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Picrylamino-substituted Heterocycles. I

2,4,6-tris(Picrylamino)-*s*-triazine and Related Compounds (1)

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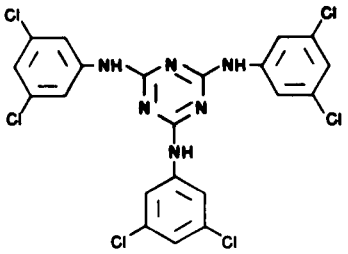
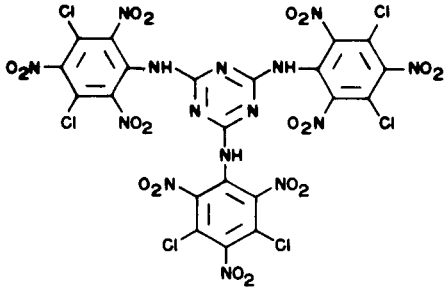
The synthesis of picrylamino-substituted heterocycles has been initiated as part of our effort to find superior heat-resistant explosives. The first of this new series of compounds, 2,4,6-tris(picrylamino)-*s*-triazine, I, was prepared by nitrating the known 2,4,6-trianilino-*s*-triazine (2) with a mixture of nitric and sulfuric acids. Further nitration of I with nitric acid in acetic anhydride gave the unstable 2,4,6-tris(picrylnitramino)-*s*-triazine, II.

The new 2,4,6-tris(3,5-dichloroanilino)-*s*-triazine, III, was obtained by refluxing cyanuric chloride with 3,5-dichloroaniline in chlorobenzene. Nitration of III with a mixture of nitric and sulfuric acids gave 2,4,6-tris(2,4,6-trinitro-3,5-dichloroanilino)-*s*-triazine, IV. Amination of IV gave 1,3,5-triamino-2,4,6-trinitrobenzene rather than the expected 2,4,6-tris(2,4,6-trinitro-3,5-diaminoanilino)-*s*-triazine.



III



IV

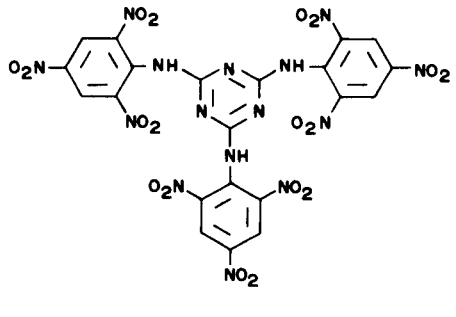
EXPERIMENTAL (3)

2,4,6-tris(Picrylamino)-*s*-triazine (I).

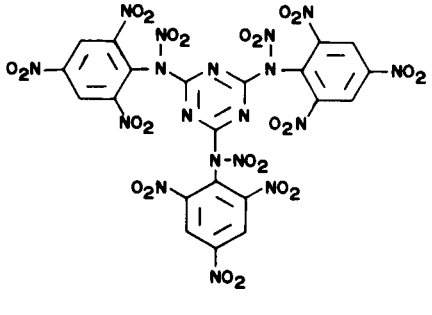
2,4,6-Trianilino-*s*-triazine (2) (2.0 g., 0.0056 mole) was added to a mixture of 15 ml. of 100% nitric acid and 15 ml. of concentrated sulfuric acid with stirring at such a rate that the temperature did not exceed 70°. The mixture was stirred at 70° for 3 hours, then cooled to 25° and poured into 150 ml. of ice and water. The solid was collected by filtration and digested in 150 ml. of boiling water for 1 hour. After the digestion was repeated once the product was collected and dried at 130°. The yield was 3.70 g. (87%). An analytically pure sample was obtained by dissolving the material in acetone, passing the solution through a barium sulfate filter to remove undissolved colloidal matter, precipitating the product by adding ethanol, then recrystallizing it from acetonitrile-ethanol.

Anal. Calcd. for $C_{21}H_9N_{15}O_{18}$: C, 33.21; H, 1.20; N, 27.67. Found: C, 33.27; H, 1.35; N, 27.73.

The compound does not melt, but begins to decompose at 300°. A DTA (differential thermal analysis) exotherm was observed at 325°. It has a crystal density of 1.75 g./ml. and a drop weight impact sensitivity of 320 cm. (4).



I



II

2,4,6-tris(Picrylnitramino)-*s*-triazine (II).

2,4,6-tris(Picrylamino)-*s*-triazine (I) (1.0 g., 0.0013 mole) was added to 8 ml. of 100% nitric acid in 20 ml. of acetic anhydride with stirring at 20°. One ml. of acetyl chloride was added and the temperature was controlled at 50° for 1 hour. After the mixture had been chilled in the freezer for 2 hours the crystals were collected by filtration and dried in a vacuum desiccator over silica gel and sodium hydroxide at 0.02 mm. for 3 hours. The product, 1.10 g. (95%) decomposes rapidly at temperatures above 100° and slowly at 0°; therefore, the elemental analysis and physical property determinations had to be performed immediately after the isolation of the product.

Anal. Calcd. for $C_{21}H_6N_{18}O_{24}$: C, 28.20; H, 0.68; N, 28.19. Found: C, 28.31; H, 1.39; N, 27.17.

The compound has a crystal density of 1.73 g./ml. and a drop weight impact sensitivity of 49 cm.

2,4,6-tris(3,5-Dichloroanilino)-*s*-triazine (III).

Cyanuric chloride (9.22 g., 0.05 mole) and 3,5-dichloroaniline (48.6 g., 0.30 mole) were refluxed in 350 ml. of chlorobenzene for 16 hours. After cooling the mixture the solid was collected by filtration, washed with benzene, air dried, washed with 2% hydrochloric acid, then with water and dried. One recrystallization from *N,N*-dimethyl formamide gave 24.0 g. (86%) of product, m.p. 283-284°.

Anal. Calcd. for $C_{21}H_{12}Cl_6N_6$: C, 44.95; H, 2.16; N, 14.98. Found: C, 44.83; H, 2.57; N, 14.89.

2,4,6-tris(2,4,6-Trinitro-3,5-dichloroanilino)-*s*-triazine (IV).

2,4,6-tris(3,5-Dichloroanilino)-*s*-triazine (III) (2.0 g., 0.0036 mole) was added to 12 ml. of 30% fuming sulfuric acid and the resulting solution was stirred at 85° for 1.5 hours. The solution was cooled in an ice bath while 18 ml. of 100% nitric acid was added at below 65°. The resulting mixture was heated at 100° for 16 hours, cooled to 25°, and poured over 300 g. of crushed ice. The solid was collected by filtration, washed with water and dried to give 3.03 g. (88%) of product which was recrystallized from ethanol-water. The product decomposes without melting at 300° and has a crystal density of 1.77 g./ml.

Anal. Calcd. for $C_{21}H_3Cl_6N_{15}O_{18}$: C, 26.11; H, 0.31; N, 21.75. Found: C, 26.17; H, 0.79; N, 21.41.

Amination of IV.

2,4,6-tris(2,4,6-Trinitro-3,5-dichloroanilino)-*s*-triazine (IV) (1.0 g., 0.00103 mole) was dissolved in 100 ml. of formamide in a pressure vessel and the solution was saturated with ammonia at 0°. The vessel was capped and allowed to shake at 25° for 16 hours. The solid which precipitated was collected by filtration, washed with water and dried. The yield was 0.76 g. (95%) of 1,3,5-triamino-2,4,6-trinitrobenzene, which was identified by comparing its infrared spectrum with that of an authentic sample and by its elemental analysis.

Anal. Calcd. for $C_6H_6N_6O_6$: C, 27.92; H, 2.34. Found: C, 27.93; H, 2.46.

REFERENCES

(1) This work was performed under the auspices of the U. S. Atomic Energy Commission.

(2) N. V. Koslova, D. F. Kutepov, D. N. Khokhlov, and A. I. Kyrmova, *Zh. Obshch. Khim.*, 33, 3303 (1963).

(3) Microanalyses by M. J. Naranjo. Crystal densities by Marion L. Clancy. Drop weight impact sensitivities by C. E. Hannaford. All melting points are corrected.

(4) All drop weight impact sensitivities were determined with a 2.5 kg. weight. The 50% points of several common explosives are: PETN, 11 cm; RDX, 23 cm; TNT, 160 cm.

Received June 23, 1966 Los Alamos, New Mexico 87544