

# Reaction of Tetraphenyl Titanate with Amines

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In the previous paper, the reaction of tetraphenyl titanate with ammonia, phenols, acetophenone and esters have been reported<sup>1)</sup>. In the course of the synthetical studies on the organo titanium compounds, it has been found that the addition compounds of tetraphenyl titanate were more stable than that of tetraalkyl titanates. In the present communication, the reaction of tetraphenyl titanate (TPhT) with aliphatic or aromatic amines are described.

When TPhT was made to react with aliphatic amines (*n*-butylamine, tri-ethylamine, tri-*n*-butylamine) in toluene solution, addition compounds of TPhT could not be isolated. However, when aromatic amines (aniline,  $\alpha$ -naphthylamine, pyridine) were used, they gave addition compounds with TPhT (molar ratio of 1:1). When the addition compound of TPhT with phenol I reacted with aromatic amines, the addition compound I was converted into the addition compounds of the corresponding amines used. They also were converted into the addition compound of TPhT with ammonia. The reaction of TPhT with hexamethylenediamine gave yellow crystals, which were considered as the addition compound of TPhT with hexamethylenediamine (molar ratio of 2:1).

## Experimental

1) **Addition Compounds of TPhT with Aromatic Amines.**—Into a solution of TPhT (8.0 g.) in toluene (50 ml.), freshly distilled aniline (2.1 g.) was added and refluxed for 15 min. After the reaction mixture was allowed to stand at room temperature, the crystals separated out were collected by filtration and dried under reduced pressure, 8.0 g. of yellowish orange crystals were obtained. They were recrystallized from toluene. M. p. 181~183°C. (Found: Ti, 9.64; N, 2.80. Calcd. for  $C_{30}H_{27}O_4NTi$ : Ti, 9.33; N, 2.73%). In a similar way the following addition compounds were obtained:  $Ti(OC_6H_5)_4 \cdot C_{10}H_7NH_2$ , orange crystals, m. p. 168~169°C.

(Found: Ti, 8.49; N, 2.60. Calcd. for  $C_{34}H_{29}O_4NTi$ : Ti, 8.50; N, 2.49%);  $Ti(OC_6H_5)_4 \cdot C_5H_5N$ , reddish orange crystals, m. p. 191~192°C. (Found: Ti, 9.53; N, 2.83. Calcd. for  $C_{29}H_{25}O_4NTi$ : Ti, 9.59; N, 2.80%).

When aliphatic amines (*n*-butylamine, tri-ethylamine, tri-*n*-butylamine) were used, addition compound of TPhT could not be isolated.

2) **Reaction of the Addition Compound  $Ti(OC_6H_5)_4 \cdot C_6H_5OH$  (I) and Aromatic Amines.**—To a solution of the addition compound I (4.0 g.), in toluene (15 ml.), aniline (2.0 g.) was added and the solution was refluxed for 15 min. After allowed to stand at room temperature, it deposited yellowish orange crystals. They were purified as described under (1), m. p. 183°C. (Found: Ti, 9.08; N, 2.86. Calcd. for  $C_{30}H_{27}O_4NTi$ : Ti, 9.33; N, 2.73%).  $Ti(OC_6H_5)_4 \cdot C_6H_5OH + C_6H_5NH_2 \rightarrow Ti(OC_6H_5)_4 \cdot C_6H_5NH_2 + C_6H_5OH$ . In a similar way, by the use of  $\alpha$ -naphthylamine or pyridine, the addition compound I was converted into the corresponding addition compounds of TPhT with the above amines respectively:  $Ti(OC_6H_5)_4 \cdot C_{10}H_7NH_2$ , m. p. 167~168°C. (Found: Ti, 8.91; N, 2.63. Calcd. for  $C_{34}H_{29}O_4NTi$ : Ti, 8.50; N, 2.49%);  $Ti(OC_6H_5)_4 \cdot C_5H_5N$ , m. p. 191~192°C. (Found: Ti, 9.67; N, 2.88. Calcd. for  $C_{29}H_{25}O_4NTi$ : Ti, 9.59; N, 2.80%).

3) **Reaction of the Addition Compound  $Ti(OC_6H_5)_4 \cdot C_6H_5NH_2$  (II) and Ammonia.**—When excess of dry ammonia gas was passed at room temperature to a solution of the addition compound II (2.5 g.), in toluene (10 ml.), the addition compound II was converted into the addition compound of TPhT with ammonia III, (molar ratio of 1:1). M. p. 201~202°C. (Found: Ti, 10.89; N, 3.17. Calcd. for  $C_{24}H_{23}O_4NTi$ : Ti, 10.95; N, 3.20%).



In a similar way, the addition compounds  $Ti(OC_6H_5)_4 \cdot C_{10}H_7NH_2$  and  $Ti(OC_6H_5)_4 \cdot C_5H_5N$  were converted into III.

4) **Reaction of TPhT with Hexamethylenediamine.**—Into a solution of TPhT (8.7 g.) in toluene (60 ml.), hexamethylenediamine (0.6 g.) was added and refluxed for 30 min. After the reaction mixture was allowed to stand at room temperature, the crystals were collected by filtration, washed with toluene and dried under reduced pressure, 4.7 g. of powdery yellow crystals were obtained. M. p. 237~239°C. The analytical data showed this compound to be an addition compound of TPhT with hexamethylenediamine (molar ratio of 2:1), (Found: Ti, 10.13; N, 3.45. Calcd. for  $C_{54}H_{56}O_8N_2Ti_2$ : Ti, 10.01; N, 2.92%).

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1) T. Yoshino et al., *J. Chem. Soc. Japan, Ind. Chem. Sec. (Kogyo Kagaku Zasshi)*, 63, 1758 (1960).