corresponding molecules, is shown in Fig. 6, indicating that this distribution is shifted toward shorter contacts for the most charged nitro groups in (II).

Quantum chemical calculations and analysis of the distribution of the intermolecular contacts in the structures of (I), (II), and (IV) show an increase in the secondary oxy-gen-halogen interactions in molecules with increasing atomic number of the halogen atom.

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REGIOCONTROLLED NITRATION OF DI(TERT-BUTYL)PHENOLS

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The nitration of 2,4-di(tert-butyl)phenol and 2,6-di(tert-butyl)phenol is accompanied by oxidative processes, leading to products of the oxidative coupling of the starting di(tert-butyl)phenols. On the other hand, the corresponding nitrophenols are formed in quantitative yield in the substitutive nitration of $6-XCH_2$ - and $4-XCH_2$ -di(tert-butyl)phenols (X = OH, OR, NR₂).

Selective aromatic substitution under certain conditions requires the use of positional protectors, namely, groups blocking ring positions from the undesired introduction of a substituent. Tert-butyl groups, which are rather readily removed from the substituted molecules, are most often used as such protective functions. However, the tert-butylation of a phenol may markedly alter the redox properties of the substrate to be substituted such that an oxidation-reduction reaction with the electrophile is possible in addition to substitution. We have encountered such a case in developing a method for the selective ortho and para mononitration of phenol using tert-butyl protection of the other ring positions. The reaction of 2,4-di(tert-butyl)phenol (I) and 2,6-di(tert-butyl)phenol (II) with NaNO₂ in acetic acid as the nitrating agent leads not only to the corresponding nitrodi(tert-butyl)phenols (III) and (IV) (in 55 and 58% yield, respectively), but also to the product of the oxidative coupling of the starting di(tert-butyl)phenols, namely, tetra(tert-butyl)bisphenol (V) (in 42% yield) and tetra(tert-butyl)diphenoquinone (VI) (in 30% yield).



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$\mathbf{R} = \mathbf{C}(\mathbf{CH}_{\mathbf{S}})_{\mathbf{S}}.$

The formation of oxidation products leads to deterioration of the material balance for substitution and hinders isolation of the desired nitrophenols as pure compounds from the reaction mixture.

We have found that the oxidative coupling may be prevented if a hydroxymethyl group is additionally introduced as a protective group in the position to be substituted in 2,4di(tert-butyl)phenol. The nitration of 6-hydroxymethyl-2,4-di(tert-butyl)phenol proceeds regiospecifically, leading to the quantitative formation of the desired product, namely, 6-nitro-2,4-di(tert-butyl)phenol (III).

The same effect is achieved using 6-alkoxy- and 6-dialkylaminomethyl protective groups.



4-XCH₂-2,6-di(tert-butyl)phenols behave analogously under these conditions to give 4-nitro-2,6-di(tert-butyl)phenol (IV) in quantitative yield.

Thus, the substitutive nitration of these CH_2X -substituted di(tert-butyl)phenols proceeds exclusively as nitrodehydroxymethylation, nitrodealkoxymethylation, or nitrodedialkylaminomethylation. The possible competitive nitrode(tert-butylation) does not occur. Such specificity is apparently a consequence of a substitution mechanism, in which the participation of the heteroatom in the CH_2X group plays the major role in all steps of this reaction. In the initial step, this role entails a coordinating interaction with the electrophile and then stabilization of the intermediate (σ -substitution complex). Finally, this role entails stabilization of the leaving group:



The overall effect of the participation gives a reduction in the energetics of this type of substitution, which becomes orientational in nature. The introduction of the CH_2X group as the substitution orientant may be used in more complex cases with subsequent removal of the tert-butyl groups.

EXPERIMENTAL

Chromatographically pure samples of 2,4- and 2,6-di(tert-butyl)phenols were obtained by single crystallization of analytical-grade commercial samples. The hydroxy-, alkoxy-, and dimethylaminomethyldi(tert-butyl)phenols were prepared according to our previous procedures [4].

<u>Nitration of 2.4-Di(tert-butyl)phenol (I).</u> A sample of 0.01 mole (2.06 g) phenol was dissolved in 50 ml glacial acetic acid and 0.03 mole (2.1 g) $NaNO_2$ was added in portions with stirring at 20°C. The conversion was monitored by thin-layer chromatography on Silufol UV-254 using 15:1 hexane-ether as the eluent. The products were analyzed by comparison with authentic samples. At the end of the reaction, the reaction mixture was diluted with

water. The products were extracted with ether and separated by fractional crystallization from hexane or preparative thin-layer chromatography. The conversion was quantitative. The following products were isolated: 1.4 g (55%) 6-nitro-2,4-di(tert-butyl)phenol (III), mp 62-63°C [1] and 1.7 g (42%) 4,4',6,6'-tetra(tert-butyl)-2,2'-bisphenol (V), mp 185-186°C [2].

<u>Nitration of 2,6-Di(tert-butyl)phenol (II)</u>. Analogously, 0.01 mole (II) gave 1.46 g (58%) 4-nitro-2,6-di(tert-butyl)phenol (IV), mp 153-154°C [3] and 0.6 g (30%) 2,2',6,6'-tetra(tert-butyl)para-diphenoquinone (VI), mp 245-246°C [5].

<u>Nitration of $6-XCH_2-2.4$ -di(tert-butyl)phenols (X = OH, OCH₃, and N(CH₃)₂).</u> Analogously to (I), 0.01 mole substrate gave 96-98% (III), mp 62-63°C.

<u>Nitration of 4-XCH₂-2,6-di(tert-butyl)phenols.</u> Analogously to (I), 0.01 mole starting phenol gave (IV) in 94% yield, mp 153-154°C.

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METALLATION AND FUNCTIONALIZATION OF o-SULFONYLDI - AND

o-SULFONYLTRIARYLCARBINOLS.

UNEXPECTEDLY FACILE CYCLIZATION OF TERT-BUTYL-

SULFONYLCARBINOL INTO A SULTINE

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The lithiation of o-sulfonyltriphenylcarbinols proceeds in the ortho position relative to the sulfonyl group, as indicated by formation of the corresponding carboxylic acids upon the action of CO_2 . Unusual facility was found for the loss of the tert-butyl group in 2-(tert-butylsulfonyl)-3-diphenylhydroxymethylbenzoic acid in acid media to give the corresponding sultime.

The ortho orienting effect of the sulfonyl group in metallation by BuLi permits us to obtain o-sulfonylbenzaldehydes, which are the starting reagents in the synthesis of stable benzonitrile oxides [1, 2].

In order to obtain new functionally substituted benzaldehydes, we studied the direction of the metallation of o-sulfonylcarbinols (Ia)-(Ic), which were obtained by the functionalization of the corresponding o-Li-phenylsulfones [3, 4].



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