STUDY OF THE THIYLATION OF VINYL PARANITROPHENYL ETHER

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In our previous communication [1] we cited data illustrating the influence of the nitro group in p-vinyloxynitrobenzene (I) on the chemical activity of the double bond. In particular, it is noted that (I), in contrast to vinyl phenyl ether, in the presence of 1% azobisisobutyrodinitrile (AIBN) does not form the corresponding addition product with butanethiol. The purpose of this work was to investigate the possibility of the interaction of (I) with butanethiol under homolytic, electrophilic, and nucleophilic conditions.

In carrying out the reaction of homolytic thiylation, we succeeded in obtaining the addition product (II) with a 53% yield by increasing the amount of AIBN to 3%. In addition, we isolated the initial (I), p-nitrophenol, and a resin. The thiylation product (II) gives a complex with an alcohol solution of mercuric chloride (without changing the pH of the medium) and is oxidized by hydrogen peroxide in acetic acid, forming the sulfone (III). The data are evidence of the addition of thiol counter to the Markovnikov rule accompanied by the formation of a product with the structure of the p-nitrophenyl ether of butylthioethylene glycol.

The presumed structure of (II), as well as (III), was confirmed by the PMR method. In the PMR spectrum of compound (II) (Fig. 1), the doublets 8.05 and 6.88 ppm belong to the protons of the aromatic ring H_a and H_b. The triplet in a strong field ($\delta_4 = 0.89$ ppm) is due to the protons of the methyl group, and that in a weak field ($\delta_1 = 4.14$ ppm) is due to the protons of the methylene group connected to the oxygen atom. The two other triplets ($\delta_2 = 2.55$ and $\delta_3 = 2.81$ ppm) belong to the protons of the CH_2 groups, bonded to sulfur. The signals of the protons of the C^5H_2 and C^6H_2 groups are believed to give an unresolved multiplet in the region of 1.14-1.74 ppm. In the PMR spectrum of the sulfone (III), the signals correspond in multiplicity to the signals of the corresponding group in the PMR spectrum of the sulfide, but differ in position, possessing the following values of the chemical shifts: $\delta_a = 8.12$, $\delta_b = 6.94$, $\delta_4 = 0.93$, $\delta_1 = 4.49$, $\delta_2 = 3.39$, $\delta_3 = 3.03$, $\delta_{5,6} = 1.18-1.87$ ppm.

The electrophilic addition of butanethiol to (I) in the presence of SO_2 as a catalyst required heating, whereas for vinyl ethers of phenol, cresols, and chlorophenols, this reaction proceeds exothermically and leads to rapid formation of products with an α-structure [2, 3]. The dinitrodiphenyl acetal of acetaldehyde (IV) and the dibutylmercaptal (V), identified by comparison with known samples [1, 4], were detected in the reaction mixture. The formation of these products leads to the conclusion that the investigated reaction proceeds according to the Markovnikov rule, following the scheme

$$CH_2 = CHOC_6H_4NO_2 + C_4H_9SH \rightarrow \underset{(VI)}{CH_3CH(OC_6H_4NO_2)(SC_4H_9)}$$

Then compound (VI), as an acetal with nonsymmetrical structure, undergoes symmetrization, characteristic of acetals, and especially thioacetals, under the conditions of synthesis:

$$\underset{(VI)}{CH_3CH\,(OC_6H_4NO_2)\,(SC_4H_9)} \rightarrow \underset{(IV)}{CH_3CH\,(OC_6H_4NO_2)_2} + \underset{(V)}{CH_3CH(SC_4H_9)_2}$$

The reaction considered, just like the data of [1], is evidence of a decrease in the ability of the double bond of compound (I) to react with electrophilic reagents. We should mention that considering the possibility of binding of the catalysts by the nitro group, we used a sufficiently large amount of SO_2.

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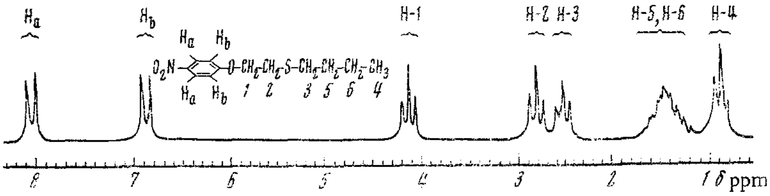


Fig. 1. PMR spectrum of the p-nitrophenyl ether of n-butylthioethyleneglycol (II).

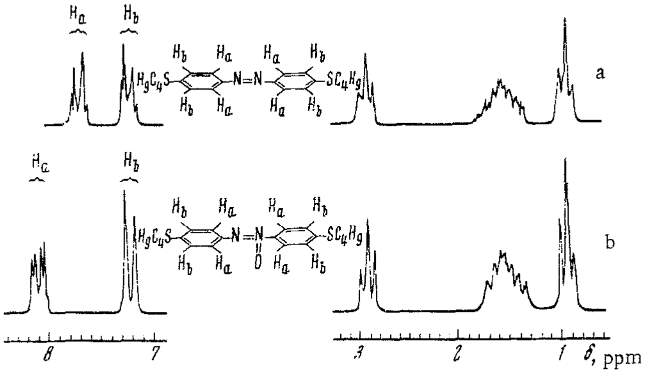
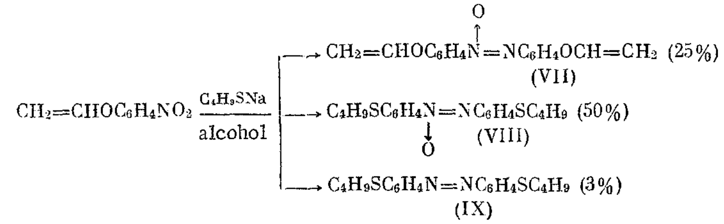


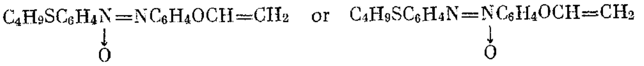
Fig. 2. PMR spectra: a) 4,4'-di-(n-butylthio)-azobenzene (IX); b) 4,4'-di-(n-butylthio)-azoxybenzene (VIII).

The passivating influence of the nitro group with respect to electrophilic conversions of the multiple bond of p-vinyloxynitrobenzene, as well as the data of a quantum chemical calculation [1], permit us to hope for the appearance of a tendency of (I) to add nucleophilic reagents. To test this hypothesis we undertook an investigation of the reaction (I) with sodium butylthiolate in a solution of abs. ethanol. Instead of the expected addition at the double bond, exchange of a vinyloxy group for a butylthiyl group and reduction of the nitro group in the initial compound and in the products of exchange, are observed:



$$CH_2{=}CHOC_6H_4NO_2 \xrightarrow[\text{alcohol}]{C_4H_9SNa} \begin{cases} CH_2{=}CHOC_6H_4\overset{O}{\overset{\uparrow}{N}}{=}NC_6H_4OCH{=}CH_2\ (25\%)\ \text{(VII)} \\ C_4H_9SC_6H_4N{=}\underset{O}{\underset{\downarrow}{N}}C_6H_4SC_4H_9\ (50\%)\ \text{(VIII)} \\ C_4H_9SC_6H_4N{=}NC_6H_4SC_4H_9\ (3\%)\ \text{(IX)} \end{cases}$$

When ethanol as the solvent is replaced by dioxane, the reduction reaction appreciably prevails over transesterification, which leads to a change in the yields of the products. Thus, (VII) was obtained in an amount of 64%, (VIII) 13%, and (IX) 2.6%. In addition, substance (X) was also isolated in small amounts; as will be shown below, it corresponds to the formula



$$C_4H_9SC_6H_4\underset{O}{\underset{\downarrow}{N}}{=}NC_6H_4OCH{=}CH_2 \quad \text{or} \quad C_4H_9SC_6H_4N{=}\underset{O}{\underset{\downarrow}{N}}C_6H_4OCH{=}CH_2$$

The reaction of nucleophilic exchange of the vinyloxy group in the series of vinyl ethers was unknown. The first appearance of this reaction was noted by us [5] in a study of the reduction of p-vinyloxynitrobenzene with alcoholic alkali for the production of the bis-vinyl ether of 4,4'-azoxyphenol (VII). Together with (VII), substantial amounts of azoxyphenetole or azoxyanisole were formed, depending on the alcohol used.

The detected nucleophilic substitution of the vinyloxy group in (I) is probably general and has the same mechanism as the known processes of transesterification of alkyl ethers of phenols [6], especially pronounced in polynitro derivatives [7, 8].

The structure of the compounds (VII)-(X) obtained was confirmed by the methods of IR and PMR spectroscopy. In this case we were able to find some criteria for the identification of azo and azoxy groups in the investigated compounds, the determination of which according to the IR spectra in aromatic compounds is a rather difficult problem. In the IR spectra of (VIII) and (IX) the bands characteristic of the vinyloxy and nitro groups are not observed. The methyl and methylene groups are identified according to the absorption in the region of 2965-2865 and 1460-1440 cm^{-1}, while the benzene rings are identified according to the bands 3075, 1580, 1480, and 1010 cm^{-1}. The spectrum of (IX) contains a single band of the nonplanar deformational vibrations of p-substituted benzene at 840 cm^{-1} and a single band of the $C_{ar}-N$ vibrations at 1270 cm^{-1}. For (VIII) a splitting of the band in the region of 840 cm^{-1} is observed, into the bands 820 and 840 cm^{-1} of approximately equal intensity, apparently due to the nonequivalence of the C–H vibrations of the ring for two hydrogen atoms standing next to one another. This splitting is due to the influence of the oxygen of the azoxy group. For the same reason, a series of bands appear in the region of 1270-1300 cm^{-1} [instead of one band, 1270 cm^{-1}, in the azo compound (IX)]. The divinyl ether of azoxyphenol (VII) is characterized by the presence of an intense band of the valence vibrations of the vinyl group at 1643 cm^{-1}. The splitting of the band in the region of 960 cm^{-1} (nonplanar deformational vibrations of =CH–) may be due to the nonequivalence of the vinyl group [5], due to the fact that the azoxy group acts as a donor with respect to one of the benzene rings, and as an acceptor with respect to the other. The splitting of the band at 1150 cm^{-1} is also apparently associated with this phenomenon.

In compound (X), in comparison with (VII), the band of the valence vibrations of the vinyl group (1643 cm^{-1}) is reduced in intensity, while nonplanar deformational vibrations of =CH– are observed in the form of a single band 957 cm^{-1}. New bands appear (2870, 2930, 2960 cm^{-1}), characteristic of the valence vibrations of the CH_2 and CH_3 groups, and the band 1460 cm^{-1} is intensified as a result of the superposition of the deformational vibrations of the indicated groups on the bands belonging to the vibrations of the benzene ring. The splitting at 1150 cm^{-1}, associated with the presence of the azoxy group, is preserved.

The data of PMR spectroscopy for compounds (VIII) and (IX) agree with the data on the IR spectra. The PMR spectrum of (IX) consists of five multiplets (Fig. 2a). The triplet in a strong field (δ = 0.93 ppm) belongs to the methyl protons. The signal of the protons of the CH_2 groups, bonded to the sulfur atom, is also represented by a triplet (2.92 ppm). The protons of the other methylene groups are responsible for the appearance of an unresolved multiplet in the region of 1.19-1.84 ppm. Finally, the two doublets (7.24 and 7.74 ppm) belong to the protons of the aromatic ring, and the signal in a stronger field corresponds to the H_b protons.

In the PMR spectrum of compound (VIII) (Fig. 2b), the signals from the protons of the butyl radicals and the H_b protons are analogous (both in positions and in multiplicity) to the signals from the corresponding protons in the spectrum of compound (IX). The signal of the H_a protons in the spectrum of compound (VIII), however, is shifted into a weak field with respect to the position in the spectrum of compound (IX) and is represented not by a doublet, but by a quartet, which is due to the superposition of two doublets (8.09 and 8.12 ppm). Consequently, replacement of an azo group by an azoxy group leads to the fact that the H_a protons are, in the first place less shielded than in (IX), and in the second place, are not chemically equivalent in pairs.

EXPERIMENTAL METHOD

Reaction of (I) with n-C_4H_9SH under Homolytic Conditions. A mixture of 4.12 g (I), 2.6 g n-C_4H_9SH, and 0.12 AIBN was heated in an ampoule at 95 ± 2° for 10 h. From the reaction mixture 0.5 g of p-nitrophenol was extracted with alkali, and 1.02 g of unreacted (I) was steam distilled off. The residue was chromatographed on Al_2O_3 (activity II). We isolated 3.35 g (53%) of the product (II) with mp. 25°. Found: C 56.31; H 6.69; S 12.61; N 5.54%. $C_{12}H_{17}NO_3$. Calculated: C 56.44; H 6.71; S 12.55; N 5.48%.

Oxidation of (II) to the Sulfone (III). A 1.55 g portion of the sulfide (II) was heated for 3 h with 2.7 g H_2O_2 in 10 ml glacial CH_3COOH at 70°. The mixture was poured out onto ice, and the solid product liberated was purified by crystallization from ethanol. White crystals were obtained with mp. 101°, yield 90%. Found: C 49.85; H 5.89; S 11.07; N 5.34%. $C_{12}H_{17}NO_5S$. Calculated: C 50.15; H 6.05; S 11.16; N 4.87%.

Reaction of (I) with n-C_4H_9SH under Electrophilic Conditions. Into a solution of 4.12 g (I) and 2.25 g n-C_4H_9SH in dry diethyl ether, SO_2 was passed for 3 min. No rise in the temperature was observed. The mixture was heated for 2 h at 30° (no reaction products were detected). The reaction was continued for another 5 h at 60°. From the reaction mixture we isolated 0.16 g (I), 0.5 g p-nitrophenol and 0.74 g bis-(p-nitrophenoxy)-ethylidene (IV) with mp. 127-128°. The melting point of a mixed sample with the known substance [1] gives no depression; the R_f values of (IV) and the standard in the system hexane – ethyl acetate, 13:1, on Al_2O_3 (activity II) coincide (0.24). In addition, we isolated 0.6 g of the dibutylmercaptal (V) (97% purity according to gas – liquid chromatography); bp. 102° (3 mm); n_D^{20} 1.4900. According to the data of [4]: bp. 64-67° (0.11 mm); n_D^{20} 1.4889. Found: C 58.46; H 10.64; S 31.35%. $C_{10}H_{22}S_2$. Calculated: C 58.22; H 10.70; S 31.08%.

Reaction of (I) with n-C_4H_9SH under Nucleophilic Conditions. An ampoule with 8.25 g (I), sodium butylmercaptide produced from 1.4 g of sodium and 4.5 g of C_4H_9SH in 25 ml of abs. ethanol was heated for 22 h at 85°. The reaction mixture with an addition of alkali was subjected to steam distillation to remove the unreacted (I) (1.5 g). The residue (5 g) was chromatographed on Al_2O_3 (activity II) in the system hexane – ethyl acetate, 13:1. After repeated preparative separation, we obtained: 4, 4'-dibutylthioazoxybenzene (VIII), 2.5 g (50%); 4, 4'-dibutylthioazobenzene (IX), 0.15 g (3%); and the divinyl ether of 4, 4'-azoxyphenol (VII), 1.25 g (25%).

Compound (VIII) was obtained in the form of yellow crystals, mp. 76-77°. Found: C 64.30; H 6.94; N 7.38; S 16.98%. $C_{20}H_{26}N_2OS_2$. Calculated: C 64.14; H 6.99; N 7.47; S 17.12%. Compound (IX) was obtained in the form of orange-red crystals, mp. 92-93°. Found: C 67.12; H 7.35; N 7.78; S 17.69%. $C_{20}H_{26}N_2 \cdot S_2$. Calculated: C 67.00; H 7.29; N 7.81; S 17.88%. Compound (VII) was obtained in the form of lemon-yellow crystals, mp. 90-92°. Found: C 68.30; H 5.07; N 9.79%. $C_{16}H_{14}N_2O_3$. Calculated: C 68.06; H 5.01; N 9.92%. Corresponds to that described earlier [5].

The method is basically analogous to that described above; only the solvent ethanol is replaced by dioxane (50 ml). The following were isolated from the reaction mixture: (I), 1 g; p-nitrophenol, 0.4 g; (VII), 3.2 g (64%); (VIII), 0.65 g (13%); (IX), 0.13 g (2.6%); resin, 0.3 g (6%); and (X), 0.1 g (2%) with mp. 110°. The IR spectra were obtained on the IR-10 spectrometer, the PMR spectra on a JNM-4H-100 spectrometer. The solvent used was CCl_4. Hexamethyldisiloxane was used as an internal standard. The chemical shifts were measured according to the δ scale, ppm.

CONCLUSIONS

1. The nitro group in the p-nitrophenoxyethylene molecule has a passivating influence on homolytic and electrophilic thiylation at the double bond, without changing the direction of the addition, characteristic of vinylalkyl and vinylaryl ethers.

2. Under conditions of nucleophilic thiylation, exchange of the vinyloxy group for an alkylthiyl group is observed, along with reduction of the nitro group both in the initial p-nitrophenoxyethylene and in the products of exchange.

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