# A New Method for the Selective Synthesis of Biphenyl by Dehydrogenative Coupling of Benzene

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**Synopsis.** A method has been developed for the direct preparation of biphenyl by the thermal dehydrogenative coupling of benzene in the vapor phase on the surface of heater at 1000—1200 °C. Biphenyl was obtained at a high selectivity of more than 94% over the wide range of benzene conversion (3—77%).

Biphenyl was first reported by Fittig, and then identified by Berthelot as the main product obtained by passing benzene vapor through a hot tube.[1] Since then many methods have been developed for the preparation of this compound.[2-4] Biphenyl is now important as the starting material for heating oil, high aromatic solvent, electric insulating oil and other synthetic use in industry. The modern commercial production process of biphenyl is the thermal dehydrogenation of benzene in a hot tube. In this method, however, the higher is the conversion of benzene, the lower is the biphenyl selectivity due to additional coupling of biphenyl to terphenyls and quaterphenyls. Therefore, the conversion is to be kept below 15% to obtain biphenyl in high selectivity (88—92%).[5] Biphenyl is also obtained as a by-product of benzene production by hydrodealkylation of toluene.[6] A further purification of biphenyl is necessary in this process. A novel method to prepare pure biphenyl in high selectivity and yield will be described in this paper. The characteristic feature of the present method is the temperature gradient system of the reactor heated by a heater from inside. In such a system, the thermal diffusion effect is significant, and the product of the higher molecular weight was separated at the cold wall of the reactor. The highly selective synthesis of ethylene from methane by the thermal diffusion reactor has recently been reported by one of the authors.[7]

## Experimental

An electric heater was placed inside of a 1 L three-necked separable flask fitted with a reflux condenser. The heater was made of a nickel chromium steel wire of 0.5 mm in diameter and 25 cm in length made in a spiral. The flask containing 50 g of benzene was heated by a heating mantle under nitrogen. After the boiling of benzene was started, the power of the heater inside was turned on, and the vapor of benzene was contacted with the heater. The surface temperature of the heater was monitored by a radiation pyrometer (Minolta IR-120) and controlled. The reaction mixture was sampled periodically and analyzed by a gas chromatograph (Shimadzu GC-9A).

## Results and Discussion

Figure 1 shows the dependence of the benzene conversion on the surface temperature of the heater. The reaction started substantially at 1000 °C. The conversion of benzene increased exponentially with the surface temperature, reaching 77% at 1150 °C. At 1200 °C the color of the benzene vapor near the heater turned brown, suggesting a considerable carbonization. In fact fairly large amount of carbonaceous material deposited on the surface of the nickel chromium steel wire under these conditions. The results are summarized in Table 1 with experimental details. The selectivity of biphenyl remained almost the same 94% over a wide range of benzene conversion. Even at the high conversion of benzene 77.5%, the selectivity of biphenyl was 94.0%. This high selectivity of biphenyl at high conversion of benzene is one of the advantages of this new method over the conventional one, in which benzene vapor is passed through a hot tube heated from outside. In the conventional method, the high selectivity of biphenyl of 90% is obtained only when the one path conversion of benzene is below 15%.

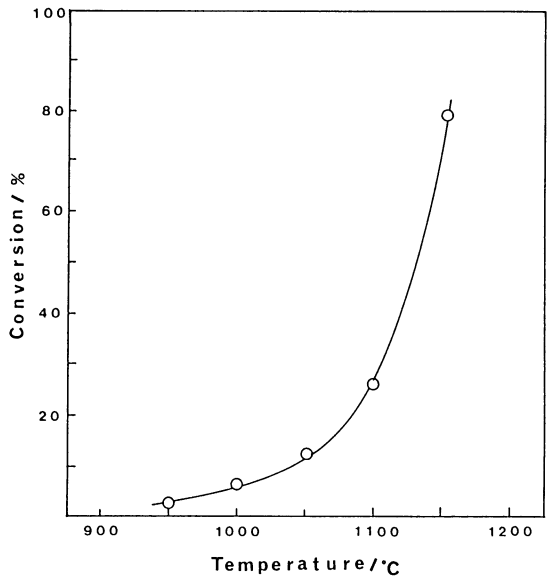


Fig. 1. Dependence of benzene conversion on the surface temperature of the heater (reaction time 6 h).

The phenomenon giving high selectivity of biphenyl may be due to the thermal diffusion effect. The thermal diffusion caused by the temperature gradient between the surface of the heated wire and the cold wall of the reactor effects the produced biphenyl molecule, which is of higher molecular weight than benzene, to leave the heated surface of the heater for the cold wall immediately after its production and

Table 1. Product Distribution of Benzene Coupling

| Surface temp. | Reaction time | Benzene conv. | Selectivity[a] | | | |
|---|---|---|---|---|---|---|
| | | | Biphenyl | *o*-Terphenyl | *m*-Terphenyl | *p*-Terphenyl |
| °C | h | % | % | % | % | % |
| 950 | 6 | 1.8 | 97.0 | 0.4 | 1.7 | 0.9 |
| 1000 | 6 | 5.7 | 95.4 | 0.6 | 2.6 | 1.4 |
| 1050 | 6 | 12.4 | 94.5 | 0.8 | 3.0 | 1.7 |
| 1100 | 3 | 8.2 | 95.3 | 0.6 | 2.3 | 1.5 |
| | 6 | 25.4 | 94.2 | 0.8 | 3.2 | 1.8 |
| 1150 | 1 | 3.5 | 95.4 | 0.6 | 2.5 | 1.5 |
| | 2 | 11.1 | 94.7 | 0.7 | 3.0 | 1.6 |
| | 3 | 20.6 | 96.1 | 0.5 | 2.2 | 1.2 |
| | 4 | 31.8 | 95.4 | 0.6 | 2.6 | 1.4 |
| | 5 | 47.5 | 95.5 | 0.6 | 2.4 | 1.5 |
| | 6 | 77.5 | 94.0 | 0.9 | 3.3 | 1.8 |

a) Values for selectivities were based on the weight of the products.

thus prevents the molecule from further reaction to terphenyls or quaterphenyls.

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