REACTION OF SALICYLIC ACID DERIVATIVES WITH ACETYLENE

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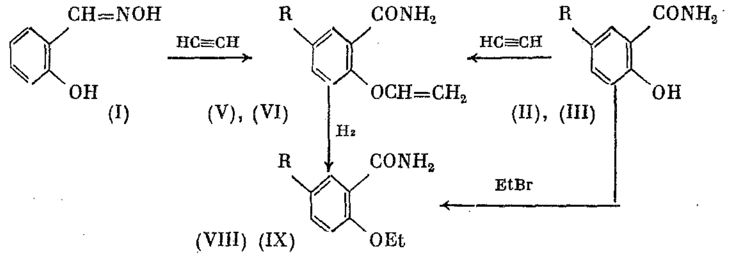
Previously we had shown that 1,3-benzoxazinones are formed under the conditions for the vinylation of salicylanilides [1, 2].

The reactions of acetylene with salicylaldoxime (I), salicylamide (II), 5-bromosalicylamide (III), and salicylhydrazide (IV) were studied in the present paper.

The reactions of oxime (I) and amides (II) and (III) with acetylene were run in dioxane at 180-190°C for 1-1.5 h. The formation of either 2-vinyloxybenzamide (V) or 2-vinyloxy-5-bromobenzamide (VI) is observed in all cases.



R = H (II), (V), (VIII); Br (III), (VI), (IX).

KOH, CdO, and Cd(OAc)$_2$ were used as catalysts. The reaction of (I)-(III) with acetylene in the presence of KOH gave neither vinyl ethers nor cyclization products. Amides (II) and (III) are recovered from the reaction slightly contaminated with phenol, while oxime (I) is converted mainly to amide (II), apparently via the intermediate formation of the nitrile, which gives the amide as the result of subsequent hydration [3]. A small amount of 2-vinyloxybenzonitrile (VII) was isolated when aqueous KOH solution is used as the catalyst, whose structure is confirmed by the PMR spectrum of the $CH_2=CHO$ group (δ, ppm): 6.59 (H_X), 4.57 (H_A), 4.85 (H_B): SSCC (J, Hz): 6 (AX), 14 (BX); IR spectrum (ν, cm^{-1}): 2230 (C≡N), 1645 and 956 ($CH_2 = CH$).

2-Vinyloxybenzamide (V) is formed in 35% yield when oxime (I) is reacted with acetylene in the presence of Cd(OAc)$_2$. The use of the KOH–CdO system lowers the yield of ether (V) by half. The direct vinylation of salicylamide (II) in the presence of either Cd(OAc)$_2$ or the KOH–CdO system gave ether (V) in respective yields of 73 and 60%. The vinylation of the bromo-substituted amide (III) also gives the corresponding vinyl ether (VI) in 40% yield.

The structure of ethers (V) and (VI) was proved by their hydrogenation over Raney Ni to the ethoxy-substituted amides (VIII) [4] and (IX), which were obtained by counter synthesis from amides (II) and (III) by reaction with ethyl bromide. When compared with the starting amides (II) and (III), the IR spectra of ethers (V) and (VI) have the bands (ν_1 cm^{-1}): 1642, 970, 947 (C=C), 1243-1148 (COC); the spectrum of (VI) retains the 525 band (CBr). The PMR spectra of (V) and (VI) have the signals of the $CH_2=CHO$ group (δ, ppm): 6.52 (H_X), 4.56 (H_A), 4.83 (H_B); SSCC (J, Hz): 2 (AB), 6 (AX), 14 (BX).

In contrast to oxime (I) and amides (II) and (III), hydrazide (IV), depending on the catalyst, reacts differently with acetylene.

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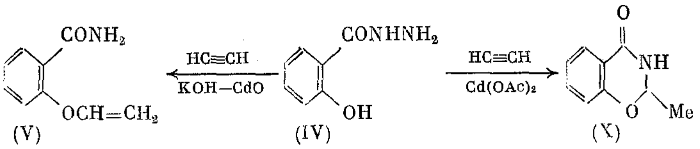

In the presence of KOH a high-melting (> 300°) water-insoluble product is formed, while vinyl ether (V) was detected in the reaction products when the KOH–CdO system is used. Samples of ether (V), obtained from amide (III), oxime (I), and hydrazide (IV), were identified via the PMR and IR spectra, and also via the mixed melting points with an authentic sample. In the presence of $Cd(OAc)_2$ a very low yield (1%) of 2-methyl-2,3-dihydro-4H-1,3-benzoxazin-4-one (X) was isolated from the reaction mixture, which was identified via the constants described in [5]. The IR spectrum of (X) has the bands (ν, cm^{-1}): 3200-3090 (NH), 2990, 2940, 2890 (CH_3), 1695-1680 (N–C=O). The structure of (X) was confirmed by the PMR spectrum.

It may be assumed that when hydrazide (IV) is reacted with acetylene in the presence of $Cd(OAc)_2$ the N atom of the imino group of the hydrazide is the reaction center and cyclization to the benzoxazine system is accomplished through the N-vinyl derivative. The probability of the starting hydrazide decomposing increases in the presence of the KOH–CdO system and a transfer of the reaction center to the O atom of the hydroxyl group occurs in the formed products, while the vinyl ethers are not cyclized to benzoxazines under these conditions.

Products (V), (VI), and (VIII)-(X) are white crystalline substances that are soluble in most organic solvents and hot water; ether (VII) is an oily liquid.

EXPERIMENTAL

The PMR spectra were taken on a Tesla BS-487C spectrometer (80 MHz) in $CDCl_3$ solution, using HMDS as the internal standard. The IR spectra were taken on a UR-20 instrument as KBr pellets. The purity of the products was checked by TLC on Al_2O_3 (4:1 ether–hexane). The column chromatography was run on Al_2O_3 using a 3:1 ether–hexane mixture as the eluant.

2-Vinyloxybenzamide (V). a) Into a 500-ml autoclave was charged a mixture of 13.7 g of amide (II) and 5.3 g of $Cd(OAc)_2$ in 90 ml of dioxane. Acetylene was added (10-11 ati) (gauge atmosphere) and the mixture was kept for 1 h at 180-185°. The dioxane was removed and the residue was recrystallized from water to give 11.9 g (73%) of ether (V), mp 121-123°. R_f 0.42. Found: C 66.55; H 5.63; N 8.57%. $C_9H_9NO_2$. Calculated: C 66.24; H 5.55; N 8.58%.

b) In a similar manner, from 13.7 g of (II), 2.8 g of KOH, and 1.3 g of CdO we isolated 9.7 g (60%) of ether (V), mp 121-123°.

c) In a similar manner, from 6.8 g of oxime (I) and 2.6 g of $Cd(OAc)_2$ at 190-195° for 1.5 h we obtained 2.9 g (35%) of ether (V), mp 122-124°.

d) In a similar manner, from 6.8 g of (I), 1.1 g of KOH, and 0.64 g of CdO we isolated 1.5 g (18%) of ether (V), mp 122-123°.

e) A mixture of 6 g of hydrazide (IV), 1.1 g of KOH, and 0.64 g of CdO in 80 ml of dioxane was charged into the autoclave, acetylene was added, and the mixture was kept for 1.5 h at 180-190°. The residue from removal of the solvent was passed through a column to give 0.5% of (V) with mp 123-124°.

2-Vinyloxy-5-bromobenzamide (VI). Obtained by method a) in 40% yield, mp 127-129° (water), R_f 0.53. Found: C 44.96; H 3.28; Br 33.27; N 5.42%. $C_9H_8BrNO_2$. Calculated: C 44.65; H 3.33; Br 33.00; N 5.78%.

2-Ethoxy-5-bromobenzamide (IX). a) A mixture of 3 g of ether (VI) and 1 g of Raney Ni in 60 ml of abs. EtOH was placed in a 250-ml autoclave, hydrogen was added (40 ati), and the mixture was kept for 4-5 h. We isolated 90% of (IX), mp 132-134° (water), R_f 0.44. Found: C 44.27; H 3.96; Br 32.49; N 5.99%. $C_9H_{10}BrNO_2$. Calculated: C 44.28; H 4.12; Br 32.73; N 5.73%.

b) A mixture of 4.3 g of amide (III), 15 ml of 50% NaOH solution, and 22 g of EtBr in 20 ml of EtOH was refluxed for 12 h. We isolated 80% of (IX), mp 132-134°.

2-Ethoxybenzamide (VIII). Method a) gave a 96% yield, and method b gave a 20% yield of (VIII) with mp 131-132° (water) (cf. [4]), R_f 0.36.

2-Methyl-2,3-dihydro-4H-1,3-benzoxazin-4-one (X). A mixture of 6 g of hydrazide (IV) and 2.6 g of $CD(OAc)_2$ in 80 ml of dioxane was charged into an autoclave, acetylene was added, and the mixture was kept for 1.5 h at 180-190°. The obtained liquid was passed through a column. We isolated 1% of (X) with mp 145-147° (water) (cf. [5]). The mixed melting point with an authentic sample was not depressed.

CONCLUSIONS

The reactions of acetylene with salicylamide, salicylaldoxime, and salicylhydrazide gave the vinyl ethers of salicylamide and its bromo derivative. Depending on the catalyst, the vinylation of salicylhydrazide gives either the vinyl ether of salicylamide or 2-methyl-2,3-dihydro-4H-1,3-benzoxazin-4-one.

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ALKALI-CATALYZED HYDRATION OF STEREOISOMERIC 3,4-EPOXYCARANES

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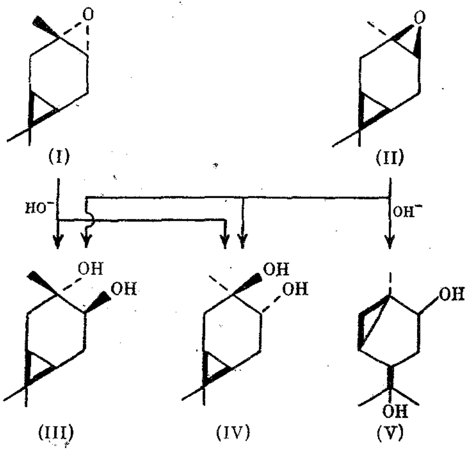
Comparative data are given in the literature on the direction of the acid- and base-catalyzed hydration of the stereoisomeric norcarene epoxides [1]. The results of studying the hydration of the trans- (I) and cis-epoxides (II) of 3-carene in the presence of a base are reported in the present paper.

trans-Diols (III) and (IV) were isolated in an 85:15 ratio when trans-epoxide (I) was treated with aqueous alkali solution.



Glycols (III), (IV), and (V) are formed in a 1:2:1 ratio when cis-epoxide (II) is treated in a similar manner. The previously described [2, 3] products were identified by direct comparison with authentic samples.

As a result, the base-catalyzed hydration of the cyclic oxide occurs at both of the C−O bonds. Here, if in the trans-epoxide (I) the reaction proceeds predominantly at the secondary center, then in the cis-isomer (II) the products of opening at both of the C−O bonds are represented to equal degree. The fact that, together with

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