Treating 12-oxo-*cis*-9-octadecenoic acid (II) first with methylmagnesium bromide (3 molar proportions) and then with diazomethane gave the same product III, b.p. 139–144° (0.1 mm.), n_D^{25} 1.4667, but in only 20% yield.

Oxidative cleavage of methyl 12-methylricinoleate (III). Oxygen containing ozone was bubbled into a solution of 10 g. (0.031 mole) of methyl 12-methylricinoleate (III) in 70 ml. of chloroform (Baker Analyzed) at a rate of 0.36 mmole of ozone per min.[8] The reaction mixture was held at the temperature of solid carbon dioxide–kerosene. Ozonolysis was interrupted after 110 min., that is, after 0.040 mole of ozone had been introduced. At this time, the chloroform became blue, and iodine was liberated on passing the emergent gases into an acidified aqueous solution of potassium iodide.

Most of the chloroform was removed by distillation at room temperature under reduced pressure. Water (300 ml.) was added to the viscous residue, and the mixture was boiled for 2 hr. Five per cent aqueous potassium permanganate (150 ml.) and 10% aqueous sodium hydroxide (25 ml.) were added to the cooled mixture, which was boiled again and then cooled in an ice bath. Excess 5% sulfuric acid (200 ml.) was slowly introduced followed by enough 5% aqueous sodium hydrogen sulfite to transform all the permanganate and manganese dioxide to manganese(II). The colorless, faintly turbid solution was extracted with six 50-ml. portions of ether, and the combined extracts were extracted in turn with two 10-ml. portions of 10% aqueous sodium hydroxide. After the combined alkaline solutions were washed with two 20-ml. portions of ether (discard), concentrated hydrochloric acid was added dropwise with cooling until the *p*H was close to 1. The white, precipitated azelaic acid (VI) was collected on the funnel, was washed free of inorganic acid with ice water, and was air dried.

This product (3.7 g.; m.p. 94–97°), on crystallization from water yielded 3.3 g. (57%) of pure material, which melted either alone or admixed with authentic azelaic acid (m.p. 104.5–106°) at 105–106°. The observed neutralization equivalent, 95.0, agreed with the value calculated (94.1) for azelaic acid. The cleavage azelaic acid (VI) mixed with 7-carbon pimelic acid (m.p. 104–105°) showed m.p. 85–95°. The reported melting points of the 8-carbon suberic acid and the 10-carbon sebacic acid are 140° and 133°, respectively.[9]

Pyrolysis of methyl 12-methylricinoleate (III).[10] A 25-ml. flask fitted with a 25-cm. Vigreux column and condenser, and containing 10.0 g. (0.031 mole) of methyl 12-methylricinoleate (III) was dipped into a metal bath at 400°. After 10 min., distillation became slower, and the bath was heated to 525° and held at this temperature for 5 min. The pyrolysis products, which came over at vapor temperatures fluctuating between 270 and 330°, were collected in a receiver cooled with solid carbon dioxide.

Redistillation of the products through a 5-cm. Vigreux column afforded the following fractions: (a) 0.61 g. of a colorless, pungent liquid, b.p. 64–75° (atm. press.), n_D^{25} 1.3767; (b) 1.3 g. of faintly yellow liquid, b.p. 97–101° (54 mm.), n_D^{25} 1.4192; (c) 1.82 g. of faintly yellow liquid, b.p. 137–140° (25 mm.), n_D^{25} 1.4392; and (d) 3.2 g. of brown residue.

Fraction (b) was shown to be 2-octanone (IV) by formation of the semicarbazone.[9] The 2-octanone (0.50 g.) furnished 0.61 g. of once-crystallized white needles, m.p. 114–117°, which were recrystallized once from water. The pure derivative melted at 121–122°; its melting point was unchanged on admixture with an authentic sample of 2-octanone semicarbazone, m.p. 121.5–122°. The derivative was crystallized twice from water before analysis.

Anal. Calcd. for $C_9H_{19}N_3O$: C, 58.34; H, 10.34; N, 22.68. Found: C, 58.6; H, 10.5; N, 22.5.

Distillate fraction (c) was taken as methyl undecylenate (V). Purification by chromatography was effected by placing 0.77 g. of fraction (c) dissolved in 10 ml. of petroleum ether (b.p. 30–60°) on a 1.7 cm. chromatography column containing 15 g. of alumina (Merck, acid washed) and eluting with 120 ml. of petroleum ether. Each 20-ml. portion of eluate was freed of solvent by exposure at 100° to a jet of pure nitrogen. In this way, 0.32 g. of analytically pure methyl undecylenate (V) was obtained.

Anal. Calcd. for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.5; H, 11.2.

The index of refraction, n_D^{25} 1.4372, agreed with the value, n_D^{25} 1.43727,[11] reported for methyl undecylenate. Infrared absorption curves taken with neat samples of pyrolysis methyl undecylenate (V) and of authentic methyl undecylenate were the same.

Under similar pyrolysis conditions, methyl ricinoleate gave heptanal and methyl undecylenate in roughly double the yields of 2-octanone (IV) and methyl undecylenate (V) from methyl 12-methylricinoleate (III).

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(8) The ozonolysis was modeled after the ozonolysis of ricinoleic acid (I), A. C. Noorduyn, *Rec. trav. chim.*, **38**, 323 (1919).

(9) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds*, Fourth edition, John Wiley & Sons, Inc., New York, New York, 1956.

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Alkaline Epoxidation of α,β-Unsaturated Aldehydes

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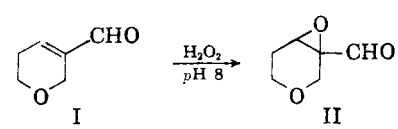
The technique recently described[1] for the epoxidation of acrolein and methacrolein by hydrogen peroxide has been applied to a variety of other α,β-unsaturated aldehydes. Table I summarizes the results obtained with crotonaldehyde, tiglaldehyde (2-methyl-2-butenal), cinnamaldehyde, citral, and the "acid dimer" of acrolein, 3-formyl-5,6-dihydro-2H-pyran (I).



I II

The epoxy aldehydes obtained from I, citral, and tiglaldehyde are new compounds. That from croton-

(1) G. B. Payne, *J. Am. Chem. Soc.*, **81**, 4901 (1959).

TABLE I

α,β-EPOXYALDEHYDES

R_1	R_2	Yield, %	B.P.	Mm.	n_D^{20}	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Oxirane Oxygen, % Calcd.	Oxirane Oxygen, % Found	2,4-Dinitrophenylhydrazone Derivative M.P.	2,4-Dinitrophenylhydrazone Derivative Formula	Nitrogen, % Calcd.	Nitrogen, % Found
CH_3	H	56[a]	60–61	80	1.4179	$C_4H_6O_2$	55.8	55.3	7.0	7.1	18.6	17.5[b]	136–138	$C_{10}H_{10}N_4O_6$	21.0	21.0
CH_3	CH_3	46	58–59	60	1.4198	$C_5H_8O_2$	60.1	60.4	8.1	8.1	16.0	14.6[b]	—[e]	—	—	—
C_2H_5	H	24	70–72	0.3	1.5448	$C_5H_8O_2$	73.0	73.1	5.4	5.6	10.8	7.2[c]	138–139	$C_{11}H_{12}N_4O_6$	17.0	16.9
Citral		75	63–67	1	1.4609	$C_{10}H_{16}O_2$	71.4	71.3	9.6	9.6	9.5	9.1[d]	—[e]	—	—	—
3-Formyl-5,6-dihydro-2H-pyran		70	56–57	2	1.4739	$C_6H_8O_3$	56.2	56.4	6.3	6.4	12.5	11.7[b]	136–136.5	$C_{12}H_{12}N_4O_6$	18.1	18.3

[a] Yield of anhydrous product; the yield of product as a flashed aqueous solution was 77%. [b] Hydrochloric acid in aqueous magnesium chloride; see J. L. Jungnickel, E. D. Peters, A. Polgar, and F. T. Weiss, *Organic Analysis*, Vol. 1, Interscience Publishers, Inc., New York, 1953, p. 134. [c] Hydrochloric acid in dioxane; see footnote (b), p. 135. [d] Hydrobromic acid in acetic acid; A. J. Durbetaki, *Anal. Chem.* 28, 2000 (1956). [e] No pure derivative isolated.

aldehyde has been prepared by oxidation with hypochlorite,[2] while β-phenylglycidaldehyde was recently obtained from cinnamaldehyde in high yield by epoxidation using alkaline *t*-butyl hydroperoxide.[3]

For the epoxidation of relatively water-insoluble unsaturated aldehydes (I, citral and cinnamaldehyde), methanol was used as solvent. This meant that the *p*H as determined by a meter was generally about 1 unit higher than that determined by indicator paper; it varied somewhat with the amount of water (from the hydrogen peroxide and from the aqueous caustic used for *p*H control) introduced into the system.

EXPERIMENTAL

2,3-Epoxybutyraldehyde from crotonaldehyde. The procedure used was exactly the same as that described earlier for the epoxidation of methacrolein.[1] The crude yield of epoxide was 86% by titration for oxirane oxygen. Flashed aqueous epoxyaldehyde was secured in 77% yield based on crotonaldehyde charged. Anhydrous product was isolated in 56% overall yield, b.p. 60–61° (80 mm.); n_D^{20} 1.4179 (lit.[2] values: b.p. 66–68° (100 mm.); n_D^{20} 1.4185).

3-Formyl-3,4-epoxytetrahydropyran. To a 1-l., five-neck, round-bottom flask equipped with mechanical stirrer, dropping funnels, thermometer, and standard electrodes connected to a Beckman *p*H Meter were charged 300 ml. of methanol and 0.55 mole of 30% hydrogen peroxide. This mixture was stirred at 35–40° while 56 g. (0.50 mole) of 3-formyl-5,6-dihydro-2H-pyran[4] was added dropwise with cooling at a meter *p*H of about 9 (true *p*H of about 8 as determined by indicator paper) over a 10-min. period; *N* sodium hydroxide was used for *p*H control. After 1.5 hr. longer, an iodometric titration indicated the presence of only 0.03 mole of peroxide; 19 ml. of caustic had been consumed. The mixture was concentrated under vacuum to remove the bulk of the methanol; the concentrate was saturated with ammonium sulfate and extracted with three 150-ml. portions of chloroform. The combined chloroform extract, after a wash with saturated ammonium sulfate solution, was dried over magnesium sulfate and concentrated to low volume on the steam bath. Distillation through a 0.7 × 50 cm. glass spiral-packed column afforded 45 g. (70% yield) of 3-formyl-3,4-epoxytetrahydropyran, b.p. 56–57° (2 mm.).

β-Phenylglycidaldehyde from cinnamaldehyde. To a 2-l. flask equipped as above were charged 1000 ml. of methanol and 0.10 mole of 30% hydrogen peroxide. To this stirred mixture held at 35–40° were added simultaneously (a) a solution of 132 g. (1.0 mole) of cinnamaldehyde in 100 ml. of methanol, (b) 1.0 mole of 30% hydrogen peroxide and (c) 1*N* aqueous sodium hydroxide solution. The addition was made over 1 hr. with the peroxide leading the aldehyde; the meter *p*H was held at 11.0–10.5 (*true* *p*H 8–8.5 as determined by indicator paper). After an additional hour at meter *p*H 10.0–10.5 and 35°, an iodometric titration indicated the utilization of 1.01 mole of hydrogen peroxide.

The mixture was concentrated under vacuum to a volume of about 300 ml., diluted with 1 l. of water, and extracted with three 300-ml. portions of ether. The combined ether extract was washed with water, dried over magnesium sulfate, and concentrated at room temperature to a constant weight of 136 g. A titration for organic peroxide[5] indicated the presence of 0.08 mole of such material. In order to obviate any difficulty due to peroxide decomposition during

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(3) G. B. Payne, *J. Org. Chem.*, 25, 275 (1960).

(4) B. P. Geyer and R. H. Mortimer, U. S. Patent 2,514,156 (1950).

distillation, the residue was dissolved in 150 ml. of benzene and hydrogenated over 3 g. of 5% palladium on charcoal catalyst in a bottle shaken at 50 pounds pressure and room temperature. Hydrogenation was halted after 0.5 hr. and 0.09 mole absorption of hydrogen. After removal of catalyst by filtration, the solution was Claisen-distilled to give 79 g. of crude product, b.p. 65–90° (0.5 mm.). Redistillation through a 10-tray Oldershaw column afforded 34 g. (24% yield) of β-phenylglycidaldehyde, b.p. 70–72° (0.3 mm.); n_D^{20} 1.5448 [lit.[3] values: b.p. 66–68° (0.2 mm.); n_D^{20} 1.5447].

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(5) A sample was added to a mixture of 5 ml. of acetic acid and 50 ml. of 2-propanol; 2 ml. of saturated aqueous sodium iodide was added and the stoppered solution held in the dark for 30 min. at room temperature. The liberated iodine was titrated with 0.1*N* sodium thiosulfate to the disappearance of yellow color.

2,6-Diethyl Homologs of Bromobenzene, Benzonitrile, Benzamide, and Benzoic Acid

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In connection with another project, we had occasion to prepare the heretofore unknown 2,6-diethylbenzoic acid. The conversion of the readily available[1] 2,6-diethylaniline to 2,6-diethylbenzoic acid was carried out by two alternate sequences of reactions. The 2,6-diethyl homologs of bromobenzene, benzonitrile, and benzamide are also unreported in the literature. These intermediates were isolated and their physical properties determined. The hydrolysis of 2,6-diethylbenzonitrile to 2,6-diethylbenzamide rather than 2,6-diethylbenzoic acid, even under the vigorous conditions employed, indicates a considerable steric factor.[2]

EXPERIMENTAL

2,6-Diethylbenzonitrile. 2,6-Diethylaniline was converted into 2,6-diethylbenzonitrile, b.p. 85–86° (1 mm.), n_D^{20} 1.5210; d_4^{27} 0.9614 in a 21% yield *via* the diazonium salt.[3] 2,6-Diethylbenzonitrile was also prepared from 2,6-diethylbromobenzene and cuprous cyanide[4] in an 86% yield.

Anal. Calcd. for $C_{11}H_{13}N$: C, 82.97; H, 8.23. Found: C, 83.02; H, 8.2.

2,6-Diethylbromobenzene. 2,6-Diethylaniline was converted into 2,6-diethylbromobenzene, b.p. 234° (742 mm.); n_D^{20}, 1.5456; d_4^{27}, 1.264 in a 24% yield according to the general direction for the Gatterman reaction.[5]

Anal. Calcd. for $C_{10}H_{13}Br$: C, 56.36; H, 6.15. Found: C, 56.31; H, 6.2.

2,6-Diethylbenzamide. Basic hydrolysis[4] of 2,6-diethylbenzonitrile gave a 91% yield of 2,6-diethylbenzamide, m.p. 136–136.5°, after recrystallization from hexane or water. Hydrolysis of 2,6-diethylbenzonitrile with 90% sulfuric acid gave a 55% yield of 2,6-diethylbenzamide. There was no evidence for the formation of 2,6-diethylbenzoic acid in either the acidic or basic hydrolysis even after an extended reaction time.

Anal. Calcd. for $C_{11}H_{15}NO$: N, 7.90. Found: N, 7.82.

2,6-Diethylbenzoic acid. Eighteen grams (0.1 mole) of 2,6-diethylbenzamide was dissolved in 180 g. of 85% phosphoric acid and heated to 130°. Within 15 min. the clear reaction mixture became opaque and after 1-hr. two layers had formed. The organic layer solidified on cooling and after recrystallization from hexane 2,6-diethylbenzoic acid, m.p. 92–93°, was obtained in a 91% yield.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.36; H, 8.1.

2,6-Diethylbenzoic acid was also obtained in a 72% yield from the carbonation of 2,6-diethylphenyllithium, prepared from 2,6-diethylbromobenzene and lithium wire in ethyl ether. The physical and spectroscopic properties of 2,6-diethylbenzoic acid prepared by the two alternate methods were identical.

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The Stereochemistry of the Free Radical Addition of Hydrogen Bromide to 1-Methylcycloheptene[1]

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Since the work of Goering[2] and his group on the stereochemistry of the radical addition of hydrogen bromide to 1-bromocyclohexene and 1-methylcyclohexene, in which stereospecific *trans* addition was observed, the use of cyclic olefins in the study of free radical reactions has become increasingly more important. The effect of a number of factors on radical additions to cyclic olefins has been studied. Of considerable interest has been the influence of ring size on the stereospecificity of the reaction. King Howe[3] reported that the free radical addition of hydrogen bromide to 1-methylcyclopentene afforded at least 94.3% of the *trans* addition product, *cis*-1-methyl-2-bromocyclopentane. Abell and Chiao[4] investigated the radical addition of hydrogen bromide to 1-bromocyclobutane, 1-bromocyclo-

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(1) This work was performed under Contract No. DA-19-020-ORD-3171, OOR Project 1037, of the Office of Ordnance Research, U. S. Army. Support for this work is gratefully acknowledged.

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