

The Synthesis of Some Alcohoxy Acetones and Related Compounds

by Masaaki ITO and Kazuo ABE

(Received October 28, 1966)

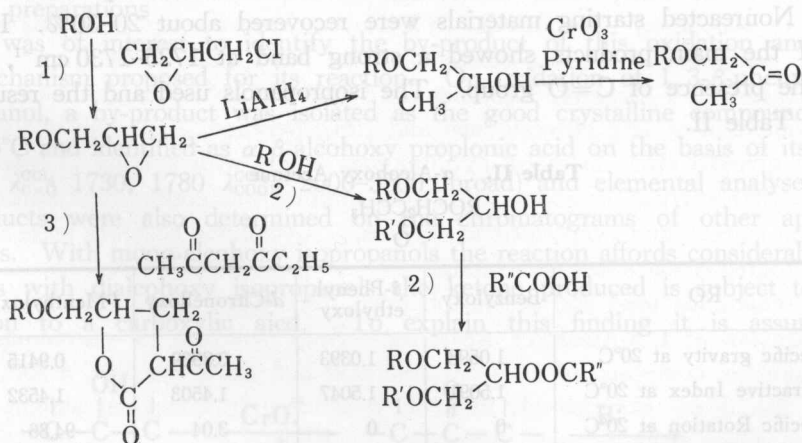
Abstract

1- and 1,3-Alcohoxy acetones were prepared by chromium acid-pyridine complex oxidation of the isopropanols derived from the appropriate glycidyl ethers. α , β -Alcohoxy propionic acids were isolated as by-product at the oxidation of 1,3-alcohoxy isopropanol.

The formation mechanism of these acids was assumed that based according with the rearrangement of hydroxyketones formed with enolisation of the ketone.

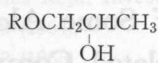
In addition to the glycidyl ethers of perfumery alcohols, described in the preceding paper¹⁾, we have prepared the derivatives of these ethers as raw material for the potential aromatics^{2),3)}. This article reports the synthesis of 1- and 1,3-alcohoxy isopropanols and corresponding acetones.

Also, the same synthesis of alkyl methyl heptenoxy acetones have been studied⁴⁾ by one of the present author at the laboratory of M^{me} MOUSSERON, École Nationale Supérieure de Chimie de Montpellier, in FRANCE.



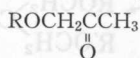
1-Alcohoxy isopropanols were prepared by lithium aluminum hydride reduction of the appropriate epoxides. An unsymmetrical epoxide form a secondary alcohol by nucleophilic attack on carbon by complex hydride ion⁵⁾. The expected products were obtained in excellent yields. Infrared spectra of these products showed a strong band at 3530 cm^{-1} , which indicate the presence of OH group. The epoxides used and the results obtained are summarized in Table I.

This paper was read at the 10th Symposium on the Chemistry of Terpenes, Essential Oils and Aromatics, at Tokyo, August, 1966.

Table I. α -Alcohoxy Isopropanol

RO	Benzyloxy	β -Phenyl ethyloxy	<i>d</i> -Citronelloxy	<i>l</i> -Menthylxy	
$^{\circ}\text{C}$, B.p./10 mmHg	123	131.5	134.5	128-128.5	
Specific gravity at 20°C	1.0352	1.0171	0.8904	0.9260	
Refractive Index at 20°C	1.5081	1.5050	1.4528	1.4575	
Specific Rotation at 20°C	0	0	2.09	-83.41	
R_f value, T.L.C.	0.25	0.26	0.40	0.52	
%, Yield	86.4	87.3	88.6	87.1	
Formula	$\text{C}_{10}\text{H}_{14}\text{O}_2$	$\text{C}_{11}\text{H}_{16}\text{O}_2$	$\text{C}_{13}\text{H}_{26}\text{O}_2$	$\text{C}_{13}\text{H}_{26}\text{O}_2$	
Carbon, %	{Calcd.	72.26	73.30	72.84	72.84
	{Found	72.15	73.10	72.57	72.61
Hydrogen, %	{Calcd.	8.49	8.95	12.23	12.23
	{Found	8.47	8.67	12.01	12.03
$\nu_{\text{OH}}^{\text{CCl}_4}$, IR	3530	3530	3530	3530	

The chromium acid-pyridine complex oxidation of 1-alcohoxy isopropanols at room temperature gave predominantly the appropriate acetones in yields of 50 to 60%. The alcohoxy acetones have been isolated from the reaction mixtures by column chromatography, because they could not be isolated by fractional distillation. Nonreacted starting materials were recovered about 20-30%. Infrared spectra of the main products showed a strong band at $1725\text{--}1730\text{ cm}^{-1}$, which indicate the presence of C=O group. The isopropanols used and the results are shown in Table II.

Table II. α -Alcohoxy Acetone

RO	Benzyloxy	β -Phenyl ethyloxy	<i>d</i> -Citronelloxy	<i>l</i> -Menthylxy	
Specific gravity at 20°C	1.0598	1.0393	0.8939	0.9415	
Refractive Index at 20°C	1.5091	1.5047	1.4503	1.4532	
Specific Rotation at 20°C	0	0	3.04	-94.86	
R_f value, T.L.C.	0.38	0.40	0.58	0.70	
%, Yield	58	50	55	49	
Formula	$\text{C}_{10}\text{H}_{12}\text{O}_2$	$\text{C}_{11}\text{H}_{14}\text{O}_2$	$\text{C}_{13}\text{H}_{24}\text{O}_2$	$\text{C}_{13}\text{H}_{24}\text{O}_2$	
Carbon, %	{Calcd.	73.15	74.13	73.54	73.54
	{Found	72.86	73.88	73.36	73.34
Hydrogen, %	{Calcd.	7.37	7.92	11.39	11.39
	{Found	7.27	7.88	11.15	11.19
$\nu_{\text{C=O}}^{\text{CCl}_4}$, IR	1725	1725	1725	1730	

enolisation⁷ of dialcohoxy ketone based according with the relative I effects of and alcohoxyl groups occurred and α -oxyketone formed rearranged to a propionic acid by way of intermediated formation of a cyclopropanone as same as the Favorskii rearrangement⁸ of α -haloketone.

Experimental

Materials.—The alcohoxo glycidyl ethers and dialcohoxy isopropanols were essentially the same used in previous work³.

Isolation of Reaction Products.—Isopropanols were isolated by fractional distillation. Alcohoxo acetones were isolated by column chromatography on silica gel and elution with pet. ethers (b.p. 50–60°C)—ethyl ether.

Identification of Reaction Products.—Products were identified in most of the cases by comparison of their infrared spectra and elemental analyses. The products and reaction mixtures were chromatographed on thin-layer of silica gel (Merck G) and developed with a solution of n-Heptane and methylethylketone (80 : 20).

Preparation of 1-Alcohoxo Isopropanols.—To a suspension of 0.075mole lithium aluminum hydride in ether, a solution of 0.1 mole 1-alcohoxo glycidyl ether in ether was added with stirring at room temperature. The reaction mixture was then heated under reflux with stirring for about 2hrs. When the reaction was completed, the mixture was decomposed by adding a saturated aqueous solution of Rochelle salt. The solution was filtered from the insoluble salts, dried over sodium sulfate, and evaporated to dryness. Fractional distillation of the crude product gave 1-alcohoxo isopropanols. Thin-layer chromatography showed a single spot. The compounds used and results obtained were listed Table I.

Preparation of 1-Alcohoxo Acetones.—To a solution of chromium acid-pyridine complex composed of 10 g chromic acid and 100 g pyridine, a solution of 0.05 mole 1-alcohoxo glycidyl ether in 50 ml pyridine was added with stirring at room temperature. After stirring for about 50hrs., the mixture was poured into water, dried over sodium sulfate, and evaporated to dryness. 1-Alcohoxo acetones were isolated by chromatography on silica gel column.

The compounds used and results obtained were listed Table II.

Preparation of 1, 3-Alcohoxo Acetones.—To a solution of chromium acid-pyridine complex composed of 10 g chromic acid and 100 g pyridine, a solution of 0.03 mole dialcohoxy isopropanols in 50 ml pyridine. In a manner similar to the above, dialcohoxy acetones were prepared.

The compound used and results were listed Table III.

Isolation and Identification of α, β -Phenylethyloxy Propionic Acid in Above Oxidation.—A crystalline compound was isolated by column chromatography of the crude product in above oxidation of di- β -phenylethyloxy isopropanol. Recrystallisation from a mixed solvent composed of petroleum ether and ethyl ether gave white needles, m.p. 80–80.5°C. Thin-layer chromatogram on silica gel (n-Hept. MeCOEt, 80–20): 1 spot $R_f=0.11$.

Anal. Calcd. for $C_{19}H_{22}O_4$: C, 72.59; H, 7.05. Found: C, 72.41; H, 6.83.

Molecular Weight. Calcd. for $C_{19}H_{22}O_4$: 314.38. Found (by titrating method): 315.

The infrared spectra showed carbonyl bands at 1730 and 1780 in CCl_4 , and combined hydroxyl band $2500\sim 3000\text{ cm}^{-1}$ (broad).

Acknowledgment.—The authors are very grateful to the Takasago Perfumery Co. for its financial support.

References

- 1) M. Ito, K. Abe: *Memoirs of the Kitami Institute of Technology*, **1**, 19-25 (1963).
- 2) *ibenda*, **2**, 43-51 (1964).
- 3) *ibenda*, **4**, 59-64 (1966).
- 4) C. Levallois, M. Ito, M. Mousseron-Canet and B. Bosc: *Synthèse de Quelques Nouveaux Éthers Tetrahydrofuranniques* *Bull. Soc. Chim. France*, in printing.
- 5) L. W. Trevoy, W. G. Brown: *J. Am. Chem. Soc.*, **71**, 1675 (1949).
- 6) R. P. Mariella, J. L. Leech: *ibenda*, **71**, 3558 (1949).
- 7) J. Kenner, G. N. Richards: *J. Chem. Soc.*, **1953**, 2240.
- 8) J. D. Cram, Hammond: *Organic Chemistry*, p. 499, McGraw-Hill Book Co., Inc., New York (1964).

$$N_a = P_{-a} = \{x : 0 \leq x \leq c \text{ for every } b, c \in R^+ \text{ and } a = b - c\}.$$

we suppose in R the following postulates:

- 1) $P_a = \{0\}$ implies $a \leq 0$,
- 2) $P_{a+b} \subset P_a + P_b$ for every element $a, b \in R$.

We shall call such a semi-ordered linear space *semi-lattice ordered* (we write *s.l.o.l.* space).

We shall investigate a method of imbedding an Archimedean s.l.o.l. space in R on a compact Hausdorff space.

The principles and methods in this paper due to I. Amemiya in [3].

C. Properties of semi-lattice ordered linear spaces

Let R be a s.l.o.l. space. By the definition of P_a in R , we have the following:

- (1) $a \leq b$ implies $P_a \subset P_b$.
- (2) $x \in P_a$ implies $P_x \subset P_a$.
- (3) $a \in P_a$, if and only if $a \geq 0$.
- (4) $P_{-a} = aP_a$ for every $a \geq 0$.

We have by the postulate 1):

$$(5) P_a \cap P_b = \{0\}, a, b \geq 0 \text{ implies } a \sim b = 0.$$

$$(1) R^+ = \{x : 0 \leq x \in R\}$$

$$(2) P_a + P_b = \{x + y : x \in P_a \text{ and } y \in P_b\}$$