Some Derivatives of 4-Dimethylamino-3,5-dinitrobenzoic Acid

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For separation of colourless substances it may sometimes be convenient to use chromatographic adsorption of coloured derivatives of these substances. Thus some alcohols have been separated as azobenzene carboxylates, aldehydes in form of their dinitrophenylhydrazones etc.

We have tried the azide and chloride of 4-dimethylamino-3,5-dinitrobenzoic acid (chrysanisic acid) as reagents for alcohols and amines, with which they give intensely coloured and well crystallized derivatives. These were, however, not especially suited for chromatographic separation, so the investigation has been discontinued and the purpose of this paper is only to describe some new compounds prepared in the course of the work.

4-Dimethylamino-3,5-dinitrobenzoic acid. Ten grams of 4-chlorobenzoic acid were dissolved in 200 g of conc. sulphuric acid and at a temperature of 80°, 33 g of potassium nitrate were added gradually. The temperature rose to 120—140° and was kept there for one and a half hour. The cooled solution was poured upon ice and the crystals of 4-chloro-3,5-dinitrobenzoic acid filtered by suction. After one crystallization from alcohol the melting point was 152°. Yield 98 %. The melting point of the pure compound is 158°, but it was found, that the over-all yield of 4-dimethylamino-3,5-dinitrobenzoic acid was larger, if no further purification of the chloro acid was performed. If desired, however, the acid may be purified via its sodium salt, which is sparingly soluble in cold sodium hydroxide solution.

A suspension of 15 g of 4-chloro-3,5-dinitrobenzoic acid in 60 ml of 33 % dimethylamine in alcohol was heated in a closed vessel at 100° for 4 hours. The solution was then evaporated to a small volume. By addition of hydrochloric acid yellow crystals of 4-dimethylamino-3,5-dinitrobenzoic acid separated. Yield 14 g, with a melting point of 210—220°. The crude product was dissolved in the minimum amount of hot alcohol and the solution filtered. By cooling large orange-yellow crystals separated. Yield 11 g + 1 g from the mother liquor, *i. e.* 77 %. M. p. 248°.

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which further amounts of the *epi*-form could be isolated.

$C_{24}H_{26}O_8$ (442.5)
Calc. OCH_3 14.0 Found OCH_3 14.0

Epi-pinoresinol. Epi-pinoresinol diacetate (1.0 g) was dissolved in hot ethanol (25 ml) and potassium hydroxide (0.5 g) in water (0.5 ml) was added. The potassium salt precipitated at once. After cooling, it was collected on a filter, washed with ethanol, acetone and ether, dissolved in a small amount of water, and precipitated with acetic acid. The *epi*-pinoresinol (0.6 g) was recrystallized twice from ethanol. M. p. 140.5—141.5°. $[\alpha]_D^{20}$ + 126° (Chloroform, $c = 2$).

$C_{20}H_{22}O_6$ (358.4)
Calc. OCH_3 17.3 Found OCH_3 17.2

A small amount of *epi*-pinoresinol was methylated with dimethyl sulfate and alkali. The dimethyl ether was isolated and recrystallized from ethanol. The melting point of the substance was 129—130°, alone or as admixture of pure *epi*-pinoresinol dimethyl ether, kindly supplied by Dr. J. Gripenberg.

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4-Dimethylamino-3,5-dinitrobenzoyl chloride. A solution of 5 g of 4-dimethylamino-3,5-dinitrobenzoic acid and 5 ml of thionyl chloride in 25 ml of dry benzene was refluxed for half an hour. By cooling the acid chloride crystallized in large yellow plates. By concentration of the mother liquor a second crop was obtained. Yield 80 %.

After recrystallization from benzene + petroleum ether the m. p. was 118—119°.

$C_9H_8O_6N_3Cl$ (273.6)

Calc.	N 15.36	Cl 12.96
Found	» 15.62	» 12.93

4-Dimethylamino-3,5-dinitrobenzoylazide. Sodium azide (1.5 g) was added to a cold solution of the acid chloride (5 g) in acetic acid and the solution was heated at 50° for 15 minutes. The azide crystallized on cooling, and was recrystallized from acetic acid. Yield 66 %. M. p. 125°.

$C_9H_8O_5N_6$ (276.2)

Calc.	N 30.42
Found	» 29.82

N,N′ -bis-(4-dimethylamino-3,5-dinitro-phenyl)-urea. A mixture of 0.5 g of the azide, 0.5 ml of water and 5 ml of xylene was refluxed for one hour. On cooling crystals separated, which were filtered and recrystallized from dilute alcohol. Dark violet-red crystals. M. p. 231°.

$C_{17}H_{18}O_9N_8$

Calc.	N 23.43
Found	» 23.29

Methyl 4-dimethylamino-3,5-dinitrophenylcarbamate. A mixture of 0.5 g of the azide, 1 ml of dry methanol and 5 ml of xylene was refluxed for 3 hours. The xylene was removed in vacuo and the residue recrystallized from a mixture of benzene and petroleum ether. Orange-red crystals. Melting point 175—176°.

$C_{10}H_{12}O_6N_4$ (284.3)

Calc.	N 19.76
Found	» 19.85

Ethyl 4-dimethylamino-3,5-dinitriphenylcarbamate. Prepared in the same way as the methyl urethane. Orange-red crystals. Melting point 91—92°.

$C_{11}H_{14}O_6N_4$ (298.3)

Calc.	N 18.74
Found	» 18.72

The two urethanes may be separated by chromatographic adsorption from benzene-petroleum ether solution on aluminium oxide, the methyl derivative forming the upper zone.

Amides of 4-dimethylamino-3,5-dinitrobenzoic acid. The amides of aliphatic amines were prepared by dissolving the acid chloride and the amine in pyridine and refluxing for 10—15 minutes. The amides separated by addition of water and hydrochloric acid and were recrystallized from benzene. The methyl- and ethylamide were also prepared by addition of the acid chloride to cold ethanolic solutions of the amine. By this method, however, the ethyl ester is easily formed. The aromatic amides were prepared by refluxing a solution of the acid chloride and the amine in benzene and were recrystallized from ethanol. All the amides crystallize in yellow to orange needles.

			N %		
			calc.	found	M. p.
Methylamide	$C_{10}H_{12}O_5N_4$	(268.2)	20.90	21.11	203°
Ethylamide	$C_{11}H_{14}O_5N_4$	(282.2)	19.86	20.42	148°
iso-Propylamide	$C_{12}H_{16}O_5N_4$	(296.3)	18.91	18.77	162°
n-Butylamide	$C_{13}H_{18}O_5N_4$	(310.3)	18.05	17.87	86°
Anilide	$C_{15}H_{14}O_5N_4$	(330.3)	16.96	17.46	248°
o-Toluidide	$C_{16}H_{16}O_5N_4$	(344.3)	16.27	16.19	213°
p-Toluidide	$C_{16}H_{16}O_5N_4$	(344.3)	16.27	16.10	234°

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