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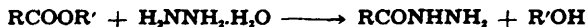
## Anomalous Behavior of Methylhydrazines In Reactions With Esters

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In the course of preparing a series of hydrazides for biological testing, syntheses of certain *N*-substituted methyl and dimethyl derivatives were attempted. Hydrazinolysis of esters is usually the method employed for preparing hydrazides:



When this type reaction was carried out with methyl- or *as*-dimethylhydrazine instead of hydrazine hydrate, little or no hydrazide was obtained even when reaction times were extended to twenty-four hours. Similar behavior on the part of *as*-dimethylhydrazine with methyl benzoate has been reported recently by Hinman (1956).

The sole product from the reaction of ethyl *p*-nitrobenzoate and methylhydrazine proved to be diethyl azobenzene-4,4'-dicarboxylate:



The same product was obtained with this ester and *as*-dimethylhydrazine, or with 85% aqueous methylhydrazine. The latter result was in direct contrast to the behavior of hydrazine hydrate (85%) which formed *p*-nitrobenzoic hydrazide readily under the same conditions. Busch and Schulz (1929) and Furst and Moore (1957) have reported the production of azoxy-, azo-, and hydrazobenzenes from reactions of hydrazine with nitrobenzene. These reactions were carried out in the presence of palladized

calcium carbonate or Raney nickel catalysts. No reaction took place in the absence of catalyst (Furst & Moore, 1957). Also Kuhn (1951) found it was necessary to add Raney nickel to reduce aromatic nitro compounds to the corresponding amines with 100% hydrazine. The difference in the nitro compounds employed prohibits a direct comparison of these previous results with those of the present study. It is interesting, however, that the azobenzene product reported here was produced in good yield in the absence of any catalyst.

#### EXPERIMENTAL

*Diethyl azobenzene-4,4'-dicarboxylate (I)*. A solution of 9.76 g. (0.050 mole) of ethyl p-nitrobenzoate and 3.45 g. (0.075 mole) of methylhydrazine in 10 ml. of 95% ethanol was refluxed for 24 hours. The orange-red crystals, which had formed after several hours refluxing, were collected and purified from chloroform-ethanol mixtures to yield 40% of I, m.p. 141°; lit. m.p. 143° (Tomlinson, 1956). Calcd. for  $C_{18}H_{18}N_2O_4$ : C, 66.24; H, 5.56; N, 8.58 Found: C, 65.92; H, 5.83; N, 8.86.

I was obtained in comparable yields using *as*-dimethylhydrazine or 85% aqueous methylhydrazine. For comparative purposes, a solution of 0.01 mole of the ester and 0.02 mole of hydrazine hydrate in 2 ml. of 95% ethanol was refluxed for 24 hours. The product proved to be p-nitrobenzoic hydrazide, m.p. 213-214°; lit. m.p. 210° (Classen et al., 1954).

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