A SEARCH FOR PESTICIDES IN THE N,N'-DI(CARBOXYPROPYL)-BENZIMIDAZOLIN-2-ONE SERIES

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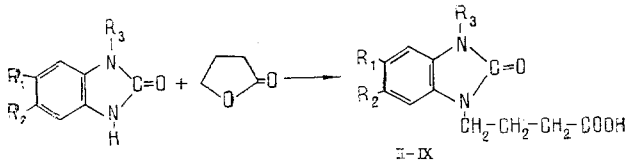
The reaction of benzimidazolin-2-ones with γ-butyrolactone has given N-mono- and N,N'-dicarboxypropylbenzimidazolin-2-ones. It has been shown that the yields and structures of the compounds synthesized depend on the nature of the substituent in the benzene nucleus of the benzimidazolin-2-ones.

The products of the carboxylation of benzimidazolin-2-one and its derivatives by γ-butyrolactone can be considered as analogs of the purine nucleosides containing the benzimidazolone ring, and the structure of which is similar to that of the natural purines, as the purine base, and with the carbohydrate moiety replaced by a polymethylene chain. Such compounds are of interest by the fact that on their possible association with nucleic acids they will affect definite functions of the latter and thereby cause the most induced biological effects [1, 2].

We have previously performed the N-carboxyalklation of N-isopropenylbenzimidazolin-2-one with γ-butyrolactone [3]. In the present paper we give the results of the N-carboxyalkylation of benzimidazolin-2-one (I) and its 5,6-substituted derivatives with γ-butyrolactone in dry dimethylformamide (DMFA) using a simplified method for isolating the desired products. Depending on the nature of the substituents, N-mono- and N,N'-dicarboxypropylbenzimidazolin-2-ones were obtained (Table 1).



I-IX

It was established that electron-donating substituents in the benzene nucleus of (I) decrease and electron-accepting groups increase the yields of reaction products. In the case of 5-nitrobenzimidazolin-2-one the N-monocarboxypropyl derivative was obtained, and with 5-chlorobenzimidazolin-2-one the product was N,N'-dicarboxypropyl-5-chlorobenzimidazolin-2-one, which can be explained by the greater electron-accepting influence of the nitro group, which promotes the nonequivalence of the nitrogen atoms of the heterocyclic nucleus of (I).

The structures of the compounds synthesized were shown by the results of elementary analysis and by IR and PMR spectra.

In the PMR spectra of (II-IX), signals at 3.73 ppm correspond to the two methylene groups of the side chain in the γ position to the nitrogen of the imidazolinone ring, those at 2.23 ppm to the α-methylene protons, and multiplets at 1.93 ppm to the β-methylene protons. The signals of aromatic protons appear at 6.6-7.3 ppm. The signals of the COOH protons are present at 10.54 ppm. For compound (IX) the methyl signals of $CH_3-\overset{|}{C}-N-$ appear at 2.14 and 2.19 ppm, and the signals of disubstituted vinyl protons, $=CH_2-$ at 5.05-5.20 ppm in the form of a quadruplet with J_{gem} = 1.5-2 Hz.

In the IR spectra of (III, IV, and VII-IX) there are absorption bands of a 1,2,4-substituted benzene ring at 810-820 cm^{-1}, and in (V) the absorption bands of 1,2,4,5-substitution at 860-870 cm^{-1}. In the spectra of (II-IX), the frequencies of the C=O stretching vibrations

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TABLE 1. Physical Constants of the Products of the N-Carboxyalkylation of Benzimidazolin-2-ones

Compound	R_1	R_2	R_3	Yield, %	mp, deg C
II. N,N'-Dicarboxypropylbenzimidazolin-2-one	H	H	$(CH_2)_3COOH$	20	98–99
III. N,N'-Dicarboxylpropyl-5-methylbenzimidazolin-2-one	CH_3	H	$(CH_2)_3COOH$	19	161–162
IV. N,N'-Dicarboxypropyl-5-chlorobenzimidazolin-2-one	Cl	H	$(CH_2)_3COOH$	64	76–77
V. N,N'-Dicarboxypropyl-5,6-dimethylbenzimidazolin-2-one	CH_3	CH_3	$(CH_2)_3COOH$	8	177–178
VI. N-Carboxypropylbenzimidazolin-2-one	H	H	H	30	175–176
VII. N-Carboxypropyl-5-chlorobenzimidazolin-2-one	Cl	H	H	3	182–183
VIII. N-Carboxypropyl-5(6)-nitrobenzimidazolin-2-one	NO_2	H	H	30	197–198
IX. N-Isopropenyl-N'-carboxypropyl-5-chlorobenzimidazolin-2-one	Cl	H	$CH_3CH=CH_2$	33	200–201

of the carboxy group appear at 1675-1680 cm^{-1} and those of the C=O group of the imidazoline ring at 1715-1720 cm^{-1}.

The pesticidal activities of the N-mono- and N,N'-dicarboxypropylbenzimidazolin-2-ones synthesized will be discussed separately.

EXPERIMENTAL

IR spectra were recorded on a UR-20 spectrometer (tablets with KBr), and PMR spectra on a JNM-4H-100/100 MHz instrument in trifluoroacetic acid (HMDS, δ scale). The results of elementary analysis corresponded to the calculated figures.

The Disodium Salt of (I). In a three-necked flask fitted with a stirrer and reflux condenser with a calcium chloride tube, 4.6 g (0.1 g-atom) of metallic sodium was added in portions to 100 ml of absolute ethanol. Then, with stirring, 13.4 g (0.1 g·mole) of (I) was added over 20-30 min. The excess of ethanol was distilled off to dryness in vacuum in an oil bath. The yield of the disodium salt of (I) was 17.8 g (100%). The mono- and disodium salts of the other benzimidazolin-2-ones were obtained similarly.

N,N'-Dicarboxypropylbenzimidazolin-2-one (II). To 8.9 g (0.05 mole) of the dry finely ground disodium salt of (I) were added 10 ml (10% excess) of freshly distilled γ-butyrolactone and 20 ml of dry DMFA, and the mixture was heated with stirring at 160-170°C for 2 h. The excess of DMFA was distilled off; the cooled residue was hydrolyzed with 50 ml of 4 N hydrochloric acid. The crude product deposited in the form of an oil, which crystallized on standing. When it was treated with 10% $NaHCO_3$ solution followed by acidification with 4 N HCl, it gave 3.0 g of (II). Evaporation of the hydrochloric acid filtrate gave an additional 0.2 g of (II).

Compounds (III-V) were obtained similarly.

N-Carboxypropylbenzimidazolin-2-one (VI). Similarly, 9.85 g (0.05 mole) of the monosodium salt of N-isopropenylbenzimidazolin-2-one and 10 ml of γ-butyrolactone in 20 ml of DMFA gave 3.4 g of (VI), (VIII), and (IX). When the hydrochloric acid filtrate after the isolation of (IX) was evaporated, (VII) was obtained.

SUMMARY

The possibility has been shown of carboxyalkylating benzimidazolin-2-one with γ-butyrolactone. Depending on the nature of the substituent in the benzene ring, N-mono- and N,N'-dicarboxypropylbenzimidazolin-2-ones are obtained.

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