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SOME REACTIONS OF 3 - MERCAPTO - 6 - P– BROMOPHENYL - PYRIDAZINE

By

F. M. Abd - El - Motti

National Research Centre, Dokki, Cairo, Egypt.

ABSTRACT

The synthesis of N - imido -, 1, 3, 4 - oxadiazole and other derivatives of p - bromophenyl - 3 - mercaptopyridazine are reported. The structures of these compounds are established on the bases of elemental analysis, IR ^{1}H-NMR and mass spectoscopy.

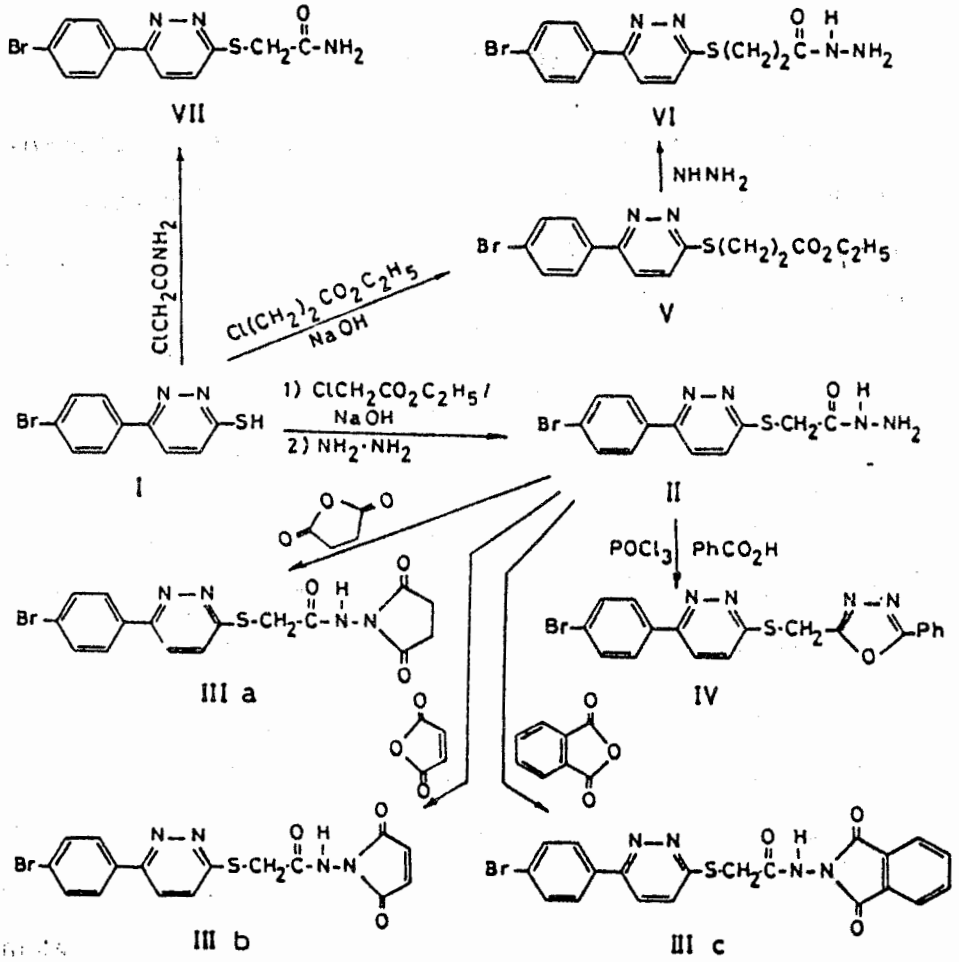
INTRODUCTION

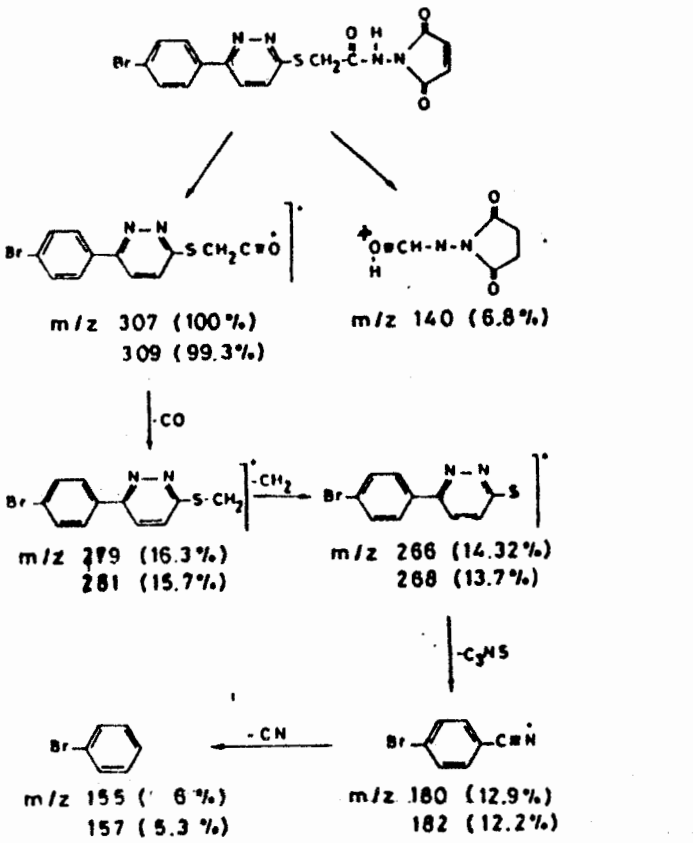
The fact that many pyridazine derivatives were established as chemotherapeutic agents[1], insecticides[2], bactericides, fungicides and herbicides[3] has led us to synthesize some of their new derivatives.

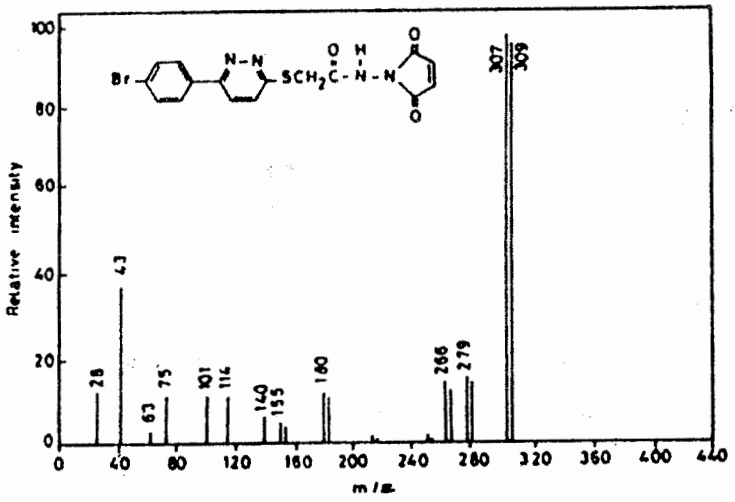
The N - imido - derivatives IIIa - c were obtained by treating the hydrazide II[4, 5] with succinic, maleic or phthalic anhydrides, respectively. The IR spectra of IIIa - c showed strong absorption bands at 1750 - 1620 cm^{-1} (2 CO) and 3200 - 3100 cm^{-1} (NH). The mass spectrum of compound III_b did not show the molecular ion peak M^+ at m / z 419, which shows that

it possesses a very low stability towad electron impact. It also showed a base peak at m / z 307, 309 (100, 99.3 %) which indicates the presence of a bromine atom in the molecule.

On heating a mixture of the hydrazide II, benzoic acid and $POCl_3$ [6 - 8] compound IV was obtained. The IR spectrum of IV revieled the absence of the carbonyl group and absorption bands at 1625 cm^{-1} (C = N) and 1130 - 1035 cm^{-1} (C - O - C).




m/z 307 (100%)
309 (99.3%)
m/z 140 (6.8%)
-CO
-CH2
m/z 279 (16.3%)
281 (15.7%)
m/z 266 (14.32%)
268 (13.7%)
-C3NS
-CN
m/z 155 (6 %)
157 (5.3 %)
m/z 180 (12.9%)
182 (12.2%)


Relative intensity
m/z
307
309
43
28
75
101
116
140
155
180
266
279

The ethylpropionate V and its acid hydrazide VI were obtained by reaction of the corresponding 3 - mercaptopyridazine I with ethyl chloropropionate[4, 5] and then on treating the ethyl ester V with hydrazine hydrate compound VI was obtained. The ^1H - NMR spectrum of VI showed signals at δ 3.5 (4H, m, $2CH_2$), δ 4.2 (2H, s, NH_2), δ 7.6 (4H, m, Ar - H), δ 8.2 (2H, d, H - pyridazine) and δ 9.1 (1H, b. s. NH).

The acid amide VII was obtained in a good yield from the reaction of 3 - mercaptopyridazine. I with chloroacetamide. The IR spectrum VII showed amide carbonyl band at 1630 cm^{-1} and sharp doublet at 3300 and 3150 cm^{-1} (NH_2).

EXPERIMENTAL

The melting points are uncorrected. IR spectra were recorded (KBr) on a Pye Unicam SP. 1000 Spectrophotometer. Microanalytical data were obtained from microanalytical lab. N. R. C Cairo Mass spectrum was run at 70 e.v. using Finigan Mass Spectrometer.

S - (6 - p - Bromophenylpyridazine - 3 - yl -) thioglycolic acid amide - N - (Succinimido -, maleinimido - or phthalimido) (IIIa - c) :

On addition of succinic, maleic or phthalic anhydride (0.01 mole) to a solution of the hydrazide II (0.01 mol) in dry xylene and the reaction mixture was heated under reflux for 2h, a white precipitate was formed then, filtered off. The product was recrystallized from the proper solvent.

2 - [S - (6 - p - Bromophenylpyridazine - 3 - yl)] - thiomethyl - 1, 3, 4 - oxadiazol - 5 - phenyl (IV) :

A mixture of the hydrazide II (0.05 mol) and benzoic acid (0.05 mol) in $POCl_3$ (5 ml) was refluxed for 2 h. The reaction mixture was slowly added to ice - water. The solid formed was filtered off, washed with water and recrystallized from ethanol.

Ethyl β - [S - (6 - p - Bromophenylpyridazine - 3 - yl)] - thiopropionate V and its corresponding hydrazide VI :

To a solution of I (0.1 mol) in ethanolic sodium hydroxide solution (0.01 mole NaOH in 50 ml ethanol) ethyl cholropropionate (0.01 mole) was added. A white precipitate was formed. The reaction was completed by warming on a water bath for 2 h. After removal of the solvent, the residual solid was recrystallized from Pet. ether 40 - 60 to give V. On refluxing a mixture of V (0.01 mol) and hydrazine hydrate (0.015 mol) in 100 ml abs. ethanol for 2 h, the acid hydrazide VI was obtained. The solid formed was filtered off washed with water, dried and recrystallized from ethanol.

S-(6-p-Bromophenylpyridazine-3-yl)-thioglycolamide VII :

To a solution of I (0.01 mol) in ethanolic sodium hydroxide (0.01 mol NaOH in 50 ml abs. ethanol) chloroacetamide (0.01 mol) was added. After heating under reflux for 2 h, the reaction mixture was cooled. The solid precipitate was collected by filteration washed several times with water, dried and recrystallized from ethanol.

Table I. Physical and analytical data of the new compounds.

Comp. No.	Yield %	m.p °C	Solvent of cryst.	Mol. Formula Mol.wt.	Analysis Calc/Found C	H	N
III_a	85	223	n.butanol	$C_{16}H_{13}BrN_4O_3S$	45.61	3.09	13.30
				421	44.90	3.20	12.46
III_b	80	216	ethanol	$C_{16}H_{11}BrN_4O_3S$	45.82	2.62	13.37
				419	45.70	2.60	12.88
III_c	85	23-	n.butanol	$C_{20}H_{13}BrN_4O_3S$	51.17	2.77	11.94
				469	51.10	2.77	12.18
IV	62	236	ethanol	$C_{19}H_{13}BrN_4OS$	53.65	3.06	13.18
				425	53.10	2.70	12.80
V	70	95	Pet.ether	$C_{15}H_{15}BrN_2O_2S$	49.05	4.09	7.63
			40-60	367	49.70	4.40	7.31
VI	75	194	methanol	$C_{13}H_{13}BrN_4OS$	44.19	3.64	15.86
				353	44.50	3.00	15.15
VII	90	212	ethanol	$C_{12}H_{10}BrN_3OS$	45.61	3.09	12.96
				324	44.90	3.20	12.51

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Some Reactions of 3- Mercapto - 6-P- Bromophnyl - Pyridazine

بعض التفاعلات لمشتق ٣ - مركابتو - بارا - بروموفينيل - بيريدازين

فايزة محمد عبد المعطى

المركز القومى للبحوث - دقى - القاهرة - مصر

يشمل هذا البحث تحضير مشتقات ن - إميدو ١، ٣، ٤ - أوكساديازول - ٥ - فينيل، استرالبربيونات، الهيدرازيد المقابل لهذه الاستر والأميد لمركب ٣ - مركابتو - بارا - بروموفينيل بيريدازين. وقد ثبت صحة الصيغة التركيبية للمركبات الناتجة بواسطة التحاليل الدقيقة وطيف الأشعة تحت الحمراء والرنين النووى المغناطيسى وطيف الكتلة.