4-BROMO-5-(4'-HYDROXYMETHYLTRIAZOLYL)PYRIDAZIN-3-ONE AND ITS DERIVATIVES

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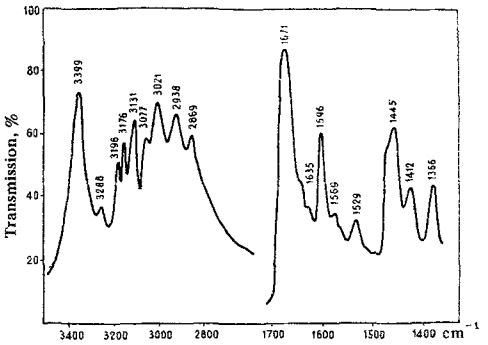
4-Bromo-5-(4'-hydroxymethyltriazolyl)pyridazin-3-ones have been obtained for the first time by the reaction of 5-azido-4-bromopyridazin-3-ones with propargyl alcohol. They have been converted into 4-bromo-5-(4'-halogenomethyltriazolyl)pyridazin-3-ones.

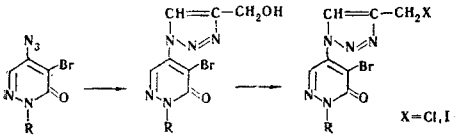
Since many pyridazinone derivatives possess herbicidal and plant growth stimulating properties, it appeared of interest to obtain and study the chemical properties of triazolylpyridazinones and to test their biological activity.



IR Spectrum of the hydroxymethyltriazolylpyridazinone IIa.

By the reaction of 4,5-dibromopyridazin-3-ones with sodium azide we have [1, 2] obtained 5-azido-4-bromopyridazin-3-ones, the properties of which have been studied in more detail in the present work. Like the alkyl and aryl azides [3–8] they take part in addition reactions with unsaturated compounds.

When 5-azido-4-bromopyridazin-3-one (Ia) was heated with propargyl alcohol in dioxane solution, the hydroxymethyltriazolylpyridazinone (IIa) was obtained. A similar reaction takes place with other derivatives of 5-azido-4-bromopyridazin-3-one (see table). On the basis of the structural features of the azido group and literature information [6–8] we assume that the hydroxymethyl group is present on the fourth carbon atom of the triazole ring.



I II a–e III a–d

a R=H; b R=CH$_3$; c R=C$_6$H$_5$; d R=CH$_2$CH$_2$CN; e R=CH$_2$CH$_2$OH

The IR spectra of IIa exhibit the absorption band of an amide carbonyl at 1671 cm^{-1}, and in the 3300–2870 cm^{-1} region there is a broad absorption band of medium intensity extending over several peaks which we ascribe to the absorption of NH groups. The band of the azido group has disappeared and at 3399 cm^{-1} there is the absorption band of a hydroxyl group (see figure).

The 4-bromo-5-(4'-hydroxymethyltriazolyl)pyridazin-3-ones (II) readily react with thionyl chloride to form 4'-chloromethyl derivatives (III, X = Cl), and when these are treated with potassium iodide the chlorine atom is replaced by iodine; they also take part in nucleophilic substitution reactions, and a subsequent paper will be devoted to these.

EXPERIMENTAL

4-Bromo-5-(4'-hydroxymethyltriazolyl)pyridazin-3-one (IIa). A mixture of 1.1 g (~5 mM) of 5-azido-4-bromopyridazin-3-one (Ia)

4-Bromo-5-(4'-hydroxymethyltriazolyl)pyridazin-3-ones and Their Derivatives

Compound	Mp, °C	Empirical formula	Found, %		Calculated, %		ν, cm^{-1}		Yield, %
			Br	N	Br	N	CO	OH	
IIb	159–160	$C_8H_8BrN_5O_2$	27.88	24.36	27.93	24.48	1631	3405	82
IIc	151–152	$C_{13}H_{10}BrN_5O_2$	22.95	20.14	22.95	20.11	1651	3314	82
IId	115–116	$C_{10}H_9BrN_6O_2$	24.51	26.10	24.58	25.85	1630	3414	52
IIe	149–151	$C_9H_{10}BrN_5O$	25.38	22.31	25.27	22.15	1641	3394 3284 3161	80
IIIb	106–107	$C_8H_7BrClN_5O$*	26.20	22.87	26.24	22.99	—	—	80
IIIc	186	$C_{13}H_9BrClN_5O$**	21.87	19.32	21.79	19.10	—	—	86
IIIe	107–108	$C_{10}H_8BrClN_6O$***	23.02	24.61	23.25	24.46	—	—	70

*Found, %: Cl 11.60. Calculated, %: Cl 11.64.
**Found, %: Cl 9.70. Calculated, %: Cl 9.66.
***Found, %: Cl 10.21. Calculated, %: Cl 10.31.

and 2 ml (~40 mM) of propargyl alcohol was heated to the boil in dioxane solution for 6 hr. After cooling, the precipitate that had deposited was recrystallized from dioxane, giving 1.1 g (81%) of IIa in the form of a crystalline product with mp 204° C. Found, %: C 31.14; H 2.40; Br 29.34; N 25.71. Calculated for $C_7H_6BrN_5O_2$, %: C 30.88; H 2.21; Br 29.41; N 25.73. The other 4-bromo-5-(4'-hydroxymethyltriazolyl)-pyridazin-3-ones (IIb–IIe, see table) were obtained similarly.

4-Bromo-5-(4'-chloromethyltriazolyl)pyridazin-3-one (IIIa, X = = Cl). A mixture of 0.3 g of IIa and an excess of thionyl chloride was heated to the boil for 2 hr and was poured onto ice. After recrystallization from dilute dioxane (2 : 1), 0.25 g (86%) of crystalline IIIa (X = Cl) was obtained with mp 196–197° C (decomp.). Found, %: Br 27.58; Cl 12.23; N 24.07. Calculated for $C_7H_5BrClN_5O$, %: Br 27.51; Cl 12.20; N 24.10. The other 4-bromo-5-(4'-chloromethyltriazolyl)pyridazin-3-ones (IIIb–IIId, X = Cl, see table) were obtained similarly.

4-Bromo-5-(4'-iodomethyltriazolyl)-2-phenylpyridazin-3-one (IIIc, X = I). To a solution of 0.4 g (~1 mM) of IIIc (X = Cl) dissolved in 15 ml of hot dioxane was added a solution of 0.4 g (~2.4 mM) of potassium iodide in 5 ml of water. This mixture was heated to the boil for 10 min and was then poured into water. The precipitate was recrystallized from dilute dioxane, giving 0.4 g (83%) of colorless crystals of IIIc (X = I), mp 200–201° C (decomp). Found, %: N 15.16. Calculated for $C_{13}H_9BrIN_5O$, %: N 15.29.

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