8. E. Larsson, J. Prakt. Chem., 323, 988 (1981).
9. B. Holmberg, Ark. Kem., 2, 567 (1950).
10. A. Gordon and R. Ford, The Chemists Companion, Wiley, New York (1973).
11. D. J. Cram, Fundamentals of Carbanion Chemistry, Academic Press, New York (1965).
12. M. Friedmann, T. F. Cavins, and T. S. Wall, J. Am. Chem. Soc., 87, 3672 (1965).
13. F. Kurzer and P. M. Sanderson, J. Chem. Soc., 230 (1962).
14. M. I. Rybinskaya, Zh. Vses. Khim. Ova. im. D. I. Mendeleeva, 12, No. 1, 11 (1967).
15. S. I. Miller, C. E. Orzech, C. A. Welch, et al., J. Am. Chem. Soc., 84, 2020 (1962).

OXIDATION OF 2,6-DISUBSTITUTED PHENOLS AS A ROUTE TO 3,5,3',5'-TETRASUBSTITUTED DIPHENOQUINONES AND 4,4'-DIHYDROXYDIPHENYLS

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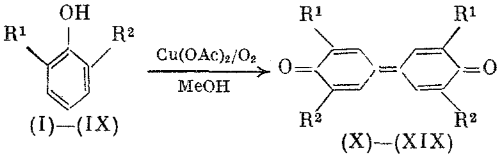
It is known [1, 2] that oxidation of 2,6-dialkylphenols (DAP) occurs smoothly forming 2,6,2',6'-tetraalkyldiphenoquinones. Nonetheless, this reaction has been used for only a limited number of materials. It was therefore of interest to broaden the scope of using oxidative dimerization for preparing diphenoquinones (DPQ) and their derivatives 4,4'-dihydroxydiphenyls which are potential antioxidants [3].

We have previously studied the oxidation of 2,6-di-tertbutylphenol (2,6-DTBP) by atmospheric oxygen [4]. In this work we have investigated 2,6-disubstituted phenols (I-IX) as substrates with catalysis by the copper acetate ammonium complex.

It should be noted that polyphenyleneoxide polymers were formed upon oxidation of 2,6-dimethyl-, 2,6-diphenyl-, and 2,6-dicyclohexylphenols. This was particularly rapid for the oxidative polycondensation of 2,6-diphenylphenol, 80% of which was converted to polymer.

As seen in Table 1, the diphenoquinone:polymer ratio resulting from phenol oxidation depended upon the degree of shielding of the hydroxyl group. The highest selectivity for the diphenoquinone was found for 2,6-DTBP, 2-tertbutyl-6-α-methylbenzyl, and 2,6-di-α-methylbenzylphenols with oxidation of 2,6-dinorbornylphenol (IX) being a little less.

The corresponding diphenoquinones X-XVIII were separated and characterized:



(I)—(IX)

(X)—(XIX)

$R^1 = R^2 = Me$ (I), (X); $R^1 = Me$, $R^2 = t\text{-}Bu$ (II), (XI); $R^1 = R^2 = t\text{-}Bu$ (III), (XII); $R^1 = Me$, $R^2 = Ph(Me)CH$ (IV), (XIII); $R^1 = t\text{-}Bu$, $R^2 = Ph(Me)CH$ (V), (XIV); $R^1 = R^2 = Ph(Me)CH$ (VI), (XV); $R^1 = R^2 = Ph$ (VII), (XVI); $R^1 = R^2 = C_6H_{11}$ (VIII), (XVII); $R^1 = R^2 =$  (IX), (XVIII).

Conversion of the diphenoquinones to the 4,4'-dihydroxydiphenyls was carried out in conjugative reaction of the quinone with 2,6-dialkylphenol in 82-98% yield. The compounds were characterized by their IR and PMR spectra which showed characteristic differences for the quinone and phenol structures.

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TABLE 1. Properties of 3,3',5,5'-Tetralkyl-4,4'-diphenoquinones (X-XVIII) and the Corresponding 4,4'-Dihydroxydiphenyls (XIX-XXVIII)

Compound	Yield, percent		mp, deg C	Compound	Yield, percent	mp, deg C
	product	polymer				
(X)	60–70	30–40	168–172	(XIX)	80,0	173–174
(XI)	95,0	–	63,5–64,0	(XX)	87,0	181,5–182,5
(XII)	98–99	–	246	(XXI)	87–89	186,0
(XIII)	69–70	–	146–147	(XXII)	83,0	liquid
(XIV)	92,0	–	210–214	(XXIII)	85,0	162,0
(XV)	96,0	–	73–80	(XXIV)	97,0	liquid
(XVI)	20–25	75–80	160–164	(XXV)	82,0	93–95
(XVII)	67–70	23–30	248–250	(XXVI)	89,0	275–278
(XVIII)	80,0	–	230–233	(XXVII)	87,0	liquid
				(XXVIII)	80,0	280–282

The IR spectra of the dihydroxydiphenyls showed OH group absorption in the region 3380-3650 cm^{-1} and the diphenoquinones showed very intense bands at 1580-1600 cm^{-1} (which were typical of $C=O$ absorptions in alkyl-substituted diphenoquinones [5]).

Formation of the diphenoquinones caused the PMR spectral signals for the OH group to disappear with a change in the chemical shifts of the remaining group fragments (excluding the Ph protons) because of a redistribution in electron density affecting virtually the whole molecule. Proton signals for the quinone ring were shifted by 0.4-0.5 ppm downfield of the corresponding phenol ring protons in the region 7.5-7.6 ppm.

EXPERIMENTAL

IR spectra were recorded on a UR-20 spectrophotometer as vaseline mulls and PMR spectra on a Tesla BS-487 instrument (80 MHz) referred to HMDS as internal standard. GLC analysis was carried out on a Tsvet-100 with flame ionization detection and 2% neopentylglycolsuccinate on Chromaton (0.20-0.25 mm) applied using chloroform. The carrier gas was helium (50 ml/min) and 1-2 ml of a 5-10% solution were taken using a MSh-10 microsyringe.

The 2,6-disubstituted phenols used were 98% pure, solvents were pure grade, and atmospheric oxygen was used without further purification.

General Method for Oxidation of 2,6-Disubstituted Phenols. Oxidation was carried out in a cyclic, thermostatted reactor of mixing volume 50 ml with continuous passage of air in combination with a buret which was constructed for measurement of a working system with an excess air pressure of 3 mm Hg. Contact between the reaction mixture and oxygen was brought about by vigorous stirring. Catalyst (0.21 g) was added with stirring at ~ 20°C to a solution of 2,6-DAP (2.06 g, 0.01 moles) in MeOH (23.24 ml). When 60°C had been reached in the reactor, air was added and this time taken as the beginning of the reaction. The oxidation was continued for 6 h, the precipitated crystals filtered off, thoroughly freed from catalyst residues by washing with hot water and methanol, and dried. The yield and conversion of starting material were calculated and the yields are reported in Table 1.

General Method for Reduction. A glass ampul of volume 8-10 ml was filled with 2,6-DAP (1.24 g, 6 mmoles), DPQ (0.82 g, 2 mmoles), and methanol (2.61 ml). The ampul was cooled, sealed, and heated in an oil thermostat for 8-10 h at 180°C. It was then opened and the precipitate (in the case of I, III, VII, and VIII) washed with methanol (2.61 ml), dried, and the yield and purity of the product determined. For reduction of IV-VI, IX, and X, crystals did not form, hence the ampul contents were distilled to remove methanol and excess phenol, and the residue was distilled in vacuo (for yields see Table 1).

CONCLUSIONS

Oxidation of 2,6-disubstituted phenols by atmospheric oxygen in the presence of a cuprammonium complex gave 3,3',5,5'-tetraalkyldiphenoquinones which were converted to the corresponding 4,4'-dihydroxydiphenyls.

LITERATURE CITED

1. V. V. Ershov, G. A. Nikiforov, and A. A. Volod'kin, Sterically Hindered Phenols [in Russian], Khimiya, Moscow (1972).
2. L. M. Strigun, A. A. Volod'kin, and A. I. Prokof'ev, Usp. Khim., 37, 969 (1968).
3. V. V. Ershov, A. A. Volod'kin, A. I. Prokof'ev, and S. P. Solodovnikov, Usp. Khim., 42, 1622 (1973).
4. M. Sh. Vakhitova, G. A. Tolstikov, and B. I. Pantukh, Zh. Prikl. Khim., 8, No. 10, 863 (1985).
5. L. J. Bellamy, Advances in Infrared Group Frequencies, Methuen, London (1968), p. 161.

ACYLATION OF AROMATIC AMINODICARBOXYLIC ACIDS

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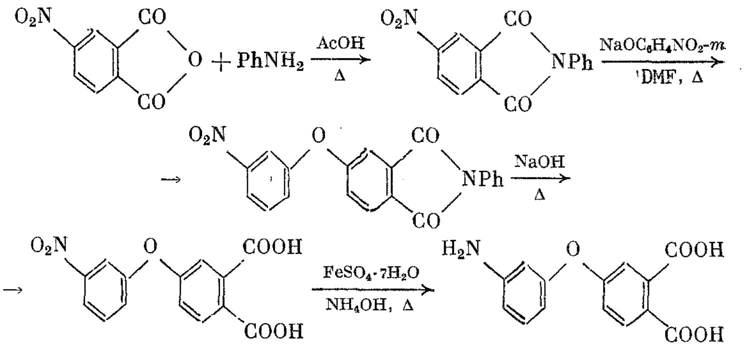
For the synthesis of thermostable polymers polyfunctional compounds that can undergo polycondensations are of interest, for example 4-aminobenzoylbenzoic acid, which forms polyamides, and 4-aminophthalic acid (4-APA), from which novel types of polyimides have been synthesized [1, 2]. However, polyimides with a high molecular weight have not been prepared from 4-APA. Obviously, the coming closer together of the carboxyl and amino groups in 4-APA gives rise to lowering of their reactivities. It is known that the effect of the substituents decreases sharply when they are separated by two benzene nuclei and becomes insignificant in three-nucleus systems [3].

It was shown earlier by us that from 4-aminophenoxyphthalic acid (4-APPA) high-molecular-weight polyimides can be obtained by linear polycondensation under the action of $(PhO)_3P$ [4]. The combination of carboxyl groups that are inactive in the usual reactions with an active amino group makes it possible to use aminodicarboxylic acids for the synthesis of polyamidoimides (PAI) and copolyimides. The successful application of these monomers in the synthesis of polymers is mainly determined by the basicity of the amino group. The rate of acylation of the amines bears a linear relation to their basicities. In connection with this, in the present study we have synthesized various aminodicarboxylic acids and studied the kinetics of their acylation with the anhydride and the acid chloride of trimellitic acid. Both 2- and 4-APPA and 3- and 4-aminobenzoylphthalic acid were prepared in analogy to [4, 5]; 3-APPA was prepared according to the following scheme:



The IR spectra of these aminodicarboxylic acids are characterized by the absence of the absorption of the free amino group and the presence of bands at 3070 (NH_3^+) and at 1600 and 1380 cm^{-1} (COO^-). The intensity of the absorption of the COO^- groups of the APPAs changes in the

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