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SYNTHESIS OF 3-AMINOBENZO-1,2,4-TRIAZINE 4-OXIDES

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o-Quinone monooxime guanylhydrazones, obtained from copper complexes of o-nitrosophenols, are cyclized to give the previously unknown 3-aminobenzo-1,2,4-triazine 4-oxides.

1,2-Naphthoquinone oxime guanylhydrazones, obtained from α-nitroso-β-naphthol or β-nitroso-α-naphthol and aminoguanidines, are readily cyclized to the corresponding 2-aminonaphtho[1,2-*l*]-1,3,4-triazine 1-oxides and 3-aminonaphtho[2,1-*l*]-1,2,4-triazine 4-oxides [1]. Compounds of this sort were not formed from o-nitrosophenol and 4-nitrosoresorcinol. However, we did synthesize o-benzoquinone monooxime guanylhydrazones from copper complexes of o-nitrosophenols [2]. These guanylhydrazones were easily converted to the previously undescribed 3-aminobenzo-1,2,4-triazine 4-oxides (I-IV, Table 1). Compound V was obtained from the readily accessible potassium salt of 2-nitroso-4-methylphenol and aminoguanidine sulfate without isolation of o-toluquinone monooxime guanylhydrazone, which is unstable at high temperatures.

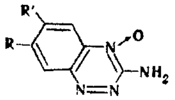
The IR spectra of triazines I-V contain intense absorption bands of the triazine C = N bond (1620-1650 cm^{-1} [3] and the N→O bond of heterocyclic compounds (1350-1370 cm^{-1}) [4]. Bands of an NH_2 group are present at 3000-3400 cm^{-1} [4].

The slow conversion of the stable copper complexes to the less stable free o-nitrosophenols, which react with excess aminoguanidine, promotes the formation of the guanylhydrazones.

EXPERIMENTAL

3-Aminobenzo-1,2,4-triazine 4-Oxides (I-IV). A 10-mmole sample of the copper complex of o-nitrosophenol was shaken at room temperature for 100 h with 70 ml of water, 40 ml of alcohol, 10 ml of 56%

TABLE 1. 3-Aminobenzo-1,2,4-triazine 4-Oxides



Compound	R	R′	mp, °C (aqueous ethanol)	Empirical formula	Found, %		Calc., %		λ_{max}, nm	lg ε	Yield, %
					N	hal	N	hal			
I	H	Cl	214—215	$C_7H_5N_4ClO$	28,4	17,8	28,4	18,1	260	4,70	75
II	CH_3	Cl	215	$C_8H_7N_4ClO$	26,5	16,9	26,6	16,9	260	4,68	92
III	H	Br	222—223	$C_7H_5N_4BrO$	23,1	32,7	23,2	33,1	260	4,59	73
IV	CH_3	Br	225	$C_8H_7N_4BrO$	21,6	31,5	21,9	31,4	265	4,66	80
V	H	CH_3	211	$C_8H_8N_4O$	31,9	—	31,8	—	255	4,71	76

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HNO_3, and 3.44 g (25 mmole) of aminoguanidine nitrate. The resulting yellow precipitate was removed by filtration and washed with a small amount of water. The yields of o-benzoquinone monooxime guanylhydrazone nitrates ranged from 80 to 95%. A 1.5-g sample of the appropriate hydrazone was heated with stirring in 150 ml of water to 70°, after which the hot mixture was filtered, and the filtrate was heated at 80-90° for 15-20 min. The filtrate was then cooled and filtered to give I-IV.

6-Methyl-3-aminobenzo-1,2,4-triazine 4-Oxide (V). A 1.75-g (10 mmole) sample of the potassium salt of 2-nitroso-4-methylphenol was heated with stirring at 50° with 25 ml of water, 25 ml of alcohol, and 2.64 g (10 mmole) of aminoguanidine sulfate for 15 min, after which the mixture was heated at 80° for 30 min. The product was isolated by filtration of the cooled mixture. Found: C 54.3; H 4.7%. $C_8H_8N_4O$. Calculated: C 54.5; H 4.5%.

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