# HALOGENATION OF 3,6-DI-tert-BUTYLPYROCATECHOL WITH RETENTION OF THE ALKYL SUBSTITUENTS

 $R = Me_3C$ .

V. B. Vol'eva, I. A. Novikova, I. S. Belostotskaya, UDC 542.944:547.565.2 É. V. Dzhuaryan, and V. V. Ershov

3,6-Di-tert-butylpyrocatechol (I) and some of its derivatives are efficient antioxidants and acceptors of hydrogen halides, which assures their practical use [1, 2]. In this connection, it seems of interest to expand the series of (I) derivatives by inserting substituents in the free positions of the ring. Our previous attempts to effect direct electrophilic substitution in (I) proved unsuccessful [3]. Thus, when (I) is brominated one alkyl substituent is lost and two Br atoms enter the ring to give 5,6-dibromo-3-tert-butylpyrocatechol (II), independent of the ratio of the reactants [half of the starting (I) remains unchanged at an equimolar ratio of (I) and  $Br_2$ ]. On this basis it was concluded that the substitutive bromination of (I) predominates which, however, does not agree with the fact that the normal monobromination product is formed when bromine acts on the isopropylidene ether (III). Taking these results into account, and also the data obtained by us on the behavior of substituted (I) derivatives in the presence of acids [4, 5], it becomes possible to formulate the



following concepts regarding the mechanism of the transformations of (I) and its derivatives when reacted with electrophiles: 1) the initial attack of the electrophile is directed to the free position of the ring of the substrate; 2) the formed  $\sigma$  complex can either deprotonate or undergo isomerization to the arenonium ion of a new structure and the cleavage of tertbutyl cation. The key step of this reaction (Scheme 1) is the formation of the  $\sigma$  complex (IV). It is known that in the halogenation of phenols and aromatic amines [6, 7] the step of forming the  $\sigma$  complex is not limiting. As a result, also in our case the lifetime of the  $\sigma$ complex (IV) should be quite long, and the composition of the reaction products should depend



Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1416-1419, June, 1983. Original article submitted November 12, 1982.

Reaction conditions	Reaction products, yield, g (%)	
	(IIa)	(Va)
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	$\begin{array}{c} 0,1831 \ (45,9) \\ 0,0565 \ (14,2) \\ 0,2733 \ (68,5) \\ 0,1478 \ (37,0) \\ 0,1797 \ (45,0) \\ 0,2800 \ (70,5) \\ 0,2072 \ (52,3) \end{array}$	$\begin{array}{c} 0,0267 & (7,0) \\ 0,0433 & (11,7) \\ 0,0672 & (18,1) \\ 0,0678 & (18,5) \\ 0,0345 & (9,3) \\ 0,0037 & (1,0) \\ 0,1813 & (49) \\ 0,0123 & (3,3) \\ 0,0789 & (21,4) \end{array}$

# TABLE 1. Bromination of 3,6-Di-tert-butylpyrocatechol (I)

on the relative contribution of the equilibrium paths for its transformations. The deprotonation of the  $\sigma$  complex (path a) leads to 4-bromo-3,6-di-tert-butylpyrocatechol (V), the monosubstitution product, while isomerization and subsequent cleavage of the tert-butyl cation (paths b and c) leads to dibromopyrocatechol (II). An increase in the basicity of the medium should facilitate the contribution of path a, which leads to an increase in the amount of (V) in the bromination products. This is confirmed by a change in the ratio of the (II):(V) yields, the bromination products of (I), from 6.6 in benzene to 1.2 in xylene (Table 1). It is evident that a further increase in the proton-acceptor properties of the medium should lead to an increase in the yield of 3,6-di-tert-butyl-o-benzoquinone (VI). Actually, as we had shown earlier [3], quinone (VI) is formed in 98% yield when (I) is brominated in an ether-water-pyridine mixture.

Path a proves to be dominant when ether (III) is brominated. In this case, the predominant deprotonation of the  $\sigma$  complex and the formation of the monobromination product are explained by the possibility of an intramolecular shift of a proton to the heterocyclic fragment of the molecule to give the oxonium ion.



It is obvious that the bromination of pyrocatechol (I) can also be directed either predominantly or even exclusively along path  $\alpha$  by a special selection of the conditions. This is evidenced by the comparative data on the bromination of (I) in CCl<sub>4</sub> and its complex with the related 3,6-di-tert-butyl-o-benzoquinone (VI), which is an efficient proton acceptor (it was shown that inherently quinone (VI) does not react with bromine). The presence of a proton-acceptor in the complex with (I) facilitates deprotonation of the  $\sigma$  complex and leads to increasing the yield of 4-bromo-3,6-di-tert-butylpyrocatechol (V) from 9.3 to 49%.

The chlorination of (I), similar to the bromination, leads to 4-chloro-3,6-di-tert-buty1pyrocatechol (VIII).



Chloropyrocatechol (VIII) is not changed on further treatment with chlorine. On this basis we excluded the possibility of forming the dihalo derivatives (II) and (IX) by the direct halogenation of (V) and (VIII). Apparently, they are obtained directly from (I) via substitutive debutylation (Scheme 1).

An analysis of the reaction mixtures reveals that the amount of (V) in the system decreases with time; this is explained by its dealkylation (paths c and d) and the formation of (II) in an irreversible process. It should be mentioned that in not one of the studied

cases did we record the formation of the postulated intermediate product, namely 5-bromo-3tert-butylpyrocatechol (VII). Apparently, the rate of the subsequent bromination of (VII) is much faster than that of the starting (I). This can be explained by a decrease in the steric hindrance for the attack of bromine on (VII) when compared with (I), and also to a difference in the basicity of (I) and (VII), due to which the liberated HBr protonates predominantly the starting (I) and thus passivates it toward electrophilic substitution. The effect of the last factor can counterbalance the use of a medium with an acidity that is adequate for the efficient protonation of (I) and (VII). Taking this into account, we ran the bromination of (I) in an ether-sulfuric acid system (75:1). The selection of an acid with a hard anion was made on the basis of a maximum decrease in the degree of dealkylation of the substrate, which was based on the data given in [4] on the behavior of protonated (I) derivatives, modeling the  $\sigma$  complex of substitution, as a function of the nature of the anion of the acid. The selected conditions proved to be optimum for the synthesis of the desired pyrocatechol (V), which was formed as the sole reaction product. This result testifies to the entering of sulfate ion into the composition of the key  $\sigma$  complex of substitution. The involvement of sulfate ion in the process is possible both via a change in the nature of the electrophilic agent (Br<sup>+</sup>HSO<sub>4</sub>) and as the result of anionic exchange of the  $\sigma$  complex (IV) with the medium. The last possibility seems especially interesting. Proof of its realization can serve as a criterion when determining the limiting step of the substitution. With this in mind we brominated (I) in the presence of a neutral electrolyte with a like ion, and specifically tetrabutylammonium sulfate in acetonitrile. In this case, the yield of pyrocatechol (V) increases sevenfold when compared with the reaction without the salt additive, which unequivocally indicates anionic exchange in the  $\sigma$  complex. A similar salt effect for electrophilic substitution in the aromatic series is apparently observed for the first time.



#### EXPERIMENTAL

Bromination of (I). All of the experiments were run using a constant ratio of the reactants (the experimental data are given in Table 1). To a solution of (I) (0.275 g, 1.24•  $10^{-3}$  mole) in 15 ml of solvent was added 15 ml of a solution of Br<sub>2</sub> (0.1 ml, 1.95•10<sup>-3</sup> mole) in the same solvent. For convenience in isolation, after 2.5 h the mixture of starting pyrocatechol (I) and formed (II) and (V) was oxidized with Ag<sub>2</sub>O to the corresponding quinones (VI), (IIa), and (Va), which were separated by chromatography on Silufol UV-254 in the system: 6:1 pentane ether. (IIa): mp 105° (cf. [3]), R<sub>f</sub> 0.42. (Va): mp 59-60° (from hexane), R<sub>f</sub> 0.80, UV spectrum (hexane):  $\lambda_{max}$  390 nm ( $\varepsilon$  2219) and  $\lambda_{max}$  581 nm ( $\varepsilon$  73.6). PMR spectrum ( $\delta$ , ppm): 1.23 s (9H, Me<sub>3</sub>C), 1.43 s (9H, Me<sub>3</sub>C), 6.80 s (1H, ring). Found: C 56.34; H 6.44%. C<sub>14</sub>H<sub>19</sub>O<sub>2</sub>Br. Calculated: C 56.18; H 6.35%. (VI): mp 199° (cf. [3]), R<sub>f</sub> 0.55.

<u>4-Bromo-3,6-di-tert-butylpyrocatechol (V)</u>. The pure (V) was obtained by reducing quinone (Va) with Zn in AcOH. To a solution of (Va) (0.75 g,  $2.5 \cdot 10^{-3}$  mole) in 30 ml of AcOH was added Zn (1.5 g,  $2.3 \cdot 10^{-2}$  g·at). After decolorization the solution was diluted with water and the product was extracted with ether. The ether fraction was washed and dried. The residue from the evaporation was recrystallized twice from hexane to give 0.302 g (40%) of (V), mp 57-58°C. PMR spectrum ( $\delta$ , ppm): 1.45 s (9H, Me<sub>3</sub>C), 1.75 s (9H, Me<sub>3</sub>C), 5.76 s (1H, OH), 5.84 s (1H, OH), 7.15 s (1H, ring).

<u>Chlorination of (I)</u>. A stream of Cl<sub>2</sub> was passed for 1 h through a solution of (I) (0.275 g,  $1.24 \cdot 10^{-3}$  mole) in 30 ml of ether. The formed mixture of pyrocatechols (I), (VIII), and (IX) was oxidized with Ag<sub>2</sub>O to the corresponding quinones (VI), (VIII), and (IXa), which were separated by chromatography on Silufol UV-254 in the system: 6:1 pentane—ether. We obtained 0.535 g (17%) of (VIIIa) and 0.1494 g (52%) of (IXa). (VIIIa):  $R_{f}$  0.79 mp 50-51° (from hexane). UV spectrum (hexane):  $\lambda_{max}$  390 nm ( $\varepsilon$  2215) and  $\lambda_{max}$  580 nm ( $\varepsilon$  69.3). Found: C 66.40; H 7.65%. C<sub>14</sub>H<sub>19</sub>O<sub>2</sub>Cl. Calculated: C 66.14; H 7.48%. (IXa):  $R_{f}$  0.40, mp 108-109° (from hexane). UV spectrum (hexane):  $\lambda_{max}$  416 nm ( $\varepsilon$  2215) and  $\lambda_{max}$  580 nm ( $\varepsilon$  36.8). Found: C 51.52; H 4.41%. C<sub>10</sub>H<sub>10</sub>O<sub>2</sub>Cl<sub>2</sub>. Calculated: C 51.50; H 4.29%.

<u>Chlorination of (VIII)</u>. Cl<sub>2</sub> was passed for 1 h through a solution of (VIII) (0.254 g,  $1 \cdot 10^{-3}$  mole) in 30 ml of ether. Chromatographic analysis of the reaction mixture disclosed that it contained only the starting (VIII).

## CONCLUSIONS

1. 3,6-Di-tert-butylpyrocatechol can be brominated and chlorinated with retention of the tert-butyl groups.

2. The yield of the 4-bromo-3,6-di-tert-butylpyrocatechol that is formed during bromination is quite dependent on the nature of the solvent and the character of the counterion in the composition of the intermediate  $\sigma$  complex.

### LITERATURE CITED

- N. A. Azatyan, G. V. Karpukhina, I. S. Belostotskaya, and N. L. Komissarova, Neftekhimiya, 13, 435 (1973).
- I. S. Belostotskaya, N. L. Komissarova, V. B. Vol'eva, and V. V. Ershov, Transactions of Third All-Union Conference on the Degradation and Stabilization of Polymers [in Russian], Moscow (1977).
- I. S. Belostotskaya, É. V. Dzhuaryan, and V. V. Ershov, Izv. Akad. Nauk SSSR, Ser. Khim., 1100 (1977).
- 4. I. A. Novikova, V. B. Vol'eva, N. L. Komissarova, I. S. Belostotskaya, and V. V. Ershov, Izv. Akad. Nauk SSSR, Ser. Khim., 2110 (1981).
- 5. V. B. Vol'eva, I. A. Novikova, I. S. Belostotskaya, N. L. Komissarova, and V. V. Ershov, Izv. Akad. Nauk SSSR, Ser. Khim., 2128 (1981).
- 6. E. Grovenstein and D. Kilby, J. Am. Chem. Soc., <u>79</u>, 2972 (1957).
- 7. E. Shilov and F. Weinstein, Nature, 182, 1300 (1958).

### QUANTUM-CHEMICAL ESTIMATE OF ACTIVATION ENERGY

FOR RUPTURE OF C-NO<sub>2</sub> BOND

V. A. Shlyapochnikov, K. I. Rezchikova, V. N. Solkan, and S. V. Zakharkinskaya UDC 530.145:542.92:541.57

The experimental determination of the activation energy for rupture of the C-NO<sub>2</sub> bond  $(E_{\alpha})$  is quite complicated. A correct theoretical determination of the activation energy requires employing a very laborious formalization of the RRKM theory [1]. In this connection it is helpful to attempt constructing relationships between the activation energies and certain calculated characteristics of the starting molecules, and also of the molecular particles that are formed as a result of their homolytic decomposition. Such relationships have a definite physical meaning in the case of homolytic monomolecular decomposition reactions, where the activation energy can serve as an estimate of the value of the enthalpy of reaction  $\Delta H_r$ .\* On the other hand, the value of the enthalpy of reaction is an estimate of the activation energy. In the present paper, two similar relationships are used to calculate the  $E_{\alpha}$  for rupture of the C-NO<sub>2</sub> bond.

Previously, it was established that the thermal rupture of the C-NO<sub>2</sub> bond in R-NO<sub>2</sub> compounds is an endothermic reaction, which proceeds with the formation of two radicals R<sup>•</sup> and NO<sub>2</sub><sup>•</sup> [2-6]. The following inequality can be written for the activation energy value of this process:

\*Starting with the principle of microscopic reversibility, the direct elementary reaction proceeds by the same path as the reverse reaction. Consequently, a reaction representing the recombination of two radicals should proceed with a small activation energy [1].

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1420-1421, June, 1983. Original article submitted November 15, 1982.