

### *N*-Alkylation of Metanilic Acid

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While the alkylation reaction of amino compounds with alcohol in the presence of iodine is well known, the method does not always give satisfactory results. The present investigation was undertaken to see if a practical method could be worked out for the preparation of *N,N*-diethylmetanilic acid using iodine, red phosphorus and boric acid as a catalyst.<sup>3)</sup>

Metanilic acid was treated with ethanol in the presence of iodine, red phosphorus and boric acid at 200–250°C for a few hours to give *N,N*-diethylmetanilic acid. The condition used in various alkylations and the yields of *N,N*-diethylmetanilic acid of individual reactions are given in Table 1.

In the reaction at 250°C, the main product was oily materials as a result of presumable desulfonation. Whereas at 210°C or below the reaction did not proceed. The best condition seemed to be heating at about 230°C (*cf.* DEM-5,10,11). An optimum reaction time was estimated to be 3 hr as a longer heating decreased the yield (*cf.* DEM-2,10). Without red phosphorus only 17.6% of metanilic acid was ethylated, and the rest was recovered unchanged. Both reactions without boric acid and without iodine and red phosphorus gave only unreacted metanilic acid. The best condition for the preparation of *N,N*-diethylmetanilic acid can be seen in run numbers DEM-10 and PE-7.

TABLE 1. REACTION CONDITION AND THE YIELD OF *N,N*-DIETHYLMETANILIC ACID  
Metanilic acid 8.88 g, Ethanol 39.4 g

Run No.	Iodine (g)	Red phosphorus (g)	Boric acid (g)	Reac. temp. (°C)	Reac. time (hr)	Yield (%)
DEM-2	0.147	0.016	0.212	230	5	68.2
DEM-3	0.224	0.045	0.278	240	5	76.6
DEM-5	0.025	0.035	0.104	240	3	79.2
DEM-8	0.072	0.004	0.093	240	3	77.2
DEM-9	0.146	0.014	0.214	240	3	69.0
DEM-10	0.129	0.019	0.215	230	3	81.8
DEM-11	0.135	0.016	0.224	210	3	— <sup>3)</sup>
DEM-12	0.143	—	0.187	240	3	17.6
DEM-16	—	—	2.105	230	3	— <sup>3)</sup>
DEM-18	0.129	0.018	—	230	3	— <sup>3)</sup>
PE-2 <sup>1)</sup>	0.51	1.54	2.05	200	10	7.2
PE-7 <sup>2)</sup>	0.53	1.60	2.14	230	3	82.9
PE-9 <sup>1)</sup>	0.53	1.60	2.14	220	10	78.1
PE-10 <sup>1)</sup>	0.53	0.16	2.14	220	5	77.0
PE-11 <sup>1)</sup>	0.51	0.15	2.05	210	5	5.9

1) Metanilic acid 88.8 g, Ethanol 530 g

2) Metanilic acid 88.8 g, Ethanol 1063 g

3) The yield was negligible.

### Experimental

For a typical run (DEM-10), 8.88 g (0.0513 mol) of metanilic acid, 39.4 g (50 ml, 0.85 mol) of ethanol, 0.129 g (0.000508 mol) of iodine, 0.215 g (0.00348 mol) of boric acid and 0.019 g (0.000154 mol) of red phosphorus were placed in an autoclave. The reaction

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mixture was heated at 230°C for 3 hr. After cooling the reaction mixture was filtered and washed with ethanol to give 10.17 g of a crude product. This product was dissolved in hot water. After removal of a hot-water-insoluble part, the filtrate was concentrated to

yield 9.95 g of *N,N*-diethylmetanilic acid (84.7% of the theoretical amount). The purity of this product was estimated to be 96.5% by a functional group analysis. Thus total yield was calculated to be 81.8%.

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