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Dedicated to the light memory of Prof. A.M. Belousov

Reaction of Triphenyl Borate with 1,3,5-Trioxane

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Abstract—Triphenyl borate was prepared by reaction of boric acid with phenol in xylene. Its reaction with 1,3,5-trioxane involved replacement of protons in the *para* positions of the benzene rings by methylene group.

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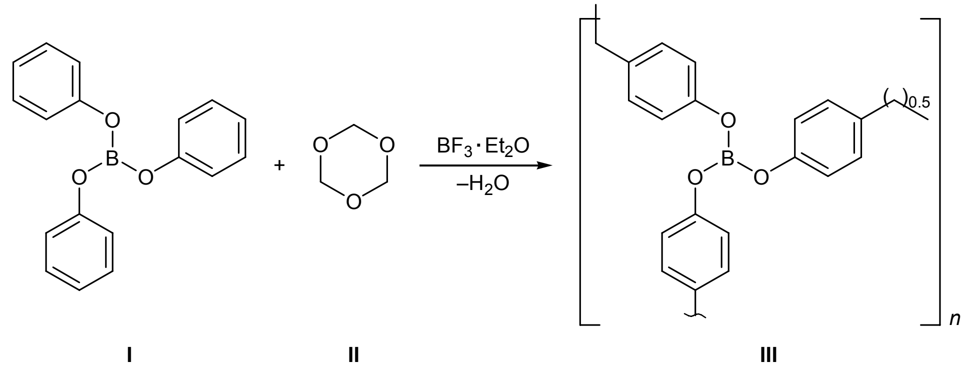
Triphenyl borate (**I**) is used as a weak Lewis acid and complexing agent toward nitrogen-containing compounds. It also attracts interest as model compound for the preparation of poly(methylenetriphenyl borates). Published data on the properties of triphenyl borate (**I**), in particular on its melting point, are strongly different [1–3]. Several procedures for the preparation of triphenyl borate (**I**) have been reported. It can be obtained by esterification of boric acid with excess phenol in methylene chloride, followed by separation of phenol–water mixture by fractional distillation. Compound **I** is also synthesized by exchange reactions of boron trichloride with phenyl acetate at –80°C or of boric acetic anhydride with phenol with subsequent distillation of the resulting mixture at 360°C. We believe that the most convenient procedure is based on the reaction of boric acid with 3 equiv of phenol in *o*-xylene with simultaneous removal of water as azeotrope [3].

The goal of the present work was to synthesize pure triphenyl borate (**I**) and examine its reaction with 1,3,5-trioxane (**II**) as a model process in the preparation of heat-resistant polymeric boric acid methylenephenyl esters. Reactions of phenols with formaldehyde are commonly carried out in a solvent. A classical procedure implies polycondensation of phenols or boric acid phenyl esters with 1,3,5-trioxane or paraformaldehyde in xylene under an inert gas [3–6]. We examined polycondensation of triphenyl borate (**I**) with 1,3,5-trioxane (**II**) using boron trifluoride–ether complex as catalyst and xylene as solvent (Scheme 1).

Triphenyl borate (**I**) becomes liquid above 101°C. We also performed its reaction with trioxane in melt, following a procedure analogous to the synthesis in

Scheme 1.



I **II** **III**

o-xylene as solvent. In this case, smaller amount of the catalyst was necessary. Exothermic reaction started after addition of even 33% of the catalyst. The reaction was carried out with simultaneous removal of water by distillation, so that the reaction mixture became more viscous. Nevertheless, there was no need of changing the experimental setup, for the required amount of 1,3,5-trioxane was added before termination of stirring. The spectral parameters of the products obtained by the two methods were identical.

The IR spectrum of dry product **III** contained absorption bands typical of 1,4-disubstituted benzene ring (δ_{CH} 818 cm^{-1} (cf. [7]). A strong absorption band at 1224 cm^{-1} was assigned to stretching vibrations of the C–O bonds. Stretching vibrations of the B–O bonds gave rise to a strong broadened absorption band at 1348 cm^{-1} [8], while bending vibrations of the C_{sp^3}–H bonds (methylene groups) were characterized by a strong band at 1454 cm^{-1}. Absorption bands at 1503 and 1599 cm^{-1} are typical of stretching vibrations of aromatic C=C bonds, and the strong band at 2918 cm^{-1} belongs to stretching vibrations of aromatic C–H bonds. In addition, a strong diffuse band was observed in the region 3013–3600 cm^{-1} with its maximum at 3365 cm^{-1}; this band arises from intermolecular H-bonds between the polymer molecules [7].

The structure of polymeric product **III** followed from its ^1H NMR spectrum, as well as from the spectrum of its hydrolysis product. The ^1H NMR spectrum of **III** contained doublet signals at δ 6.71 and 6.81 ppm from protons in the *ortho* and *meta* positions of benzene rings, respectively, and a singlet at δ 3.84 ppm from the methylene protons. Compound **III** was subjected to hydrolysis; the hydrolysis product was extracted into benzene, while the aqueous phase contained mainly boric acid. In the ^1H NMR spectrum of the hydrolysis product we observed a singlet at δ 3.98 ppm due to methylene protons and two doublets centered at δ 6.91 and 7.11 ppm from protons in the *ortho* and *meta* positions, respectively. The intensity ratio for the aromatic and methylene protons was 24 : 6. The intensity ratio for the *ortho*- and *meta*-proton signals in the spectrum of **I** was 1 : 1.

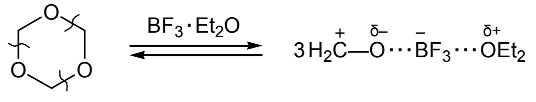
Elemental analysis revealed larger than theoretical percentage of carbon in the polymeric product, which may be due to partial hydrolysis of the boric acid ester moiety with water liberated during the polycondensation process. This is confirmed by separation of some amount of boric acid (1–2 wt %) upon evaporation of an alcoholic solution of the reaction mixture and liberation of phenol while drying the product under reduced pressure. The ^{11}B NMR spectrum of **III** contained a singlet at δ_B 18.45 ppm, which is typical of boric acid esters, as well as a minor singlet at δ_B 0.34 ppm, which belonged to residual boron trifluoride–ether complex.

Thus the IR, ^1H and ^{11}B NMR, and analytical data indicate that the reaction of triphenyl borate (**I**) with 1,3,5-trioxane (**II**) gives a polycondensation product consisting of *p*-methylene-substituted triphenyl borate units.

Our results unambiguously show that the solvent-free procedure is more advantageous, for it does not require removal of solvent and its regeneration. In addition, the amount of the catalyst necessary to initiate the process is approximately three times as small, which is important taking into account its cost and toxicity. The polymeric product obtained under solvent-free conditions had a higher characteristic viscosity by a factor of 1.75; i.e., its molecular weight is greater than that of a sample obtained in *o*-xylene.

From the mechanistic viewpoint, the reaction of triphenyl borate (**I**) with 1,3,5-trioxane (**II**) is analogous to the formation of phenol–formaldehyde resins in the presence of acid catalyst [9]. In the first step, cleavage of the trioxane ring by the action of boron trifluoride–ether complex gives rise to oxymethylene cation which then acts as hydroxymethylating agent (Scheme 2).

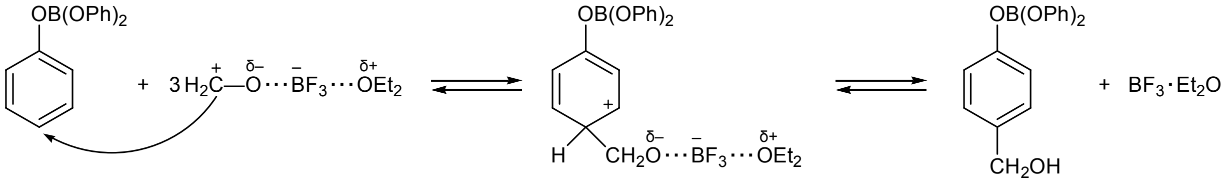
Scheme 2.



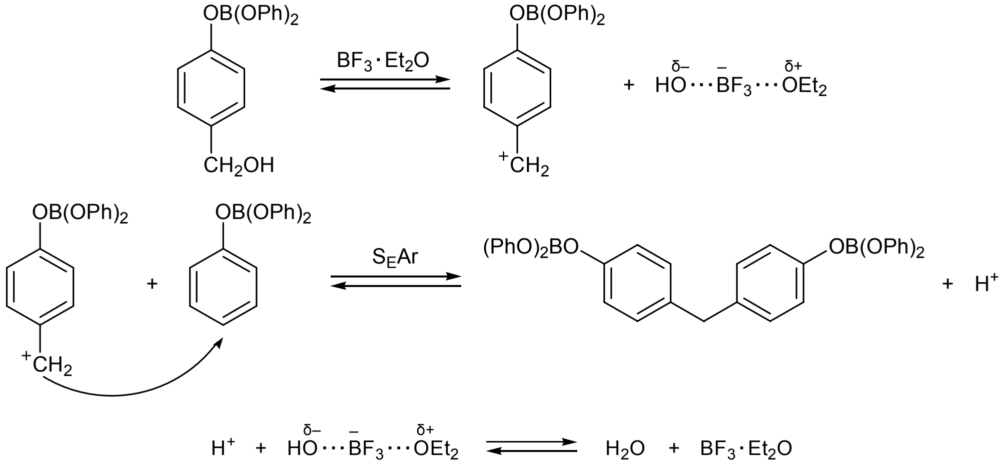
The next step is relatively slow, and its rate determines the overall rate of the process. It involves electrophilic attack by the carbocation at the *para*-position of the benzene ring in triphenyl borate (Scheme 3). Hydroxymethyl group in acid medium readily loses hydroxide ion to give stable electrophilic benzyl cation which rapidly replaces hydrogen atom in the *para* position of benzene ring in another triphenyl borate molecule to produce diphenylmethane derivative as shown in Scheme 4.

According to published data, hydroxymethylation of phenol in alkaline medium gives hydroxymethylphenols as the major products, whereas such compounds cannot be isolated in acid medium. Electrophilic substitution by both hydroxymethyl and methylene groups in acid medium occurs mainly at the *para* position, but the formation of *ortho*- and *ortho,para*-

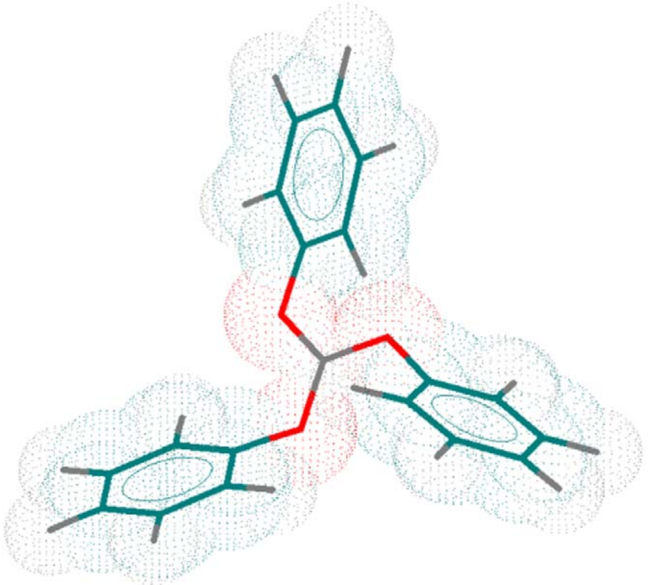
Scheme 3.



Scheme 4.



substituted products cannot be excluded [9]. For example, the reaction of triphenyl borate with paraformaldehyde at 90–130°C was reported [10] to give both *para* and *ortho* isomers, but the *o*/*p* ratio was not given. In the examined reactions, despite the presence of excess 1,3,5-trioxane, only the corresponding *para*-substituted derivatives were formed. Presumably, the reason is steric factor. Figure shows the structure of triphenyl borate molecule according to PM3 semiempirical quantum-chemical calculations performed with the use of HyperChem 7.1 software. It is seen that *ortho* positions in the benzene rings of molecule **I** are sterically shielded by both oxygen atoms and neighboring phenyl groups. Therefore, electrophilic attack occurs exclusively at more accessible *para* positions.



Structure of the molecule of triphenyl borate (**I**) according to PM3 calculations.

EXPERIMENTAL

The NMR spectra were recorded on Bruker AM-400 (400.13 MHz for ^{1}H) and Bruker DRX-500 (500.13 MHz (1H, ^{11}B) spectrometers; the ^{1}H chemical shifts were determined relative to residual proton signals of the solvent ($CDCl_3$, δ 7.24 ppm; CD_3OD, δ 3.34 ppm). The IR spectra were measured in KBr on a Bruker Vector-22 instrument. Elemental analysis was performed on a Carlo Erba 1106 CHN analyzer. The ash content was determined after burning a sample in oxygen. The characteristic viscosities of solutions of the polymers in acetone were determined at 25°C using a VPZh-2 glass capillary viscometer.

Commercially available *o*-xylene of pure grade, distilled phenol of analytical grade, boric acid of pure grade, freshly distilled 1,3,5-trioxane of pure grade, and freshly distilled boron trifluoride–ether complex of pure grade were used.

Triphenyl borate (I). A three-necked flask equipped with a mechanical stirrer, thermometer, Dean–Stark trap, and reflux condenser capped with a drying tube was charged with 11.45 g (0.185 mol) of boric acid, 57.52 g (0.611 mol) of phenol, and 77 ml of *o*-xylene. The mixture was heated to the boiling point (129.5°C) and heated for 3 h under reflux until 9.5 ml of water separated. The solvent and unreacted phenol were distilled off under reduced pressure (1 mm), and the residue was distilled in a vacuum. Yield 49.90 g (92%), bp 230–240°C (1 mm), mp 98–101°C. IR spectrum, ν, cm^{-1}: 2839, 1599, 1450, 1377, 1304, 899, 721. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 7.15 t (3H, *p*-H, *J* = 7.4 Hz), 7.20 d (6H, *o*-H, *J* = 8.4 Hz), 7.37 t (6H, *m*-H, *J* = 8.4, 7.4, 1.6 Hz). ^{11}B NMR spectrum ($CDCl_3$): δ_B 16.39 ppm, s.

Reaction of triphenyl borate (I) with 1,3,5-trioxane (II). *a*. A four-necked flask equipped with a mechanical stirrer, thermometer, Dean–Stark trap, and reflux condenser capped with a drying tube was charged with 49.90 g (0.172 mol) of triphenyl borate (**I**) and 50.0 ml of *o*-xylene. The reaction was carried out in a stream of dry nitrogen. The mixture was thoroughly stirred to obtain a uniform suspension and heated to 80°C, 2.5 g (0.022 mol) of boron trifluoride–ether complex was added, the mixture was stirred for 25 min, and 12.84 g (0.143 mol) of 1,3,5-trioxane (**II**) was added in 0.5–1.0-g portions at such a rate that the temperature of the mixture did not exceed 110°C. When the addition was complete, the mixture was stirred for 1 h at 90°C, the solvent was distilled off under reduced pressure (1 mm), and the residue was dried for 2 h at 90°C. The polymeric product was dissolved in five volumes of ethanol, the solution was filtered, the filtrate was evaporated under reduced pressure (1 mm) until alcohol no longer liberated, and the residue was dried for 1 h at 150°C under reduced pressure (1 mm). Yield of polymer **III** 50.23 g (94%). Characteristic viscosity 0.056 dl/g. IR spectrum, ν, cm^{-1}: 3600–3013, 2918, 1599, 1503, 1454, 1348, 1224, 818. ^1H NMR spectrum (CD_3OD), δ, ppm: 3.84 s (6H, CH_2), 6.71 d.d (12H, *o*-H, *J* = 8.4, 1.7 Hz), 6.81 d.d (12H, *m*-H, *J* = 8.4, 2.8 Hz). ^{11}B NMR spectrum (CD_3OD), δ_B, ppm: 0.34 s ($BF_3 \cdot OEt_2$), 18.45 s (BO_3). Found, %: C 78.00; H 4.95. $[C_{19.5}H_{14}BO_3]_n$. Calculated, %: C 76.00; H 4.92.

b. The reaction of triphenyl borate (**I**) with 1,3,5-trioxane (**II**) was carried out in melt in a stream of dry nitrogen. A flask was charged with 49.90 g (0.172 mol) of compound **I** and heated to 105°C, 0.83 g (0.007 mol) of $BF_3 \cdot Et_2O$ was added, the mixture was stirred for 25 min, and trioxane **II** was added in 0.5–1.0-g portions. The mixture was then treated as described in *a*. Yield of **III** 50.49 g (94%). Characteristic viscosity 0.098 dl/g. ^1H NMR spectrum (CD_3OD), δ, ppm: 3.84 s (6H, CH_2), 6.74 d.d (12H, *o*-H, *J* = 8.2, 1.7 Hz), 6.83 d.d (12H, *m*-H, *J* = 8.2, 2.4 Hz).

Hydrolysis of polymer III. The hydrolysis was performed with water at 100°C (reaction time 24 h). The mixture was extracted with benzene (5 × 100 ml), the extract was evaporated on a rotary evaporator, and the residue was dried for 1 h at 150°C under reduced pressure. ^1H NMR spectrum (CD_3OD), δ, ppm: 3.98 s (6H, CH_2), 6.91 d.d (12H, *o*-H, *J* = 8.4, 1.7 Hz), 7.11 d.d (12H, *m*-H, *J* = 8.4, 2.8 Hz).

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