TRANSFORMATION OF UNSYMMETRICAL DIACETYLENIC GLYCOLS OF ARALKYL SERIES UNDER THE INFLUENCE OF SULFURIC ACID

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The isomeric transformations of acetylenic δ-glycols $RR^1C(OH)C{\equiv}CCH_2CH(OH)R^2$ under the influence of alcoholic H_2SO_4 solutions were described previously [1, 2]. As a continuation of studying their diacetylenic analogs [3-4] we made a study of the acetylene–allene anionotropic isomerization of some diacetylenic glycols of the aralkyl series (I) and (II). Only the rearrangement of the symmetrical diacetylenic glycols to the diethylenic α-diketones, caused either by $HgSO_4$ [5, 6] or NH_4OH and NH_4Cl [7], was described up to now.

In a 4% alcohol solution of H_2SO_4, at 35-40°C, glycols (I) and (II) are easily etherified at the OH group attached to the atom bound to the aromatic radical, which was mentioned earlier for acetylenic glycols [1]

$$\underset{\text{(I), (II)}}{RR^1C(OH)C{\equiv}CC{\equiv}CCH_2CH(OH)R^2} + C_2H_5OH \xrightarrow{4\%\ H_2SO_4} \underset{\text{(III), (IV)}}{RR^1C(OC_2H_5)C{\equiv}CC{\equiv}CCH_2CH(OH)R^2}$$

$$R = R^1 = C_6H_5,\ R^2 = H(Ia), (III);\ R = CH_3,\ R^1 = C_6H_5,\ R^2 = H(Ib), (IV);$$
$$R = R^1 = C_6H_5,\ R^2 = CH_3(IIa);\ R = R^2 = CH_3,\ R^1 = C_6H_5(IIb)$$

The IR spectra of the diacetylenic hydroxy ethers (III) and (IV) are characterized by the absorption bands of a triple bond (2250 cm^{-1}) and an associated hydroxyl (in the 3200-3400 cm^{-1} region).

The acetylene–allene isomerization of glycols, containing two phenyl groups [(Ia) and (IIa)], occurs under more drastic conditions, under the influence of 18% H_2SO_4 solution, at 60-70°. However, the expected enyne keto alcohols (V) could not be isolated. The frequencies of the OH group are absent in the IR spectra of the reaction products, but the absorption bands of conjugated double bonds (1612, 1617 cm^{-1})

TABLE 1. Physicochemical Constants of Diacetylenic Glycols

Compound No.	Compound	Yield, %	Mp., °C	Found, %		Empirical formula	Calculated, %		Characteristic frequencies, cm^{-1}
				C	H		C	H	
(Ia)	1,1-Diphenyl-2,4-heptadiyn-1,7-diol	93,4	110–111 (benzene-cyclohexane)	81,97	5,84	$C_{19}H_{16}O_2$	82,68	5,79	3360 s. w. 2260 m
(Ib)	2-Phenyl-3,5-octadiyn-2,8-diol	92,0	79–80,5 (benzene)	77,80	6,38	$C_{14}H_{14}O_2$	78,50	6,54	3300 s, w 2265 m
(IIa)	1,1-Diphenyl-2,4-octadiyn-1,7-diol	83,8	—	82,05	6,38	$C_{20}H_{18}O_2$	82,75	6,26	3330 s, w 2260 s
(IIb)	2-Phenyl-3,5-nonadiyn-2,8-diol	89,5	—	78,11	7,47	$C_{15}H_{16}O_2$	78,94	7,01	3360 s (v.w) 2251 m

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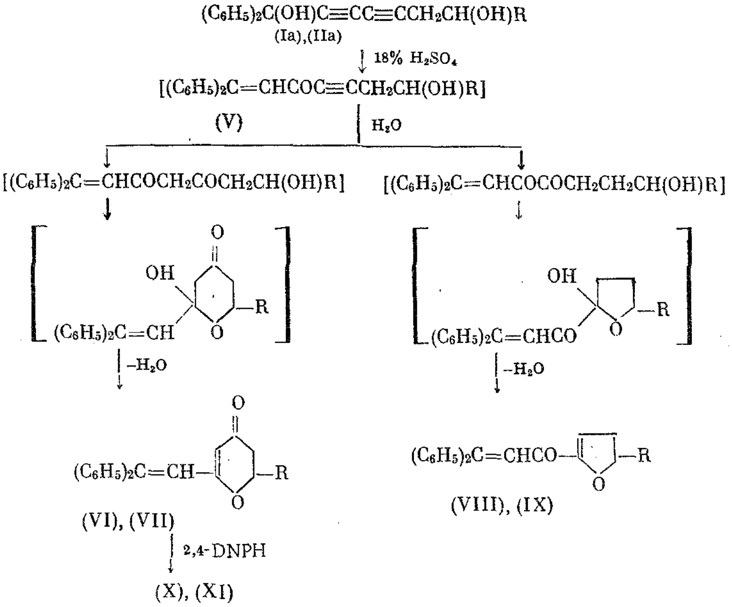
TABLE 2. Constants of Diacetylenic Hydroxy Ethers and 6-(β,β-Diphenylvinyl)-2,3, dihydro-γ-pyrones

Compound No.	Compound	Yield, %	Mp., °C	Found, %			Empirical formula	Calculated, %			Characteristic frequencies, cm^{-1}
				C	H	N		C	H	N	
(III)	1-Ethoxy-1,1-diphenyl-2,4-heptadiyn-7-ol	96,43	—	81,93	6,53	—	$C_{21}H_{20}O_2$	82,59	6,48	—	3375 s (v.w) 2253 s
(IV)	2-Ethoxy-2-phenyl-3,5-octadiyn-8-ol	93,6	—	79,04	7,42	—	$C_{16}H_{18}O_2$	79,3	7,43	—	3330 s (v. w) 2257 s
(VI)	6-(β,β-Diphenylvinyl)-2,3-dihydro-γ-pyrone	92,5	109—110° (heptane)	82,54	5,84	—	$C_{19}H_{16}O_2$	82,68	5,70	—	1676 v. s 1617 v. s
(VII)	2-Methvl-6-(β,β-Diphenylvinyl)-2,3-dihydro-γ-pyrone	90,00	123—124,1 (heptane)	82,05	6,16	—	$C_{20}H_{18}O_2$	82,75	6,26	—	1658 v. s 1612 v. s
(X)	2,4-DNPH of (VI)	—	178,5—179,5 (alcohol —benzene	65,57	4,52	12,53	$C_{25}H_{20}O_5N_4$	65,79	4,38	12,28	3306 w 1627 s
(XI)	2,4-DNPH of (VII)	—	158—161,5 (alcohol —benzene	66,37	4,71	11,67	$C_{26}H_{22}O_5N_4$	66,38	4,80	11,91	3311 m 1613 s

and of the CO group (1655 and 1676 cm^{-1}) are present. Based on the elemental analysis data, the obtained compounds have the same composition as the starting diacetylenic glycols. It is possible to assume that under the reaction conditions enyne ketones (V) are hydrated, with the subsequent cleavage of a molecule of water and the formation of either 6-(β,β-diphenylvinyl)-2,3-dihydro-γ-pyrones (VI) and (VII) or of the 5-(β,β-diphenylvinyl)ketones of the 2,3-dihydrofuran series (VIII) and (IX)



R=H (VI), (VIII), (X); CH_3 (VII), (IX), (XI)

The NMR spectrum of the isomerization product of glycol (Ia) unequivocally testifies to the fact that the reaction product is the vinyl derivative of 2,3-dihydro-γ-pyrone. Thus, the NMR spectrum of (VI) contains triplets with τ 7.73 and 5.93 ppm (J = 6.4 Hz), which correspond to the protons of the methylene groups in the 2 and 3 positions of the dihydropyran ring, and singlets (τ 3.74 and 4.34 ppm) that correspond to the methine protons found in the α- and γ-positions to the CO group. The signal at 2.80 ppm corresponds to the protons of the phenyl rings. The isomerization product of glycol (IIb) has an analogous structure (VII).

The reaction of (VI) and (VII) with 2,4-dinitrophenylhydrazine gave their dinitrophenylhydrazones (X) and (XI). The acetylenic glycols (Ib) and (IIb), with R = CH_3 and R^1 = C_6H_5, undergo tarring under the given conditions.

As a result, depending on the H_2SO_4 concentration and the nature of the substituents R and R^1 attached to the tertiary carbon atom, the primary and secondary–tertiary diacetylenic glycols of the aralkyl series

(I) and (II), are either etherified at the OH group, found α to the diacetylenic fragment and attached to the C atom bearing either one or two aromatic radicals, or they undergo acetylene–allene rearrangement with the end formation, when $R = R^1$, of aryl-6-(β,β-diarylvinyl)-2,3-dihydropyrones.

EXPERIMENTAL METHOD

Diacetylenic glycols (I) and (II) were obtained by the Chodkiewicz–Cadiot reaction under the conditions given in [3]. Their yields and constants are given in Table 1.

Synthesis of Diacetylenic Hydroxy Ethers. To 25 ml of a 4% alcohol solution of H_2SO_4 was added 2.0 g of glycol (Ia). The reaction mixture was heated at 35-40° for 5 h, neutralized with aqueous Na_2CO_3 solution, extracted with ether, and dried over $MgSO_4$. After removal of the solvent the residue was chromatographed on a column filled with Al_2O_3 (eluant = 30:1 $CHCl_3$–CH_3OH). We isolated 2.12 g (96.4%) of 1-ethoxy-1,1-diphenyl-2,4-heptadiyn-7-ol (III).

2-Ethoxy-2-phenyl-3,5-octadiyn-8-ol (IV) was obtained in a similar manner.

Isomerization of 1,1-Diphenyl-2,4-heptadiyn-1,7-diol (Ia). A mixture of 2.0 g of (Ia) and 20 ml of 18% H_2SO_4 solution was heated at 60-70° for 9 h. The reaction mixture was neutralized with aqueous Na_2CO_3 solution, and the reaction products were extracted with ether. After drying over $MgSO_4$ and removal of the solvent we obtained 1.85 g (92.5%) of 6-(β,β-diphenylvinyl)-2,3-dihydro-γ-pyrone (VI).

The isomerization of 1,1-diphenyl-2,4-octadiyn-1,7-diol (IIa) was accomplished under analogous conditions. The NMR spectrum of the obtained ketone (VII) contains the doublet of a methyl group with τ 9.10 ppm (J = 7.5 Hz) and a doublet with τ 7.85 (J = 8.5 Hz), which corresponds to a methylene group. Singlets at 3.69 and 4.76 ppm correspond respectively to the methine protons that are found α and γ to the carbonyl group. The multiplet at τ 5.89 ppm belongs to the proton in the 2 position of the dihydropyran ring, while the signal with τ 2.80 ppm belongs to the protons of the phenyl rings.

The constants of the obtained 6-(β,β-diphenylvinyl)-2,3-dihydro-γ-pyrones, their 2,4-DNP hydrazones, and of the diacetylenic hydroxy ethers, are given in Table 2.

The NMR spectra of compounds (VI) and (VII) were taken in CCl_4 solution on a Tesla BS487B spectrometer (80 MHz), using HMDS as the internal standard.

CONCLUSIONS

Etherification of the hydroxyl group, found on the carbon atom attached to the aromatic radical, occurs when aralkyl primary and secondary–tertiary diacetylenic glycols are treated with 4% alcoholic sulfuric acid solution. In the presence of 18% H_2SO_4 solution, glycols that contain two aromatic substituents on a tertiary carbon atom undergo anionotropic acetylene–allene isomerization. Under the reaction conditions the intermediately formed enyne keto alcohols are converted to 6-(β,β-diphenylvinyl)2,3-dihydro-γ-pyranones.

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