The Synthesis of Thermally Stable Oils by the Benzylation of Biphenyl with Benzyl Chloride Catalyzed by Iron(III) Oxide

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Synopsis. The benzylation of biphenyl with various amounts of benzyl chloride was performed at 80 °C or at room temperature in the presence of iron(III) oxide prepared by calcining, at 300 °C, iron(III) hydroxide which has been precipitated by hydrolyzing $FeCl_3$ with ammonia. The products with various viscosities were thermally stable up to 200—300 °C, and no chlorine was detected in the products.

Several works concerning the decomposition of PCB by methods using pyrolysis,[1] radiolysis,[2] photolysis[3] and plasma[4] have been reported. On the other hand, some workers have investigated the alkylations of biphenyl in the presence of Friedel-Crafts catalysts in order to use the products as liquid heat stabilizers.[5,6] Biphenyl is also used as a high-boiling heating medium by mixing it with diphenyl ether as a liquid at room temperature.[7] Previously, we reported that the iron(III) oxide thus prepared is an exceedingly effective catalyst for the polycondensation of benzyl chloride, and that the product is poly(*p*-phenylenemethylene) and stable up to 400 °C.[8] In this work, we wish to report that thermally stable oils with various viscosities can be synthesized with ease by the benzylation of biphenyl with benzyl chloride in the presence of the iron(III) oxide catalyst.

Experimental

The iron(III) oxide catalyst was prepared by calcining iron(III) hydroxide in a glass tube in air at 300 °C for 3 h; it was then stored in a glass ampoule until use. The iron(III) hydroxide was precipitated by hydrolyzing $FeCl_3$ with aqueous ammonia. The hydroxide was washed, dried at 100 °C, and finally powdered below 100 mesh. The benzyl chloride (guaranteed reagent of Wako Pure Chemical Co.) and biphenyl (Wako Pure Chemical Co.) were used without further purification.

Benzylation was carried out in bulk following two methods: (A): 10—60 ml of benzyl chloride were stirred, in 2-ml portion, into a mixture of 20 g of biphenyl (mp, 70 °C) and 0.1 g of the catalyst at 80 °C. Each reaction occurred immediately, with a violent evolution of HCl. Benzyl chloride was added at intervals of 10—30 s for the first 20 ml, and afterwards at 1—2 min intervals, without any additional catalyst. (B): 10—50 g of biphenyl were dissolved in 50 ml of benzyl chloride at room temperature, after which the benzylation was performed by stirring with 0.2 g of the catalyst. The reaction started immediately, with an evolution of HCl gas, and was completed within 7—10 min in every reaction. After the reactions by both methods, the reaction mixture was diluted with benzene, separated from the catalyst by filtration, washed with water several times, and dried; finally, the benzene was removed by vacuum evaporation.

Results and Discussion

Table 1 shows the yields and viscosities of the products. Brownish oils with various viscosities were obtained in high yields depending on the amount ratios of benzyl chloride and biphenyl reacted. In the cases of excess amounts of benzyl chloride (Runs 3—6), the products are considered to also contain poly(*p*-phenylenemethylene), judging from the high activity of the catalyst for the polycondensation of benzyl chloride to poly(*p*-phenylenemethylene).[8] Elemental analysis showed no chlorine in any of the products in the table. NMR spectroscopy showed a singlet peak at 3.85 ppm (CH_2) and a multiplet at 6.7—7.5 ppm (phenylene H) in the ratio 1:7 for the samples in Runs 2 and 8.

The TG analyses of the products were done in nitrogen; some of the results are shown in Fig. 1, together with that of biphenyl. The products were thermally stable up to 200—300 °C, above which decomposition occurs, and they decomposed completely at 550 °C. The weight decrease in biphenyl was 100%

TABLE 1. BENZYLATION OF BIPHENYL WITH BENZYL CHLORIDE

Run	Amount of benzyl chloride ml	Amount of biphenyl ml	Reaction temperature °C	Yield g	Viscosity[a] η_{rel}
1	10	20	80	25	2.76
2	20	20	80	34	3.37
3	40	20	80	47	4.74
4	60	20	80	60	5.97
5	50	10	RT[b]	43	8.95
6	50	20	RT	53	5.58
7	50	30	RT	65	3.88
8[c]	50	50	35	82	3.31

a) Relative viscosity of a 50 wt% benzene solution to benzene determined at 25 °C in a Cannon-Fenske viscosity. b) Room temperature. c) Since the biphenyl was not all soluble in benzyl chloride at room temperature, the reaction was carried out at 35 °C.

below 200 °C.

The molecular-weight distribution of the sample in Run 3 was determined by gel-permeation chromatography, as is shown in Fig. 2. The main products have a molecular weight of 220—380; this indicates that the degree of the benzylation of biphenyl is predominantly 1—3.

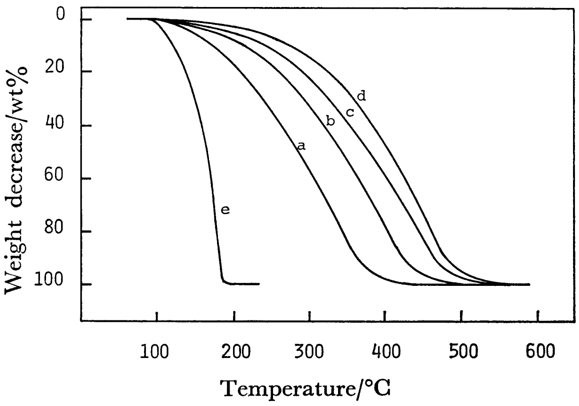

Fig. 1. TG curves of products.
a, b, c, and d refer to the products given by Runs 2, 3, 6, and 4, respectively. e: Biphenyl, heating rate: 5 °C/min.

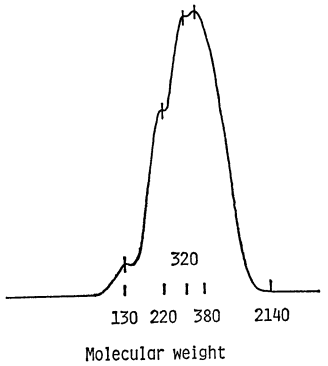

Fig. 2. GPC curve of the sample produced by Run 3. Concentration: 0.4 g in 100 ml of THF, flow rate: 1 ml/min.

The present synthesis was carried out with $AlCl_3$ and $FeCl_3$, typical Lewis acid catalysts, under the same conditions. The reaction was complete when 28 ml of benzyl chloride was added, in 2-ml portions, to a mixture of 20 g of biphenyl and 0.1 g of $AlCl_3$ at 80 °C. However, further reactions did not occur with additional benzyl chloride, in spite of another addition of the catalyst. It is considered that the oily product poisoned the acidic sites of the catalyst surface. Another run was performed at room temperature with 30 g of biphenyl dissolved in 50 ml of benzyl chloride and 0.2 g of $FeCl_3$, but the reaction was extremely slow; 1.38% chlorine was detected in the product after a reaction of 45 min.

The product obtained by the present easy method of synthesis with the conventional and active iron(III) oxide catalyst can replace PCB, whose synthesizing method is to liquidize biphenyl by chlorination. The present method could also be applicable to naphthalene as well as biphenyl, both of which are produced in great quantities in petroleum industries.

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References

1) L. Karlson and E. Rosen, *Chem. Scripta*, **1**, 61 (1971).
2) T. Tawai and Y. Shinozaki, *Chem. Lett.*, **1972**, 865.
3) T. Nishiwaki, J. Ninomiya, S. Yamanaka, and K. Ando, *Nippon Kagaku Kaishi*, **1972**, 2225.
4) K. Hiroaki, K. Mitsumori, and S. Mochizaki, *Chem. Lett.*, **1979**, 739.
5) D. B. Friddy, *I. E. C. Prod. Res. Develop.*, **8**, 239 (1969).
6) K. Ajimoto, Japan Pat. 74104890 (1974).
7) Monsanto Industrial Chemicals, *Chem. Process*, **39**, 118 (1976).
8) M. Hino and K. Arata, *Chem. Lett.*, **1979**, 1141.