May, 1985] © 1985 The Chemical Society of Japan NOTES Bull. Chem. Soc. Jpn., 58, 1611—1612 (1985) 1611

# Iodination of Benzene with Iodine and Metal Salts in Acidic Solvents

Atsushi SHIMIZU,* Kazunori YAMATAKA,* and Toshiro ISOYA
*Technical Development Department of Petrochemical Intermediates, Asahi Chemical Ind. Co., Ltd.*
*Nagahama-cho 4-3401, Nobeoka, Miyazaki 882*

(Received December 12, 1984)

**Synopsis.** Iodobenzene was obtained by a reaction of benzene with molecular iodine in trifluoromethanesulfonic acid in oxygen atmosphere in the presence of vanadium salt as a catalyst. The method affords a new aromatic iodination process in which benzene is iodinated directly with molecular iodine.

Aromatic compounds can be brominated or chlorinated with bromine or chlorine in the presence of a catalyst, most often iron. On the other hand, iodine is the least reactive of the halogens in aromatic halogenation reactions where an oxidizing agent is normally required to oxidize iodine to a better electrophile, as opposed to the case of active substrates. Generally, iodination of benzene can be accomplished by iodine in the presence of nitric acid.[1] Recently several synthetic methods of iodoarens have been reported, which include (1) iodination of aromatics with molecular iodine in the presence of oxidizing agents,[2–4] (2) iodination of aromatics with a potent iodine donor[5,6] (3) decomposition of arylthallium compounds with potassium iodide or iodine,[7,8] and (4) electrochemical iodination of aromatics.[9,10] These procedures have some deficiencies. Metal salts are required as stoichiometric agents, iodine donors are hard to be prepared, or iodine is lost from the reaction as hydrogen iodide or metallic iodide.

Recently fluorine containing compounds such as trifluoromethanesulfonic acid or trifluoroacetic acid have been used as catalysts or solvents in various reactions to show remarkable effects. We have found that iodination of benzene with molecular iodine occurs in trifluoromethanesulfonic acid in the presence of sodium vanadate(V) and oxygen gas. The present paper will describe a new catalytic iodination of benzene.

## Experimental

*The Typical Procedures.* In a 200-ml three-necked glass autoclave were placed 5.08 g (65.1 mmol) of benzene, 2.03 g (8.00 mmol) of iodine, 0.33 g (2.7 mmol) of sodium vanadate(V), and 12.5 g of trifluoromethanesulfonic acid. The mixture was magnetically stirred at 100 °C under 10 atm of air. When the colour of iodine was discharged and the solution became black after 1.5 h, the mixture was poured into 300 ml of ice-water containing 10% of sodium thiosulfate, and the products were extracted with 100 ml of hexane. Removal of hexane left 3.13 g of an oil which contained 2.99 g (14.7 mmol) of iodobenzene, 0.13 g (0.39 mmol) of *p*-diiodobenzene, and 0.01 g (0.04 mmol) of *o*-diiodobenzene. The yields based on iodine were 91.9, 2.5, and 0.2% respectively. All the products were characterized by comparison of NMR spectra, mass spectra, and GC retention times with those of authentic samples.

## Results and Discussion

The results of the iodination in trifluoromethanesulfonic acid are shown in Table 1.

The reaction was performed as a two-layer system. The upper layer was benzene and the lower layer was trifluoromethanesulfonic acid. An increase in the quantity of trifluoromethanesulfonic acid was accompanied by an increase in the yield of iodobenzene. The presence of oxygen was essential in the reaction because iodobenzene was not obtainable without oxygen. Iodinations were examined in various combinations of solvents and metal salts, and the use of vanadium salt and trifluoromethanesulfonic acid gave an excellent yield of iodobenzene. The molar ratio of the iodobenzene to the metal salt reveals that the metal salt acts as a catalyst. Since the molar ratio

TABLE 1. IODINATION OF BENZENE IN $CF_3SO_3H$

| Run | Benzene | Iodine | Metal Salt | | $CF_3SO_3H$ | Press | | Temp | Time |
|---|---|---|---|---|---|---|---|---|---|
| | mmol | mmol | mmol | | g | kg/cm² | | °C | h |
| 1 | 65.1 | 8.00 | $NaVO_3$ | 2.71 | 12.5 | air | 10 | 100 | 1.5 |
| 2 | 67.2 | 15.1 | $V_2O_5$ | 1.37 | 12.5 | $O_2$ | 2 | 100 | 5.5 |
| 3 | 129 | 15.1 | $V_2O_5$ | 8.25 | 1.19 | $O_2$ | 5 | 100 | 9.0 |
| 4 | 64.1 | 15.0 | $V_2O_5$ | 1.38 | 12.5 | $N_2$ | 5 | 100 | 8.0 |

| Run | IB/M[a] | $C_6H_5I$ | Select.[b] of $C_6H_5I$ | Select.[b] of $p$-$C_6H_4I_2$ | Select.[b] of $o$-$C_6H_4I_2$ | Conv. of Benzene |
|---|---|---|---|---|---|---|
| | | mmol | % | % | % | % |
| 1 | 5.4 | 14.7 | 91.9 | 2.5 | 0.2 | 27.6 |
| 2 | 17.9 | 24.5 | 81.1 | 6.7 | 1.0 | 44.7 |
| 3 | 0.21 | 1.74 | | | | |
| 4 | | trace | | | | |

a) IB/M is a molar ratio of the iodobenzene to the metal salt. b) Selectivity was based on iodine.

Table 2. Iodobenzene/catalyst molar ratio in $CH_3SO_3H$ (100 °C, 8 h)

| Cat. | $C_6H_5I$/Cat. | Cat. | $C_6H_5I$/Cat. | Cat. | $C_6H_5I$/Cat. |
|---|---|---|---|---|---|
| $FeCl_2 \cdot 4H_2O$ | 1.0 | $VCl_3$ | 3.7 | $ZnCl_2$ | 0.0 |
| $FeCl_3$ | 1.0 | $TiCl_4$ | 2.7 | $CdCl_2 5/2H_2O$ | 0.0 |
| $Fe_2O_3$ | 0.5 | $ZrCl_4$ | trace | $Ag_2O$ | 0.65 |
| $Fe(OH)_3$ | 1.0 | $Co_3O_4$ | 0.51 | TlCl | trace |
| $Fe(AcAc)_3$ | 0.0 | NiO | 0.0 | $MnO_2$ | 1.3 |
| $CuCl_2$ | 3.0 | $PdCl_2$ | trace | $SbCl_3$ | trace |
| CuO | 1.0 | $CrO_4$ | 1.6 | $V_2O_5$ | 1.8 |
| $MoO_3$ | trace | $NaVO_3$ | 1.6 | $WO_3$ | 0.0 |

Other reaction conditions are as follows: $Ag_2O$, $Fe_2O_3$, $V_2O_5 = 1.35$ mmol; $Co_3O_4 = 0.9$ mmol; others $= 2.7$ mmol; $C_6H_6 = 5$ g; $CH_3SO_3H = 12.5$ g; $O_2 = 5$ kg/cm$^2$.

Table 3. Iodination of benzene in $CF_3COOH$

| Run | $C_6H_6$ mmol | Iodine mmol | Cat. mmol | $CF_3COOH$ g | Press. kg/cm$^2$ | Temp °C | Time h | $C_6H_5I$ mmol |
|---|---|---|---|---|---|---|---|---|
| 1 | 65.3 | 15.2 | $V_2O_5$ 1.37 | 12.5 | air 10 | 100 | 5.5 | 2.60 |
| 2 | 128.0 | 23.6 | $FeCl_2 \cdot 4H_2O$ 0.352 | 10.5 | $O_2$ 2 | 100 | 48.0 | 2.56 |

of consumed benzene to iodine was about 2:1, the overall reaction can be shown as follows:

$$2C_6H_6 + I_2 + 1/2O_2 \longrightarrow 2C_6H_5I + H_2O$$

The iodobenzene also gave diiodobenzene by a reaction with iodine.

Activities of various metal salts in the iodination were examined in methanesulfonic acid. All the results are summarized in Table 2.

Cu, Ti, Fe, and Mn salts were comparatively effective. Since the sorts of counter ions of metal ions do not seem to be important, we may describe that the metal salts were oxidizing catalysts, and not Lewis acids.

Trifluoroacetic acid could also be used as the solvent. Table 3 gives the results.

The iodination rate was dependent on the acidity of the solvent because the iodination rate decreased in the order $CF_3SO_3H > CH_3SO_3H > CF_3COOH$ and was nearly zero in $CH_3COOH$. The combination of acidic solvent, oxygen gas, and oxidizing catalyst are indispensable in the iodination reaction. We may describe the reaction pathways as follows:

$$CF_3SO_3H + I_2 \longrightarrow CF_3SO_3^- + HI_2^+$$

$$HI_2^+ \longrightarrow HI + I^+$$

$$I^+ + C_6H_6 \longrightarrow C_6H_5I + H^+$$

$$HI \longrightarrow H^+ + I^-$$

$$I^- + V^{5+} \longrightarrow 1/2I_2 + V^{4+}$$

$$V^{4+} + H^+ + 1/4O_2 \longrightarrow V^{5+} + 1/2H_2O$$

Although the reactive intermediate is represented as iodine ion in the pathways, possible intermediates other than iodine ion are HIO, $CF_3SO_3I$, $CH_3SO_3I$, or $CF_3COOI$.[3,4] It is not clear which is the true active intermediate.

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