Benzylation of β-hydroxy ester III *to give* VII. To a stirred suspension of 0.1 mole of lithium amide in 300 ml. of anhydrous liquid ammonia was added 15 g. (0.5 mole) of β-hydroxy ester III in 25 ml. of anhydrous ether. After stirring the resulting suspension for 20 min., 6.33 g. (0.5 mole) of benzyl chloride in 15 ml. of ether was added slowly. A gray precipitate formed immediately. The mixture was stirred for 1 hr. and was then inversely neutralized with ammonium chloride. The ammonia was evaporated and replaced by ether. Water was added and the aqueous layer was thoroughly extracted by ether. The combined ether solution was dried over magnesium sulfate and evaporated to a colorless oily residue having the odor of benzyl chloride. Treatment of the residue with 95% ethanol permitted crystallization of 3 g. (10%) of *t*-butyl α-benzyl-β-hydroxy-β,β-diphenylpropionate (VII) in the form of needle-like crystals, m.p. 104–105°. The infrared spectrum showed carbonyl absorption at 5.8 μ, and hydroxyl absorption at 2.75 μ.

Anal. Calcd. for $C_{26}H_{28}O_3$: C, 80.37; H, 7.26. Found: C, 80.29; H, 7.19.

The filtrate from above was reduced in volume and cooled to yield 8.6 g. (57%) of recovered starting ester III, m.p. 92–93° after a second crystallization from ethanol.

Treatment of ethyl acetate with excess lithium amide followed by benzyl chloride. To a stirred suspension of 1.0 mole of lithium amide in 600 ml. of liquid ammonia was added 44 g. (0.5 mole) of ethyl acetate in an equal volume of ether. The resulting gray suspension was stirred for 2 min. and 126.6 g. (1.0 mole) of benzyl chloride in 80 ml. of ether was added. After stirring for 1 hr. the ammonia was replaced by ether and the resulting mixture neutralized with cold, dilute hydrochloric acid. There was obtained 33 g. (26%) of recovered benzyl chloride b.p. 66–68° at 20 mm., and 18.2 g. (22%) of ethyl hydrocinnamate, b.p. 245–248° at 758 mm.; reported[20] b.p. 247° at 760 mm. The temperature of the distillate then rose rapidly to about 300°, at which temperature stilbene began to clog the column and apparatus. There was obtained 15.2 g. (17%) of crude stilbene, m.p. 119–120°. After recrystallization from ethanol (Norit), the product melted at 122–123°; reported[21] m.p. 124°.

Treatment of benzophenone with lithium amide followed by ethyl acetate. To a stirred suspension of 0.4 mole of lithium amide in 400 ml. of liquid ammonia was added 36.4 g. (0.2 mole) of benzophenone in 100 ml. of anhydrous ether. The gray suspension was stirred for 20 min., and 17.6 g. (0.2 mole) of ethyl acetate in an equal amount of ether was added. The resulting dark black solution was stirred for 1 hr. and was then neutralized with ammonium chloride. There was obtained 30.2 g. (84%) of recovered benzophenone, m.p. 47–48°, none of β-hydroxy ester I being isolated.

Condensation of lithioethyl acetate with acetone. To a stirred suspension of 0.62 mole of lithium amide in 400 ml. of anhydrous liquid ammonia was added 44 g. (0.5 mole) of ethyl acetate in an equal volume of ether. The resulting gray suspension was stirred for 2 min., and 21 g. (0.5 mole) of acetone (dried over magnesium sulfate) in a little anhydrous ether was added. The resulting black solution was stirred for 1 hr. and was then inversely neutralized with ammonium chloride. The ammonia was replaced by 300 ml. of ether, and 150 ml. of cold water was added. After thorough extraction of the aqueous layer with ether, the combined ethereal solution was dried and evaporated. The residue was distilled to give 16 g. (25%) of ethyl β-hydroxy-β-methylbutyrate (VIII), b.p. 175–176° at 738 mm.; reported[22] b.p. about 180°.

Anal. Calcd. for $C_7H_{14}O_3$: C, 57.51; H, 9.65. Found: C, 57.41; H, 9.65.

When the reaction was repeated allowing the condensation to proceed for 1 hr. instead of 10 min., a 25% yield of hydroxy ester VIII was obtained.

DURHAM, N. C.

---

[20] W. H. Perkin, *J. Chem. Soc.*, **69**, 1025 (1896).

[21] T. W. J. Taylor and A. R. Murray, *J. Chem. Soc.*, 2079 (1938).

[22] A. Semljanizen and A. Saytzeff, *Ann.*, **197**, 73 (1897)

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, UNION CARBIDE CHEMICALS CO.]

The Oxidation of Unsaturated Acetals and Acylals with Peracetic Acid

DONALD L. HEYWOOD AND BENJAMIN PHILLIPS

Received March 18, 1960

A series of unsaturated dioxolanes, acetals, and acylals based on α,β-unsaturated aldehydes were prepared and oxidized with peracetic acid. The major products in most cases were the anticipated epoxides, but when noncyclic acetals were used, or when the reaction was catalyzed by sulfuric acid, the predominant products of oxidation were the corresponding unsaturated esters. The novel peracid oxidation of acetals to esters was found applicable to saturated acetals also.

The literature concerning epoxides of α,β-unsaturated aldehydes and their acetals and acylals is very sparse. The simplest member of the series, 2,3-epoxypropionaldehyde, has been referred to often in connection with the autoxidation of fats but was synthesized and statisfactorily characterized only recently.[1] Kögl prepared 2,3-epoxybutyraldehyde by lead tetraacetate cleavage of 2,3-6,7-diepoxyoctane-4,5-diol,[2] and the epoxides of 2-ethyl-2-hexenal and crotonaldehyde were prepared by sodium hypochlorite oxidation of the unsaturated aldehydes.[3] The diethyl and ethylene glycol acetals of 2,3-epoxypropionaldehyde were prepared by dehydrochlorination of the chlorohydrins,[4] and three other acetals (the diethyl and ethylene glycol acetals of 2,3-epoxypropionaldehyde and the ethylene glycol acetal of 2,3-epoxy-3-phenylpropionaldehyde) were prepared by perbenzoic acid

---

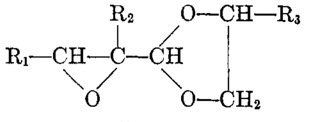
[1] G. B. Payne, *J. Am. Chem. Soc.*, **80**, 6461 (1958); **81**, 4901 (1959).

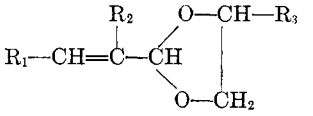
[2] F. Kögl and H. Veldstra, *Ann.*, **552**, 1 (1942).

[3] C. Shaer, *Helv. Chim. Acta*, **41**, 614 (1958).

[4] K. Taufel and P. Sadler, *Z. Untersuch. Lebensm.*, **65**, 540 (1933); *Chem. Abstr.*, **27**, 4702 (1933).

oxidation of the olefins.[5] The diethyl acetal of 2,3-epoxypropionaldehyde was also studied recently by Wright.[6] In the total synthesis of lysergic acid an intermediate of this type was also prepared.[7] Reaction of 2,3-dichloroaldehydes with sodium methoxide in methanol leads to the formation of the dimethyl acetals of 2,3-epoxyaldehydes.[8] Finally, an acylal, the diacetate of 2,3-epoxybutyraldehyde, and its hydrolysis to methylglyceraldehyde were reported recently.[9]


Epoxyalkyl dioxolanes
VI. $R_1 = C_6H_5$; $R_2 = H$; $R_3 = CH_3$


Unsaturated dioxolanes
VIa. $R_1 = C_6H_5$; $R_2 = H$; $R_3 = CH_3$

A series of epoxides of the cyclic acetals of α,β-unsaturated aldehydes were conveniently prepared in good yield by epoxidation of the unsaturated dioxolanes with peracetic acid in ethyl acetate solution.[10] Epoxides so prepared are listed in Table I; the unsaturated dioxolanes were prepared by standard methods by acid-catalyzed acetalization of the glycol and unsaturated aldehyde.

An unexpected reaction was observed when a noncyclic acetal (crotonaldehyde di-*n*-butyl acetal, VII) was oxidized with peracetic acid. A higher temperature of reaction for a comparable conversion (based on peracid consumption) was required than for epoxidation of the cyclic acetals, and the major product was the unsaturated ester, butyl crotonate, VIII, in 73% yield.

$$\underset{\text{VII}}{CH_3CH{=}CHCH(OC_4H_9)_2} \xrightarrow{CH_3CO_3H} \underset{\text{VIII}}{CH_3CH{=}CHCO_2C_4H_9}$$

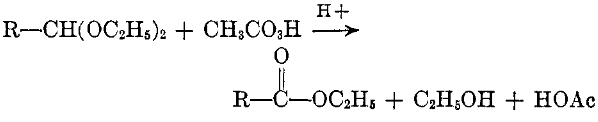
TABLE I

UNSATURATED DIOXOLANES AND EPOXIDES

Compound	Name	R_1	R_2	R_3
I	2-(1,2-Epoxypropyl)-1,3-dioxolane	CH_3	H	H
Ia	2-(1-Propenyl)-1,3-dioxolane	CH_3	H	H
II	2-(1,2-Epoxypropyl)-4-methyl-1,3-dioxolane	CH_3	H	CH_3
IIa	2-(1-Propenyl)-4-methyl-1,3-dioxolane	CH_3	H	CH_3
III	2-(1,2-Epoxy-1-methylethyl)-1,3-dioxolane	H	CH_3	H
IIIa	2-Isopropenyl-1,3-dioxolane	H	CH_3	H
IV	2-(1,2-Epoxy-1-ethylpentyl)-1,3-dioxolane	*n*-C_3H_7	C_2H_5	H
IVa	2-(1-Ethyl-1-pentenyl)-1,3-dioxolane	*n*-C_3H_7	C_2H_5	H
V	2-(1,2-Epoxy-1-ethylpentyl)-4-methyl-1,3-dioxolane	*n*-C_3H_7	C_2H_5	CH_3
Va	2-(1-Ethyl-1-pentenyl)-4-methyl-1,3-dioxolane	*n*-C_3H_7	C_2H_5	CH_3
VI	2-(1,2-Epoxy-2-phenylethyl)-4-methyl-1,3-dioxolane	C_6H_5	H	CH_3
VIa	2-(β-Styryl)-4-methyl-1,3-dioxolane	C_6H_5	H	CH_3

This reaction was found to be catalyzed by sulfuric acid. In fact, in the oxidation of an unsaturated cyclic acetal (VIa) from which the epoxide (VI) was isolated (45% yield) in the non-acid-catalyzed oxidation, none of the epoxide could be isolated from the acid-catalyzed oxidation. Only a high-boiling liquid which was difficult to purify could be isolated from the latter. The infrared spectrum and analysis of this liquid could be interpreted on the basis of a propylene glycol monocinnamate. The fairly large residues formed in the preparation of most of the epoxy-acetals may be attributable to this competing reaction.

Three saturated acetals (the diethyl acetals of butyraldehyde, benzaldehyde, and β-phenyl-β-ethoxypropionaldehyde) were oxidized with peracetic acid in the presence of sulfuric acid. These oxidations proceeded readily to give the corresponding ethyl esters, in yields of 69, 90, and 61%



$$R{-}CH(OC_2H_5)_2 + CH_3CO_3H \xrightarrow{H^+} R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OC_2H_5 + C_2H_5OH + HOAc$$

IX. $R = n\text{-}C_3H_7{-}$
X. $R = C_6H_5{-}$
XI. $R = C_6H_5{-}CH(OC_2H_5){-}CH_2{-}$

respectively. It was observed qualitatively that the oxidation proceeds most readily for those acetals in which an electron deficiency on the "aldehyde" carbon can be stabilized by an adjacent unsaturation.

In all the literature of peracids there is no indication of this reaction. The oxidation of acetals to the corresponding acids by air or oxygen is known,[11] but the free acid is the exclusive or major product. Very little free acid was observed in the present peracid oxidation, and concentrations of the (presumed) alcohol coproduct could not have been high enough for a mechanism involving intermediate formation of free unsaturated acid followed

---

(5) J. P. Fourneau and S. Chantalou, *Bull. Soc. Chim. France*, **12**, 845 (1945); *Chem. Abstr.*, **40**, 6465 (1946).

(6) J. B. Wright, *J. Am. Chem. Soc.*, **79**, 1694 (1957).

(7) E. C. Kornfeld, *et al.*, *J. Am. Chem. Soc.*, **78**, 3087 (1956).

(8) S. Searles, Jr., E. K. Ives, and H. M. Kash, *J. Org. Chem.*, 22, 919 (1957).

(9) G. Zasaki, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **78**, 113 (1957); *Chem. Zentr.*, **1957**, 6713.

(10) B. Phillips, F. C. Frostick, Jr., and P. S. Starcher, *J. Am. Chem. Soc.*, **79**, 5982 (1957).

(11) J. C. Martin and J. P. Hawk, U. S. Patent **2,887,512**, May 19, 1959.

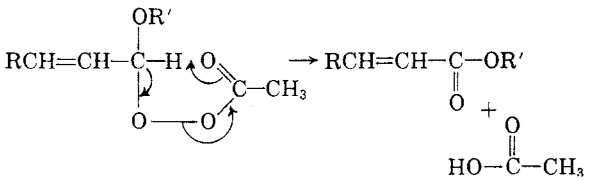
TABLE II

UNSATURATED DIOXOLANES

Compound	Yield, %	B.P., Mm.	n_D^{30}	Notes	Formula	Analysis Calcd. C	Calcd. H	Calcd. Equiv. Wt.	Found C	Found H	Found Equiv. Wt.[a]
Ia	35	71/50	1.4380	b,c	$C_6H_{10}O_2$	—	—	114	—	—	117
IIa	55	71–73/40	1.4304	d	$C_7H_{12}O_2$	65.59	9.44	128	64.80	9.28	132
IIIa	—	31/10	1.4311 at 21°	e	$C_6H_{10}O_2$	—	—	—	—	—	—
IVa	71	86–88/10	1.4486		$C_{10}H_{18}O_2$	70.54	10.66	170	70.59	10.64	171
Va	41	92–95/10	1.4441	c	$C_{11}H_{20}O_2$	71.69	10.94	184	71.74	11.04	187
VIa	90	109/2	1.5428	d	$C_{12}H_{14}O_2$	75.76	7.42	190	76.33	7.62	189

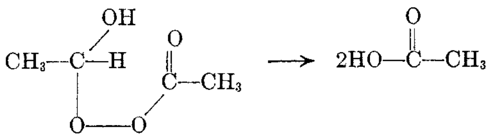
[a] See ref. 15. [b] Reported[5] b.p. 147°/760 mm. [c] No acid catalyst used. [d] 0.025% p-Methoxyphenol inhibitor added, and orthophosphoric acid catalyst used. [e] Prepared by H. A. Stansbury of this department.

by esterification. The ferrous ion induced decomposition of α-hydroperoxy ethers to esters is formally similar, although probably not mechanistically related, to the present oxidation.[12] It is possible that oxidation of the acetal to the ester proceeds through a hemiacetal peracetate (A), the formation of which would be catalyzed by strong acid



A

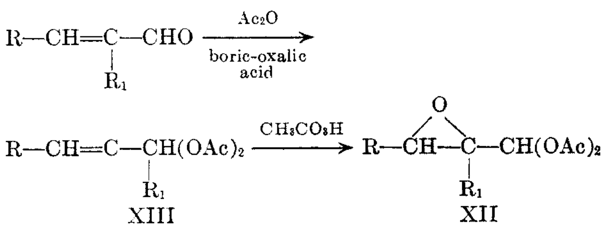
and which could decompose as indicated. A formal analogy is seen in the decomposition of acetaldehyde monoperacetate (B) to two molecules of acetic



B

acid.[10] However, other plausible mechanisms for oxidation of the unsaturated acetal to ester may be written, and it is not possible at present to define the most likely.

Two 1,1-diacetoxy-2-alkyl-2,3-epoxyalkanes (XII) were also prepared by peracetic acid epoxidation of the unsaturated acylals (XIII); the latter



were made by reaction of the unsaturated aldehydes with acetic anhydride, catalyzed by mixed boric-oxalic acid.[13] These were 1,1-diacetoxy-2-ethyl-2,3-epoxybutane (XII, R = CH_3, R_1 = C_2H_5) and 1,1-diacetoxy-2-ethyl-2,3-epoxyhexane (XII, R = n-C_3H_7, R_1 = C_2H_5.

EXPERIMENTAL

Preparation of unsaturated dioxolanes. The following preparations of *2-(1-ethyl-1-pentenyl)-1,3-dioxolane* (IVa) illustrates the method which, with minor modifications, was used for the other dioxolanes listed in Table II.

The following mixture was refluxed for 13 hr. in a flask equipped with a condenser and Dean-Stark trap for continuous removal of water as formed: 378 g. (3.0 moles) of 2-ethyl-3-propylacrolein, 186 g. (3.0 moles) of ethylene glycol, 1000 ml. of benzene, and 1.9 g. of p-toluenesulfonic acid monohydrate. During this time 55 g. of water was removed. The reaction mixture was neutralized with 1.06 g. of sodium carbonate and fractionated to give 361 g. (71% yield) of 2-(1-ethyl-1-pentenyl)-1,3-dioxolane, b.p. 86–88°/10 mm., n_D^{30} 1.4486; lit.,[14] b.p. 98–101°/20 mm., n_D^{25} 1.4510.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.54; H, 10.66; equiv. wt., 170.24. Found: C, 70.59; H, 10.64; equiv. wt., 171.[15]

Epoxidation of unsaturated dioxolanes. The preparation of *2-(1,2-epoxypropyl)-4-methyl-1,3-dioxolane* (II) is illustrative of the method used for preparation of the epoxides listed in Table III.

To 128 g. (1.0 mole) of 2-(1-propenyl)-4-methyl-1,3-dioxolane (IIa) was added 349 g. of a solution of peracetic acid in ethyl acetate[10] (24.0%; *i.e.*, containing 84 g. or 1.1 moles peracetic acid) over a period of 4 hr. During this period the reaction mixture was stirred vigorously, and the temperature was maintained at 40°. After an additional 7 hr. at 40°, titration for peracetic acid[10] indicated that 93% of the theoretical peracetic acid has been consumed. The cooled reaction mixture was fed into ethylbenzene under reflux at 30–40 mm. pressure, and a mixture of acetic acid, ethylbenzene, and ethyl acetate was removed at the head of the column. Fractionation of the residue gave 67 g. (46% yield) of 2-(1,2-epoxypropyl)-4-methyl-1,3-dioxolane, b.p. 81–83°/15 mm., n_D^{30} 1.4291.

---

(12) N. A. Milas, R. L. Peeler, Jr., and O. L. Mageli, *J. Am. Chem. Soc.*, **76**, 2322 (1954).

(13) This method of preparing acylals was developed and kindly furnished to us by L. W. McTeer, Development Department, Union Carbide Chemicals Company, U. S. Patent **2,866,813**, December 30, 1958.

(14) H. R. Nace and E. P. Goldberg, *J. Am. Chem. Soc.*, **75**, 3646 (1953).

(15) Double bond equivalent weights were determined by titration with bromine–sodium bromide reagent in methanol, a modification of the method outlined in S. Siggia, *Quantitative Organic Analysis via Functional Group*, 2nd ed., J. Wiley & Sons, N. Y., 1954, pp. 69–71.

TABLE III

EPOXYALKYL DIOXOLANES

Compound	Yield, %	B.P., Mm.	n_D^{30}	Formula	Analysis Calcd. C	Analysis Calcd. H	Analysis Found C	Analysis Found H
I	28	70–73/9[a]	1.4337	$C_6H_{10}O_3$	—	—	—	—
II	46	81–83/15	1.4291	$C_7H_{12}O_3$	58.31	8.39	57.83	8.32
III	64	78/20	1.4344	$C_6H_{10}O_3$	55.37	7.75	55.17	7.72
IV	67	90–93/5	1.4426	$C_{10}H_{18}O_3$	64.49	9.74	63.79	9.55
V	66	57–60/.4	1.4382	$C_{11}H_{20}O_3$	65.97	10.07	66.49	10.26
VI	45	111–112/1	1.5197	$C_{12}H_{14}O_3$	69.88	6.84	70.79	7.16

[a] Reported[5] b.p. 80°/18 mm.

Anal. Calcd. for $C_7H_{12}O_3$: C, 58.31; H, 8.39; equiv. wt., 144. Found: C, 57.83; H, 8.32; equiv. wt.,[16] 149.

Oxidation of crotonaldehyde dibutyl acetal with peracetic acid. Crotonaldehyde dibutyl acetal was prepared by a known method[17] and exhibited the following properties b.p. 96–99°/10 mm., n_D^{31} 1.4247.

Peracetic acid in ethyl acetate (117 g. of a 22.9% solution; *i.e.*, containing 26.8 g. or 0.352 mole peracetic acid) was added over a period of 1 hr. to 64 g. (0.32 mole) crotonaldehyde dibutyl acetal. The temperature was maintained at 60°, and titration for peracetic acid at the end of this period indicated that the theoretical amount was consumed. The cooled reaction mixture was fed into ethylbenzene under reflux at 35 mm., and ethylbenzene, acetic acid, and ethyl acetate were removed at the head of the column. Fractionation of the residue gave 33 g. (73% yield) of butyl crotonate, b.p. 75–80°/20 mm. A redistilled sample exhibited the following properties: b.p. 75–78°/20 mm., n_D^{30} 1.4286.

Anal. Calcd. for $C_8H_{14}O_2$: C, 67.57; H, 9.93; sapon. equiv. 142. Found: C, 68.26; H, 9.92; sapon. equiv. 139.5.

A portion of the butyl crotonate obtained above was saponified and acidified in the usual fashion, giving crystalline crotonic acid, m.p. and mixed m.p. with authentic *trans*-crotonic acid, 69–72°.

Oxidation of n-butyraldehyde diethyl acetal. The starting acetal[18] was prepared by reaction of the aldehyde with ethanol in the presence of calcium chloride and exhibited the following properties: b.p. 142°, n_D^{30} 1.3904.

To *n*-butyraldehyde diethyl acetal (10 g., 0.07 mole) containing 1 drop of concd. sulfuric acid was added 23 g. of a solution of peracetic acid (5.7 g., 0.075 mole) in ethyl acetate over a period of 30 min. The mixture was warmed to 40° and held there for 11 hr., at the end of which time titration for peracetic acid indicated a consumption of 99.3% of the theoretical. The cooled solution was washed with aqueous sodium carbonate, the layers were separated, and the organic layer was fractionated. There was obtained 4.0 g. of pure ethyl butyrate (b.p. 118–120°, n_D^{30} 1.3864), in addition to 6.0 g. of a mixed ethyl acetate and ethyl butyrate fraction (b.p. 80–118°) which, by gas chromatographic analysis, contained 1.6 g. of ethyl butyrate. Yield was thus 5.6 g. or 69%. The infrared spectrum of the isolated ethyl butyrate was identical with the standard (Sadtler) spectrum.

Oxidation of benzaldehyde diethyl acetal. The starting acetal[18] was prepared by reaction of benzaldehyde and ethyl orthoformate catalyzed by ammonium nitrate and exhibited the following properties: b.p. 75°/4 mm., n_D^{30} 1.4742.

Benzaldehyde diethyl acetal (54 g., 0.3 mole) containing 2 drops of concd. sulfuric acid was treated with 109 g. of a solution of peracetic acid (26.6 g., 0.35 mole) in ethyl acetate. The addition required 3 hr., during which time the temperature was maintained at 26–40° by ice-water cooling. After standing for 20 hr., the mixture was titrated for peracid, and it was found that the theoretical amount had been consumed. The solution was worked up as in the preceding experiment to give 41 g. (90% yield) of ethyl benzoate, b.p. 87–90°/10 mm., n_D^{30} 1.4993, the infrared spectrum of which was identical with that of an authentic specimen. From the distillation residue a small amount (*ca.* 0.5 g.) of benzoic acid (melting point and mixed melting point with an authentic sample, 117–119°) was isolated.

Oxidation of β-phenyl-β-ethoxypropionaldehyde diethyl acetal. The starting acetal was prepared by the method of Haworth and Lapworth[19] and exhibited the following properties: b.p. 127–130°/6 mm., n_D^{30} 1.4721.

β-Phenyl-β-ethoxypropionaldehyde diethyl acetal (37 g., 0.146 mole) was mixed with 67 g. of a solution of peracetic acid in ethyl acetate (a 22.5% solution; *i.e.*, containing 15 g. or 0.198 mole peracetic acid) and held at 40–60° for 7 hr. At this point 42% of the theoretical amount of peracid was consumed; upon adding 4 drops of concd. sulfuric acid the reaction became exothermic and warmed to 92°. After cooling, the solution was treated with 1 drop of cobalt naphthenate (to destroy peroxides) and 1.34 g. sodium acetate (to neutralize the sulfuric acid). Direct distillation of the reaction mixture gave 20 g. (61% yield) of ethyl β-phenyl-β-ethoxypropionate, b.p. 122–130°/10 mm., n_D^{30} 1.4866.

The ester (6.4 g.) was saponified with potassium hydroxide (3.6 g.) in ethanol-water in the usual fashion to give crystalline β-phenyl-β-ethoxypropionic acid (5.0 g.), m.p. 74–75° (ligroin).

Anal. Calcd. for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27; equiv. wt., 194.2. Found: C, 68.47; H, 7.34; equiv. wt., 195.3.

The melting point reported in the literature for this acid

---

[16] Equivalent weight was determined by titration of epoxide group with pyridinium chloride–pyridine solution. See J. J. Jungnickel, E. D. Peters, A. Polgar, and F. T. Weiss in *Organic Analysis*, Vol. I, Interscience Publishers, Inc., N. Y., 1953, p. 136.

[17] R. H. Saunders, U. S. Patent **2,573,678,** November 6, 1951.

[18] These acetals were prepared by H. E. Johnson of this department, to whom we are indebted for furnishing generous samples.

[19] Utilization of a literature method for preparing cinnamaldehyde diethyl acetal [R. D. Haworth and A. Lapworth, *J. Chem. Soc.*, **121,** 83 (1922)] gave, in our hands, β-phenyl-β-ethoxypropionaldehyde diethyl acetal as the only isolable product; the boiling point of this product was indistinguishable from the boiling point of cinnamaldehyde diethyl acetal (127–130°/6 mm.) prepared by another method [M. M. Kreevoy and R. W. Taft, Jr., *J. Am. Chem. Soc.*, **77,** 5590 (1955)], the structure of which was confirmed by elemental analysis, infrared absorption spectrum, and oxidation by the method of this paper to ethyl cinnamate. The index of refraction of the unsaturated acetal was appreciably higher (1.5091 at 30°) than that of the β-ethoxy compound.

is 75°;[20] these authors also reported its conversion to cinnamic acid by boiling hydrochloric acid, a result which we duplicated. A sample of the acid (0.6 g.) was heated to boiling with 25 cc. 6.0*N* hydrochloric acid and gave, on cooling, crystalline cinnamic acid (0.45 g.), melting point and mixed melting point with authentic cinnamic acid, 130–132°.

Oxidation of 2-(β-styryl)-4-methyl-1,3-dioxolane (VIa) *with peracetic acid catalyzed by sulfuric acid.* To 76 g. (0.4 mole) of 2-(β-styryl)-4-methyl-1,3-dioxolane containing 0.76 g. of sulfuric acid was added with stirring 157 g. of a 24.3% solution of peracetic acid in ethyl acetate (*i.e.*, containing 38.0 g. or 0.5 mole peracetic acid) over a period of 1 hr. The reaction was exothermic from the outset, and the temperature was maintained at 25–33° by ice-water cooling. After an additional 4 hr. at 30°, titration for peracetic acid indicated the theoretical amount had been consumed. Sodium acetate, 1.25 g., was added to neutralize the sulfuric acid. Distillation through a glass helix-packed column gave, after recovery of solvent and acetic acid, 23 g. (28% yield) of impure propylene glycol monocinnamate, b.p. *ca.* 195°/1.25 mm., n_D^{30} 1.5483.

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 71.92; H, 7.25.

1,1-Diacetoxy-2-ethyl-2-butene. To acetic anhydride (217 g., 2.15 moles) containing 0.34 g. of a mixed boric-oxalic acid catalyst[13] (1:1 molar ratio) was added 139 g. (1.42 moles) of 2-ethylcrotonaldehyde over a period of 35 min. The solution was stirred constantly, and slight cooling was required to maintain a temperature of 30°. After the mixture had stood for an additional 20 hr., the catalyst was neutralized with 0.93 g. of sodium acetate, and the reaction mixture was fractionated directly to give 212 g. (75% yield) of 1,1-diacetoxy-2-ethyl-2-butene, b.p. 88–90°/4 mm., n_D^{30} 1.4339.

Anal. Calcd. for $C_{10}H_{16}O_4$: C, 59.98; H, 8.05. Found: C, 60.58; H, 8.21.

1,1-Diacetoxy-2,3-epoxy-2-ethylbutane. To 200 g. (1.0 mole) of 1,1-diacetoxy-2-ethyl-2-butene was added 396 g. of a solution containing 23.0% peracetic acid in ethyl acetate (91 g. or 1.2 moles peracetic acid). The addition and subsequent stirring (both at 60°) required 4 hr., at the end of which time the theoretical quantity of peracid was consumed. The cooled reaction mixture was fed to ethylbenzene under reflux in a still at 30 mm. pressure while acetic acid and unchanged peracetic acid was removed continuously at the still head as an ethylbenzene azeotrope. Fractionation of the residue gave 119 g. (55% yield) of 1,1-diacetoxy-2,3-epoxy-2-ethylbutane, b.p. 95–96°/3.0 mm., n_D^{30} 1.4289.

Anal. Calcd. for $C_{10}H_{16}O_5$: C, 55.54; H, 7.46. Found: C, 55.46; H, 7.42.

1,1-Diacetoxy-2-ethyl-2-hexene. This preparation based on 2-ethyl-3-propyl acrolein and acetic anhydride was similar to that for 1,1-diacetoxy-2-ethyl-2-butene. Yield of 1,1-diacetoxy-2-ethyl-2-hexene was 75%, b.p. 91–95°/2.0 mm., n_D^{30} 1.4366.

Anal. Calcd. for $C_{12}H_{20}O_4$: C, 63.13; H, 8.83. Found: C, 63.48; H, 8.82.

1,1-Diacetoxy-2,3-epoxy-2-ethylhexane. The epoxidation of the above olefin was analogous to the preparation of 1,1-diacetoxy-2,3-epoxy-2-ethylbutane with the following results. Yield of 1,1-diacetoxy-2,3-epoxy-2-ethylhexane was 72%, b.p. 102–103°/1.25 mm.; n_D^{30} 1.4308.

Anal. Calcd. for $C_{12}H_{20}O_5$: C, 59.00; H, 8.25. Found: C, 59.17; H, 7.90.

SOUTH CHARLESTON, W. VA.

---

(20) W. Schreuth, W. Schoeller and R. Streunsee, *Ber.*, **44**, 1432 (1911).

[CONTRIBUTION FROM THE SUMMIT RESEARCH LABORATORIES, CELANESE CORP. OF AMERICA]

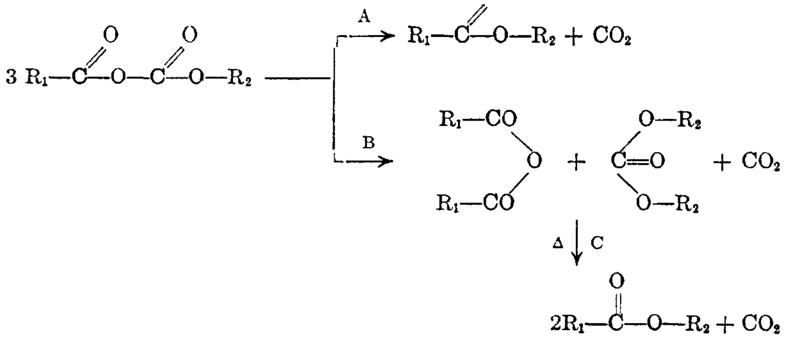
Decomposition of Mixed Carboxylic-Carbonic Anhydrides[1a]

THOMAS B. WINDHOLZ[1b]

Received June 22, 1959

The decomposition of a number of mixed carboxylic-carbonic anhydrides has been investigated and the occuring reactions established. It was found that the structures of both the carboxylic (R_1) and carbonic (R_2) components have directing influences on the possible paths of decomposition. Polar and steric effects as well as proposed reaction mechanisms are discussed. A method of preferential ester formation from mixed anhydrides is demonstrated for ethyl benzoate.

The preparation and characterization of stable carboxylic-carbonic anhydrides was first reported by Tarbell and Leister.[2] Since then it has been established[3a,3b] that mixed carboxylic-carbonic anhydrides decompose according to Equations A and B



---

(1)(a) Part of this work has been presented before the Division of Organic Chemistry at the 136th Meeting of the American Chemical Society, Atlantic City, September 1959.

(1)(b) Present Address: Merck Sharp and Dohme Research Laboratories, Rahway, N. J.