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Abstract

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A NEW METHOD FOR PREPARING POLYENE ALDEHYDES

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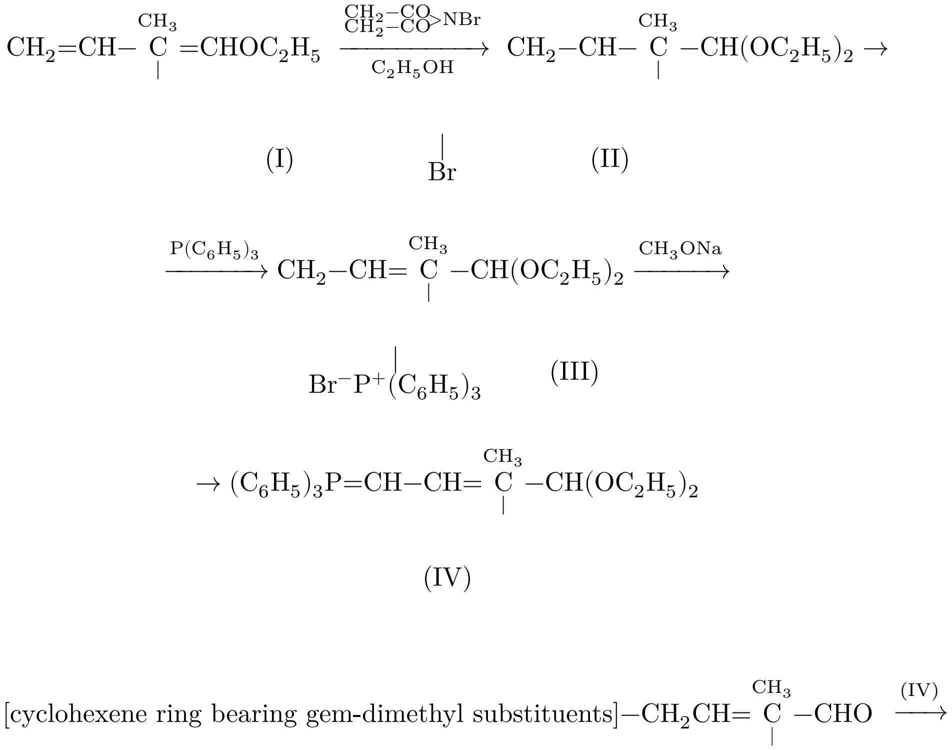
Among polyene aldehydes, β-C_{19}-aldehyde (VII), or 8-(2^1,6^1,6^1-trimethylcyclohexen-1^1-yl)-2,6-dimethyloctatrien-2,4,6-al-1, is of special importance, being the main product in the synthesis of β-carotene (^{1}). The present communication describes a new method for preparing β-C_{19}-aldehyde from β-C_{14}-aldehyde (V) and the acetal of γ-bromotiglic aldehyde (II) by the Wittig reaction. The possibility of using haloacetals in this reaction had not previously been known. The use in the Wittig reaction of various haloacetals, readily obtainable from 1-alkoxydienes, opens a simple route for the synthesis of polyene aldehydes.



$$CH_2{=}CH{-}\underset{|}{\overset{CH_3}{C}}{=}CHOC_2H_5 \xrightarrow[C_2H_5OH]{\substack{CH_2-CO\\CH_2-CO}>NBr} CH_2{-}CH{-}\underset{|}{\overset{CH_3}{C}}{-}CH(OC_2H_5)_2 \rightarrow$$

(I) $\underset{Br}{|}$ (II)

$$\xrightarrow{P(C_6H_5)_3} CH_2{-}CH{=}\underset{|}{\overset{CH_3}{C}}{-}CH(OC_2H_5)_2 \xrightarrow{CH_3ONa}$$

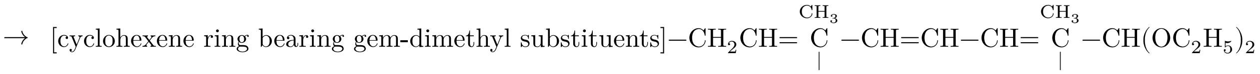
$$\overset{|}{Br^-P^+(C_6H_5)_3}$$ (III)

$$\rightarrow (C_6H_5)_3P{=}CH{-}CH{=}\underset{|}{\overset{CH_3}{C}}{-}CH(OC_2H_5)_2$$

(IV)

$$\text{[cyclohexene ring bearing gem-dimethyl substituents]}{-}CH_2CH{=}\underset{|}{\overset{CH_3}{C}}{-}CHO \xrightarrow{(IV)}$$

(V)



$$\rightarrow \text{[cyclohexene ring bearing gem-dimethyl substituents]}{-}CH_2CH{=}\overset{CH_3}{\underset{|}{C}}{-}CH{=}CH{-}CH{=}\overset{CH_3}{\underset{|}{C}}{-}CH(OC_2H_5)_2$$

(VI)

$$\xrightarrow{10\%\ H_3PO_4} \text{[cyclohexene ring bearing gem-dimethyl substituents]}{-}CH_2CH{=}\overset{CH_3}{\underset{|}{C}}{-}CH{=}CH{-}CH{=}\overset{CH_3}{\underset{|}{C}}{-}CHO$$

(VII)

1-Ethoxy-2-methylbutadiene-1,3 (I) (^{2}), under the action of bromosuccinimide and alcohol, is converted into the diethyl acetal of γ-bromotiglic aldehyde (II). The latter is introduced, in ether solution, into reaction with triphenylphosphine, as a result of which 4-(1,1-diethoxy-2-methylbuten-2-yl)-triphenylphosphonium bromide (III) is obtained. This entire process is carried out without isolation of the intermediate products, essentially in a single operation.

Subsequently, β-C_{14}-aldehyde (V) and the phosphonium salt (III) are dissolved in methanol and treated with sodium methylate. In this process the phosphonium salt (III), eliminating hydrogen bromide, is converted into the phosphorylene compound (IV), which reacts with β-C_{14}-aldehyde (V) to form the diethyl acetal of β-C_{19}-aldehyde (VI).

The yield, based on the β-C_{14}-aldehyde that entered into reaction, is 78.5%. On hydrolysis of the diethyl acetal of β-C_{19}-aldehyde (VI) with 10% phosphoric acid, β-C_{19}-aldehyde (VII) is formed as a mixture of two stereoisomeric forms. The β-C_{19}-aldehyde (VII) obtained has an absorption band characteristic of trienals, $\lambda_{\max}$ (in alcohol) 327.5 mμ (ε23500). The structure of the aldehyde (VII) obtained is also confirmed by the IR absorption spectrum. Figure 1 shows the IR absorption spectrum of an 8.65% solution of β-C_{19}-aldehyde (VII) in CCl_4. Below, for comparison, is given the IR absorption spectrum of a 9.45% solution in CCl_4 of the fully trans-β-C_{19}-aldehyde known from the literature (^{1}) (m.p. 64–65°).

Fig. 1: IR absorption spectrum of β-C_{19}-aldehyde.

The individual stereoisomeric forms were isolated as 2,4-dinitrophenylhydrazones by crystallization from alcohol. The high-melting and less soluble fully trans isomer has m.p. 199–200° and gives no depression on mixed melting with the 2,4-dinitrophenylhydrazone of an authentic sample of fully trans-β-C_{19}-aldehyde. $\lambda_{\max}$ (in isooctane) 396 mμ.

The more soluble cis isomer has m.p. 167-169°, $\lambda_{\max}$ (in isooctane) 397 mμ. Since in the Wittig reaction a double bond having the trans configuration is usually obtained, it is probable that in the isomer obtained the double bond having the cis configuration is in the 2–3 position. However, additional investigations are needed to prove this assumption.

Experimental Part

β-Ionone was obtained by cyclization of pseudoionone with 100% sulfuric acid in a nitromethane solution (^{3}). B.p. 80° (0.07 mm), n_D^{20}1.5181, $\lambda_{\max}$ (in alcohol) 222 mμ (ε6980), 296.5 mμ (ε10300).

β-C_{14}-aldehyde was obtained from β-ionone by the Darzens reaction (^{4}). n_D^{20}1.5095, $\lambda_{\max}$ (in isooctane) 224 mμ (ε17000), 280 mμ (ε600).

4-(1,1-Diethoxy-2-methylbuten-2-yl)-triphenylphosphonium bromide (III). To a solution of 22.4 g of 1-ethoxy-2-methylbutadiene-1,3 (I) in 40 ml of anhydrous ethyl alcohol at a temperature of 10–15° in a nitrogen atmosphere and with vigorous stirring over 45 min, 36.5 g of bromosuccinimide was added in portions. The mixture was stirred at 20° for 1.5 h, after which the precipitated succinimide was filtered off, washed on the filter with ether, and the mother liquor, containing 4-bromo-1,1-diethoxy-2-methylbutene-2 (II), was added to a solution of 52.4 g of triphenylphosphine in 300 ml of dry ether. The reaction mixture was stirred at 20° for 10 h, and then for 4 h at the boiling point of ether. The precipitated 4-(1,1-diethoxy-2-methylbuten-2-yl)-triphenylphosphonium bromide (III) was filtered off and dried in a vacuum desiccator. Weight 71.2 g (70%). The product was used in the next reaction without recrystallization.

Found, %: C 64.42; 64.28; H 5.93; 5.98; P 6.20; 5.87
$C_{27}H_{32}BrO_2P$. Calculated, %: C 64.93; H 6.47; P 6.22

After recrystallization from alcohol, salt (III) has m.p. 244°.

Diethyl acetal of β-C_{19}-aldehyde (VI). To a solution of 68 g of phosphonium salt (III), 100 ml of methanol, and 18 g of β-C_{14}-aldehyde (V), under a stream of nitrogen and with stirring at 55° for 15 min, was added a solution of 3 g of sodium in 80 ml of methanol, and then the reaction mixture was stirred at 60° for 8 hr. The methanol was evaporated in vacuo, and the residue was thoroughly extracted with low-boiling petroleum ether. The ethereal solution was washed with water and dried over magnesium sulfate. After removal of the petroleum ether the product was distilled in vacuo. This gave 7.3 g of the starting β-C_{14}-aldehyde with b.p. 76–83° (0.08 mm), n_D^{20} 1.5085, and 14.1 g of diethyl acetal of β-C_{19}-aldehyde (VI) with b.p. 145–147° (0.08 mm), n_D^{20} 1.5465.

$C_{23}H_{38}O_2$. Found, %: C 79.56; 79.46; H 10.83; 10.84
Calculated, %: C 79.71; H 11.05

β-C_{19}-aldehyde VII. A mixture of 4 g of diethyl acetal of β-C_{19}-aldehyde (VI), 15 ml of dioxane, 7 ml of 10% phosphoric acid, and traces of hydroquinone was stirred in a nitrogen atmosphere at 80–90° for 3 hr. The reaction product was treated with ether and water. The ethereal layer was separated, washed with 5% potassium hydroxide solution and with water, and dried over magnesium sulfate. The ether was distilled off in a slight vacuum, and the residue was kept in vacuo at 0.5 mm for an hour. This gave 3.07 g of undistilled β-C_{19}-aldehyde, n_D^{20} 1.5838, $\lambda_{\max}$ (in alcohol) 327 mμ (ε 22300). On distillation in vacuo, β-C_{19}-aldehyde has b.p. 135–138° (0.02 mm), n_D^{20} 1.5805, $\lambda_{\max}$ (in alcohol) 327.5 mμ (ε 23500).

$C_{19}H_{28}O$. Found, %: C 83.40; 83.90; H 10.45; 10.37
Calculated, %: C 83.77; H 10.36

2,4-Dinitrophenylhydrazones of the isomeric β-C_{19}-aldehydes. To 0.4 g of 2,4-dinitrophenylhydrazine were added 2 ml of conc. hydrochloric acid, 2 ml of water, and 10 ml of alcohol. The solution was filtered, and to it was added 0.3 ml of the previously obtained β-C_{19}-aldehyde, dissolved in 20 ml of alcohol. After 2 hr, the precipitated mixture of isomeric 2,4-dinitrophenylhydrazones was filtered off and subjected to fractional recrystallization from alcohol. The crystals were heated in alcohol (100–120 ml) in such a way that the readily soluble 2,4-dinitrophenylhydrazone of cis-β-C_{19}-aldehyde passed into solution, while the remaining insoluble 2,4-dinitrophenylhydrazone of trans-β-C_{19}-aldehyde could be rapidly filtered off from the hot solution. After several recrystallizations from alcohol, the isomeric 2,4-dinitrophenylhydrazones were isolated individually in approximately equal amounts.

The 2,4-dinitrophenylhydrazone of all-trans-β-C_{19}-aldehyde (bright purple crystals) has m.p. 199–200°, $\lambda_{\max}$ (in isooctane) 396 mμ and gives no depression on mixed melting with an authentic sample of the 2,4-dinitrophenylhydrazone of all-trans-β-C_{19}-aldehyde.

$C_{25}H_{32}N_4O_4$. Found, %: N 12.60; 12.32
Calculated, %: N 12.38

The 2,4-dinitrophenylhydrazone of cis-β-C_{19}-aldehyde (dark-brown crystals) has m.p. 167–169°, $\lambda_{\max}$ (in isooctane) 397 mμ.

$C_{25}H_{32}N_4O_4$. Found, %: N 12.35; 12.09
Calculated, %: N 12.38

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named after M. V. Lomonosov

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