amide. For example, 4-nitrochlorobenzene 15 g. (0.1 mol.), cupric sulfate 10 g. (0.04 mol.) and dimethylformamide 50 ml. were refluxed with stirring for 16 hr., and then about 25 ml. of dimethylformamide was distilled off from the reaction mixture. The residue was poured into a large quantity of water, and the precipitate separated was collected and extracted with benzene. The benzene solution was evaporated, and the residue was recrystallized from methanol. 4-Nitrodimethylaniline was obtained as yellow crystals, yield, 13 g. (78%), m. p. 163°C (m. p. 163°C)[1]. Found: C, 57.83; H, 6.06; N, 16.38. Calcd. for $C_8H_{10}N_2O_2$: C, 57.82; H, 6.06; N, 16.86%. 2, 4-Dinitrochlorobenzene in the same way gave 2, 4-dinitrodimethylaniline in a 77% yield.

The same results were obtained when cuprous cyanide was used as a catalyst in place of cupric sulfate. 2, 4-Dinitrochlorobenzene 20 g. (0.1 mol.), cuprous cyanide 10 g. and dimethylformamide 50 ml. were refluxed with stirring for 16 hr., then the mixture was added to a mixture of ferric chloride 20 g., concentrated hydrochloric acid 5 ml. and water 30 ml., and kept at 70~80°C for 30 min. After cooling, the precipitate separated was filtered and recrystallized from methanol. Yield, 7 g. (34%), m. p. 87°C (m. p. 87°C)[2]. Found: C, 45.6; H, 4.51; N, 19.8. Calcd. for $C_8H_9N_3O_4$: C, 45.38; H, 4.29; N, 19.89%. 4-Nitrochlorobenzene in the same way gave 4-nitrodimethylaniline in a 13% yield.

2-Nitrochlorobenzene could not be converted into 2-nitrodimethylaniline in the presence of cupric sulfate, and 2-nitrobenzonitrile was obtained when cuprous cyanide was used.

Industrial Research Institute
Osaka Prefecture
Enokozima Nishi-ku, Osaka

1) A. Weber, *Ber.*, **10**, 760 (1877).
2) K. H. Mertens, ibid., **19**, 2124 (1886).

Dimethylamination by Dimethylformamide

By Masao WAKAE and Kiyoshi HAMANO

(Received October 22, 1962)

The formylation reaction by dimethylformamide is well known, but the dimethylamination by the same reagent is not reported yet. We have found the substitution reaction of halogen atom on halonitrobenzenes by dimethylform-