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Deacylation of N-Acetylated Amines with Alcohol and Boron Trifluoride

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On attempting to prepare 3,4-dinitro- α -naphthylamine¹ from its acetyl derivative it was found that the usual methods of deacylation were unsatisfactory, side reactions accompanying deacylation.

As stated in another investigation¹ 3,4-dinitro- α -naphthylamine is quantitatively transformed to 4-chloro-3-nitro-naphthalene diazonium chloride when heated with *hydrochloric acid*.

With *dilute sulphuric acid* it was found that acetaldehyde was formed when the acetyl compound was refluxed in a mixture

of equal amounts of ethanol and 50 % sulphuric acid which may suggest the formation of a diazonium compound that in its turn is reduced by the alcohol. The reaction with sulphuric acid is obviously similar to that with hydrochloric acid.

Attempts to split off the acetyl-group by heating the acetyl compound for a short time in *concentrated sulphuric acid* as described by Blankema² also failed, sulphonation apparently taking place.

Roon, Verkade, and Wepster³ have reported that many aromatic acetyl compounds are converted to the corresponding amine by heating with *absolute alcoholic hydrogen chloride*. However, this method was not successful in the case of 3,4-dinitroaceto- α -naphthalide. A product exploding very violently at ca. 150 °C was formed. It was not investigated further.

Treatment of the acetyl compound with *alcoholic aqueous sodium hydroxide* yielded chiefly products other than 3,4-dinitro- α -naphthylamine. The formation of ammonia indicated that the amino-group was split off.

Attempts were also made to deacylate the acetyl compound in boiling *alcohol with sodium alcoholate as a catalyst* as described by Verkade and Witjens⁴ and this method was found to give satisfactory results.

Table 1. The results of deacylation with methanol and boron trifluoride.

Compound	Time min.	Temp. °C	M.p. * of the crude product °C	M. p. of the pure amine °C
Acetanilide	60	65	liquid ($n_D^{20} = 1.586$)	liquid ($n_D^{20} = 1.586$)
<i>o</i> -Nitroacetanilide	10 35 **	65 65	71—72 71—72	71—72
<i>m</i> -Nitroacetanilide	20	65	112—13	114—15
<i>p</i> -Nitroacetanilide	15	65	149—50	150—51
2,3-Dinitroacetanilide	20	65	124—25	126—27
2,6-Dimethylacetanilide	2 160	110	4—6 ($n_D^{20} = 1.556$)	9—11 ($n_D^{20} = 1.561$)
2,6-Dimethyl-N-methyl-acetanilide	2 160	110	94—95 (unchanged starting material)	liquid
4-Nitroaceto- α -naphthalide	25	65	192—93	196—97
2,3-Dinitroaceto- α -naphthalide ¹	60	65	(unchanged starting material)	232 (decomp.)
3,4-Dinitroaceto- α -naphthalide	65	65	201 (decomp.)	201 (decomp.)

* All melting points are corrected.

** Deacylation in a solution containing 0.01 g BF₃/ml.

According to Sowa and Nieuwland⁵ amides can be esterificated by alcohols and phenols in the presence of boron trifluoride. It might, therefore, be expected that acetylated amines would be deacylated in the acidic solution formed from boron trifluoride and an alcohol. This was also found to be the case, and 3,4-dinitroacetone-naphthalide and some other acetyl compounds (see Table 1) were easily deacylated when heated in methanol containing boron trifluoride (0.10 g/ml, 4–8 mole/mole acetyl compound) giving the corresponding amine in almost theoretical yield. The time required for complete reaction was determined only approximately. Samples were taken out at suitable intervals and investigated. The relation between the rate of deacylation and the amount of boron trifluoride was not investigated. In the case of *o*-nitroacetanilide, however, an experiment was carried out with one tenth of the above mentioned amount of boron trifluoride; an increase of the time of reaction from 10 to 35 minutes was required.

As can be seen from the Table the sterically hindered 2,6-dimethylacetanilide was very slowly deacylated even at 110 °C, and its *N*-methyl derivative remained unchanged when heated to this temperature for 36 hours. For comparison it may be pointed out that the former compound can not be hydrolysed in boiling concentrated hydrochloric acid but when heated to 200 °C in 70–75 % sulphuric acid it is hydrolysed in about 6 hours⁶. The *N*-methyl derivative remains unchanged when boiled in 80 % sulphuric acid for 9 hours or heated to 220 °C in concentrated alcoholic potassium hydroxide for 11 hours⁷.

Experimental. The acetyl compound (0.30 g) was refluxed in methanol (6 ml) containing boron trifluoride (0.60 g) and at suitable intervals samples were taken out and investigated (m.p. and/or refractive index). When the deacylation was complete the reaction solution was worked up in one of the following alternative ways.

1. After the introduction of ammonia to bind the boron trifluoride as $\text{NH}_3 \cdot \text{BF}_3$ the methanol was evaporated and the residue extracted with ether. Evaporation of the ether yielded the free amine. By treatment of the ether insoluble residue with sulphuric acid as described by Sowa and Nieuwland⁵ practically all the boron trifluoride was liberated.

2. Water insoluble amines forming compounds with boron trifluoride which decom-

pose in aqueous solution (e. g. 2,3-dinitroaniline) were precipitated by diluting the reaction solution with water. The precipitated amine was collected and washed with water.

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The Compressibility of Acetylene at 25.0° C

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In connection with equilibrium and solubility determinations earlier described¹, the compressibility of acetylene was measured at pressures below 1.5 atm.

It proved advantageous to use the same type of apparatus as for the solubility determinations, even if more accurate compressibility measurements may be performed by other methods. The apparatus consists of a thick-walled glass flask in a water thermostat; the flask is connected to a manometer and a gas-burette, the latter provided with a separate thermostat. The gas contents of ducts and manometer can be calculated from the pressure and the inner reading of the manometer, using a function which has been determined by separate calibration.

During the measurements V and T are kept constant and the relation between p and n is studied. The measurement of the gas quantity (which is volumetrically performed under suitable standard conditions), however, does not give n but n_a ,