obtained in the preceding experiment may have contained some of the isomer, α-methoxyllydracrylaldehyde.

(17) The periodic acid method for α-glycols (ref. 14) was modified by using sodium periodate in buffered neutral solution. With this reagent, the theoretical values were obtained with glyceraldehyde and other α-hydroxy aldehydes.

[CONTRIBUTION FROM THE NATIONAL RESEARCH COUNCIL, OTTAWA 2, CANADA]

Co-catalysis in Friedel–Crafts Reactions. III. Reaction between 2-Butene and Anhydrous Perchloric Acid

BY STEPHEN J. TAUBER* AND A. M. EASTHAM

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The preparation and handling of anhydrous perchloric acid in a vacuum system are described. Reaction of the acid with *cis*-2-butene in ethylene dichloride solution leads to very rapid absorption of two or three moles of olefin per mole of acid, but the rate of isomerization of the olefin is very slow. The spectrum of the reaction mixture shows three absorption bands in the visible region, each apparently corresponding to a different compound or complex, but no structures have been assigned to the chromophores.

The concept of co-catalysis in Friedel-Crafts reaction was put forward by Polanyi, Evans and coworkers[1] to explain the results of their studies of isobutylene polymerization. They considered that the coördination compound of the catalyst and cocatalyst was a very strong acid which initiated polymerization by protonation of the olefin, *i.e.*

$$BF_3 + H_2O \rightleftharpoons BF_3{\cdot}OH_2 \xrightarrow{>C{=}C<} >CH{-}C^+< \;\ldots\ldots\; BF_3{^-}OH$$

It has become increasingly apparent in recent years that this simple scheme is inadequate because the reaction rates of a number of processes are dependent upon higher powers of the catalyst concentration than would be expected from the above equation. In previous papers we have reported some attempts to study the catalyst systems by measuring the rates of isomerization of *cis*- and *trans*-2-butenes brought about by boron fluoride and water.[2] The results of those experiments suggested that the rate of isomerization was given by the expression

$$dI/dt = k(BF_3)(BF_3{\cdot}H_2O)(\text{butene})$$

but subsequent experiments indicate that the order in butene may be less than one.

Concurrently with these studies we have been attempting a more direct test of the Polanyi hypothesis by employing perchloric acid as the catalyst. Because of the experimental difficulties, progress has been very slow, but the preliminary results now seem worth reporting. Perchloric acid is probably the only very strong, non-nucleophilic acid suitable for this purpose because its preparation and properties permit it to be handled entirely within a vacuum system while its solubility in numerous organic solvents should permit a study of its reactions. Unfortunately, the acid reacts readily, even in the anhydrous state, with mercury and with stopcock grease so must be handled when possible in a completely closed system using break seals for transferring materials.

Experimental

The apparatus devised for preparing and manipulating the acid is shown in Fig. 1. The method of preparation

* N.R.L. Postdoctorate Fellow, 1957–1959.

(1) A. G. Evans and J. Polanyi, *J. Chem. Soc.*, 252 (1947).

(2) A. M. Eastham, THIS JOURNAL, **78**, 6040 (1956); J. M. Clayton and A. M. Eastham, *ibid.*, **79**, 5368 (1957).