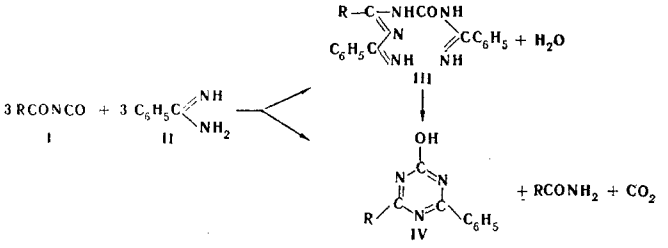
FORMATION OF sym-TRIAZINES BY THE REACTION OF ACYL ISOCYANATES WITH BENZAMIDINE

K. A. Nuridzhanyan, N. E. Mironova, and L. M. Nesterova

UDC 547.87.490.8:543.422.4

2-Hydroxy-1,3,5-triazines containing aryl or alkyl substituents in the 4,6 positions have been obtained only recently by the action on amidines of N-(α-chloroalkylidene)carbamoyl chlorides [1] or N-acylimidic esters [2].

We have established that sym-triazines of this type can be obtained by the action of acyl isocyanates (I) on benzamidine (II). Acyl isocyanates, in contrast to aryl isocyanates, which form the corresponding imidoylureas with benzamidine [3], react at room temperature in benzene simultaneously by two overall schemes [(1) and (2)]. On prolonged heating in solvents, compounds III are slowly converted with the elimination of benzonitrile and ammonia into compounds IV, the same reaction taking place rapidly at the melting point.



The reaction takes place with the liberation of heat and the evolution of gas, the oil first formed then being converted into a crystalline mixture of III and IV which can be separated by fractional crystallization. The addition of hydrogen chloride to the initial acyl isocyanate leads also to the separation of a certain amount of benzamidine hydrochloride, which is insoluble in acetone and does not react with acyl isocyanates under these conditions.

The structure of the compounds obtained was shown by elementary analysis, by the conversion of compounds IV by the action of phosphorus pentachloride [4] into the corresponding 2-chloro-sym-triazine, by independent synthesis, and by IR spectroscopy.

The following compounds have been obtained by the scheme shown: 4-(4-chlorophenyl)-2-hydroxy-6-phenyl-1,3,5-triazine (IVa), yield 99%, mp 290°C (from butanol). Found %: C 63.40; H 3.21; N 15.11. $C_{15}H_{10}ClN_3O$. Calculated %: C 63.50; H 3.53; N 14.83. Compound IVa was converted by chlorination into 2-chloro-4-(4-chlorophenyl)-6-phenyl-1,3,5-triazine, mp 142-143°C (140-141°C [1]). N'-Benzimidoyl-N-benzimidoylcarbamoyl-4-chlorobenzamidine (IIIa), yield 76.8%, mp 216-219°C (from nitromethane). Found %: C 65.40; H 4.50. $C_{22}H_{18}ClN_5O$. Calculated %: C 65.40; H 4.45. At 195-205°C, IIIa forms IVa quantitatively. From the mother liquor 4-chlorobenzamide was isolated; yield 72.1%, mp 179°C. 2-Hydroxy-4,6-diphenyl-1,3,5-triazine, yield 78.4%, mp 295-296°C (from butanol) (295°C [1]). 2-Chloro-4,6-diphenyl-1,3,5-triazine, mp 138-139°C (138-139°C [1]). 4-Ethyl-2-hydroxy-6-phenyl-1,3,5-triazine, yield 80.0%, mp 229°C (from nitromethane) (230°C [1]). 2-Hydroxy-4-(2-methylphenoxymethyl)-6-phenyl-1,3,5-triazine, yellow crystals, yield 86.5%, mp 184-185°C (from butanol). Found %: C 69.37; H 5.03; N 14.28. $C_{17}H_{15}N_3O_2$.

All-Union Scientific-Research Institute for Chemical Plant Protecting Agents, Moscow. Translated from Khimiya Geterotsiklicheskikh Soedinenii, Vol. 6, No. 7, pp. 1001-1002, July, 1970. Original article submitted November 3, 1969.

Calculated %: C 69.40; H 5.11; N 14.08. A mixture of 4-chlorobenzoylisocyanate and benzamidine hydrochloride in benzene yielded 1,3-bis(4-chlorobenzoyl)urea, yield 21%, mp 242-243°C (from butanol). Found %: C 53.31; H 3.14; Cl 20.85; N 8.28. $C_{15}H_{10}Cl_2N_2O_3$. Calculated %: C 53.40; H 2.97; Cl 21.05; N 8.30.

LITERATURE CITED

1. E. Degener, H. G. Schmelzer, and H. Holtschmidt, Angew. Chem. Inst. Ed., 5, 960 (1966).
2. M. Bel-Gacem Baccar, Compt. Rend., Ser. C, 264, 352 (1967).
3. A. Pinner, Ber., 23, 2923 (1890).
4. J. Ephraim, Ber., 26, 2226 (1893).