SOME TRANSFORMATIONS OF AROXYACETYLENES

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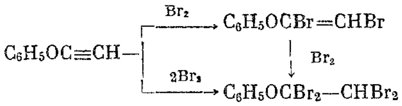
As a continuation of our studies of the reactivity of aromatic acetylenic ethers [1, 2], we reacted them with halogens, organic acids, monoethanolamine, and carbon tetrachloride.

The reaction of aroxyacetylenes with bromine is exothermic and proceeds according to the following scheme to give high yields of the reaction products

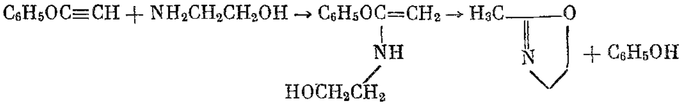


The conversion of acetylenic ethers to the tetrabromo derivatives was used by us in a number of cases to corroborate the presence of the triple bond. The constants of the synthesized bromo derivatives are given in Table 1 [compounds (I)-(VII)].

The addition of organic acids to aroxyacetylenes was accomplished in the presence of mercury acetate [3]. α-Acyloxy-substituted vinyl aryl ethers are formed under these conditions. Trichloroacetic acid adds, the same as it adds to alkoxyacetylenes, without a catalyst [4]. In contrast to phenoxyacetylene (POA) and p-tolyloxyacetylene (TOA), the acetylenic ether of p-nitrophenol (NPOA) does not react with organic acids under comparable conditions, as was shown on the example of benzoic and p-nitrobenzoic acids. An explanation of the given fact must be sought in the electron-acceptor nature of the nitro group, the effect of which, according to the spectral studies, is transmitted through the ether oxygen atom [5].

The structure of the synthesized α-acyloxy-substituted vinyl aryl ethers (compounds (VIII)-(XIII)] was corroborated by the IR spectra, in which the band in the 1685-1670 cm^{-1} region corresponds to the stretching vibrations of the C = C bond, and the band in the 1782-1750 cm^{-1} to the stretching vibrations of the carbonyl group.

The reaction of POA with monoethanolamine has an exothermic character and proceeds by a scheme that is analogous to that of aroxyacetylenes [6], with the formation of 2-methyloxazoline and phenol



Together with the discussed transformations, we ran the telomerization reaction, which is not known for acetylenic ethers. The monoadduct (XIV) and the telomer were obtained as a result. The NMR spectrum of the adduct consists of a singlet (δ 6.63 ppm), which belongs to an olefinic proton, and a multiplet, caused by the protons of the benzene ring, and occupying the region 6.79-7.40 ppm. The ratio of the integral intensities of the singlet and multiplet is 1 : 5. The polymer represents a dark brown powder with mp 157-160°, which is soluble in benzene, acetone, and dioxane. In the IR spectrum of the polymer is observed a broad band at 1640 cm^{-1}, which testifies to the presence of conjugated double bonds. The electrical conductivity of the polymer at 30° is $1 \cdot 10^{-16}$ $ohm^{-1} \cdot cm^{-1}$, and $1.2 \cdot 10^{-14}$ $ohm^{-1} \cdot cm^{-1}$ at 110°, while the activation energy is 0.89 eV.

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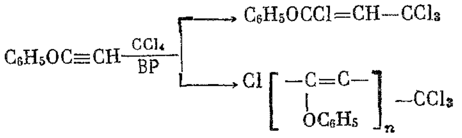
TABLE 1

Compound		Bp, °C (mm of Hg) Mp, °C	n_D^{20}	d_4^{20}	Empirical formula	Found/calculated, %			Yield, %
number	formula					C	H	Hal, N	
I	$C_6H_5OCBr{=}CHBr$	33—34	—	—	$C_8H_6OBr_2$	34,49/34,56	2,28/2,18	57,89/57,49	63
II	$C_6H_5OCBr_2{-}CHBr_2$	38—39	—	—	$C_8H_6OBr_4$	22,17/21,96	1,38/1,38	72,39/73,03	93
III	$o\text{-}CH_3C_6H_4OCBr_2{-}CHBr_2$	100—101 (2)	1,5830	1,7168	$C_9H_8OBr_4$	38,09/37,02	2,65/2,75	54,56/54,39	84
IV	$m\text{-}CH_3C_6H_4OCBr_2{-}CHBr_2$	124—125 (3)	1,5860	1,7100	$C_9H_8OBr_4$	37,16/37,02	3,02/2,75	54,32/54,39	80
V	$p\text{-}CH_3C_6H_4OCBr_2{-}CHBr_2$	115,5—116,5 (3,5)	1,5825	1,6982	$C_9H_8OBr_4$	37,01/37,02	2,68/2,75	54,87/54,39	88
VI	$p\text{-}NO_2C_6H_4OCBr_2{-}CHBr_2$	104—105	—	—	$C_8H_5O_3NBr_4$	—	—	66,06/66,20	95
VII	$p\text{-}CHBr_2{-}CBr_2{-}OC_6H_4OCBr_2{-}CHBr_2$	139—140,5	—	—	$C_{10}H_6O_2Br_8$	—	—	80,51/80,15	90
VIII	$(C_6H_5O)\,(OCOCH_3)\,C{=}CH_2$	64,5—65,5 (1)	1,5005	1,0984	$C_{10}H_{10}O_3$	67,54/67,39	5,76/5,66	—	60
IX	$(C_6H_5O)\,(OCOC_6H_5)\,C{=}CH_2$	148 (1)	1,5615	1,1486	$C_{15}H_{12}O_3$	75,27/74,98	4,92/5,04	—	88
X	$(C_6H_5O)\,(OCOCCl_3)\,C{=}CH_2$	108,5--110 (1)	1,5185	1,3517	$C_{10}H_7O_3Cl_3$	42,78/42,66	2,50/2,51	37,68/37,70	80
XI	$(C_6H_5O)\,(OCOC_6H_4NO_2)\,C{=}CH_2$	80,5—81	—	—	$C_{15}H_{11}O_5N$	62,90/63,14	4,08/3,89	N 4,84/4,91	89
XII	$(p\text{-}CH_3C_6H_4O)\,(OCOCCl_3)\,C{=}CH_2$	110—112 (1)	1,5163	1,3318	$C_{11}H_9O_3Cl_3$	44,66/44,67	2,93/3,04	35,49/36,04	75
XIII	$(p\text{-}CH_3C_6H_4O)\,(OCOC_6H_5)\,C{=}CH_2$	142—144 (2)	1,5570	1,1230	$C_{15}H_{11}O_3$	75,76/75,50	5,78/5,50	—	54
XIV	$C_6H_5OCCl{=}CHCCl_3$	94—94,8 (0,5)	1,5620	1,4342	$C_9H_6OCl_4$	39,47/39,74	2,22/2,22	51,67/52,14	13,6

Starting with the presented data and the elemental analysis results, it is possible to postulate the following reaction scheme for the telomerization of POA



EXPERIMENTAL

The starting phenoxy-, p-tolyloxy- and p-nitrophenoxyacetylenes were obtained by the procedures described in [7]; POA, bp 49-50° (12 mm); n_D^{20} 1.5160; TOA, bp 72° (12 mm); n_D^{20} 1.5148; NPOA, mp 54°.

Addition of Bromine. To 2.4 g of POA in 15 ml of CCl_4 was added, with stirring and cooling at –25 to –30°, a solution of 3.2 g of Br_2 in 5 ml of CCl_4. Recrystallization from hexane gave a substance with mp 33-34°, which, based on the analysis data, had the structure of (I). The literature data for (I) (mp 37-38° [8]) correspond more closely to the tetrabromide (II).

To 2.4 g of POA in 15 ml of CCl_4 was added, at –25 to –30°, a solution of 6.4 g of bromine in 5 ml of CCl_4. Recrystallization from hexane gave 6 g (93%) of $\alpha,\alpha,\beta,\beta$-tetrabromoethyl phenyl ether (II) with mp 38-39°.

Addition of Organic Acids. A solution of 3.34 g of p-nitrobenzoic acid in 24 ml of CH_2Cl_2 and 30 ml of acetone was added at room temperature, in 15 min, to a solution of 4.72 g of POA and 0.11 g of $Hg(CH_3\cdot COO)_2$ in 35 ml of CH_2Cl_2. The reaction mixture was heated at 35-40° for 2 h. Recrystallization from alcohol gave 5.1 g (89%) of (XI) with mp 80.5-81°.

Addition of Monoethanolamine. To a mixture of 11.8 g of POA and 0.6 g of hydroquinone was rapidly added 6.12 g of freshly distilled ethanolamine. A rapid heating up of the reaction mixture to 100° was observed within 1-2 min. This temperature was maintained for 2.5 h. The reaction product was vacuum-distilled. In a trap, cooled in dry CO_2, was collected a compound with bp 107-110° and n_D^{20} 1.4361, which had a pyridine odor, and which we assumed to be 2-methyloxazoline. From [6]: bp 109-110°. The obtained picrate of the presumed 2-methyloxazoline has mp 156-157°. From [6]: mp 158-161°. Besides the described compound, phenol was identified in the fractional distillation products.

Addition of CCl_4. A mixture of 11.8 g of POA and 0.6 g of benzoyl peroxide in 300 ml of CCl_4 was refluxed for 6 h. After removal of the CCl_4 the residue was vacuum-distilled. The isolated yield of (XIV) was 13.6%. The tarry residue (5.5 g) in the flask was reprecipitated from ethanol. We isolated 3 g of polymer, mp 157-160° (on a Koffler block).

CONCLUSIONS

1. It was shown that aromatic acetylenic ethers exhibit a high tendency to add to halogens, organic acids and ethanolamine. On the example of the reaction with acids it was shown that the nitro group in the p-nitrophenoxyacetylene molecule exerts a passivating effect on the triple bond.

2. We were the first to run the telomerization reaction of acetylenic ethers on the example of phenoxyacetylene.

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