MECHANISM OF OXIDATION OF AMINOALKYLPHENOL DERIVATIVES WITH BENZOYL PEROXIDE

COMMUNICATION 3. STUDY OF THE OXIDATION PRODUCTS OF ETHERS OF o-AMINO-p-tert-BUTYLPHENOL

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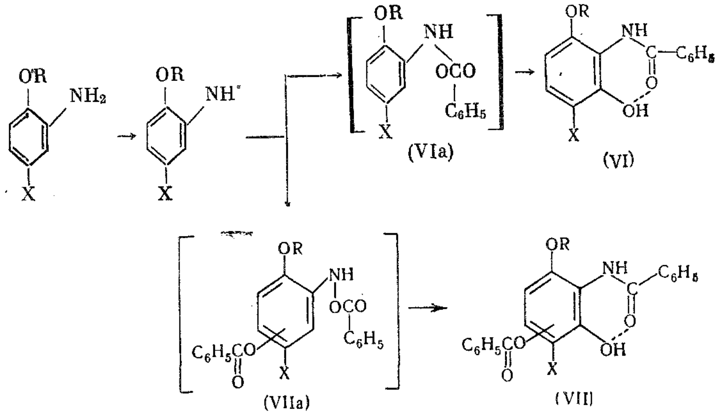
The oxidation of the ethers of o-amino-o-tert-butylphenol with benzoyl peroxide (BP) was studied in previous communications [1, 2]. The oxidation products of the methyl, ethyl, propyl, isopropyl, and butyl ethers of o-amino-p-tert-butylphenol were characterized (Tables 1 and 2), and schemes were postulated for the formation of some of them. Improvements in the chromatographic separation technique enabled us to isolate from the reaction products of the methyl ether of o-amino-p-tert-butylphenol (MEABP), in addition to those already described in [6], six pure compounds (see Table 1, III, IV, V, VIII, IX, XI). As a result, 10 compounds were detected in the oxidation products of MEABP, and the structure was established for 7 of them. Besides this, the oxidation of the ethyl and propyl ethers of o-amino-p-tert-butylphenol (EEABP and PEABP) gave the (VII) compounds, which were not detected in the experiments with MEABP.

The formation of benzoic acid (BA) (II), 4,4'-diphenylbiphenyl (III), and biphenyl(IV) as the result of oxidation can be depicted in the following manner: BP in the presence of the employed amines is easily decomposed to $C_6H_5COO^{\bullet}$, the main portion of which (up to 65%), reacting with the hydrogen of the amino group, is converted to BA. A part of the $C_6H_5COO^{\bullet}$, as will be shown later, adds to the oxidation products of the starting amine. A small amount of the benzoyloxy radical, decomposing to $C_6H_5^{\bullet}$, is converted to (III) and (IV).

The formation of the azo compounds (V) can be depicted in harmony with the previously proposed scheme via the initial formation of the ArNH• radicals [1], with the subsequent pairing of these radicals and the oxidation of the obtained hydrazo compounds



X=C(CH₃)₃

The presence of azo compounds indicates that in principle the scheme for the oxidation of the taken amines remains the same whether lead dioxide or BP is used. In both cases the cleavage of hydrogen from the starting amine occurs in the first step, with the formation of the ArNH• radical. The reaction products of this radical with the oxidizing agent or with the benzoyloxy radical are formed when BP is used.

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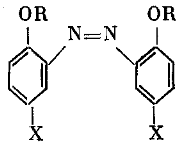
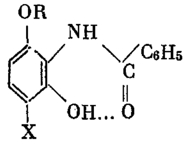
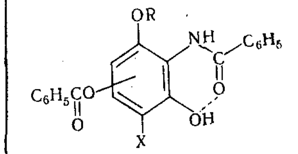
TABLE 1. Compounds Isolated from the Oxidation Products of the Ethers of o-Amino-p-tert-butylphenol

No.	Formula*	mp, °C (R)	Yield, % to sum of starting compounds
I	$C_6H_5COONH_4$	180—186 (sublimes)	3—4
II	C_6H_5COOH	122	35—40
III	$C_6H_5(C_6H_4)_2C_6H_5$	318 (sublimes)	—
IV	$C_6H_5C_6H_5$	68—68,5	—
V		150—151 (CH_3) 171—172 (C_2H_5) 140,5—141,5 (C_3H_7) 104,5—105 (C_4H_9)	1,5—2,0
VI		142—143 (CH_3) 97,5—98,5 (C_3H_7) 96,5—97,5 (C_4H_9)	3—5
VII		163—164 (C_2H_5) 153—154 (C_3H_7)	1
VIII	—	287—291 (CH_3) 259—260 (C_2H_5) 243—245 (C_4H_9)	1
IX	—	275—277 (CH_3) 245—247 (C_2H_5)	1
X	—	321—323 (CH_3) 322—323,5 (C_2H_5) 310—311 (i-C_3H_7) 264—266 (C_4H_9)	0,5
XI	$C_6H_5CONH_2$	124—125	—

* X — $C(CH_3)_3$

To compound (VI), obtained in the oxidation of MEABP, we previously [2] assigned the structure of (VIa). When the chemical properties (alkaline hydrolysis) and the IR spectra of these compounds were studied we came to the conclusion that product (VI) is N-benzoyl-2-hydroxy-6-alkoxy-3-tert-butylaniline. The latter can be formed by the isomerization of the initially obtained (VI), as was postulated in [3]. Absorption bands are observed in the IR spectra of (VI) that are characteristic for OR (~2840), tert-butyl grouping (~2900), NH (~3380 in CCl_4; ~3410 in Nujol, 3380 and 3420 cm^{-1} in KBr). The absence of bands, characteristic for OH, and also the presence of several additional bands in the 2600-3060 cm^{-1} region can be explained by the phenomenon of "chelate conjugation" [4] when an intramolecular hydrogen bond is formed between the hydrogen of the OH group and the oxygen of $C=O$.

The N-benzoyl-2-hydroxy-6-alkoxy-5(or 4)-benzoyloxyanilines (VII) were isolated only from the oxidation products of EEABP and PEABP. It is possible that they are formed from the other ethers but we were unable to detect them. The structure of these compounds was deduced on the basis of the elemental composition and an analysis of the IR spectra. In the IR spectra were observed the bands that were enumerated above for (VI), and also a band at ~1750 cm^{-1} (ester carbonyl); the position of the benzoyloxy group was not established. The formation of (VII) can occur during the reaction of either BP or $C_6H_5COO^{\bullet}$ with the $ArNH^{\bullet}$ radicals, or with (VIa) or (VI).

The structure of compounds (VIII), (IX), and (X) could not be established. On the basis of the elemental analysis, molecular weight and the IR spectra it is only possible to speak of the composition of these compounds. They are all products of the more profound oxidation of the starting amine and they each contain from 3 to 4 molecules of the latter in their composition, while compounds (IX) and (X), in addition, contain either benzoyloxy or benzoyl groups. Judging by the IR spectrum and the elemental composition, the benzoyloxy group is absent in compound (VIII). As corroboration of this can serve the fact that compound (VIII) was obtained in higher yield when the reaction of BEABP with BP was run using a 1 : 1/4 ratio

TABLE 2. Elemental Composition and Molecular Weights of Oxidation Products

Oxidation products	Starting amine															
	MEABP				EEABP				PEABP				BEABP			
	Found/Calculated, %				Found/Calculated, %				Found/Calculated, %				Found/Calculated, %			
	C, %	H, %	N, %	Mol. wt.	C, %	H, %	N, %	Mol. wt.	C, %	H, %	N, %	Mol. wt.	C, %	H, %	N, %	Mol. wt.
VI	72,18/72,23	7,32/7,07	4,98/4,68	292,00 */299,35	—	—	—	—	72,95/73,36	7,76/7,69	4,70/4,27	324,6 */327,40	74,56/73,87	8,00/7,96	4,17/4,10	332,0 */341,42
VII	—	—	—	—	71,52/72,03	6,46/6,28	3,19/3,23	—/433,4	72,24/72,46	6,82/6,52	3,16/3,12	443,60 */446,59	—	—	—	—
VIII	76,52/—	6,78/—	7,57/—	—	—	—	—	752,0 †/—	—	—	—	—	78,29/—	7,24/—	7,32/—	843,0 †/—
IX	74,63/—	6,20/—	6,63/—	660,0 †/—	74,80/—	5,95/—	6,21/—	—	—	—	—	—	—	—	—	—
X	75,80/—	7,09/—	6,21/—	—	76,15/—	7,05/—	6,89/—	637,0 †/—	—	—	—	—	—	—	—	—

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*Cryoscopically in benzene.

†Ebullioscopically in benzene.

rather than a 1 : 1 ratio, and the benzoyl peroxide was converted quantitatively to BA and the ammonium salt of benzoic acid. In this case compounds (IX) and (X) were not detected in the oxidation products. The calculations, made on the basis of the molecular weight and the elemental analysis (see Table 2), lead to the conclusion that 4 molecules of the oxidized amine, containing 4 alkoxyl groups, enters into the composition of (VIII). Compound (VIII), obtained from BEABP, is assigned the empirical formula $C_{55}H_{62}N_4O_4$. It is interesting to mention that EPR signals, with a hyperfine structure composed of 9 lines, were observed in the initially obtained product. These signals disappeared after repeated purification.

Judging by the IR spectrum of compound (IX) it is possible to assume that individual functional groups are present in it. Absorption bands are observed in the IR spectra that are characteristic for $C(CH_3)_3$ (~2900); OR (~2840), but with a lower intensity than for the starting ester; Ar–C=O (~1690), and the NH_2 grouping (~3370 and 3420 cm^{-1}). The latter gives two distinct bands in $CHCl_3$, while a broad diffuse band is observed when the spectrum is taken as a KBr pellet. It is possible to assume that the shift of the NH_2 bands toward lower frequencies in solution and the diffuse nature in the solid state occur due to the formation of an intramolecular hydrogen bond with the oxygen of the carbonyl group. The empirical formula for the (IX) obtained from MEABP is $C_{41}H_{40}N_3O_5$.

In the IR spectra of the (X) compounds, besides the absorption bands of $C(CH_3)_3$ (~2900) and Ar–C=O (~1670 cm^{-1}), are observed (in KBr) several bands in the 3050-3430 cm^{-1} region. The latter most probably correspond to complex hydrogen bonds. Not understandable is the absence of a band at 2840 cm^{-1} (OR), since the molecule contains an alkoxyl group, as can be judged by the different melting points for the (X) compounds obtained from the different ethers. The empirical formula for the (X) obtained from EEABP is $C_{44}H_{44}N_3O_4$. Benzamide (XI), the same as the ammonium salt of benzoic acid (I), is the reaction product of the oxidizing agent and the starting amine, with cleavage of the amino group.

EXPERIMENTAL METHOD

The preparation and characteristics of the starting ethers of o-amino-p-tert-butylphenol are given in [5, 6]. The oxidation of the enumerated ethers was run as described in [1] for MEABP, using a 1 : 1 ratio of amine to BP. After 24 h the oxidation mass was filtered from the precipitated ammonium benzoate (I). As a rule, the latter was obtained in an amount of 3.4-3.7%, when based on the sum of the starting products, or 6-7% when based on the BP. The filtered benzene solution was washed with 2% $NaHCO_3$ solution to remove the BA and then with water. After removing a part of the benzene by distillation the washed mass was diluted with an equal volume of petroleum ether (40-70°), and then chromatographed on a column filled with Al_2O_3 (50-140 mesh). Elution with the petroleum ether was continued until a slightly colored or colorless eluate was obtained, and then with a mixture of petroleum ether and benzene, with the amount of the latter steadily increasing from 10 up to 100%; finally, elution was with ether, acetone, and alcohol. The collected fractions had a variable color. The pure compounds were isolated after evaporation of the solvents and subsequent workup (see Tables 1 and 2).

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CONCLUSIONS

From the oxidation products of the methyl, ethyl, propyl, and butyl ethers of o-amino-p-tert-butylphenol using benzoyl peroxide were isolated and characterized 23 compounds, for 14 of which the structure was established. Schemes were proposed for the formation of the oxidation products.

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