tricyanmelamine trihydrate possesses a hexagonal unit of structure with a_0 = 10.23 Å., c_0 = 5.56 Å., containing $2Na_3C_6N_9 \cdot 3H_2O$, space-group $D^4_{3h} - C\bar{6}2c$. The tricyanmelamine ions pack together with water molecules in symmetry planes to form atomic layers which are equally spaced perpendicular to the hexagonal axis. These negatively charged layers are bound together by sodium ions (Fig. 1) each of which is octahedrally surrounded by four nitrogen and two oxygen atoms at distances agreeing with the sums of the respective ionic radii. Packing relations within this structure and the stereochemistry of the anion are compared with the corresponding data for cyanuric triazide. The stabilities of both anion and crystal are reflected in the compact and generally satisfactory nature of the structure.

ITHACA, N. Y. RECEIVED MARCH 10, 1938

[A CONTRIBUTION FROM THE PEARSON MEMORIAL LABORATORY OF TUFTS COLLEGE]

Certain Halogen and Nitro Derivatives of 3-Anilino-5-phenylisoxazole and Pyrazole

BY DAVID E. WORRALL

It was shown in a previous communication[1] that the substances obtained from phenylpropiol thioanilide by interaction with hydroxylamine and hydrazine react easily with bromine and nitric acid. Since 3,5-diphenylisoxazole does not react even with fuming nitric acid,[2] it was assumed that substitution took place solely in the aniline group, an assumption that since has been found untenable by comparison with a derivative of known structure.

The thioamide obtained from *p*-bromophenyl isothiocyanate forms an isoxazole isomeric and not identical with that resulting from the action of bromine on anilinophenylisoxazole. Furthermore, it was discovered that 2,4-dibromoaniline as well as benzoic acid could be isolated from the oxidation products of the tribromo derivative of anilinophenylpyrazole. Substitution must start with the isoxazole (or pyrazole) ring and at position four as it is otherwise stripped of hydrogen, subsequently involving the aniline group. Consequently, the substances previously reported as 3-*p*-bromoanilino-5-phenylisoxazole and 3-(2,4,-6-tribromoanilino)-5-phenylpyrazole actually are 3-anilino-4-bromo-5-phenylisoxazole and 3-(2,4-dibromoanilino)-4-bromo-5-phenylpyrazole. It follows that similar changes should be made with the nitro derivatives. The compounds previously listed as 3-(2,4-dinitroanilino)-5-phenylisoxazole and 3-(2,4,6-trinitroanilino)-5-phenylpyrazole should be recorded as 3-(4-nitroanilino)-4-nitro-5-phenylisoxazole and 3-(2,4-dinitroanilino)-4-nitro-5-phenylpyrazole.

Experimental

Phenylpropiol Thio-4-bromoanilide.—This substance was prepared using the customary technique[1] from 0.2 gram mole of *p*-bromophenyl isothiocyanate. The product, thoroughly washed with cold alcohol, amounted to about 50 g. A small portion was crystallized from benzene, separating as bright yellow needles, melting with decomposition at 132–133°. No polymer formation was observed. *Anal.* Calcd. for $C_{15}H_{10}NSBr$: Br, 25.3. Found: Br, 25.6.

3-(4-Bromoanilino)-5-phenylisoxazole.—Ten grams of the crude was added in small lots to a boiling alcoholic solution containing an excess of hydroxylamine. The precipitate thrown out by an equal volume of water was crystallized first from ethylene chlorohydrin, then twice from alcohol; final yield, 2.4 g. of colorless flat needles melting at 180–181°. *Anal.* Calcd. for $C_{15}H_{11}ON_2Br$: Br, 25.4. Found: Br, 25.5.

3-(2,4-Dibromoanilino)-4-bromo-5-phenylisoxazole was obtained by bromination in chloroform of the monobromide. The same substance resulted when the isomeric monobromo derivative and the original non-bromine containing isoxazole were mixed with an excess of bromine. An insoluble substance formed in all cases which blackened and lost hydrogen bromide on contact with wet solvents, but which dissolved in boiling alcohol with only a transitory color, separating out almost immediately as colorless, hair-like crystals, m. p. 176°. *Anal.* Calcd. for $C_{15}H_9ON_2Br_3$: Br, 50.8. Found: Br, 50.7.

3-(2-Chloro-4-bromoanilino)-4-chloro-5-phenylisoxazole was prepared by the chlorination of the bromo derivative. It was isolated from alcohol in the form of small needles, m. p. 163°. *Anal.* Calcd. for $C_{15}H_9ON_2BrCl_2$: Cl, 18.5. Found: Cl, 18.6.

3-(4-Bromoanilino)-4-nitro-5-phenylisoxazole.—By nitration slender yellow needles were obtained, sparingly soluble in alcohol, m. p. 163–164°. *Anal.* Calcd. for $C_{15}H_{10}O_3N_3Br$: Br, 22.2. Found: Br, 21.8.

3-(4-Nitroanilino)-4-bromo-5-phenylisoxazole.—Nitration of the nuclear brominated isoxazole produced this isomer which separated from glacial acetic acid as small

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[1] Worrall, THIS JOURNAL, **59**, 933 (1937).

[2] Wislicenus, *Ann.*, **308**, 249 (1899).

yellow needles, m. p. 182–183° with preliminary softening. *Anal.* Calcd. for $C_{15}H_{10}O_3N_3Br$: Br, 22.2. Found: Br, 22.5.

3-(4-Bromoanilino)-5-phenylpyrazole.—The new pyrazole was prepared with hydrazine in a manner similar to that used for the isoxazole. The product after crystallization from chlorohydrin was dissolved in boiling alcohol and concd. hydrochloric acid added dropwise. The resulting colorless precipitate, filtered while warm, was washed thoroughly with water; yield 4–5 g. It separated from dilute alcohol as lustrous small plates, m. p. 176–177°. *Anal.* Calcd. for $C_{15}H_{12}N_3Br$: Br, 25.5. Found: Br, 25.4. Bromine changed this substance into a tribromo derivative identical with that obtained from the non-halogenated pyrazole. Oxidation of this tribromo derivative in one instance using permanganate produced a small amount of material, probably the monoanilide of oxalic acid, soluble in alkali and precipitated by acid, m. p. approx. 130° with foaming. It was decomposed by boiling with dilute acid into 2,4-dibromoaniline identified by a mixed melting point and oxalic acid.

3 - (2 - Chloro - 4 - bromoanilino) - 4 - chloro-5-phenylpyrazole was prepared by the action of chlorine on the above pyrazole. It separated from alcohol as needles, m. p. 197–198°. *Anal.* Calcd. for $C_{15}H_{10}N_3BrCl_2$: Cl, 18.6. Found: Cl, 18.5. A nitro derivative was obtained from the pyrazole, but because of a poor analysis is not listed.

Summary

It has been shown that 3-anilino-5-phenylisoxazole and pyrazole form substitution products with chlorine or bromine and nitric acid in which position four of the heterocyclic ring and positions two and four of the aniline group are involved.

MEDFORD, MASS. RECEIVED FEBRUARY 28, 1938

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

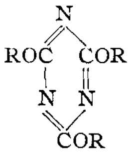
β-Methoxy-β-mesitylacrylonitriles

BY REYNOLD C. FUSON, G. E. ULLYOT AND A. J. GEHRT

β-Alkoxyacrylonitriles (I) are little known, and no general method is available for their preparation. The present paper reports the synthesis of certain β-methoxy-β-mesitylacrylonitriles and gives a proof of their structures. This study was initiated with the hope of throwing some light on the behavior of the vinylogous alkyl cyanates (II) which have never been isolated. Apparently the cyanates trimerize rapidly to give alkyl cyanurates (III).

$RO—CH═CH—CN$ I

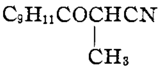
$ROCN$ II



III

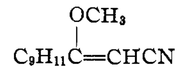
The method of synthesis is due to the discovery of Kohler and his co-workers[1] that the mesityl group favors O-alkylation. It was found, in fact, that α-cyanoacetomesitylene (IV) and α-cyanopropiomesitylene (V) gave exclusively O-methylation products.

$C_9H_{11}COCH_2CN$ IV



$C_9H_{11}CO\underset{CH_3}{\underset{|}{C}}HCN$

V



$C_9H_{11}\overset{OCH_3}{\overset{|}{C}}═CHCN$

VI (a, b, c)

While the mesityl group on the β-carbon atom would be expected to inhibit addition to the olefinic linkage, it was thought that the reactions due to the cyano group and to the methoxyl group might resemble those ascribed to methyl cyanates. This expectation was, however, not realized; the β-methoxy-β-mesitylacrylonitriles are very stable and, in particular, show no tendency to polymerize.

The unsubstituted β-mesityl-β-methoxyacrylonitriles (VI) were made by methylation of α-cyanoacetomesitylene prepared by the method of Fuson and Beveridge.[2] The reaction was carried out by two different procedures. The first involved the use of methyl sulfate in aqueous potassium hydroxide. It yielded two forms of the enol ether which melted at 66° (VIa) and 82.5–83.5° (VIb).

The second method of methylation consisted in treating IV with methyl iodide and silver oxide. Here, also, the product consisted of the isomers VIa and VIb. Under certain circumstances these forms appeared as a solid solution melting at 67–68° (VIc). For example, when a mixture of equal amounts of VIa and VIb was fused and then dissolved in high-boiling petroleum ether and the solution allowed to cool, the crystals which formed consisted entirely of VIc.

Treatment with alcoholic hydrochloric acid converted VIb and VIc into VIa. These three forms of the enol ether (VIa, VIb, VIc) when

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[1] Kohler, Tishler and Potter, THIS JOURNAL, **57**, 2517 (1935); Kohler and Potter, *ibid.*, **58**, 2166 (1936); Kohler and Thompson, *ibid.*, **59**, 887 (1937).

[2] Fuson and Beveridge, *ibid.*, **53**, 1985 (1931).