OXIDATIVE TRANSFORMATIONS OF $4-(\omega-HYDROXYALKYL)-2, 6-DI-TERT-BUTYLPHENOLS$

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The hydroxylation and alkoxylation of sterically hindered para-alkylphenols is accomplished through the corresponding methylenequinones [1]. The participation of the aliphatic hydroxy group is possible when $4-\omega$ -hydroxyalkyl-2,6-di-tert-butylphenols (I) are used in these transformations. Such transformations may be either intra- or intermolecular depending on the position of the hydroxy group in the aliphatic chain in (I).

The oxidative transformations of sterically hindered phenols to methylenequinones have been studied for a large number of examples, including $4-\beta$ -hydroxyethyl-2,6-di-tert-butylphenol (Ia) [2]. Examples of the acid hydration of $4-\gamma$ -hydroxyalkyl-2,6-dialkylmethylenequinones to the corresponding benzyl alcohol derivatives have been reported [3]. This course for the consecutive oxidative and hydrational transformations was reproduced in our laboratory for $4-\beta$ -hydroxyethyl- (Ia) and $4-\gamma$ -hydroxypropyl-2,6-di-tert-butylphenols (Ib).



The following 4-dihydroxyalkyl-2,6-di-tert-butylphenols (IIIa) and (IIIb) were obtained. We should note that an analytically pure sample of methylenequinone (IIa) converted upon storage for six months into a mixture of $(C_{16}H_{24}O_2)_n$ oligomers with mean molecular mass two or three times greater than the initial value. The formation of oligomers apparently indicates the participation of the aliphatic hydroxy group in the molecular condensation of methylenequinone (IIa).

Different behavior was noted in the transformations of $4-(\delta-hydroxybutyl)-2,6-di-tert$ butylphenol (Ic). The oxidation of this phenol by potassium hexacyanoferrate in the presence of alkali in a benzene-water medium gave a reaction mixture, which yielded two productsupon chromatography on silica gel: tetrahydrofuran derivative (IV) and hydroxyketone (V).The structure of tetrahydrofuran (IV) was indicated by spectral analysis and its furthertransformations.



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This scheme indicates that ketone (V) is the product of the further oxidation of tetrahydrofuran (IV). Indeed, methylenequinone (VII) was obtained upon the oxidation of (IV) by potassium hexacyanoferrate in alkaline medium. Methylenequinone (VII) is stable in benzene and tetrahydrofuran solution and as a solid.

The hydration of methylenequinone (VII) to give hydroxyketone (V) occurs on alumina. This transformation is similar to the reaction giving ketophenols from α -methoxymethylenequinones [4] with the difference that the fate of the leaving group may be followed in this case. This makes ketone (VII) an interesting model for studying ring-chain transformations of hydroxycarbonyl compounds [5].

These results may be used to elucidate the reason for the formation of the derivative of perhydrofuro[3,4]furan obtained by Sarkanen and Wallis [6] by the formation and subsequent cyclization of the intermediate methylenequinone.

EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrometer. The UV spectra were taken on a Specord UV-VIS spectrometer. The PMR spectra were taken on an A 56/60A (60 MHz) spectrometer using the δ scale with HMDS as the internal standard.

The starting 4- ω -hydroxyalky1-2,6-di-tert-butylphenols were products of pilot plant production at the Novosibirsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR: (Ia), mp 99-101°C; (Ib), mp 67-68°C; (Ic), mp 28-29°C.

<u>Oxidation of 4- ω -Hydroxyalkyl-2,6-di-tert-butylphenols (general procedure)</u>. A solution of 15 g (0.045 mole) potassium hexacyanoferrate and 2.6 g (0.047 mole) KOH in 50 ml water was added to a solution of 0.018 mole 4- ω -hydroxyalkyl-2,6-di-tert-butylphenol (I) in 70 ml benzene. The mixture was heated for 2.5 h at 50-55°C with rapid stirring. The organic layer was separated, washed with water, and evaporated. Then, 2 ml hexane was added to the residue and cooled to -10°C. The precipitate of methylenequinone was filtered off.

 $\frac{\alpha-\text{Hydroxymethyl-2,6-di-tert-butylmethylenequinone (IIa)}{100-101^{\circ}\text{C} (\text{from hexane}) [2]}.$ Upon standing for six months, (IIa) gave a mixture of five oligomeric products as indicated by thin-layer chromatography. The mean molecular mass was 644. β -Hydroxyethyl-2,6-di-tert-butylmethylenequinone (IIb) was obtained in 60% yield, mp 73-74°C (from hexane).

Reaction of Methylenequinones (II) with Water. A sample of 0.024 mole methylenequinone (II) was dissolved in 40 ml 60% aqueous acetone and 5 ml 10% sulfuric acid was added. The reaction mass was heated at reflux for 30 min, cooled, neutralized by the addition of aqueous sodium bicarbonate, and extracted with ether. The extract was washed with water, dried over anhydrous MgSO₄, and evaporated. A sample of 1 ml hexane was added to the residue and cooled to -10° C. The precipitate formed was washed with hexane and dried.

<u>1-(3,5-Di-tert-butyl-4-hydroxyphenyl)-1,2-ethanediol (IIIa)</u> was obtained in 63% yield, mp 119-120°C (from hexane). (3,5-Di-tert-butyl-4-hydroxyphenyl)-1,3-propanediol (IIIb) was obtained in 35% yield, mp 121-122°C (from hexane).

2-(3,5-Di-tert-butyl-4-hydroxyphenyl)tetrahydrofuran (IV). The oxidation of 5.02 g 4-(3,5-di-tert-butyl-4-hydroxyphenyl)butanol (Ic) according to the general procedure gave 3.42 g yellow crystals containing 87% tetrahydrofuran (IV) and 12% hydroxyketone (V) as indicated by gas-liquid chromatography. This mixture was placed onto a column packed with 30 g silica gel and eluted with 1:2 ether-hexane, 1:1 ether-hexane, ether, and 1:1 etheracetone. Evaporation of the first two fractions gave 2.7 g (51%) (IV) as colorless crystals, mp 124-125°C. Evaporation of the latter two fractions gave 0.5 g (9%) 1-(3,5-di-tert-butyl-4-hydroxyphenyl)-4-hydroxy-1-butanone (V) as colorless crystals, mp 74-75°C (from hexane).

2,6-Di-tert-butyl-4-(2-tetrahydrofurylidene)-2,5-cyclohexadienone (VII). A sample of 6 g (0.00181 mole) potassium hexacyanoferrate and 1.1 g (0.0187 mole) KOH in 60 ml water was

	с	H	formula	ik spectrum ; v см−1 (CCl₄)	$\substack{\substack{\lambda_{\max}, nm \\ (\log \varepsilon)}}$	MMK spectrum, ^α δ, ppm (J, Hz)
73–74	77,45 77,81	<u>10,03</u> 9,99	C ₁₇ H ₂₆ O ₂	3470-3550, 1640, 1630, 1580, 1570	228 (3,73) 304 (4,38)	1,18 s $(2C_1H_9)$, 2,18 s (OH) , 2,63 q $(CH_2, J=7)$, 3,68 t $(CH_2O, J=7)$, 6,24 t $(-CH=, J=7)$, 6,73 d $(1H, J=, 2,5)$, 7,16 d $(1H, J=, 2,5)$
127–129	78,70 78,79	9,53 9,55	C ₁₈ H ₂₆ O ₂	1635, 1570	227 (3,61) 315 (4,39)	1,18 s $(2C_4H_9)$, 2,19 m (2H), 3,06 t $(CH_2C=, J=7)$, 4,39 t $(CH_2O-, J=7)$, 7,06 d (1H, J=2,5), 7,48 d (1H, J=2,5)
119-120	72,01 72,18	<u>9.43</u> 9,77	C16H28O3	3635, 3600, 3370–3470	228 (3,78) 277 (3,13)	1,29 s $(2C_4H_9)$, 2,64 s (2OH), 3,53 d $(CH_2OH, J=7)$, 4,53 t $(CH0H, J=7)$, 4,96 s (OH) , 6,86 s $(2H)$
121-122	72,41 72,82	9,79 10,06	C17H28O3	3650, 3610, 3350—3550	228 (3.69) 275 (3,09)	1.36 s $(2C_4H_9)$, 1.8– 2.0m $(2CH_2)$, 2.56 s $(2OH)$, 3.79 t (CH_2O) , J=6), 4.79 t (CHO) , J=7), 5.11 s (OH) , 7.11 s $(1H)$
124-125	78,78 78,26	<u>9.87</u> 10,14	C18H28O2	3642, 1075	228 (3,92) 278 (3,39)	1,31 s $(2C_4H_9)$, 1,8- 2,0 m(CH ₂), 2,56 s (2OH), 3,79 t (CH ₂ O, J=6), 4,56 t (CHO, J=7), 4,91 s (OH), 6,93 s(1H)
74–75	73,96 73,93	9.63 6,65	C18H28O3	3630, 3440 -3 540, 1680	227 (4,19) 283 (4,17)	$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$
	73-74 127-129 119-120 121-122 124-125 74-75 -(V) in	$\begin{array}{c ccccc} 73-74 & \hline 77,45 \\ \hline 77,81 \\ \hline 127-129 & \hline 78,70 \\ \hline 78,79 \\ \hline 119-120 & \hline 72,01 \\ \hline 72,18 \\ \hline 121-122 & \hline 72,41 \\ \hline 72,82 \\ \hline 124-125 & \hline 78,78 \\ \hline 78,26 \\ \hline 74-75 & \hline 73,96 \\ \hline 73,93 \\ \hline \hline -(V) & \text{in CCl}_{4} \end{array}$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

TABLE 1. Indices of the Compounds Synthesized

added to a solution of 2 g (0.0072 mole) (IV) in 50 ml benzene. The mixture was heated for 4 h at 55-65°C with rapid stirring. The benzene layer was separated, washed with water, dried over anhydrous $CaCl_2$, and evaporated. The crystalline precipitate was washed with benzene to give 1.5 g (76%) (VII) as lemon yellow crystals, mp 127-129°C. Product (VII) was placed on an alumina column and eluted with ether-acetone. Evaporation of the solvents gave (V).

The physicochemical indices of the compounds obtained are given in Table 1.

CONCLUSIONS

Methylenequinones obtained by the oxidation of $4-\omega$ -hydroxyalkyl-2,6-di-tert-butylphenols undergo inter- and intramolecular transformations to give oligomers or tetrahydrofuran and hydroxyketone derivatives depending on the position of the hydroxyl group in the aliphatic chain of the para substituent.

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REACTION OF DICYCLOHEXYLBORANE WITH DIMETHYLAMINOMETHYLENE-PHENYLPHOSPHINE

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In previous work [1], we showed that the reaction of dimethylaminomethylenephenylphosphine with catecholborane gives an addition product, in which the phosphorus atom is bound to the boron atom ($\delta^{31}P = -20$ ppm). Upon heating in vacuum, this product decomposes into methylenephenylphosphine and dimethylaminocatecholborane. Methylenephenylphosphine is unstable and polymerizes.

In the present work, we carried out the reaction of dimethylaminomethylenephenylphosphine with one or two moles of dicyclohexylborane in order to study the possibility of capturing unstable methylenephenylphosphine by excess dialkylborane.

The reaction of dimethylaminomethylenephenylphosphine with one mole of dicyclohexylborane proceeded under mild conditions to give an addition product with a P-B bond, namely, dimethylaminomethyl(dicyclohexylboryl)phenylphosphine, which undergoes β -elimination at room temperature and was detected only spectrally. The ³¹P NMR spectrum of this product has a signal at -24 ppm. When the proton decoupling is removed, no splitting is found for this signal. The electron impact mass spectrum has peaks for decomposition products with m/z 122 [PhP=CH₂] and 221 [(C₆H₁₁)₂BNMe₂]. Such rapid β -elimination is in accord with the affinity of amino groups to the dialkylboryl site [2]. Vacuum distillation gave dicyclohexyldimethylaminoborane, whose electron impact mass spectrum has a molecular ion peak with m/z 221 [(C₆H₁₁)₂BNMe₂⁺] and peaks for fragment ions: C₆H₁₁BNMe₂⁺, HBNMe₂⁺, C₆H₁₁⁺, and C₆H₁₀⁺.

The reaction of dimethylaminomethylenephenylphosphine with two moles of dicyclohexylborane leads to dicyclohexylborylmethyl(phenyl)phosphine, which exists as a dimer as indicated by ebullioscopy in benzene (the molecular weight found was 630, while the calculated value is 600).

 $\begin{array}{c} \mathrm{Ph-P=CHNMe_{2}+(C_{6}H_{11})_{2}BH} \rightarrow [\mathrm{Ph-P=CH_{2}}] + (C_{6}H_{11})_{2}BNMe_{2} \rightarrow \\ \\ \xrightarrow{(C_{6}H_{11})_{2}BH} \\ & \stackrel{|}{\underset{H}{\overset{|}}} \end{array} \begin{array}{c} \mathrm{Ph-PCH_{2}B(C_{6}H_{11})_{2}} \\ & \stackrel{|}{\underset{H}{\overset{|}}} \end{array} \end{array} \begin{array}{c} \mathrm{Ph-PCH_{2}B(C_{6}H_{11})_{2}} \\ & \stackrel{|}{\underset{H}{\overset{|}}} \end{array} \begin{array}{c} \mathrm{Ph-PCH_{2}B(C_{6}H_{11})_{2}} \\ & \stackrel{|}{\underset{H}{\overset{|}}} \end{array} \end{array} \end{array}$

The ³¹P NMR spectrum of (I) shows one signal with chemical shift 17.49 ppm and ¹J_{PH} 469 Hz, which indicates a phosphorus—hydrogen bond and phosphonium character of the phosphorus atom. The dimerization of compounds with the P(III)—C—B(III) fragment was shown by Rathke and Schaeffer [3]. Product (I) dissociates in the gas phase. The electron impact mass spectrum of (I) has a molecular ion peak, PhP(H)CH₂B(C₆H₁₁)₂⁺ with m/z 300 and fragmentation peaks: PhP(H)CH₂BC₆H₁₁⁺, PhP(H)CH₂BH⁺, PhP(H)CH₂⁺, and PhPH⁺.

Thus, the addition of dicyclohexylborane to dimethylaminomethylenephenylphosphine and methylenephenylphosphine proceeds regiospecifically under mild conditions.

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