SYNTHESIS AND POLYMERIZATION OF SOME NEW BIPHENYL DERIVATIVES

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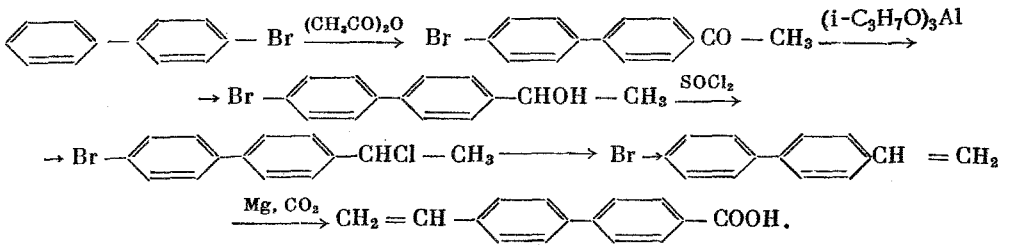
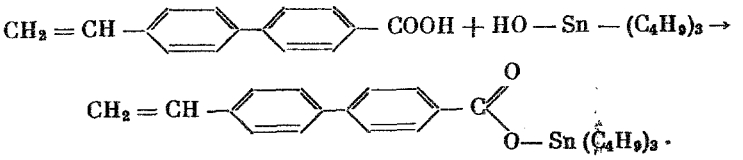
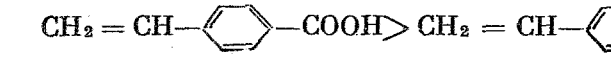
In continuation of work on the synthesis and polymerization of vinyl monomers we have synthesized new polymerizable biphenyl derivatives. We synthesized 4'-vinyl-4-biphenylcarboxylic acid and its organometallic derivative tributyltin 4'-vinyl-4-biphenylcarboxylate. In the course of the synthesis of 4'-vinyl-4-biphenylcarboxylic acid we prepared and characterized 4-bromo-4'-vinylbiphenyl. The synthesis of 4-bromo-4'-vinylbiphenyl and 4'-vinyl-4-biphenylcarboxylic acid was carried out in accordance with the following scheme:



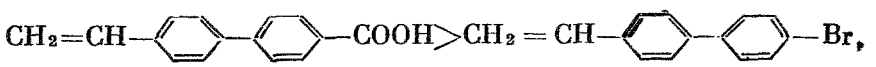
4'-Vinyl-4-biphenylcarboxylic acid was prepared from 4-bromo-4'-vinylbiphenyl by Normant's reaction [1]. Tributyltin 4'-vinyl-4-biphenylcarboxylate was prepared by the reaction of 4'-vinyl-4-biphenylcarboxylic acid with tributyltin hydroxide:



All the monomers obtained can be polymerized. To determine the polymerizability of 4-bromo-4'-vinylbiphenyl we studied the rate of its polymerization by the dilatometric method as a 0.6 M solution in toluene in presence of 0.5 mole percent of azodibutyronitrile at 80°, 90°, and 100° (Fig. 1). The activation energy for the polymerization of 4-bromo-4'-vinylbiphenyl was found from the value of the slope of the straight line plotted in the coordinates of ln $\underline{k}$ and $1/T$; its value was 15 ± 0.5 kcal/mole. A comparison was made between the rate of polymerization of 4'-vinyl-4-biphenylcarboxylic acid and those of p-vinylbenzoic acid and 4-bromo-4'-vinylbiphenyl. Their rates of polymerization were compared in 1 M solutions in N,N-dimethylformamide in presence of 0.2 mole percent of azodiisobutyronitrile (Fig. 3). From Fig. 3 it will be seen that with increase in the number of benzene rings in the molecule of the unsaturated arenecarboxylic acid the rate of polymerization falls considerably:



and with replacement of bromine by carboxyl in the vinylbiphenyl molecule the rate of polymerization increases:



EXPERIMENTAL

For the synthesis of 4'-vinyl-4-biphenylcarboxylic acid we started with 4-bromobiphenyl, which was prepared by the bromination of biphenyl in carbon disulfide [2]. 4-Bromobiphenyl had m.p. 83-85° (from alcohol).

4'-p-Bromophenylacetophenone was prepared by the acetylation of 4-bromobiphenyl (55 g) with acetic anhydride (25 ml) in carbon disulfide (200 ml) in presence of anhydrous aluminum chloride (69 g) at 35° with subsequent heating for three hours. The reaction mixture was decomposed with ice and hydrochloric acid, carbon disulfide was removed, and the 4'-p-bromophenylacetophenone was purified by crystallization from alcohol; m.p. 123-125°; yield 50%. Found: Br 29.49; 29.52%. $C_{14}H_{11}OBr$. Calculated: Br 29.09%.

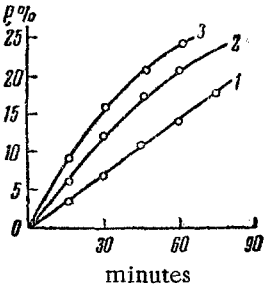


Fig. 1.

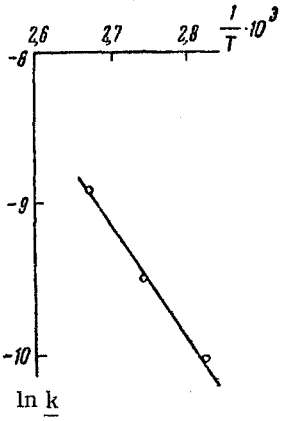


Fig. 2.

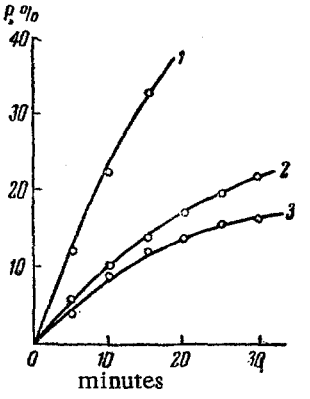


Fig. 3.

Fig. 1. Rate of polymerization of 4-bromo-4'-vinylbiphenyl (0.6 M solution in toluene) in presence of 0.5 mole percent of azodiisobutyronitrile at: 1) 80°; 2) 90°; 3) 100°.
Fig. 2. Relation of ln k to 1/T for 4-bromo-4'-vinylbiphenyl.
Fig. 3. Comparison of rates of polymerization (1 M solution in N,N-dimethylformamide) in presence of 0.2 mole percent of azodiisobutyronitrile: 1) p-vinylbenzoic acid; 2) 4'-vinyl-4-biphenylcarboxylic acid; 3) 4-bromo-4'-vinylbiphenyl.

4'-Bromo-α-methyl-4-biphenylmethanol was prepared by the reduction of 4'-p-bromophenylacetophenone (20 g) with aluminum isopropoxide (prepared from 0.7 g of aluminum) in isopropyl alcohol (55 ml) solution. The reaction mixture was decomposed with ice and hydrochloric acid. The 4'-bromo-α-methyl-4-biphenylmethanol obtained was purified by reprecipitation from benzene solution with petroleum ether and had m.p. 148-150°. For the further reaction use can be made of unreprecipitated 4'-bromo-α-methyl-4-biphenylmethanol, m.p. 145-147°, which is obtained in 95% yield.

4-Bromo-4'-(1-chloroethyl) biphenyl was prepared by reaction of a suspension of 4'-bromo-α-methyl-4-biphenylmethanol (20.0 g) in ether (120 ml) with thionyl chloride (25 ml) with cooling. As reaction proceeded the 4'-bromo-α-methyl-4-biphenylmethanol went into solution. After the removal of excess of thionyl chloride the 4-bromo-4'-(1-chloroethyl) biphenyl was crystallized from petroleum ether and had m.p. 110-112°; yield 95%.

4-Bromo-4'-vinylbiphenyl [3] was prepared by the dehydrochlorination of 4-bromo-4'-(1-chloroethyl) biphenyl by heating it with five times the amount of quinoline at 180-190° for 15 minutes. After the reaction, the reaction mixture was poured into 2 N HCl. The 4-bromo-4'-vinylbiphenyl obtained was purified by crystallization from alcohol or petroleum ether and had m.p. 137-139°. Found: C 65.08, 64.96; H 4.45, 4.14%. $C_{14}H_{11}Br$. Calculated: C 64.86; H 4.25%.

4'-Vinyl-4-biphenylcarboxylic acid. A solution of 5 g of 4-bromo-4'-vinylbiphenyl in 25 ml of tetrahydrofuran was added slowly dropwise to 1.0 g of activated magnesium, and the reaction mixture was then heated with stirring for 15 minutes. Carbon dioxide was passed into the reaction mixture with external cooling; 5% sulfuric acid was then added. 4'-Vinyl-4-biphenylcarboxylic acid had m.p. 228-232° after crystallization from benzene. Found:

C 80.36, 80.37; H 5.78, 5.56%. $C_{15}H_{12}O_2$. Calculated: C 80.36; H 5.35%. 4'-Vinyl-4-biphenylcarboxylic acid forms colorless crystals, readily soluble in N,N-dimethylformamide and dioxane.

Tributyltin 4'-vinyl-4-biphenylcarboxylate was prepared by the previously described method [4] by reaction between equimolecular amounts of 4'-vinyl-4-biphenylcarboxylic acid and tributyltin hydroxide in ethereal solution at room temperature. After the removal of ether tributyltin 4'-vinyl-4-biphenylcarboxylate was obtained as a viscous oil which decomposed when vacuum-distilled. Found: Sn 23.40, 23.28%. $C_{27}H_{38}O_2Sn$. Calculated: Sn 23.19%.

The polymers obtained were prepared by polymerization in toluene (4-bromo-4'-vinylbiphenyl and tributyltin 4'-vinyl-4-biphenylcarboxylate) or N,N-dimethylformamide (4'-vinyl-4-biphenylcarboxylic acid) solution in presence of 0.2% of azodiisobutyronitrile with gradual rise of temperature from 60°. The polymer from 4-bromo-4'-vinylbiphenyl was a high-melting colorless solid, insoluble in organic solvents. Poly-4'-vinyl-4-biphenylcarboxylic acid was a high-melting colorless polymer, soluble in N,N-dimethylformamide. Polytributyltin 4'-vinyl-4-biphenylcarboxylate was a colorless polymer, soluble in toluene; IFP thermostability 165°.

SUMMARY

New polymerizable biphenyl derivatives were prepared for the first time: 4-bromo-4'-vinylbiphenyl, 4'-vinyl-4-biphenylcarboxylic acid, and tributyltin 4'-vinyl-4-biphenylcarboxylate.

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