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Abstract

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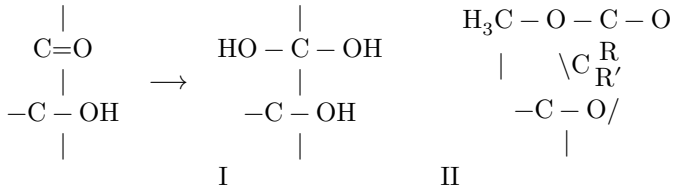
BENZYLIDENE DERIVATIVES OF THE HYDRATED FORM OF α-KETO ALCOHOLS CONTAINING 1,3-DIOXOLANE RINGS

(Presented by Academician I. N. Nazarov, 13 VII 1956)

Compounds containing 1,3-dioxolane and 1,3-dioxane rings—cyclic full ketals and acetals—are widely used in organic chemistry. They are obtained, in particular, for protecting alcoholic groups from the action of reagents during methylation and acylation of polyhydric alcohols and during transformations of monosaccharides. The stability of these rings in the presence of alkalis and their easy hydrolyzability in an acid medium to aldehydes or ketones and to the transformation products of the initial polyhydroxy compounds make it possible to carry out reactions in the desired direction. As an example one may cite the work ([1]), in which the β-methyl ether of glycerol was first obtained in the form of an α-, γ-benzylidene derivative (2-phenyl-1,3-dioxane) by protecting the terminal alcoholic groups. Passing through the same benzylidene derivative, Stimmel and King ([2]) obtained β-monoethers of glycerol and fatty acids. The greatest significance of 1,3-dioxane and 1,3-dioxolane rings has been in the chemistry of sugars, where extensive work has been carried out with acetone and benzylidene derivatives. The latter, however, especially dibenzylidene derivatives, have not been sufficiently studied. Compounds containing 1,3-dioxolane rings are obtained by two methods: by condensation of di- or polyhydric alcohols with aldehydes or ketones in the presence of catalysts (H_2SO_4, $CuSO_4$, etc.) ([3]), and by condensation of oxides with carbonyl-containing compounds in the presence of sulfuric acid or salts of heavy metals ([4]).

Since in recent years α-methoxy-α-oxy compounds (methyl lactolides of α-keto alcohols) ([5], [6]) have become readily accessible, it seemed of interest to condense them with aldehydes or ketones in order to obtain the first representatives of a new type of derivative of the hydrated form of α-keto alcohols (I)—4-methoxy-1,3-dioxolanes (II)



I II

The first attempts at condensation of the methyl lactolide of the secondary keto alcohol H-propylbenzoylcarbinol (III) with ketones were not successful*: upon interaction of the methoxyoxy compound with acetone containing 0.2% water, in the presence of sulfuric acid as catalyst, only a small amount was obtained

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* Performed by V. Ivanova.

the amount of hydrolysis product—ketospirit propylbenzoylcarbinol (IV); chiefly, however, dimerization of methyl lactolide was observed:

$$\text{III} \qquad C_6H_5{-}\overset{\overset{O}{\|}}{C}{-}CH{-}C_3H_7 \;\rightarrow\; C_6H_5CO{-}CHOH{-}C_3H_7 \;+\; \text{IV}$$

On attempting to carry out the condensation with benzophenone in a solution of carbon tetrachloride in the presence of $SnCl_4$ as catalyst, only isomerization of the methyl lactolide of propylbenzoylcarbinol into the methyl ether of phenylpropionylcarbinol occurred.

In the present work we succeeded in carrying out the condensation of the methyl lactolide of dimethylbenzoylcarbinol (V) ([6]) with benzoic, anisic, and *p*-nitrobenzoic aldehydes:

$$\text{V} \quad + \quad X{-}C_6H_4{-}CHO \;\longrightarrow\; \text{VI}$$

where $X = H$, CH_3O, or NO_2. The condensation was carried out in a solution of carbon tetrachloride in the presence of several drops of $SnCl_4$ as catalyst. The reaction takes place at the moment the oxide is added to the aldehyde complex with $SnCl_4$. The yield of the product purified by recrystallization is 40–50% of theory.

4-Methoxy-5,5-dimethyl-2-aryl-4-phenyl-1,3-dioxolanes are well-crystallizing substances; in the condensation with benzoic aldehyde and *p*-nitrobenzoic aldehyde the dioxolanes were obtained in the form of two diastereomeric forms.

In the condensation of α-methoxy oxide with benzoic aldehyde, 4-methoxy-5,5-dimethyl-2,4-diphenyl-1,3-dioxolane was obtained in the form of two diastereomeric forms: (VI, $X = H$):

α-form with m.p. 98–99°.

Found, %: C 75.9; 76.2; H 7.24; 7.15; OCH_3 10.61; 11.01

β-form with m.p. 84–86°.

Found, %: C 76.2; H 7.31; OCH_3 11.01
$C_{18}H_{20}O_3$. Calculated, %: C 76.03; H 7.09; OCH_3 10.91

In the condensation with anisic aldehyde, 4-methoxy-5,5-dimethyl-2-*p*-methoxyphenyl-4-phenyl-1,3-dioxolane (VI, $X = OCH_3$), m.p. 74–75°, was obtained.

Found, %: C 72.36; 72.40; H 7.09; 7.11; OCH_3 20.02; 19.88
$C_{19}H_{22}O_4$. Calculated, %: C 72.58; H 7.05; OCH_3 19.75

On condensation with *p*-nitrobenzaldehyde, 4-methoxy-5,5-dimethyl-2-*p*-nitrophenyl-4-phenyl-1,3-dioxolane (VI, X = NO_2) was obtained in the form of two diastereomeric forms:

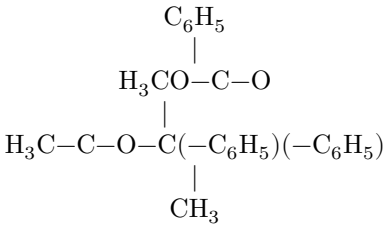
α-form with m.p. 139–140°.

Found, %: C 65.58; H 5.95; OCH_3 9.22; N 4.36

β-form with m.p. 86.88°.

Found, %: C 65.71; H 6.12; OCH_3 9.28; N 4.41
$C_{18}H_{19}O_5N$. Calculated, %: C 65.70; H 5.82; OCH_3 9.43; N 4.27

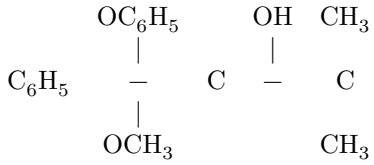
In the same way, condensation of the methyl lactolide of dimethylbenzoylcarbinol with benzophenone was carried out. The resulting 4-methoxy-5,5-dimethyl-2,2,4-triphenyl-1,3-dioxolane (VII) had m.p. 89–90°.



VII

Found, %: C 79.81; 79.84; H 6.94; 6.63; OCH_3 8.68; 8.72
$C_{24}H_{24}O_3$. Calculated, %: C 79.97; H 6.71; OCH_3 8.62

All 4-methoxy-1,3-dioxolanes, with the exception of the nitro-group-containing compound, have characteristic absorption curves in the ultraviolet region with an absorption maximum at λ 318 mμ; the same maximum is present in the spectrum, recorded by us for the first time, of the phenyl methyl ketal of dimethylbenzoylcarbinol (VIII):



VIII

The spectrum of 4-methoxy-5,5-dimethyl-2-*p*-nitrophenyl-4-phenyl-1,3-dioxolane is characterized by very intense general absorption in the region examined (340–290 mμ). In the infrared spectrum the compounds obtained by us have no absorption maxima in the region 1680–1750 cm^{-2}.

All the compounds obtained by us, representing as it were "double" full ketals and possessing a characteristic alternation in the chain of oxygen and carbon atoms, are very stable in neutral and alkaline media and withstand prolonged boiling with aqueous alkalis. In acidic aqueous medium, on the contrary, they are readily hydrolyzed both on heating and at room temperature. Since all the compounds (VI, VII) are crystalline substances, their hydrolysis on immersion in acidified water (5% H_2SO_4) proceeds very slowly in the cold. As a result of hydrolysis, a ketol alcohol—dimethylbenzoylcarbinol—the carbonyl-containing compound taken for the condensation, and methyl alcohol are formed. Identification of the hydrolysis products was carried out in the form of their 2,4-dinitrophenylhydrazones by gradual successive precipitation of derivatives of the corresponding aldehyde and then of the ketol alcohol. Methyl alcohol was not identified.

The facile hydrolysis of the compounds obtained in an acidic medium and their stability in an alkaline medium confirm their structure as methoxy-substituted 1,3-dioxolanes.

On the basis of the approximate equality of the condensation rates of aldehydes bearing substituents of opposite electrochemical character (the groups *n*-CH_3O and *n*-NO_2), and also of the facile condensation with benzophenone, it may be assumed that the reaction rate is determined chiefly by the rate of opening of the oxide ring.

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REFERENCES

[1] H. Hill, M. Whelen, H. Hibbert, J. Am. Chem. Soc., **50**, 2235 (1928).
[2] B. Stimmel, C. King, J. Am. Chem. Soc., **56**, 1724 (1934).
[3] E. Fischer, Ber., **27**, 1532 (1894); **28**, 1145 (1895); H. Hibbert et al., J. Am.

Chem. Soc., **46**, 1286 (1924); **50**, 3375, 3378 (1928); H. Ohle, I. Koller, Ber., **57**, 1566 (1924).
[4] M. Bogert, R. Roblin, J. Am. Chem. Soc., **55**, 3741 (1933); G. Willfang, T. B. Resin, Ber., **70**, 2167 (1937); **74**, 145 (1941).
[5] T. I. Temnikova, E. N. Kropacheva, ZhOKh, 1917 (1949).
[6] T. I. Temnikova, N. Almashi, ZhOKh, **23**, 1338 (1953).

Note: Figure translations are in progress. See original paper for figures.