INTERACTION OF 1,3-DIOXOLANES WITH ACETYLENE UNDER CONDITIONS OF THE IOTSICH REACTION

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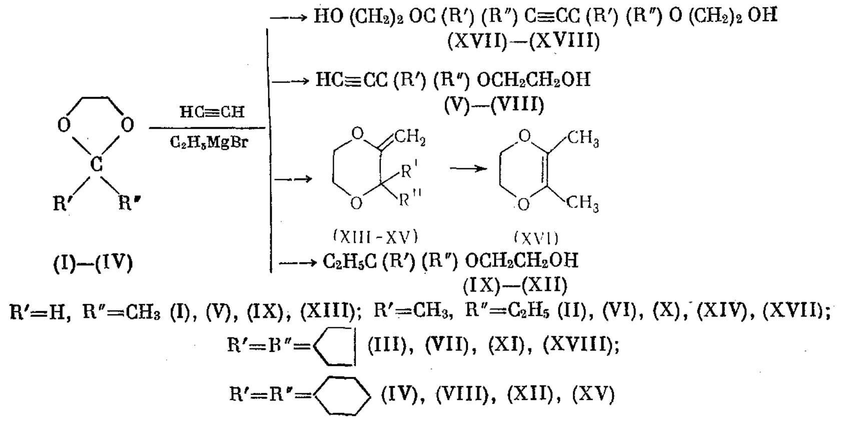
Magnesiumbromo derivatives of phenylacetylene [1, 2] and vinylacetylene [3-7] comparatively readily open the 1,3-dioxolane ring with the formation of β-hydroxyalkyl ethers of the appropriate acetylenic alcohols. Propargyl alcohol can be used in this reaction as a monosubstituted acetylene [8].

The present article is concerned with the attempt to extend this reaction to acetylene. In reference [9] on the cleavage of C–O bond by the Iotsich complex based on acetylene a study was made only of the open structure acetals. Carrying out the reaction at 95° without a solvent the researchers [9] obtained 3-phenyl-3-ethoxy-1-propyne from diethylacetal of benzaldehyde with a yield of 66%; di-n-propylformal under the same conditions gave 1,4-di-(propoxy)-2-butyne (yield 31-35%), and in the case of diethyl acetal of acetaldehyde it gave 3-methyl-3-ethoxy-1-propyne (yield not given). Similar transformations of dialkylacetals were described in [10]. Cyclic acetals (I)-(IV), as shown by our studies, are also capable of cleavage by magnesiumbromo acetylenes (MBA) at one of the C–O bonds; however, as compared with vinyl- and phenylacetylenes, the cleavage proceeded with much greater difficulty and was accompanied by side processes. The reaction was carried out at temperatures of 80-120° in different solvents: excess of reacting 1,3-dioxolane, tetrahydrofuran (THF), benzene, toluene, and xylene. Different methods were used to prepare MBA: at atmospheric pressure and in an autoclave under 12 atm (gage pressure) of C_2H_2: in ether, THF, and in aromatic solvents; on the basis of ethylmagnesium bromide (EMB) and butyl- and phenylmagnesium bromide. As a rule, the reaction gave a complex mixture containing, according to the IR spectra, alongside with the expected hydroxyacetylenes (V)-(VIII) and (XVII)-(XVIII), different products of their cyclization [for example, (XIII)-(XVI)] and saturated hydroxyethers (IX)-(XII) which correspond to the opening of the dioxolane ring by the starting Grignard reagent, mainly EMB. In all cases, the overall yield did not exceed 20%.



When, for the decomposition of the reaction mixture, dilute acid was used instead of saturated NH_4Cl solution, the unsaturated dioxanes (XIII)-(XVI) were partially hydrolyzed to give the appropriate carbonyl-containing compounds, thus indicating the presence of characteristic absorption bands of the carbonyl group

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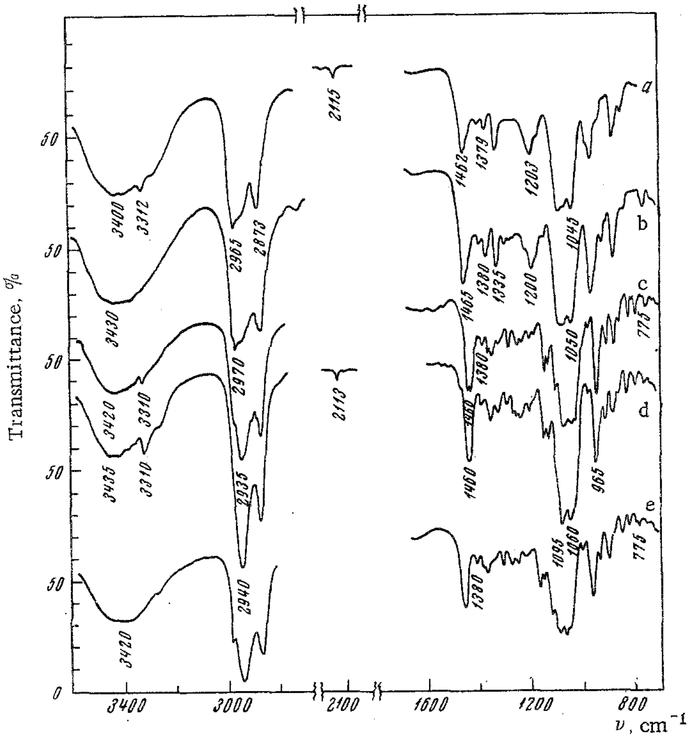
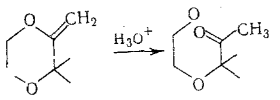


Fig. 1. IR spectra of reaction products of 2-methyl-1,3-dioxolane (I) and MBA (a-c) and of standard sec-butylcellosolve (IX) (d).



Under conditions of low yields, the separation of the resulting mixtures into individual products represents a laborious operation; therefore, the IR spectrum analysis was the main method used in these studies. Since all main components in the mixture corresponded to quite a definite set of characteristic frequencies, the spectral identification was indeed the most rational. The IR spectrum (Fig. 1, curve a) of the product isolated in the reaction of 2-methyl-1,3-dioxolane with MBA (ether, then toluene, 90-98°, 3 h), fully corresponds to the structure of 3-methyl-3-(β-hydroxyethyl)-1-propyne (V). A strong maximum in the 3300 cm^{-1} region in combination with the weak peak at 2100 cm^{-1} clearly indicate a monosubstituted acetylenic fragment ($HC \equiv C-$). An intense wide band in the 3410 cm^{-1} region confirms the presence of the hydroxyl group. A weakly resolved multiplet at 1050-1170 cm^{-1} corresponds to valence vibrations of the C–O group, $-OCH_2CH_2OH$. The product, apparently, does not contain noticeable impurities of sec-butylcellosolve (IX), since its spectrum shows no band at a frequency of 1347 cm^{-1} which is shown by the spectrum of the standard sample (IX) (Fig. 1d); instead, an intense peak is shown in the 1326 cm^{-1} region. Differences are shown in the relative intensities of the bands corresponding to the methyl group (2980, 1460, 1375 cm^{-1}). The weak bands in the region of 1650 and 1700 cm^{-1}, based on the data [11], can be ascribed to the valence vibrations of the double bond in the rings (XIII) and (XVI) present as impurities. The product of a similar interaction, carried out under more rigid conditions (THF, then toluene, 120°, 3 h) also showed no saturated hydroxyether (IX) (Fig. 1b), but the amount of 2,3-dimethyl-1,4-p-dioxane (XVI) somewhat increased (a more intense band at 1705 cm^{-1}, additional maxima in the 1000-1200 cm^{-1} region).

Reducing the time of the preparation of MBA and an elevation in the temperature resulted in the formation of sec-butylcellosolve (IX) in the reaction mixture. When the preparation of MBA was carried out for 1 h at 37-50° instead of 5 h at 0-10°, the isolated product was practically pure sec-butylcellosolve (Fig. 1c).

Similar conclusions were derived in the analysis of IR spectra (Figs. 2 and 3) of mixtures obtained under different conditions from dioxolanes (II)-(IV) (see "Experimental"). There is of interest, for example,

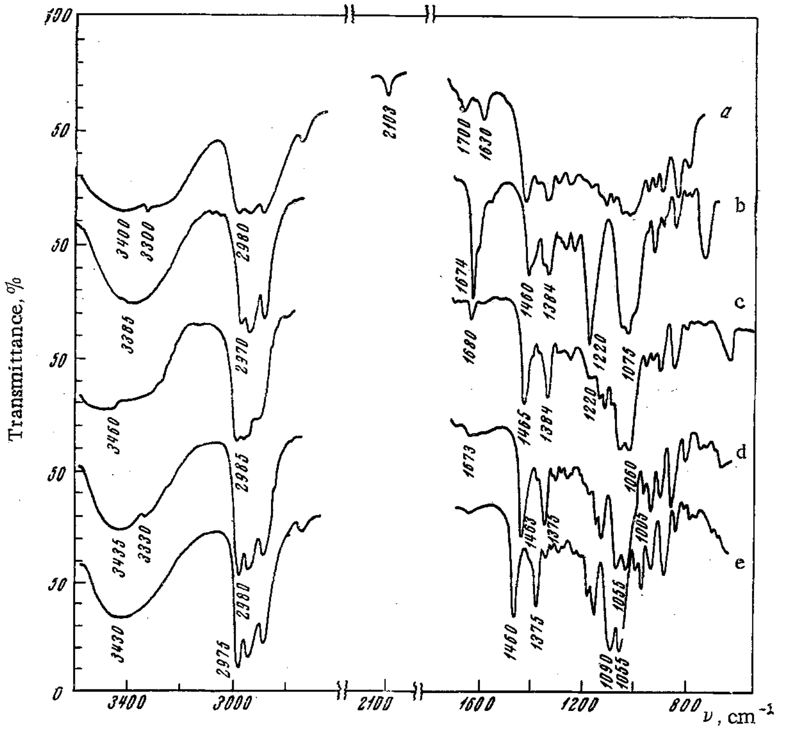


Fig. 2. IR spectra of reaction products of 2-methyl-2-ethyl-1,3-dioxolane (II) with MBA (a-d) and of standard hydroxyether (X) (e).

the spectrum illustrated in Fig. 2, curve b. The very intense bands in the region of 1674, 1220, and 1075 cm^{-1} indicate that the mixture contains considerable amounts of methylene dioxane (XIV) alongside with the saturated hydroxyether (X) (3385, 1460, and 1384 cm^{-1}): acetylenic hydroxyether (VI) is absent.

EXPERIMENTAL

Interaction of 1,3-Dioxolanes with MBA. 2-Methyl-1,3-dioxolane (I). Into an ether solution of EMB, obtained from 4.8 g of Mg, was passed purified and dried acetylene with stirring and cooling (~0 to 10°) for 5 h. The solution turned pink and became slightly hot. Acetal (I), 9 ml, and 30 ml of toluene were then added. The ether was removed and the mixture heated for 3 h on a boiling water bath. After decomposing with dilute (1 : 40) HCl and subsequent conventional treatment the mixture was fractionated in vacuo. Yield 1.9 g (16.7%) of 3-methyl-3-(β-hydroxyethoxy)-1-propyne (V), bp 68-71° (24 mm); n_D^{20} 1.4240; d_4^{20} 0.9113. Purity of the substance, according to GLC data, exceeded 95%. The IR spectrum is given in Fig. 1a. Acetylene was passed through the EMB solution (0.2 M in 100 ml of ether) for 10 min at 8-20° and for 1 h at 37-50°. This gave a thick mass to which 30 ml of toluene and 18 ml of acetal (I) were added. The mixture (without discontinuing the passage of acetylene) was heated for 2 h on a boiling water bath. Standard treatment and fractionation yielded a fraction (3.3 g) of bp 60-63° (19 mm); n_D^{20} 1.4182; d_4^{20} 0.9017, which according to the constants and spectrum (Fig. 1c) corresponds to sec-butylcellosolve (IX), [bp 73° (37 mm); n_D^{20} 1.4112, d_4^{20} 0.8964].

To THF saturated with acetylene (cooled with ice) was added dropwise for 2 h EMB, obtained from 0.5 M Mg in ether, without stopping the passage of acetylene. The mixture turned pink and, despite cooling, became hot. Acetal (I), 20.7 ml, and 100 ml of toluene were then added. After the removal of ether and THF, the mixture was heated for 3 h at 120°. This treatment yielded 3.5 g of the fraction with bp 50-62° (19 mm), which according to IR spectrum (Fig. 1b) was acetylene hydroxyether (V) with an admixture of isomerized cyclization product (XIII) (a band in 1705 cm^{-1} region) and of solvent (toluene) (bands at 1495, 1602, and 3025 cm^{-1}).

2-Methyl-2-ethyl-1,3-dioxolane (II). The Iotsich reagent was obtained in one stage by adding 38 ml (0.5 M) C_2H_5Br to 12.6 g Mg in ether with a simultaneous passage of acetylene for 4 h. To MBA thus

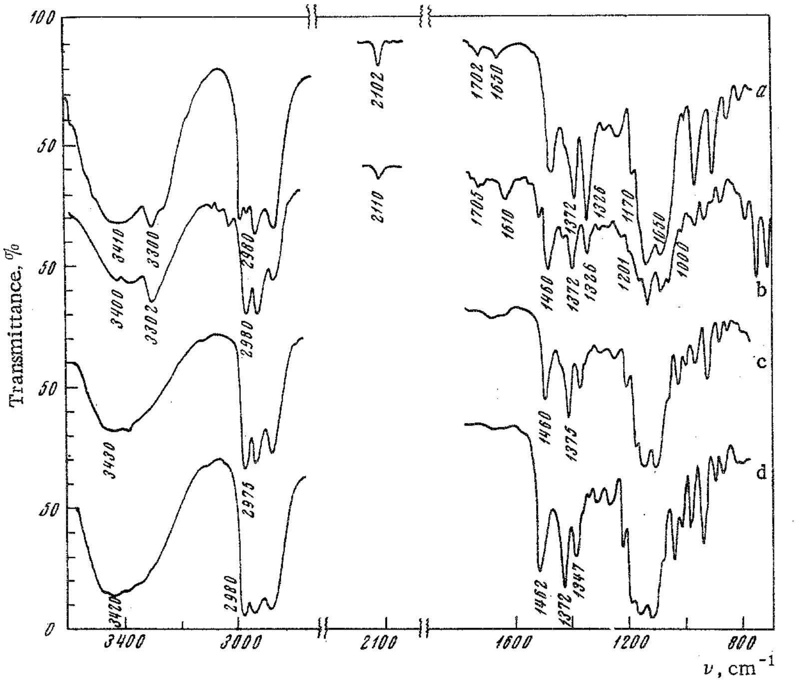


Fig. 3. IR spectra of interaction products with MBA; a) ketal (III); b) standard saturated hydroxyether (XI); c) ketal (IV); d) pure hydroxyether (XII).

prepared were added 50 ml of toluene and 0.2 M ketal. The mixture was heated for 3 h at 128°. After standard treatment, the mixture was fractionated. Yield, 5.2 g (18.2%) of 3-methyl-3-ethyl-3-(β-hydroxyethyl)-1-propyne (VI), bp 82-85° (15 mm); n_D^{20} 1.4440; d_4^{20} 0.9451. According to the data [12]: bp 89-92 (16 mm); n_D^{20} 1.4447. According to IR spectrum (Fig. 2a) the substance contained impurities (weak bands at 1630 and 1700 cm^{-1}). Content of main product, 45% [GLC, Fig. 4, analysis conditions: column 3 m long, diameter 6 mm; SP, didecylsebacate (10%) and dibutylene glycolsebacate (1%) on carrier TND treated with silane; gas-carrier, hydrogen, column temperature 160°]. The mixture also yielded 2.3 g (8.9%) of 3,6-dimethyl-3,6-di(β-hydroxyethyl)-4-octyne (XVII), bp 118-120° (1 mm); n_D^{20} 1.4715; d_4^{20} 1.0079; MR 72.59. $C_{14}H_{26}O_4$. Calculated MR: 71.98.

Acetylene was passed through a solution of 0.2 M EMB in ether at room temperature for 7 h, then 50 ml of benzene and 0.1 M ketal were added. The mixture was stirred for 1 h and allowed to stand overnight. On the following day the ether was distilled off and the mixture heated for 3 h at 78-82° (black viscous mass), cooled, and decomposed by a saturated aqueous NH_4Cl solution; dried over ($Na_2SO_4 + K_2CO_3$) and fractionated. Yield, fraction 2.7 g (19.01%), bp 50-55° (3 mm); according to IR spectrum (Fig. 2b) consists of 2-methyl-2-ethyl-3-methylene-1,4-dioxane (XIV) and saturated hydroxyether (X) [see IR spectrum of standard sample (Fig. 2e)].

Acetylene was passed through the ether solution (0.2 M) of EMB with cooling to 0-5° for 3 h. Then 30 ml of toluene and 12.4 ml of ketal were added. The ether was removed and the mixture heated for 3 h on a boiling water bath. Standard treatment yielded 3.5 g of a product with a bp 83-86° (18 mm); n_D^{20} 1.4428; d_4^{20} 0.8595. According to IR spectrum (Fig. 2c) the main product was saturated hydroxyether (X) with an admixture of acetylenic hydroxyether (VIII) and methylenedioxane (XIV).

Acetylene was passed through an ether solution of 0.2 M EMB for 5 h; then there was added 0.1 M ketal and 30 ml of toluene, and the ether removed. The mixture was heated for 3 h at 60-95°, then decomposed by dilute (1 : 40) aqueous HCl solution. Fractionation yielded 3.6 g of product with bp 80-82° (17 mm); n_D^{20} 1.4386; d_4^{20} 0.9204. According to IR spectrum (Fig. 2d), the product is a mixture of (VI), (X), and (XIV).

Spiro[4,4]-1,4-dioxononane (III). Acetylene was passed through an ether solution of 0.2 M EMB for 5 h at room temperature (18°). Then, 0.1 M ketal (III) and 30 ml of toluene added, ether removed, and the product heated for 3 h at 60-95°. The mixture was decomposed by HCl (1 : 40). Yield, 2.8 g (18.2%) of

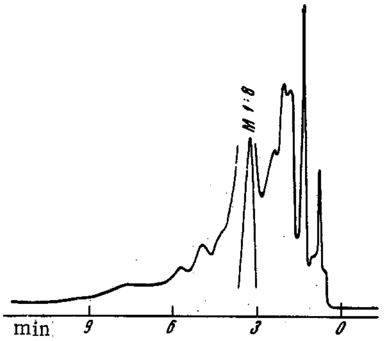


Fig. 4. Chromatogram of the product of interaction between ketal (II) and MBA.

product with bp 60-63° (1 mm); n_D^{20} 1.4598; d_4^{20} 1.0087. According to the IR spectrum (Fig. 3a), the product was a mixture of 1-ethyl-1-(β-hydroxyethoxy) cyclopentane (VII) and saturated hydroxyether (XI). The product also yielded 1.3 g of fraction with constants corresponding to bis-(1-β-hydroxyethoxy-1-cyclopentyne) acetylene (XVIII); bp 140-153° (1 mm); n_D^{20} 1.4868; d_4^{20} 1.0399.

Spiro[4,5]-1,4-dioxodecane (IV). To an ether solution of 0.2 M EMB was added 0.27 M ketal and acetylene (cooling, -4.5 to 1.5°) passed for 3 h, the ether removed, and the product heated for 3 h at 120°. Conventional treatment yielded 10.3 g of fraction with bp 67-71° (1 mm), which yielded a product with a bp of 89-90° (3 mm); n_D^{20} 1.4690; d_4^{20} 0.9814; according to IR spectrum (Fig. 3c) the product was 1-ethyl-1-(β-hydroxyethoxy)cyclohexane (XII) with an admixture of 1-ethyl-(β-hydroxyethoxy)cyclohexene (VIII). The results of GLC analysis support the derived conclusion.

Acetylene was passed through the ether solution of 0.2 M EMB (for 10 min at 5-20° and for 1 h at 30-50°), then 40 ml of toluene added and ketal added dropwise over a period of 30 min. The mixture was heated for 2 h at 70-95° and decomposed by dilute (1 : 40) HCl. Fractionation yielded 2.4 g of a product with bp 75-90° (1 mm); n_D^{20} 1.4722; d_4^{20} 0.9984. According to IR spectrum (Fig. 3d), the product was 1-ethynyl-1-(β-hydroxyethoxy)cyclohexane (VIII) with an admixture of saturated hydoxyether (XII). The spectrum of the product, differing from the spectrum of pure (XII) (Fig. 3e), showed no absorption at 2970 and 1380 cm^{-1} (CH_3), the doublet nature of the band of CH_2 (1455 cm^{-1}) disappeared and the band with frequency of 775 cm^{-1} (pendulum vibration of CH_2 in the ethyl group [13]) became much weaker.

CONCLUSIONS

1. 1,3-Dioxolanes at a temperature of 80-120° underwent cleavage by the Iotsich complex based on acetylene, with the formation of low yields of hydroxyethyl ethers of acetylenic alcohols and glycols.

2. According to IR spectroscopy data, in a number of cases, during the course of the reaction the resulting acetylenic hydroxyethers underwent cyclization to give the appropriate unsaturated 1,4-dioxanes.

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