

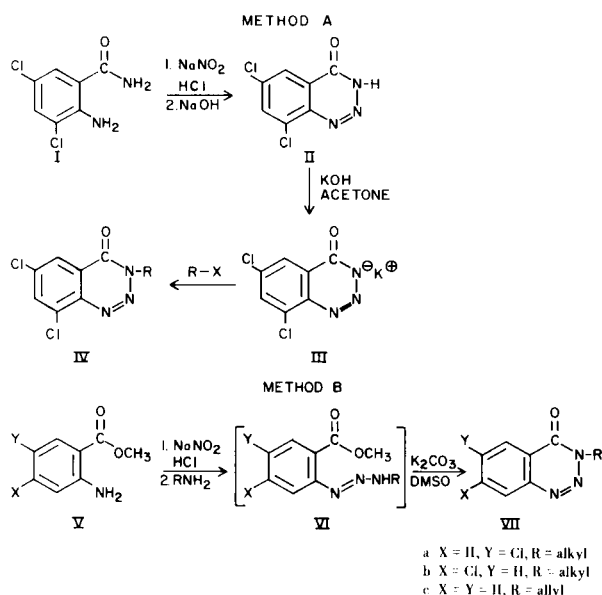
Chloro- and Dichloro-3-alkyl-1,2,3-benzotriazin-4(3H)ones (1)

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Several chloro- and dichloro-3-alkyl-1,2,3-benzotriazin-4(3H)ones have been prepared by diazotization of methyl anthranilates. A brief study was made of factors affecting the formation of 3-allyl-1,2,3-benzotriazin-4(3H)one from methyl anthranilate. Good nmr evidence was obtained to substantiate the previously proposed methyl 2-(3-allyltriazeno)benzoate (VIc) intermediate.

Three general methods have been reported for the preparation of 3-substituted 1,2,3-benzotriazin-4(3H)ones. The method most frequently used is cyclization of diazonium salts formed from anthranilamides (3). 3-Alkyl-1,2,3-benzotriazin-4(3H)ones have been prepared by alkylation of the sodium or potassium salt of 1,2,3-benzotriazin-4(3H)one (Method A) (4,5). A third, in many ways the



most convenient, method of preparation of 3-substituted 1,2,3-benzotriazin-4(3H)ones consists of treating a diazonium salt from a methyl anthranilate with an amine (Method B) (3).

In this work 6-chloro- and 7-chloro-3-alkyl-1,2,3-benzotriazin-4(3H)ones (VIIa and b) were prepared by Method B. The methyl and ethyl derivatives frequently underwent spontaneous ring closure as the amine was added to the diazonium salt. *n*-Butylamine and allylamine formed relatively stable methyl 2-(3-alkyltriazeno)-4 or 5-chlorobenzoates (VIa or b). Such an intermediate was postulated by Van Heyningen (3); however, no evidence for its existence

was given. Since we were not able to duplicate the procedure described by Van Heyningen for the preparation of 3-allyl-1,2,3-benzotriazin-4(3H)one (VIIc) from methyl anthranilate, we made a brief study of some of the factors affecting this synthesis. Whereas Van Heyningen was able to obtain 3-allyl-1,2,3-benzotriazin-4(3H)one, b.p. 105° (1.1 mm) in 50% yield, we were unable after repeated attempts to distill the crude reaction mixture. Methyl anthranilate (16-34%) was recovered. Under otherwise similar conditions, crystalline 3-allyl-1,2,3-benzotriazin-4(3H)one was obtained in 31.6-42.2% yields by warming the intermediate oil with potassium carbonate in DMSO. We obtained better yields of the intermediate oil (VIc) when the excess hydrochloric acid used in the diazotization was neutralized with either excess allylamine or preferably triethylamine.

The infrared and nmr spectra of the intermediate oil are consistent with structure VIIc.

Although methyl 4-chloro- and 5-chloroanthranilates were diazotized easily in hydrochloric acid, methyl 3,4-dichloroanthranilate did not undergo diazotization under a variety of conditions including the use of hydrobromic acid and sulfuric-phosphoric acid mixtures. Thus, the dichloro compounds were prepared by Method A (4,5).

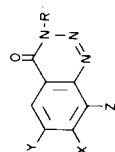
Compounds prepared during this work are listed in Table I.

EXPERIMENTAL (6)

Methyl esters of the chloro- and dichloroanthranilic acids were prepared by the method of Atkinson and Simpson (7). 2-Amino-3,5-dichlorobenzamide was prepared as previously described (4,5). 3-Methyl-6-chloro-1,2,3-benzotriazin-4(3H)one (VIIa, R = Methyl, X = H, Y = Cl).

A solution of 30.0 g. (0.16 mole) of methyl 5-chloroanthranilate and 40 ml. (0.48 mole) of concentrated hydrochloric acid in 160 ml. of water was stirred at 0-5° while a solution of 13.8 g. (0.20 mole) of sodium nitrite in 45 ml. of water was slowly added. The mixture was stirred with cooling for an additional 2 hours. Then a mixture of 12.5 g. (0.16 mole) of 40% aqueous methylamine and 32.4 g. (0.32 mole) of triethylamine was added at 0-5°.

TABLE I



X	Y	Z	R	Method	Yield %	M.p. ^o	Formula	Analyses						Ethanol λ max μ (ϵ)		
								Calcd.			Found					
								C	H	Cl	N	C	H	Cl	N	
H	H	H	allyl	B	65.7 (a)	75-76	C ₁₀ H ₉ N ₃ O	64.16	4.85	18.12	22.45	64.07	4.76	18.07	22.71	284(6,740)
Cl	H	H	methyl	B	21.9	145-146	C ₈ H ₆ ClN ₃ O	49.12	3.09	18.12	21.48	49.24	3.11	18.07	21.60	236(27,100) 290(5,470)
Cl	H	H	ethyl	B	57.4	99-100	C ₉ H ₈ ClN ₃ O	51.56	3.85	16.91	20.05	51.73	3.83	16.75	19.91	238(25,600) 290(5,200)
Cl	H	H	n-butyl	B	54.1	87-88	C ₁₁ H ₁₂ ClN ₃ O	55.58	5.09	14.92	17.68	55.48	5.11	14.77	17.46	238(26,400) 291(5,530)
Cl	H	H	allyl	B	46.6	87.8	C ₁₀ H ₈ ClN ₃ O	54.19	3.64	15.99	18.96	54.30	3.80	15.78	18.76	244(31,000) 289(6,150)
H	Cl	H	methyl	B	48.1	135.5- 136.5	C ₈ H ₆ ClN ₃ O	49.12	3.09	18.12	21.48	49.30	3.20	18.10	21.66	290(7,380)
H	Cl	H	ethyl	B	48.2	75.5- 76.5	C ₉ H ₈ ClN ₃ O	51.56	3.85	16.91	20.05	51.70	4.00	16.92	20.05	291(9,530)
H	Cl	H	n-butyl	B	34.8	47-48	C ₁₁ H ₁₂ ClN ₃ O	55.58	5.09	14.92	17.68	55.64	5.21	14.79	17.70	292(8,830)
H	Cl	H	allyl	B	41.3	67-68	C ₁₀ H ₈ ClN ₃ O	54.19	3.64	15.99	18.96	54.10	3.71	15.79	18.85	291(9,190)
H	Cl	Cl	methyl	A	88.4	131.5- 132.5	C ₈ H ₅ Cl ₂ N ₃ O	41.77	2.19		18.27	41.81	2.33		18.12	226(24,600) 298(10,800)
H	Cl	Cl	ethyl	A	55.5	89.5- 90.5	C ₉ H ₇ Cl ₂ N ₃ O	44.29	2.89		17.22	44.50	3.00		17.04	226(21,600) 299(9,770)
H	Cl	Cl	n-butyl	A	79.5	78.5- 79.5	C ₁₁ H ₁₁ Cl ₂ N ₃ O	48.55	4.07		15.44	48.70	4.17		15.51	226(23,950) 299(10,700)
H	Cl	Cl	allyl	A	50	81.0- 82.5	C ₁₀ H ₇ Cl ₂ N ₃ O	46.90	2.76		16.41	46.65	2.63		16.19	227(22,100) 298(8,940)

(a) crude yield.

The cold solution was left overnight. Chloroform was added with stirring and the chloroform was separated, dried over magnesium sulfate and evaporated to obtain 33.2 g. of a solid. Four recrystallizations, two with 95% ethanol and two with methanol, gave 15.2 g. (48.1%) of a solid, m.p. 135.5-136.5°; IR 1680 cm^{-1} (C=O), λ max (ethanol), 290 $\text{m}\mu$ (ϵ , 7,380), nmr, singlet 4.0 δ (3H, CH₃) and multiplet 7.8-8.2 δ (3H, aromatic).

3-Allyl-1,2,3-benzotriazin-4(3H)one (VIIc, R = Allyl, X = Y = H)

To a solution of 10 g. (0.066 mole) of methyl anthranilate and 16.5 ml. (0.198 mole) of concentrated hydrochloric acid in 45 ml. of water cooled to 0° was added with stirring a solution of 6.9 g. (0.10 mole) of sodium nitrite in 20 ml. of water. The mixture was stirred with cooling for 1 hour. Allylamine (9.1 g., 0.16 mole) was added at 0-3° and stirring was continued for 1.5 hours. The mixture was extracted with ether (2 x 100 ml.) and chloroform (100 ml.), the combined extract was dried over magnesium sulfate and the solvent was evaporated to obtain 10.3 g. (71.2%) of an oil, IR 3290 (NH), 1710 and 1680 cm^{-1} (COOCH₃ and N=N) and 1640 cm^{-1} weak (C=C); nmr singlet 3.8 δ (3H, CH₃O), doublet 4.35 δ (2H, N-CH₂, J = 6 cps with secondary splitting), multiplets 5.05-5.5 δ (2H, C=CH₂), 5.78-6.42 δ (1H, CH=C) and 6.68-7.92 δ (4H, aromatic).

This oil was divided into two parts. One part (5.1 g., 0.023 mole) was distilled to obtain 1.8 g. (36% recovery) of a liquid, b.p. 98-101° (0.8-0.85 mm). The infrared spectrum of this liquid is identical to the infrared spectrum of methyl anthranilate. Evolution of a gas appeared to occur during this distillation.

The second part of the oil (5.2 g., 0.024 mole) was heated at 55-75° with stirring for 3 hours with 1.93 g. (0.014 mole) of potassium carbonate in 25 ml. of DMSO. The reaction mixture was poured over ice and extracted with ether and then with chloroform. The combined extract was dried over magnesium sulfate and the solvent was evaporated to obtain 2.6 g. (42.2%) of crude VIIc, m.p. 69-71°. Recrystallization of this material from 95% ethanol gave 1.2 g. (19.4%) of VIIc, m.p. 75-76°; IR 1670 cm^{-1} (C=O), λ max (ethanol), 284 $\text{m}\mu$ (ϵ 6,740).

Under similar conditions except with the use of 11.3 g. (0.198 mole) of allylamine instead of 9.1 g. (0.16 mole), 12.2 g. (85.9%) of the intermediate oil was obtained. Distillation of 6.1 g. of this gave 1.6 g. (32% recovery) of methyl anthranilate and treatment of 6.1 g. of the oil with potassium carbonate in DMSO gave 3.2 g. (52%) of crude VIIc.

Under similar conditions except with the use of a mixture of 3.78 g. (0.066 mole) of allylamine and 13.3 g. (0.132 mole) of triethylamine instead of 9.1 g. (0.16 mole) of allylamine, 13.0 g. (90%) of the intermediate oil was obtained. This oil was heated with 4.35 g. (0.032 mole) of potassium carbonate in 45 ml. of DMSO to obtain 8.1 g. (65.7%) of crude VIIc.

REFERENCES

- (1) This work was supported by Contract Number 12-14-100-7787(51) with the Stored Product Insects Research Branch, Market Quality Research Division, Agriculture Research Service, U. S. Department of Agriculture.
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- (6) Melting points were determined using a Mel-Temp capillary melting point apparatus. The ultraviolet and infrared spectra were obtained with a Beckman DK-1 spectrophotometer and a Perkin-Elmer Model 137 Infracord spectrophotometer. The nmr spectra were determined in carbon tetrachloride or deuterated chloroform by Miss Hope Howard using a Varian A-60 spectrometer with tetramethylsilane as an internal standard. The microanalyses were performed by Galbraith Laboratories, Knoxville, Tennessee.
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