SYNTHESIS OF SOME N-TRIAZINEBENZOXAZOLINONES AND S-TRIAZINE-BENZOXAZOLYLSULFIDES

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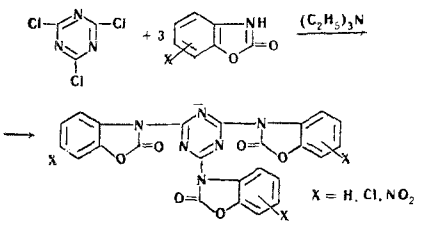
Tris(benzoxazolinonyl)triazines are obtained from cyanuric chloride and benzoxazolinone. Mercaptobenzoxazoles are converted to tris (benzoxazolylsulfido)triazines. The sodium salts of benzoxazolinone and mercaptobenzoxazole react with cyanuric chloride to give respectively mono(benzoxazolinyl)dichlorotriazines and mono(benzoxazolylsulfido)dichlorotriazines. The latter react with aliphatic amines to give benzoxazolonyldiamidotriazines or benzoxazolonylamidochlorotriazines, depending on the ratios of the reactants. Monobenzoxazolonyldichlorotriazines are fungicides for Botritis cinerea.

In continuation of a systematic study of the relationship between pesticidal properties of derivatives of benzoxazolinones and benzoxazolinylthones (mercaptobenzoxazoles) and chemical structure [1], we planned to synthesize compounds with both benzoxazole and triazine systems in the molecule.

Investigation of these compounds is of interest as many substituted triazines are widely used as herbicides [2], and 2, 4-dichloro-6-O-chloroanilino-sym-triazine is used as a fungicide [3].

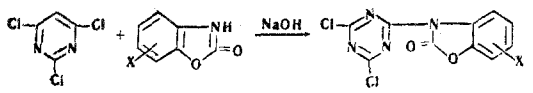
Depending on the hydrogen chloride acceptor, reaction of cyanuric chloride with benzoxazolinones gives mono- and trisbenzoxazolonyltriazines.

The tris substitution products were obtained by reacting cyanuric chloride with benzoxazolinones and triethylamine in dioxane.



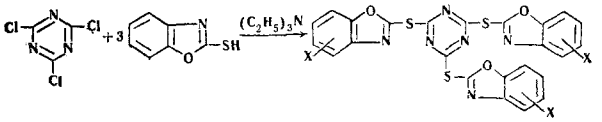
Use of pyridine as the acceptor obviously caused opening of the triazine ring. Use of acetone as the solvent in the reaction led to formation of mixtures containing, judging by their IR spectra, alkyltriazinyl compounds. The appearance in the IR spectra of maxima corresponding to alkyl groups can be explained by the known splitting of triethylamine by cyanuric chloride [4], or by formation of acetone enol esters.

We have prepared monobenzoxazolonyldichlorotriazines by adding an aqueous solution of a sodium salt of benzoxazolinones to a suspension of cyanuric chloride in aqueous dioxane.



Under the same conditions reaction of monobenzoxazolonyldichlorotriazines with aliphatic amines gives benzoxazolonyldiamidotriazines or benzoxazolonylamidochlorotriazines, depending on the ratio of the reactants. Amidodichlorotriazines and diamidochlorotriazines do not react with the sodium salt of benzoxazolinone, and do not react with benzoxazolinone in the presence of triethylamine.

Benzoxazolinthiones (mercaptobenzoxazoles) react with cyanuric chloride and triethylamine in the same way as benzoxazolinones, to give tris(benzoxazolylsulfido)triazines.



Reaction of sodium salts of benzoxazolinthiones (mercaptobenzoxazoles) with cyanuric chloride gives mainly mono(benzoxazolylsulfido)dichlorotriazines. Treatment of the sodium salt of 5-chlorobenzoxazolinthione (5-chloromercaptobenzoxazole) with cyanuric chloride gives a mixture that is difficult to separate, but from which bis(benzoxazolylsulfido)chlorotriazine and mono(benzoxazolylsulfido)dichlorotriazine are obtained.

In the present paper the formulas of triazinyl-substituted benzoxazolinones, where the triazine ring is linked to nitrogen of the benzoazolinone, are based on previous research [5], and confirmed by IR spectra, which show a marked maximum corresponding to the C=O group. Obviously triazinyl derivatives of benzoxazolinthiones (mercaptobenzoxazoles) are mainly formed from mercapto forms of benzoxazolinthiones [6], but the IR spectra of the end products show that both thiol and thione forms react.

Results of tests on the pesticidal properties of the compounds synthesized show that both benzoxazolonyldichlorotriazines and benzoxazolylsulfidodichlorotriazines are fungicidal for Botritis cinerea. Most active is 2, 4-dichloro-6-(6-chlorobenzoxazolin-2'-one-3'-yl)-sym-triazine.

Tris-substituted triazine do not show pesticidal properties.

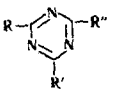
EXPERIMENTAL

a) 18.4 g (0.1 mole) Cyanuric chloride in 100 ml dioxane was put in a flask, and stirred and heated to 48°–50° C. Then 0.3 mole of the appropriate benzoxazolone or mercaptobenzoxazole plus 0.3 mole Et_3N in 75 ml dioxane was added dropwise, and the mixture left for 2 hr at room temperature.

Precipitates of substituted 2, 4, 6-tris(benzoxazol-2'-on-3'-yl)-sym-triazines or 2, 4, 6-tris(benzoxazolyl-2'-sulfido)triazines formed, and further quantities were obtained by vacuum evaporation of the mother liquors. The reaction products were purified by washing with

Table

Derivatives of the Symmetric Triazine



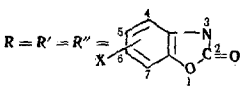
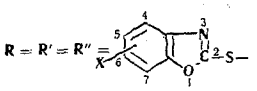
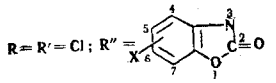
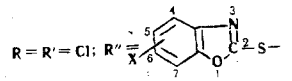
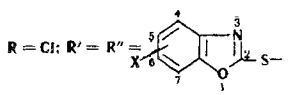
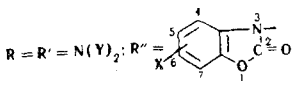
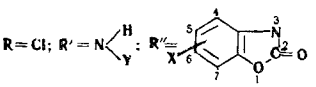
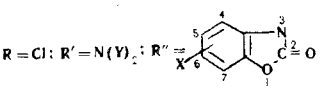
Experiment no.	X	Mp, °C	Formula	Found, %		Calculated, %		Yield, %
				N	Cl	N	Cl	
1	2	3	4	5	6	7	8	9
								
1*	H	312—314	$C_{24}H_{12}N_6O_6$	—	—	—	—	76.9
2	6-Cl	340—344	$C_{24}H_9Cl_3N_6O_6$	—	18.43	—	18.10	61.3
3	5-Cl	—	$C_{24}H_9Cl_3N_6O_6$	—	18.03 17.93	—	18.10	48.4
4	6-NO_2	276—277	$C_{24}H_9N_9O_{12}$	20.69 20.65	—	20.48		80
5	5-NO_2	262—263	$C_{24}H_9N_9O_{12}$	21.18	—	20.48	—	67
								
6	H	244—246	$C_{24}H_{12}N_6O_3I_3$	15.41	—	15.90	—	61
7	5-Cl	285—286	$C_{24}H_9Cl_3N_6O_3I_3$	—	16.99 17.01	—	16.90	88
8*	5-NO_2	205—206	$C_{24}H_9N_9O_9I_3$	—	—	—	—	44

Table (cont'd)

1	2	3	4	5	6	7	8	9
			R = R' = Cl; R'' = 					
9	H	253—255	$C_{10}H_4Cl_2N_4O_2$	19.80 19.43	24,40 24.53	19.7	24.38	84.4
10	6-Cl	219—220	$C_{10}H_3Cl_3N_4O_2$	17.10 17.38	33.08 33.24	17.6	33.5	90
11	5-Cl	—	$C_{10}H_3Cl_3N_4O_2$	17.79 17.66	—	17.6	—	65
			R = R' = Cl; R'' = 					
12*	H	—	$C_{10}H_4Cl_2N_4OS$	—	—	—	—	63
13*	5-Cl	—	$C_{10}H_3Cl_3N_4OS$	—	—	—	—	73.5
			R = Cl; R' = R'' = 					
14*	5-Cl	218—220	$C_{17}H_6Cl_3N_5O_2S_2$	—	21.72 21.63	—	22.2	77
			R = R' = N(Y)$_2$; R'' = 					
15	H Y = CH_3	175—176	$C_{14}H_{16}N_6O_2$	28.14 28.04	—	28.08	—	66.5
16	H Y = C_3H_7	210—215	$C_{22}H_{32}N_6O_2$	19.80 19.90	—	20.40	—	43
17	Y = *i*-C_3H_7	290—294	$C_{22}H_{32}N_6O_2$	20.99	—	20.40	—	48
18	H Y = *i*-C_4H_9	—	$C_{26}H_{40}N_6O_2$	18.65	—	18.01	—	44
19	6-Cl Y = CH_3	192—195	$C_{14}H_{15}ClN_6O_2$	—	10.68 10.51	—	10.60	57
			R = Cl; R' = N(H)(Y); R'' = 					
20	H Y = CH_3	265—269	$C_{11}H_5ClN_5O_2$	—	12.80 12.60	—	12.60	59
			R = Cl; R' = N(Y)$_2$; R'' = 					
21	H Y = CH_3	216—218	$C_{12}H_{10}ClN_5O_2$	—	11.90	—	12.20	77.5
22	H Y = C_2H_5	139—140	$C_{14}H_{14}ClN_5O_2$	—	10.41	—	11.10	43.5
23	H Y = C_3H_7	159—162	$C_{16}H_{18}ClN_5O_2$	—	11.00	—	10.20	67.2
24	6-Cl Y = CH_3	219—221	$C_{12}H_9Cl_2N_5O_2$	—	21.68 22.10	—	21.70	95

*For compound no. 1: found C 60.00; 60.24; H 2.45; 2.86%, calculated C 60.00; H 2.50%; no. 8: found S 15.07; 15.24%, calculated S 15.16%; no. 12: found S 9.59%, calculated S 10.70%; no. 13: found S 10.30; 10.45%, calculated S 9.59%; no. 14: found S 12.69; 12.90%, calculated S 13.2%.

water and repeated boiling with EtOH, and dried over P_2O_5 in a desiccator.

b) A solution of 18.4 g (0.1 mole) cyanuric chloride in dioxane was poured, with vigorous stirring, into ice water. Then, with cooling, 0.1 mole benzoxazolinone or mercaptobenzoxazole and 0.1 mole NaOH in 50 ml water were added with cooling, and the mixture left for 1 hr 30 min at 0°-2° C. The precipitate of 2, 4-dichloro-6-(benzoxazol-2'-on-3'-yl)-sym-triazine and 2, 4-dichloro-6-(benzoxazolyl-2'-sulfido)-sym-triazine was washed with water, recrystallized from dioxane, and dried in a desiccator over P_2O_5.

c) A solution of 2.83 g (0.01 mole) 2, 4-dichloro-6-(benzoxazol-2'-on-3'-yl)-sym-triazine or 2, 4-dichloro-6-(6-chlorobenzoxazol-2'-on-3'-yl)-sym-triazine in 80 ml dioxane was poured into well-stirred water at 18°-20° C. To the resultant suspension was added 0.02 mole of the appropriate amine, 0.02 mole NaOH in 30 ml water, and the whole heated for 12 hr at 90°-92° C. The precipitate of 2, 4-bisamino-6-(benzoxazol-2'-on-3'-yl)sym-triazine was washed with water, recrystallized from dioxane, and dried over P_2O_5 in a desiccator.

d) Reaction was carried out as in c), but using 2.83 g (0.02 mole) 2, 4-dichloro-6-(benzoxazol-2'-on-3'-yl)-sym-triazine or 2, 4-dichloro-6-(6-chlorobenzoxazol-2'-on-3'-yl)-sym-triazine, with 0.01 mole of the appropriate amine and 0.01 mole NaOH. The resultant 2-chloro-4-amino-6-(benzoxazol-2'-on-3'-yl)-sym-triazine was recrystallized from dioxane, and dried over P_2O_5 in a desiccator.

The compounds synthesized are listed in the table.

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