react in part with KBH₄ to form $K_2B_{12}H_{12}$. It is known that at 120° 9-pentaborane reacts with NaBH₄ to form Na₂B₁₂H₁₂ [6]. Probably when I decomposes without releasing gaseous products [1, 2], the evolved 9-pentaborane also reacts with hydridoborate to form a mixture of $B_{12}H_{12}^{2-}$ and $B_{10}H_{10}^{2-}$ salts. Evidently the pyrolysis equations of [1]:

$$5 \text{KB}_3 \text{H}_8 \xrightarrow{185^\circ} 3 \text{KBH}_4 + \text{K}_2 \text{B}_{12} \text{H}_{12} + 8 \text{H}_2$$
$$4 \text{KB}_3 \text{H}_8 \xrightarrow{185^\circ} 2 \text{KBH}_4 + \text{K}_2 \text{B}_{10} \text{H}_{10} + 7 \text{H}_2$$

include the intermediate stages of 9-pentaborane formation and the subsequent formation of polyhedral anions by the reaction of 9-pentaborane with KBH_{4} .

CONCLUSIONS

The thermal decomposition of KB_3H_8 in vacuum at 150° forms 9-pentaborane and potassium hydridoborate, followed by partial reaction between the latter to form $K_2B_{12}H_{12}$.

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ORTHO-ESTERS BASED ON 3,6-DI-TERT-BUTYLPYROCATECHOL

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The H atoms of the methylene unit of 3,6-di-tert-butylpyrocatechol methylene ether (I), which can be obtained from 3,6-di-tert-butylpyrocatechol (II) by synthesis in a two-phase catalytic system [1], have high hydride mobility, so that (I) can be used in the synthesis of various ortho-esters of sterically hindered pyrocatechol, for example, by hydride cleavage in reactions with triphenylmethane derivatives.



Ether (III) formed in these reactions was converted, without isolation, by alcoholysis with aliphatic alcohols (CH₃OH, C_2H_5OH) into mixed orthoformates (IVa, b), by treatment with 20% aqueous NaOH into orthoformate (V), and by the action of 3,6-di-tert-butylpyrocatechol (II) into orthoformate (VI)

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 $\mathrm{R'}=\mathrm{CH}_3$ (a), $\mathrm{C}_2\mathrm{H}_5$ (b).

Compound (VI) has also been directly synthesized by reaction of (II) with chloroform in the $CHCl_3-50\%$ aqueous NaOH two-phase system, using $(C_4H_9)_4NBr$ as an interphase transfer catalyst. Orthocarbonate (VII) could not be obtained under similar conditions using CCl_4 or benzene as the organic phase. Increase in the contact time of the reagents (up to 10 days) leads to noticeable oxidation of (II) into a related quinone (VIII) and



to the appearance of product (IX) as the result of the reaction of (VIII) with the dianion of the initial (II). Orthocarbonate (VII) could be obtained in the presence of CuCl as a cocatalyst under the conditions of interphase catalysis



It is natural to assume that transformations with the participation of $CHCl_3$ and CCl_4 leading to orthoesters differ in their mechanisms. With CCl_4 , a nucleophilic substitution activated by the copper catalyst takes place. In the case of $CHCl_3$, probably a carbenium mechanism takes place, whose key stages are the formation of dichloromethylene and its introduction at the O-H bond of the hydroxyl group of (II).



The formation of the $:CCl_2$ group in the reaction system was confirmed by the isolation of its adducts with quinone (VIII) with a 1:1 (X) and 1:2 (XI) composition



EXPERIMENTAL

Reaction of 3,6-Di-tert-butylpyrocatechol Methylene Ether (I) with Triphenylmethane Derivatives. Triphenylmethyl perchlorate Ph₃CClO₄ was added to a solution of 1 mmole of (I) in 10 ml of CH₂Cl₂. The reaction mixture was held until complete decoloration. The disappearance of initial (I) and the formation of Ph₃CH was established by the TLC method on Silufol UV-254 in various systems of solvents (identified by comparison with a standard sample, and isolated preparatively by chromatography in hexane, yield 87%, mp 93-94°C). The reactions of (I) with Ph₃CCl · MCl₂ (M = Zn, Hg) were carried out in a similar way. The reaction mixture was further treated with a) excess of alcohol (CH₃OH, C₂H₅OH), b) 20% aqueous NaOH, c) a solution of pyrocatechol (II) in CH₂Cl₂. The following compounds were isolated by preparative TLC in the hexane-ether (8:1) system: a) esters (IVa) and (IVb); (IVa): Rf 0.6 colorless oily liquid. Found: C 72.70; H 9.02%. C₁₆H₂₄O₃. Calculated: C 72.72; H 9.09%. UV spectrum: λ_{max} 285 nm. (IVb): Rf 0.6, mp 52-53°C (from acetone). Found: C 73.46; H 9.38%. C₁₇H₂₆O₃. Calculated: C 73.38; H 9.35%. UV spectrum: λ_{max} 285 nm; b) orthoformate (V): Rf 0.75, mp 156-158°C (from acetone). Found: C 75.00; H 8.71%. C₃₀H₄₂O₅. Calculated: C 74.69; H 8.70. PMR spectrum (δ , ppm): 1.11 s (18H), 5.33 s (2H), 3.60 s (1H); c) orthoformate (VI): Rf 0.7, mp 228°C (from acetone). Found: C 76.48; H 9.26%. Ester (VI) was oxidized by Ag₂O in benzene into the corresponding phenoxyl radical.

<u>Reaction of 3,6-Di-tert-butylpyrocatechol (II) with Chloroform.</u> A 2-mmole portion of Bu_4NBr and 1 ml of 50% aqueous NaOH were added to a solution of 1 mmole of (II) in 10 ml of $CHCl_3$, and the mixture was stirred for 7 days at ~20°C. The organic phase was separated, washed with water to a neutral reaction, and partially evaporated. The ortho-ester (VI) was isolated by preparative TLC on Silufol UV-254 in the hexane-ether (6:1) system, $R_f 0.9$, mp 222-223°C, yield 10%; no depression of a mixed melting point with a sample obtained by the preceding method was observed.

<u>Reaction of 3,6-Di-tert-butylpyrocatechol with Carbon Tetrachloride.</u> A $2 \cdot 10^{-3}$ -mole portion of Bu₄NBr and 1 ml of 50% aqueous NaOH solution were added to a solution of 1 mmole of (II) in 10 ml of CCl₄. The reaction was carried out in the presence of CuCl catalyst at ~20°C for seven days, with vigorous stirring. The organic phase was separated, washed with water, CCl₄ was partially evaporated, and the residue was chromatographed on Silufol UV-254 in the hexane-water (6:1) system. The layer with Rf 0.9 was eluted by hexane. The yield of ortho-ester (VII) was 10%, mp 254-255°C (from hexane). Found: C 77.06; H 8.70%. C₂₉H₄₀O₄. Calculated: C 77.0; H 8.84%. PMR spectrum (δ , ppm): 1.25 s (9H), 5.43 s (1H).

A 2-mmole portion of Bu_4NBr and 1 ml of 50% aqueous NaOH were added to a solution of 1 mmole of (II) in 10 ml of CCl_4 . The reaction was carried out in the absence of a catalyst. By chromatography on Silufol UV-254 in the hexane-ether (6:1) system, a lemon-yellow layer was collected with Rf 0.8, which was eluted by hexane, and hexane was evaporated. The yield of (IX) was 20%, mp 253°C (from acetone). Found: C 76.50; H 9.09%. $C_{14}H_{20}O_2$. Calculated C 76.36; H 9.09%. PMR spectrum (δ , ppm): 1.1 s (9H), 1.2 s (9H), 1.4 s (18H), 7.1 s (1H), 7.35 s (2H), 8.1 s (1H).

Reaction of 3,6-Di-tert-butyl-o-benzoquinone with Chloroform. A solution of 1 mmole of quinone (VIII) and $2 \cdot 10^{-3}$ mole of Bu₄NBr in 10 ml of CHCl₃ was vigorously shaken for 2 min with 1 ml of 50% aqueous NaOH. The gray-brown color of the solution turned lemon-yellow. The organic phase was separated, washed with water, CHCl₃ was partially evaporated, and the residue was chromatographed on Silufol UV-254 in the hexane-ether system. Two layers were collected: a pale yellow one with Rf 0.8 and lemon-yellow one with Rf 0.55. Elution by hexane gave (X) (Rf 0.55) and (XI) (Rf 0.8). Compound (X): yield 30%, mp 130-132°C (from hexane). Found: C 59.63; H 6.52%. C₁₅H₂₀O₂Cl₂. Calculated: C 59.45; H 6.60%. PMR spectrum (δ , ppm): 1.2 s (9H), 1.25 s (9H), 2.77 d (1H, J = 6 Hz), 6.94 d (1H, J = 6 Hz). Compound (XI): yield 60%, mp 149-150°C. Found: C 50.02; H 5.32%. C₁₆H₂₀O₂Cl₄. Calculated: C 49.71; H 5.18%. PMR spectrum (δ , ppm): 1.14 s (9H), 2.60 s (1H).

CONCLUSIONS

1. Methods for the synthesis of ortho-esters based on 3,6-di-tert-butylpyrocatechol have been developed.

2. Concepts on the mechanisms of formation of orthoformate and orthocarbonate in the reaction of 3,6-di-tert-butylpyrocatechol with chloroform and carbon tetrachloride in two-phase catalytic systems have been formulated.

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REACTION OF 3,6-DI-TERT-BUTYLPYROCATECHOL WITH THIONYL CHLORIDE IN THE PRESENCE OF DIMETHYLFORMAMIDE

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We found that the composition of products of the reaction of 3,6-di-tert-butylpyrocatechol (I) with thionyl chloride (TC) in the presence of dimethylformamide (DMFA) in ether depends on the ratio between the reagents. At an equimolar ratio, the main product is 3,6-di-tert-butyl-o-phenylene sulfite (II). 3,6-Di-tert-butyl-



pyrocatechol dimethylaminomethylene ether hydrochloride (III) is formed in parallel in a low yield together with DMFA hydrochloride. The formation of (III) is the result of the formation of Vilsmeier reagent (VR)dichloro-N,N-dimethylaminomethane, followed by its reaction with (I). This was confirmed by the reaction of



(I) with the specially prepared VR, leading to the formation of (III). When (III) is treated with an acetone solution of KOH, the free base (IV) is isolated. An unusual type of transformation proceeds in the reaction of (I) with TC in DMFA at a ratio (I): TC = 2:1. In this case, the formation of not only sulfite (II) is observed, but also of elemental sulfur and 3,6-di-tert-butyl-o-benzoquinone (V). It is possible that sulfur and quinone (V) are



products of the simultaneous fragmentation of the unstable sulfuran (VI), formed by the action of excess of (I) on sulfite (II). This serves as an indirect confirmation of the previously discovered [1,2]tendency of (I), as a bidentate ligand, to substitute a maximal number of coordinational vacancies of the element in compounds of

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