MIGRATION OF ALKYL GROUPS OF o-tert-BUTYL-SUBSTITUTED HYDROXYAROMATIC COMPOUNDS UNDER HIGH PRESSURE IN COMBINATION WITH SHEARING STRESS

V. B. Vol'eva, V. A. Zhorin,
A. L. Khristyuk, V. V. Ershov,
and N. S. Enikolopyan

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o-tert-Butyl substituted hydroxyaromatic compounds, sterically hindered phenols, are widely used for stabilization of polymeric substances. Technological schemes for production of polymeric products include, as a rule, the action of high pressure and shearing stress, which emphasizes the practical importance of the study of the behavior of sterically hindered phenols under such conditions.

EXPERIMENTAL

We study the behavior of four compounds of the class of sterically hindered phenols, 4-methyl-2,6-di-tert-butylphenol (I), 2,4,6-tri-tert-butylphenol (II), 3,5-di-tert-butylcatechol (III), and 3,6-di-tert-butylcatechol (IV), under the influence of high pressure and shearing stress. This was done in a Bridgman anvil-type apparatus at pressure intervals from 2000 to 6000 MPa at about 20°C, the weight of samples recovered being about 30 mg. The transformed products were analyzed by means of analytical preparative thin-layer chromatography on Silufol UV-254 using a hexane—ether solvent system with various ratios of components. For preparative separations we used combined quantities of reaction mixtures from six to seven separate runs (∿200 mg). Identification of products was carried out by comparison with standard samples, differentiated not only by R_f values, but by the colors of the spots [1] on the chromatogram.

Isomerization of (III) to (IV). Formation of (IV) was established chromatographically; (III) gave a raspberry colored spot on the chromatogram; (IV) gave a green-brown spot. Estimation of the amount of (IV) was made by comparison with standard mixtures of (III) and (IV) containing comparable amounts of these components.

The System 2,4,6-tri-tert-Butylphenol (II)—Titanium Salt of Catechol (V) (1:1). The recovered starting phenol (II) (∿15%) had mp 131°C and showed no depression in melting point when mixed with authentic samples; 2,4-di-tert-butylphenol (VI) (80% yield) mp 59°C, was identical with the standard sample; 3-tert-butylcatechol (VII) (60% yield), bp 97-98°C (1 mm Hg), corresponds to that of [2] and is identical with a standard sample; it gave a black spot on the chromatogram; 4-tert-butylcatechol (VIII) (∿20% yield) mp 47°C, gave a lilac-colored spot on the chromatogram.

The System 2,4,6-tri-tert-Butylphenol (II)—Catechol—p-Toluenesulfonic Acid (1:1:0.2). Analysis was carried out immediately after removal of the high pressure. Acid-catalyzed isomerization yields (VII) and (VIII), just as in the previous instance, with comparable ratios of (VII) to (VIII). Yields: (II), 25%; (VI), 60%; (VII), 40%; (VIII), ∿15%. Identification is analogous with that described above.

The titanium salt of catechol (V) is prepared from catechol and $TiCl_3$ (2:1) in acetone; the brown precipitate of (V) is dried under vacuum.

The mixed manganese salt of monomethoxy- and dimethoxy-di-tert-butyl catechol is prepared by interaction of 3,5-di-tert-butylbenzoquinone with manganese diacetate in methanol [3]. Three or four days after mixing the reagents, black shiny crystals of the mixed manganese salts are formed. The action on them of high pressure (2000 MPa) and shearing stress results in the formation of 4-methoxy-3,6-di-tert-butyl-o-benzoquinone (X) and 4,5-dimethoxy-3,6-di-tert-butyl-o-benzoquinone (VI) (mp. 98°C and 70°C), corresponding to those given in [3]. Quinones (X) and (XI) are identical with standard samples; (X) — brown spot on the chromatogram; (XI) — orange-red spot.

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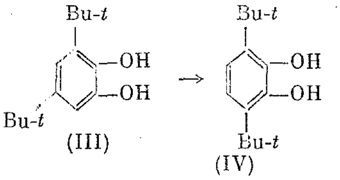
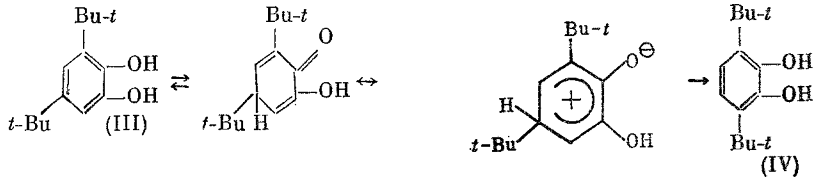
DISCUSSION OF THE PRODUCTS OBTAINED

Compounds (I), (II), and (IV) remain practically unchanged up to pressures of 6000 MPa with shearing stress, the corresponding angle of rotation of the upper part of the anvil being relatively low at 1000°. In the case of (III), the symmetrically substituted isomer (IV) was observed in the product (1% at 4000 MPa).

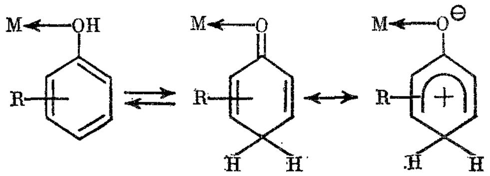


This fact is extremely interesting and deserves special attention. It might be predicted that under high-pressure conditions the more hindered isomer (IV) would be thermodynamically more stable and the conversion (III)-(IV) would be accompanied by decreased yield due to closer packing. The action of high pressure ought to favor the isomerization of (III) and (IV) as well as the subsequent change in acidity of the substituted catechol. Isomer (IV) is less acid than (III) and the change from (III) to (IV) is accompanied by a decrease in the total number of particles.

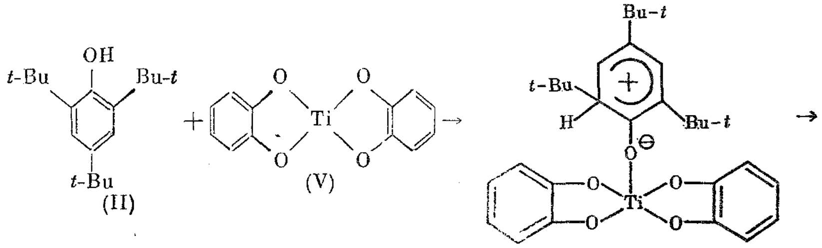
The observed regrouping with alkyl migration can occur via two mechanisms, intra- and intermolecular, but the absence of any dealkylation products in the sample after removing the high pressure attests to the likelihood of the intramolecular mechanism. Because of this it is highly probable that the migrating capability of the tert-butyl group in position 5 is brought about by the tautomerization of (III) to a keto form with a para-quinoid structure.

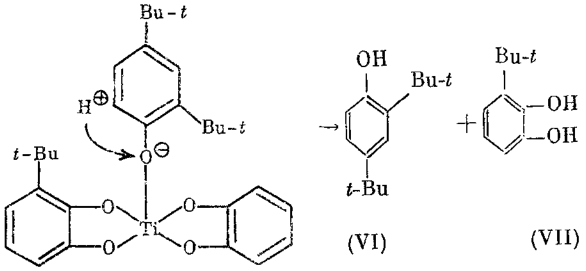


The mechanism of such a tautomerization may include the catalytic action of the metal surface of the anvil, causing the formation of coordinate bonds between the atoms of the metal and oxygen atoms of the hydroxyl group, similar to the interaction of alkoxy aromatic compounds with aluminum halides and other Lewis acids [4].

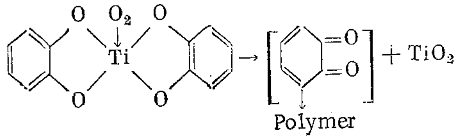


The mechanism of metal complex catalysis of alkyl migration is evidently a factor in another system investigated by us, the system phenol (II)—titanium salt of catechol (V), where (V) fulfills the function of a catalyst and an acceptor of the tert-butyl group. By analysis of this system immediately after removal of the high pressure, we discovered the formation of 2,4-di-tert-butylphenol (VI) (80%) and a mixture of the isomeric 3- and 4-di-tert-butylcatechols (VII) and (VIII) in which isomer (VII) predominates, the (VII):(VIII) ratio being 3:1. The observation of ortho selectivity of the tert-butyl group entering into the catechol ligand indicates ortho transfer via a complex of reactants.

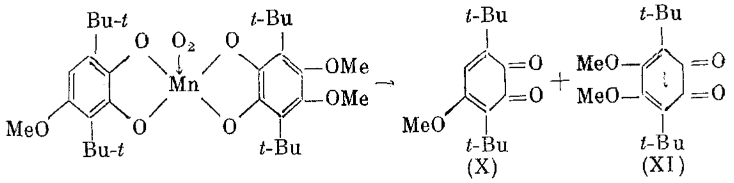



(VI) (VII)

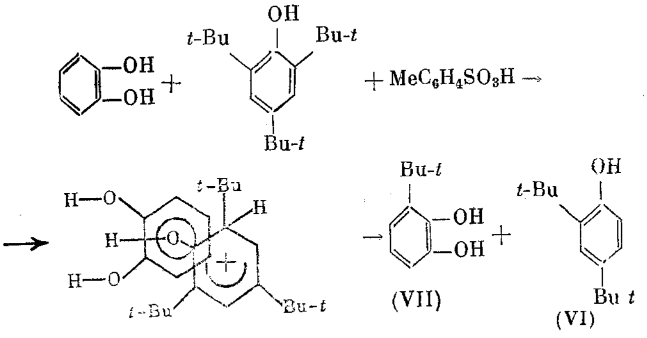
Analogous results are obtained for the system 4-methyl-2,6-di-tert-butyl phenol (I) with the titanium-catechol salt (V). In both systems we observed the formation of notable quantities of tarry substances, chromatographically identified as being formed by the action of high pressure and shearing stress on the catechol salt (V). The reason for the appearance of tars is evidently the polymerization of unsubstituted o-benzoquinone, the formation of which is highly probable and linked to the presence in (V) of O_2 bonded to titanium.



The ability of transition metals linked to catechol to bond reversibly with O_2 has been noted in [5]. This ability was confirmed by us for the mixture of the manganese salts of mono and dimethoxy-di-tert-butylcatechol.


(X) (XI)

The role of complex formation under high pressure and shearing stress is evidently generally quite important, as in the appearance of ortho-selective alkyl migrations, which were found in the systems of phenols (I) or (II) with catechol and p-toluenesulfonic acid. The predominant formation of 3-tert-butylcatechol (VII) effectively accounts for the reaction via donor—acceptor complexes where the reciprocal arrangement of the components is fixed by hydrogen bonding in the position most favorable to the transfer of the tert-butyl groups to the ortho position of the catechol fragment.


(VII) (VI)

CONCLUSIONS

1. By the concurrent action of high pressure and shearing stress, we demonstrate an unusual conversion of 3,5-di-tert-butyl catechol to the more sterically strained 3,6-isomer, and we propose a mechanism for the observed isomerization.

2. Ortho-selective transfer of tert-butyl groups from 2,4,6-tri-tert-butylphenol to the unsubstituted catechol is demonstrated. Conclusions are drawn as to the important role of complex formation between the reactants under high pressure and shearing stress.

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OXIDATION OF TRIARYL- AND DIARYLMETHANES BY OXYGEN IN THE SYSTEM KOH—DIMETHOXYETHANE—18-CROWN-6-ETHER AND CLEAVAGE OF TRIARYLCARBINOL AND DIARYL KETONE INTERMEDIATES

G. A. Artamkina, A. A. Grinfel'd,
and I. P. Beletskaya

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Oxidation by oxygen of carbanions obtained in situ from CH acids treated with bases is a promising method for obtaining oxygen-containing compounds. However, up to the present time this oxidation method has practically not been used. This is apparently explained by the difficulty of generating the carbanions, especially from weak CH acids, since usually strong bases must be used in aprotic media. For sufficiently low pK_a values for the CH acids ($pK_a <$ 17-18), when generation of the carbanions is a rather simple problem, complications in the use of this method are due to the stability of the carbanions relative to O_2.

The first difficulty can be rather successfully overcome by using such solvents as dimethylsulfoxide (DMSO) or hexamethylphosphoramide (HMPA). In the DMSO—t-BuOH (20%)—t-BuOK system [1, 2], oxidation of a large number of CH acids ($pK_a \cong$ 18-33) has been successfully carried out. The purpose of this work is to study the reaction mechanism. The use of DMSO in the synthesis has substantial limitations due to its relatively high cost and difficulties connected with the isolation of reaction products from this solvent. New promising directions in this field have been opened up to phase transfer catalysis, which has allowed us to significantly extend the pK_a limits for the hydrocarbons from which we may generate carbanions in situ [3, 4]. The use of this method has made it possible to carry out oxidation by oxygen of fluorene, xanthene, and anthracene and to obtain fluorenone, xanthone, and anthraquinone in practically quantitative yields [5]. Recently we have shown that the system KOH—dimethoxyethane—18-crown-6-ether allows us to generate and oxidize by oxygen or air carbanions from di- and triphenylmethanes, the pK_a of which are, respectively, equal to 33 and 31.5 [6]. We note that metallation of hydrocarbons of the di- and triphenylmethane type has not yet been accomplished even with treatment with potassium hydride; positive results have been achieved only when using KH in the presence of 18-crown-6-ether [7] or potassium amide [8]. However, recently in the system xylene—50% solution of KOH in water—quaternary ammonium salt, isomerization of allyl benzene has been accomplished. This means that under the given conditions it is possible to form a carbanion from a CH acid with pK_a 34 [9], which agrees with our results.

In this work, we have carried out an investigation of the oxidation of hydrocarbons of the di- and triphenylmethane type in alkaline medium by oxygen in the presence of the phase transfer catalysts Bu_4NBr, $C_{16}H_{33}(CH_3)_3NBr$, and 18-crown-ether. As the solvents we used dimethoxyethane (DME), tetrahydrofuran (THF), and benzene. The R_4NX salts exhibit low activity compared with the crown ether, which probably is explained by their low solubility in the given solvents. The oxidation of di- and triphenylmethanes in the presence of crown ether proceeds most easily in DME, somewhat less easily in THF, and rather slowly in benzene. Below

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