and water to a constant melting point, 187–190°, $[\alpha]^{24}\text{D}$ $-$ 125°, and specific absorption coefficient, α = 80.0.

Anal. Calcd. for $C_{18}H_{26}O_2$: C, 78.79; H, 9.55. Found: C, 78.68, 78.69; H, 9.45, 9.50.

Summary

The structure of neoabietic acid has been proved with the aid of Woodward's rules for unsaturated systems, and by the isolation of acetone, a 1,5-dialkylated naphthalene, and a substituted α,β-unsaturated ketone.

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[CONTRIBUTION FROM THE CENTRAL RESEARCH DEPARTMENT, MONSANTO CHEMICAL COMPANY]

N,N'N''-Triacylmelamines

BY WILLIAM S. EMERSON AND TRACY M. PATRICK, JR.

Ostrogovich[1] has reported that treatment of melamine with acetic anhydride gives 96% of diacetylmelamine and with benzoic anhydride gives 100% of tribenzoylmelamine. Diacetylmelamine can be further acetylated with a large excess of acetic anhydride to triacetylmelamine.[1] Triacetylmelamine also can be prepared by acetylating melamine with acetic anhydride in the presence of sodium acetate.[2]

We have found that aliphatic anhydrides above acetic give triacylmelamines as the sole products, and have prepared eleven such compounds by this method in 85–99% yields. We have also prepared diacetylmelamine by Ostrogovich's method.

Attempts to hydrolyze tripropionylmelamine to less highly acylated products were unsuccessful. The compound was unaffected by boiling water but was completely hydrolyzed to melamine by hot aqueous sodium hydroxide or sodium carbonate. Hot aqueous hydrochloric acid not only removed the propionyl groups but also hydrolyzed the melamine to what was probably a mixture of ammeline and ammelide.

Our tribenzoylmelamine melted at 201–203° in contrast to the 142–143° reported by Ostrogovich. His product was probably solvated.

Experimental

Preparation of Triacylmelamines.—These compounds were prepared by heating melamine with the appropriate acid anhydride. In the smaller runs a large test-tube (1 in. by 10 in.) with a thermometer as the stirrer, served as the reaction vessel. The larger runs were conducted in three-necked flasks of suitable dimensions. In all cases the temperature was raised by means of an oil-bath to the value indicated in the table and held there for five to thirty minutes. Upon cooling, the reaction mixture was diluted with some solvent such as methanol, ethanol, acetone or ethyl acetate, and filtered. The solid was washed with additional solvent and dried to obtain the crude yield. Further purification was effected by crystallization from glacial acetic acid or from the anhydride used in the preparation of the compound in question. The compounds prepared are summarized in Table I.

TABLE I

N,N',N''-TRIACYLMELAMINES

Acyl	Mol.[b] ratio	—Reaction— Temp., °C.	Time, min.	Yield, %	M. p.,[c] °C.	Nitrogen, % Calcd.	Found
Acetyl[a]	12	132	15	99[d]	312[e]	40.0	39.6
Propionyl	8.1	158	15	94	282	28.6	28.6[f]
n-Butyryl	12	160	30	98	258	25.0	24.6
n-Valeryl	10	172	30	94	228–229	22.2	22.4[f]
Isovaleryl	12	167	15	85	216–218	22.2	21.8
Caproyl	8.8	175	15	91	220	20.0	19.9
Oenanthyl	10	160	5	90	210	18.2	18.2
Caprylyl	9.3	175	15	94	209	16.7	16.7
Pelargonyl	6.3	185	5	88	194–195	15.4	15.3
Lauryl	6.5	192	15	99	178–179	12.5	12.5
Stearyl	3.5	200	30	93	159–161	9.08	9.66[f]
Oleyl	4.0	197	30	99	138–140	9.14	9.49
Benzoyl	8.3	172	60	84	201–203[g]	19.2	19.2

[a] Diacetylmelamine. [b] Molar ratio of anhydride to melamine. [c] All melting points corrected. [d] Ostrogovich[1] obtained a 96% yield, m. p. 305–306°. [e] Decomposed. [f] Microanalyses by the Oakwold Laboratories, Alexandria, Virginia. [g] Ostrogovich[1] gives m. p. 142–143°.

Hydrolyses of Tripropionylmelamine.—When 5 g. of tripropionylmelamine and 100 cc. of water were boiled under reflux for one hour the tripropionylmelamine was recovered unchanged, m. p. 275–276° (282°).

A 5-g. sample of tripropionylmelamine was boiled one hour with 100 cc. of 5% aqueous sodium hydroxide. Upon cooling, the mixture was neutralized with acetic acid and filtered. The 1.7 g. (81%) of dried solid proved to be melamine, m. p. 350° uncor. (347°).[1]

A similar experiment in which 100 cc. of 5% aqueous sodium carbonate was used yielded 1.7 g. (81%) of melamine, m. p. 353–354° uncor. (347°).[1]

A mixture of 5 g. of tripropionylmelamine and 100 cc. of 5% aqueous hydrochloric acid was boiled under reflux for one hour, cooled and neutralized with aqueous sodium bicarbonate. The solid was separated by filtration, washed with water and dried. It weighed 1.8 g. When heated on a spatula it did not melt but slowly decomposed and sublimed. It was soluble in dilute alkali.

Anal. Found: N, 50.8, 50.7. Calcd. for ammeline: N, 55.1. Calcd. for ammelide: N, 43.8.

Summary

Eleven new triacylmelamines have been prepared in 85–99% yield by treating melamine with the appropriate acid anhydride.

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[1] Ostrogovich, *Gazz. chim. ital.*, **65**, 566 (1935).

[2] Cason, THIS JOURNAL, **69**, 495 (1947).