

rate of gas evolution was markedly increased but the yield of pure product was somewhat decreased (13–16%).

3-Carboxy-4-(p-methoxy-m-tolyl)-5-methyl-3-hexenoic acid. The crude diacid (16.5 g., m.p. 114–116°) was refluxed for 6.5 hr. in 10% sodium hydroxide. The semicrystalline product isolated in the usual way (13 g., 83%) gave on recrystallization from benzene-petroleum ether (b.p. 90–100°) 9.5 g. of one relatively pure stereoisomer, m.p. 155–156°. Further recrystallization from the same solvent, aqueous methanol, and benzene-hexane gave the pure diacid, m.p. 162–163°. The same product was obtained in a preliminary experiment on the pure half ester.

Anal. Calcd. for $C_{14}H_{18}O(COOH)_2$: neut. equiv., 146.2. Found, neut. equiv., 146.6, 146.8.

From the preceding benzene petroleum ether mother liquors there was isolated 1.0 g. of crystalline material m.p. 119–120° which has the composition of γ -(*p*-methoxy-*m*-tolyl)- γ -isopropylitaconic anhydride. The melting point changes on exposure to air, apparently by absorption of moisture. A pure sample was prepared by repeated recrystallization from benzene-petroleum ether; m.p. 121–121.5°.

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 70.05; H, 6.61. Found: C 70.33, 70.59; H, 6.53, 6.81.

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Glycol Esters of 3-Alkoxypropionic Acids

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Received August 12, 1957

The probability that glycol esters of 3-alkoxypropionic acids would be useful as plasticizers and lubricants prompted the synthesis of a number of these materials.

While the preparation of numerous monohydric esters of 3-alkoxypropionic acids by the base-catalyzed addition of an alcohol to an alkyl acrylate has been previously reported,^{1,2} the synthesis of a glycol ester appears to be novel.

TABLE I
3-ALKOXYPROPIONIC ACIDS: $R-O-CH_2CH_2CO_2H$

R	B.P., ³ °C.	Mm.	n_D^{20}
$CH_2=CHCH_2-$	110	5	1.4383
$(CH_2CH_2)_2CHCH_2-$	144	10	1.4301
$CH_3(CH_2)_3(CH_3CH_2)CHCH_2-$	142	5.5	1.4350

R	d_4^{20}	Purity, % ^a	Yield, %
$CH_2=CHCH_2-$	1.0562	98.1	73
$(CH_2CH_2)_2CHCH_2-$	0.9641	95.8	85
$CH_3(CH_2)_3(CH_3CH_2)CHCH_2-$	0.9248	99.7	82

^a Based on titration with 0.1N sodium hydroxide.

(1) M. B. Dixon, C. E. Rehberg, and C. H. Fisher, *J. Am. Chem. Soc.*, **70**, 3733 (1948).

(2) C. E. Rehberg, M. B. Dixon, and C. H. Fisher, *J. Am. Chem. Soc.*, **69**, 2966 (1947).

(3) All temperatures are uncorrected.

TABLE II
GLYCOL ESTERS OF 3-ALKOXYPROPIONIC ACIDS: $(ROCH_2CH_2CO_2)_2R'$

R	R'	B.P., °C./mm.	n_D^{20}	d_4^{20}	Purity, ^a %	Yield, %	Calcd., %		Found, %	
							C	H	C	H
$CH_3(CH_2)_3(CH_3CH_2)CHCH_2-$	$-CH_2CH_2-$	154/0.2 ^b	1.4439	0.9582	98.8	75	67.0	10.7	66.9	10.6
$CH_3(CH_2)_3(CH_3CH_2)CHCH_2-$	$O(CH_2CH_2)_2$	180/0.2 ^b	1.4464	0.9747	101	81	65.8	10.5	65.5	10.4
$CH_3(CH_2)_3(CH_3CH_2)CHCH_2-$	$-(CH_2)_6-$	181/0.25 ^b	1.4472	0.9455	100	94	67.8	11.1	68.1	10.8
$(CH_3CH_2)_2CHCH_2-$	$-(CH_2CH(CH_3)O)-_2$	Residue	1.4431	0.9860	98.5	99	63.5	10.2	63.5	10.4
$CH_2=CHCH_2-$	$-CH_2CH_2-$	180/0.8	1.4533	1.0876	104.6	16	58.7	7.74	58.3	7.45

^a Based on saponification and titration with 0.1N hydrochloric acid. ^b Falling film molecular still.

3-Alkoxypropionic acids were readily prepared by the cyanoethylation of an alcohol⁴ and hydrolysis of the 3-alkoxypropionitrile thus formed with mineral acid.⁵ Esterification was accomplished by the usual azeotropic technique. Physical properties for the several 3-alkoxypropionic acids are given in Table I and the data concerning the glycol esters are shown in Table II.

Acknowledgment. The author is grateful to Messrs. H. C. Shue and J. Smith, Jr. for technical assistance.

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(4) H. A. Bruson, *Org. Syntheses*, **V**, 122 (1948).

(5) R. V. Christian and R. M. Hixon, *J. Am. Chem. Soc.*, **70**, 1334 (1948).

Cyclic Peroxide By-product from the Alkaline Epoxidation of Mesityl Oxide

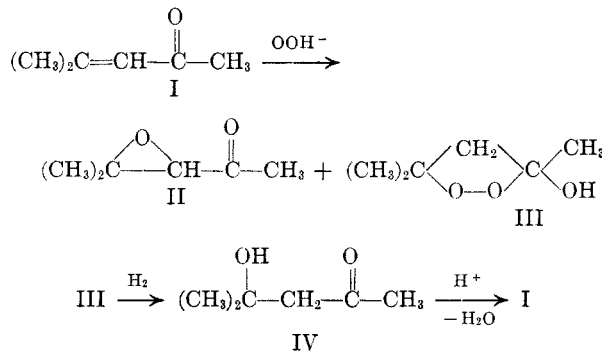
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Received August 14, 1957

The alkaline epoxidation of mesityl oxide, 4-methyl-3-penten-2-one (I), to give 3,4-epoxy-4-methyl-2-pentanone (II), has been carried out several times in the past.¹ Nazarov and Akhrem,^{1d} however, were the only ones to separate and purify a slightly higher boiling by-product. They established its formula as $C_6H_{11}O_2(OH)$ by carbon and hydrogen and hydroxyl analysis.

Using a modification of the procedure employed by Wilder and Dolnick^{1b} we have carried out the epoxidation of mesityl oxide and obtained the high boiling impurity in 3% yield along with an 85% yield of II. Its structure has been established as 3-hydroxy-3,5,5-trimethyl-1,2-dioxacyclopentane (III) by ultimate analysis, peroxide titration, qualitative reaction with ferrous ion and by quantitative hydrogenation to 4-methyl-4-hydroxy-2-pentanone (IV). The latter, when allowed to react with 2,4-dinitrophenylhydrazine under acidic conditions, afforded the 2,4-dinitrophenylhydrazone of mesityl oxide (I). An authentic sample of IV exhibited this same behavior.

(1) (a) Weitz and Scheffer, *Ber.*, **54**, 2327 (1921); (b) Wilder and Dolnick, U. S. Patent **2,431,718** (Dec. 2, 1947); (c) Bunton and Minkoff, *J. Chem. Soc.* 665 (1949); (d) Nazarov and Akhrem, *J. Gen. Chem. (U.S.S.R.)*, **20**, 2183 (1950); *Chem. Abstr.*, **45**, 7062 (1950); (e) House and Wasnon, *J. Am. Chem. Soc.*, **78**, 4394 (1956).



The infrared spectrum of III, with the exception of the presence of a strong band for hydroxyl, was markedly similar to that recently given for 3,3,5,5-tetramethyl-1,2-dioxacyclopentane.²

EXPERIMENTAL

3-Hydroxy-3,5,5-trimethyl-1,2-dioxacyclopentane (III) and *3,4-epoxy-4-methyl-2-pentanone* (II). To a 3-l. round-bottom flask equipped with stirrer, thermometer, and dropping funnel were charged 450 ml. of water and 392 g. (4.0 moles) of freshly distilled mesityl oxide. With stirring was added a solution of 8 g. of sodium hydroxide in 100 ml. of water followed by 5 g. of magnesium sulfate dissolved in 50 ml. of water. With vigorous stirring and ice bath-cooling to maintain a temperature of 25–30°, there was then added 555 g. (5.0 moles) of 30% hydrogen peroxide over a period of 40 min. After stirring an additional 2 hr., 200 g. of sodium sulfate was added followed, 0.5 hr. later, by 400 ml. of benzene. After another 0.5 hr. of stirring, excess salt was removed by filtration and washed with 50 ml. of benzene. Distillation of the benzene layer of the filtrate through a 10-tray Oldershaw column afforded 387 g. (85%) of *3,4-epoxy-4-methyl-2-pentanone*, b.p. 61–62° (20 mm.); n_D^{20} 1.4235 (reported^{1b} values: b.p. 155.5–157.5°; n_D^{20} 1.4238).

The 28 g. residue from the above distillation was distilled through an 18-in. glass spiral packed column to give 16 g. (3%) of *3-hydroxy-3,5,5-trimethyl-1,2-dioxacyclopentane*, b.p. 69–70° (10 mm.); n_D^{20} 1.4320 (reported^{1d} values: b.p. 79–81°/15 mm.; n_D^{20} 1.4328).

The infrared spectrum exhibits strong bands at 2.91 μ (hydroxyl) and at 6.88, 7.32, 7.68, 10.31, 11.25, 11.52 (probably O—O stretching) and 12.6 μ . 3,3,5,5-Trimethyl-1,2-dioxacyclopentane is reported² to exhibit strong bands at 6.86, 7.32, 7.67, 11.47, and 12.55 μ along with weaker bands at 10.28 and 11.22 μ .

Anal. Calcd. for $C_6H_{12}O_3$: C, 54.5; H, 9.2; active O, 12.1. Found: C, 54.5; H, 9.2; active O, 11.8.³

Reaction of III with hydrogen. Conversion to *4-methyl-4-hydroxy-2-pentanone* (IV). Ten g. of cyclic peroxide III (0.076 mole) and 100 ml. of methanol were charged to a 450 ml. capacity glass hydrogenation bottle along with 1 g. of 5% palladium on barium sulfate catalyst. The mixture was shaken at room temperature with hydrogen at a starting pressure of 50 lb. Within 1 hr., 0.074 mole of hydrogen had been absorbed and the rate of uptake was then very slow. Distillation of the filtered solution afforded 7.2 g. of *4-methyl-4-hydroxy-2-pentanone*, b.p. 56–61° (10 mm.); n_D^{27} 1.4204. The refractive index of Eastman Kodak Co. White Label diacetone alcohol, taken at the same time, was n_D^{27} 1.4200.

(2) Criegee and Paulig, *Ber.*, **88**, 712 (1955).

(3) Sample heated with 56% aqueous hydrogen iodide in glacial acetic acid at 60° for 45 minutes, liberated iodine titrated with standard thiosulfate; milder methods of analysis gave lower values.