

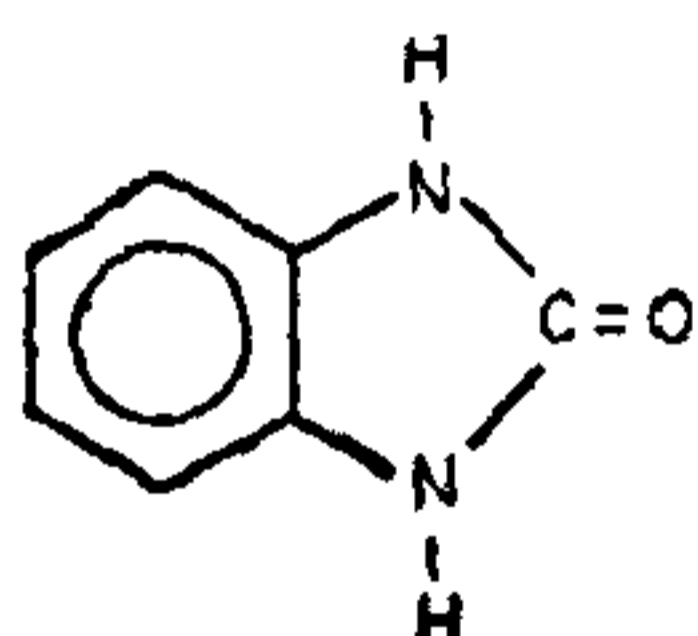
SYNTHESIS OF 1,3-BIS-(ANILINOMETHYL) BENZIMIDAZOLONE-2-N-MANNICH BASES AND THEIR BIOLOGICAL EVALUATION

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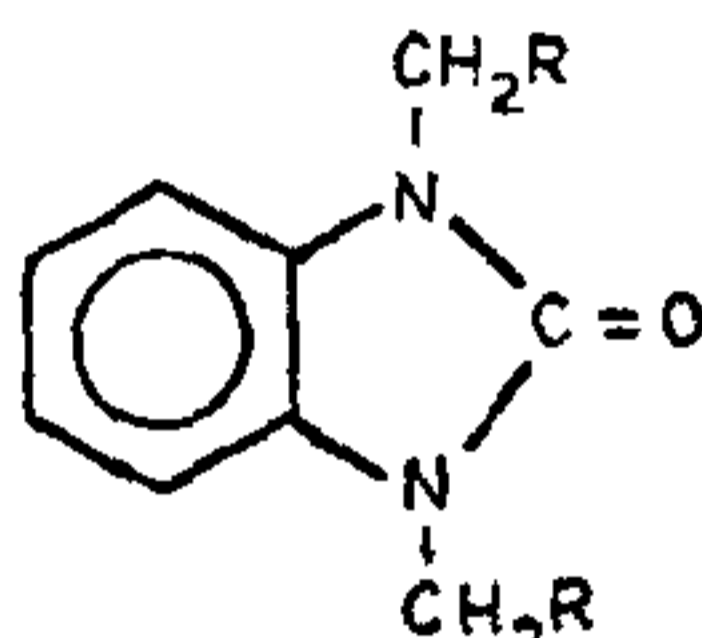
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A series of 1,3-Bis-(anilinomethyl)benzimidazolone-2-N-Mannich bases have been synthesised from benzimidazolone-2 and several primary aromatic amines in presence of formaldehyde. The representative compounds have been screened for their antibacterial and insecticidal activities.

COMPOUNDS having an active hydrogen atom on nitrogen such as salicylamide¹, succinimide², phthalimide³, 4-nitrophthalimide⁴, isatins⁵ and benzimidazoles⁶ have been reported to undergo ready Mannich condensations furnishing N-Mannich bases in good yields. Hydrogen atoms attached to nitrogen in benzimidazolone-2 should as such be appreciably labile to participate in the Mannich condensation. Since benzimidazoles have been reported to possess antibacterial⁷ and insecticidal⁸ activities, it was considered of interest to treat I with a few primary aromatic amines to furnish N-Mannich bases (II). The condensation reaction was possible with aromatic amines having electron donating as well as electron withdrawing substituents.



I



II

EXPERIMENTAL

Melting points were taken in open capillaries and were not corrected. Infrared spectra were recorded on Perkin-Elmer 137G spectrophotometer in KBr. Benzimidazolone-2 was prepared according to the published method⁹.

1,3-Bis-(anilinomethyl)benzimidazolone-2-N-Mannich bases (II)

An intimate mixture¹⁰ of I (0.01 mole), formalin (0.02 mole) and aniline (0.02 mole) in 20 ml of ethanol was warmed on a water bath with stirring for 30 min and thereafter it was allowed to stand overnight at room temperature. The solid product, which separated, was filtered and recrystallised from ethanol. Other compounds, thus synthesised, are given in Table I.

TABLE I

Corresponding K.D. values for 1,3-Bis(anilinomethyl)benzimidazolone-2-N-Mannich bases (II)

Sl No.	R from Amines	M.P. °C	Insecticidal activity Knocking Down values (hr)	
			0.5%	0.1%
1.	Anilino	175	9.5	13
2.	<i>p</i> -carbomethoxy-anilino	185	10	12
3.	<i>p</i> -carbopropoxy-anilino	166	9	11
4.	<i>p</i> -carboxyanilino	125	6	8
5.	<i>p</i> -toluidino	192	7	10.5
6.	<i>m</i> -toluidino	182	10.5	12.5
7.	<i>o</i> -toluidino	146	8	12
8.	<i>p</i> -anisidino	195	8	12.5
9.	<i>p</i> -nitroanilino	228	6	10
10.	<i>m</i> -nitroanilino	196	7	9
11.	2,4-dinitroanilino	160	6	8
12.	<i>p</i> -chloroanilino	178	9	12
13.	<i>p</i> -bromoanilino	200	10	13
14.	<i>p</i> -iodoanilino	230	8	10
	Parathione	..	4	..

- (i) Yields varied from 70–90%.
 (ii) The compounds were recrystallised from ethanol.
 (iii) The elemental analyses were found to be within satisfactory limits.
 (iv) IR (μ) 2. 2.95 (NH), 5.8 (C=O).
 9. 3.00 (NH), 6.60 and 7.60 (NO₂).

BIO-ASSAY

Antibacterial Activity

The method, developed by Varma and Nobles¹¹, was employed for the determination of the antibacterial spectrum of the compounds (Table I). The test organisms, maintained at Public Analytical Laboratory to the U.P. Government, included *Staphylococcus*

aureus and *Bacillus subtilis*. It was observed that compounds No. 9 and 10 inhibited *B. subtilis* only, while other compounds had no effect on the bacilli.

Insecticidal Activity

The compounds in two concentrations¹² (0.5% and 0.1% in acetone) were injected in the 3/4 abdominal segment of the adult male and female cockroaches (*Periplaneta americana*) with the help of microsyringe. The tests were repeated and the control was done with parathione. The knocking down (K.D.) periods (hr) of II are given in Table I. The K.D. values for acetone and parathione were 42 hr and 4 hr respectively. It was observed that the compounds associated with nitro and carboxyl groups showed significant activity. Further substitution with methyl, and propyl groups in the carboxylic group decreases (increases the K.D. value) the activity as in compound Nos. 2 and 3 of Table I.

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REPUBLIC DAY AWARDS

The award of *Padma Vibhushan* has been given to Prof. Satish Dhawan; *Padma Bhushan* to (a) Shri A. P. J. Abdul Kalam, (b) Prof. M. K. Vainu Bappu, (c) Shri Prabhat Kumar Mukherjee and (d) Dr. Prafulla

B. Desai; *Padma Shri* to (a) Dr. Gurucharan Singh Kakat, (b) Dr. H. K. Jain, (c) Dr. J. S. Bajaj, (d) Dr. V. K. Thiruvengadam and (e) Dr. Madhav Dhananjaya Gadgil.