REACTION OF 2,4,6-TRI-TERT-BUTYLPHENOXYL WITH OXYGEN IN THE

PRESENCE OF METAL COMPOUNDS

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The reaction of 2,4,6-tri-tert-butylphenoxyl (I) with oxygen leads to the formation of the peroxide which was initially characterized as the p-diquinolide p,p-II [1]. In our subsequent work [2], we showed that the product formed is a mixture of p,p-II and the isomer with o,p-fusion of the quinolide fragments o,p-II



Here and subsequently, $R = Me_3C$. According to our previous work [2], the p,p-(II)/o,p-(II) ratio is 3. Phenoxyl (I) is usually obtained by the oxidation of 2,4,6-tri-tert-butylphenol (II) by compounds of metals with variable valence such as PbO₂, Ag₂O, MnO₂, K₃[Fe(CN)₆], and Mn(OAc)₃. We have shown that some of these compounds may be used not only as stoichiometric oxidizing agents but as coordination catalysts (in reduced form) of the subsequent reaction of (I) with oxygen. The ratio of the isomeric peroxides formed depends on the nature of the metal and the medium. Quantitative analysis of the isomeric composition of the peroxides was carried out by the thin-layer chromatographic separation of p,p-(II) and o,p-(II).

However, the separation of the isomeric quinones, 3,5-di-tert-butyl-o-benzoquinone (IV) and 2,6-di-tert-butyl-p-benzoquinone (V) formed upon treating the peroxide mixture consecutively by CF_3CO_2H and Ag_2O in CH_2CI_2 was found to be more convenient



The results obtained are given in Table 1.

The homogeneous system of (III) + $Mn(OAc)_3$ which shows the greatest change in regioselectivity of the attack of phenoxyl (I) by oxygen was studied in greatest detail. A special experiment showed identical results for the reaction of (III) + $Mn(OAc)_3$ when (I) and $Mn(OAc)_2$ are generated during the course of the reaction and the reaction of (I) + O_2 in the presence of $Mn(OAc)_2$ with the independent preparation of phenoxyl (I) by the action of another oxidizing agent, $K_3[Fe(CN)_6]$.

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Oxidant/Reduced form	Solvent (phase state of the sys tem)	Total yield of p,p-(II) and o,p-(II), %	$\frac{p,p-(\mathrm{II})}{o,p-(\mathrm{II})}$	(V) (IV)
Ag_2O/Ag	Benzene (hetero- geneous)	98	2,75	6,5
Same	Methanol (hetero- geneous)	97	1,75	4,5 ·
PbO ₂ /PbO	Benzene (hetero- geneous)	97	3,0	7,0
Same	Methanol (hetero- geneous)	95	1,5	4,0
$Mn (OAc) _3/Mn (OAc) _2$	AcOH (homo-	86 -	1,25	3,5
Same	Methanol (homo- geneous)	92	1,1	3,2

TABLE 1. Reaction of 2,4,6-Tri-tert-butylphenoxyl with Oxygen

The latter variant was selected for the kinetic study of the step involving the reaction of (I) with O_2 . Phenoxyl (I) was obtained according to Muller and Ley [3] which provides for 98% purity of the product. The kinetic parameters were found for the reactions of (I) + O_2 in pure methanol and in the presence of an equimolar amount of Mn(OAc)₂.

The process was carried out such that it was pseudomonomolecular relative to (I) with a large excess of dissolved oxygen $[O_2] = 10^{-3}$ mole/liter [4]. At 20°C and 2·10⁻⁴ mole/liter initial phenoxyl concentration, the addition of an equimolar amount of Mn(OAc)₂ accelerates the reaction of (I) with oxygen by a factor of about 2 (the rate constants are 3.3·10⁻³ and 5.7·10⁻³ sec⁻¹, respectively). The change in the concentration of (I) was followed spectrophotometrically relative to the decrease in optical density at 402 nm.

The rate constants imply that the addition of $Mn(OAc)_2$ leads to a marked acceleration of the reaction. These results, in conjunction with the data for the change in the isomeric composition of the peroxides formed in the presence of $Mn(OAc)_2$, indicate a coordination catalytic mechanism involving the simultaneous coordination of (I) and oxygen at the metal.

The possibility of changing the regioselectivity of the attack of (I) by oxygen by the action of low-valence metal compounds has practical importance since it opens a new approach for going from phenol (III) to pyrocatechol derivatives.

EXPERIMENTAL

Oxidation of 2,4,6-tri-tert-butylphenol (III). A sample of 10 mmoles (III) was dissolved in 50 ml benzene, methanol or acetic acid and 20 mmoles PbO_3 or AgO_2 or 10 mmoles $Mn(OAc)_3$ was added. The mixture was stirred at 20°C in an open vessel. The solution was evaporated in vacuum and the mixture of peroxides was extracted from the residue with hexane. Isomers p,p-(II) and o,p-(II) were separated by thin-layer chromatography on Silufol UV-254 plates with 38:12:5 hexane-benzene-chloroform as the eluent, R_f p,p-(II) 0.7, R_f o,p-(II) 0.6, mp 130.5-131.0°C and 129-129.5°C, respectively [2].

<u>Decomposition of the Peroxides by the Action of CF_3CO_2H .</u> A sample of o,p-(II) was added to a solution of 0.2 ml CF_3CO_2H in 10 ml CH_2Cl_2 and maintained for 0.5 h at 20°C, washed with water, and 2 mmoles Ag₂O was added. The mixture was stirred for 0.5 h, partially evaporated in vacuum and separated on Silufol UV-254 with 5:1 hexane)—ether as the eluent to yield 1 mmole quinone (IV), R_f 0.3, mp 113-114°C [5] and 1 mmole quinone (V), R_f 0.6, mp 67-68°C [6].

The decomposition and analysis of mixtures of p,p-(II) and o,p-(II) were performed analogously. The results were treated by the equation: p,p-(II)/o,p-(II) = [(V)/(IV) - 1]/2 (peroxide p,p-(II) forms only quinone (V)).

<u>Reaction of 2,4,6-tri-tert-butylphenoxyl (I) with O_2 .</u> A sample of 2 mmoles $Mn(OAc)_2$ was dissolved in 20 ml methanol and then 2 mmoles (I) obtained according to Muller [3] was introduced. The mixture was left in the air until decolorized. The peroxide mixture obtained was analyzed as indicated above. The p,p-(II)/o,p-(II) ratio was found to be 1.1. The kinetic measurements were carried out on a Specord UV-VIS spectrophotometer in 3-ml quartz cells with 1 cm pathlength.

CONCLUSIONS

A dependence was found for the isomer composition of the quinolide peroxides formed upon the oxidation of 2,4,6-tri-tert-butylphenol on the coordination capacity of the metal compounds used for the oxidation and the medium. Kinetic measurements showed that the reaction of 2,4,6-tri-tert-butylphenoxyl with oxygen is accelerated in the presence of manganese diacetate.

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CATALYTIC ACTIVITY OF DIASTEREOMERS OF DICYCLOHEXANO-18-CROWN-6

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The diastereomers of dicyclohexano-18-crown-6 (DCH-18-C-6) have been found to differ in their capacity to complex with alkali metal cations [1].

In the present work, we have found that DCH-18-C-6 diastereomers display different activity upon their use as phase transfer catalysts (PTC) for the reaction of benzyl chloride with potassium acetate. The characteristics of the DCH-18-C-6 diastereomers used are given in Table 1.

Diastereomer A was found to have the greatest activity, which exceeds that of 18-crown-6 (18-C-6). Diastereomer B is less active than 18-C-6. Diastereomer C is comparable in activity to dibenzo-18-crown-6 (DB-18-C-6). The experimental results are given in Table 2.

The use of isomeric mixtures of DCH-18-C-6 obtained by the hydrogenation of DB-18-C-6 in the presence of palladium and nickel catalysts as PTC leads to different results. This finding is apparently related to the different isomer composition of the mixtures.

The partition coefficients for K⁺ cations between aqueous and organic phases were determined according to Laskorin et al. [3] in order to evaluate the extraction capacity of the DCH-18-C-6 diastereomers. The extraction capacity of the DCH-18-C-6 diastereomers was found to decrease in the series A > B > C.

EXPERIMENTAL

The ¹³C NMR spectra were taken on a Bruker WP-200 spectrometer at 50.323 MHz in CDCl₃. The gas-liquid chromatographic analysis was carried out on a Tsvet-104 chromatograph using a 3 m × 3 mm column packed with 15% SKTFT-50Kh on Chromatone N-AW-DMCS and nitrogen as the gas carrier. Acetonitrile was dried by distillation over P_2O_5 . The electromotive force of the circuit was measured using a Radelkis OP-208 precision pH-meter.

<u>Reaction of Benzyl Chloride with Potassium Acetate.</u> A sample of 14.7 g (0.15 mole) potassium acetate and 1.5 mmole crown ether were added consecutively to a solution of 12.6 g (0.1 mole) benzyl chloride in 50 ml acetonitrile. The mixture was stirred for 0.5 h at 60°C and then cooled. A sample of 500 ml water was added and the organic layer was separated. The aqueous layer was extracted with three 50-ml portions of chloroform. The organic layer and

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