Syntheses and Odor of 6-Oxohexanoic Acids Having 1,3-Dioxane Moiety.

Hiromi HAMAMATSU, Yoshinobu NAOSHIMA, Shoji WAKABAYASHI*, Shuichi HAYASHI

Department of Chemistry, Faculty of Science, Okayama University of Science, [REDACTED]

Such cyclic monoethers as rose oxide and linalool oxide are known to possess floral note, but to our knowledge, organoleptic properties of cyclic diethers are unknown. In the course of our work on acid-catalyzed aldol-condensation of alkyl cyclohexanones with formaldehyde¹⁾, two ethyl esters of 6-oxohexanoic acids having 1,3-dioxane moiety, i. e., ethyl 5-(4-oxobutyl)-1,3-dioxane-5-carboxylate (**4**) and ethyl 4-(5-formyl-1,3-dioxan-5-yl)butyrate (**5**), and their derivatives were prepared to know their odor.

These ethyl esters **4** and **5** were synthesized by oxidation with lead tetraacetate of 2,4-dioxaspiro [5.5] undecan-7-one¹⁾. The first oxidation was carried out in acetic acid to give acetoxy ketone **1**. Hydrolysis of **1** gave a tautomeric mixture of α -hydroxy ketones (**2** and **3**) which could not be separated by GLC or elution chromatography. The hydrolyzed products (**2** and **3**) were subjected to the second oxidation in benzene-ethanol to afford a mixture of the ethyl esters **4** and **5** by cleavage of the cyclohexane ring with relative ratio of 1 : 24.

The ethyl esters (**4** and **5**) were changed to acetals **7** and **8**. The ethyl ester **5** was converted to 4-(5-formyl-1,3-dioxan-5-yl) butyric acid **6**, ethyl 4-(5-hydroxymethyl-1,3-dioxan-5-yl) butyrate **9** (50.6 % yield), and ethyl 4-[5-(1-hydroxyethyl)-1,3-dioxan-5-yl] butyrate **10** (52.5 % yield) by treating with alkali, with lithium aluminum hydride, and with methylmagnesium iodide, respectively.

In addition, the ethyl ester **5** was heated with 2-(6,6-dimethyl-2-norpinen-2-yl) ethyl alcohol (nopol) in the presence of sodium to afford nopyl esters of 4-(5-formyl-1,3-dioxan-5-yl) butyric acid **11**, 4-(1,3-dioxan-5-yl) butyric acid **12**, and 2,4-dioxaspiro [5.4] dec-7-ene-8-carboxylic acid **13** in 18 %, 5 % and 6 % yield. The compound **12** is a decarboxylated product. The reaction of **5** with sodium gave ethyl esters **14** and **15**, and **5** was gradually changed to **14** on standing at room temperature.

No. 81-004-2/2

The ethyl esters **4**, **5**, **7-10**, **14** and **15** had apple-like fruity odor similar to those ethyl esters of the corresponding 6-oxohexanoic acids. Therefore, it was found that the 1, 3-dioxane moiety does not cause any influence to the odor of 6-oxohexanoic acids, but the odor became long lasting due to increase of molecular weight. The nopyl esters **11**, **12** and **13** showed refreshing woody note.

- 1) F.Hirano, S.Wakabayashi, *Bull. Chem. Soc. Jpn.*, **48**, 2579 (1975), **50**, 3059 (1977), **52**, 799 (1979)
(原報: 6 ページ, 図 1, 引用文献 1)

次 号 予 定

「生体関連微量金属をめぐる最近の話題」特集号

巻 頭 言

日本の合成化学者の活躍と関連分野との協力.....石井 義郎

特 集

序にかえて.....	平川 芳彦
生体必須微量重金属元素と海洋の化学環境.....	北野 康
スーパーオキシドジスムターゼの化学.....	花木 昭
非ヘム鉄.....	大倉 一郎 北島 信正
チトクローム-p-450	佐藤 了
ポルフィリンおよびその関連物質の金属錯体.....	生越 久靖 青山 安宏
ビタミン B ₁₂ の生化学における最近の進歩.....	虎谷 哲夫
亜鉛酵素—特にアルコール脱水素酵素について—.....	松本 和子 不破敏一郎
Mo 酵素とそのモデル化合物.....	中村 晃 上山 憲一
重金属とメタロチオネイン.....	鈴木 和夫
重金属の代謝と体内分布.....	森田 昌敏
ブレオマイシンの DNA 切断活性と金属錯体.....	杉浦 幸雄
金属と疾病.....	山根 靖弘 坂井 和男
微量金属と植物.....	高橋 英一
食品中の有害金属.....	細貝祐太郎

報 文

Alkylation of Phenylacetonitrile Under Organic-aqueous Alkali Hydroxide Two Phase System in the Presence of Poly (ethylene glycol)s or Their Ethers.須方 一明

REVINDEX, 新しい合成, ほか