SYNTHESIS OF SUBSTITUTED 1-ISOPROPENYL- AND 1-ALKYLBENZIMIDAZOLONES

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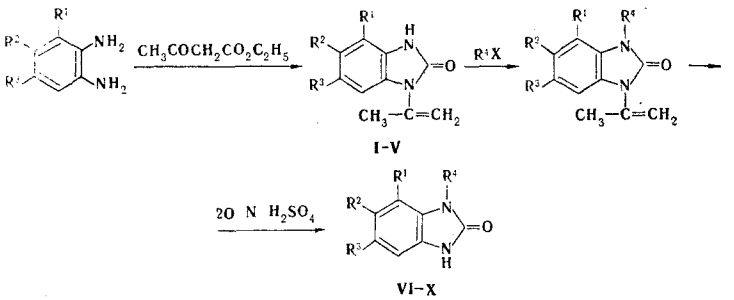
1-Isopropenylbenzimidazolones, the alkylation of which with alkyl halides and γ-butyrolactone proceeds in the 3 position, were obtained by reaction of o-phenylenediamine and its aromatic ring-substituted derivatives with acetoacetic ester.

Benzimidazole and its derivatives are traditional objects in the search for pesticides [1, 2], but 1-monosubstituted benzimidazolones have not been investigated as herbicides.

We have used the condensation of o-phenylenediamine and its derivatives with acetoacetic ester for the synthesis of benzimidazolones. It is known that the process may go in several directions, depending on the conditions [3, 4]. In the present research, the condensation of o-phenylenediamine and its 4-chloro, 3,5-dimethyl, 3,5-dichloro, and 4,5-dichloro derivatives with acetoacetic ester was carried out under conditions for which one might have expected the formation of 1-isopropenylbenzimidazolones (I-V). The highest yields could be obtained when the condensation was carried out in refluxing xylene in neutral media with removal of the liberated water and alcohol by distillation. In addition to benzimidazolones I-V (Table 1), we isolated ethyl β-(o-aminoanilino)crotonates:



The 5-chloro-1-isopropenylbenzimidazolone structure (II) was confirmed by alkylation and subsequent hydrolysis to the known 6-chloro-1-ethyl- and -1-allylbenzimidazolones [5], and also by the PMR spectra. The 4,6-dimethyl- (III) and 4,6-dichloro-1-isopropenylbenzimidazolone (IV) structures were proved by preparation of 3-acyl derivatives and comparison of the PMR spectra. The signals of the protons of the aromatic ring of III and IV are found at δ 6.71 and 6.66 ppm. The position of the signals of the aromatic protons is retained for the 3-acyl derivatives. This means that the allyl group does not enter the 1 position, otherwise one should have expected an appreciable anisotropic effect of the acyl C=O group on the shift of 7-H. The presence of signals of allyl methyl groups at 2.15 and 2.20 ppm and of the signals of vinyl protons at 5.05-5.20 ppm in the form of two doublets with J = 1.5-2 Hz in the PMR spectra of benzimidazolones I-V proves the formation of 1-isopropenylbenzimidazolones and excludes the structure of substituted dihydrobenzo-2-diazepinones, in the spectra of which the protons of the methylene group resonate at strong field at 3.07 ppm [6]. Signals of aromatic protons at 6.7-7.3 ppm are observed in all of the spectra. The signals of the protons of the two aromatic methyl groups for III form two singlets at 2.30-2.34 ppm.

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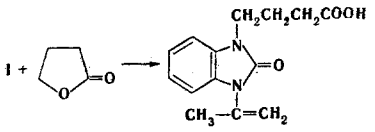
TABLE 1. Substituted 1-Isopropenylbenzimidazolones and Their Alkylation Products

Compound	R¹	R²	R³	R⁴	mp, deg C	Empirical formula	Found, %			Calc., %			Yield, %
							C	H	N	C	H	N	
I	H	H	H	—	119—120[5]	$C_{10}H_{10}N_2O$							60
II	H	Cl	H	—	186—189	$C_{10}H_9ClN_2O$	56,9	4,3	13,8	57,5	4,3	13,4	41
III	CH_3	H	CH_3	—	215—218	$C_{12}H_{14}N_2O$	60,1	6,8	13,7	59,4	6,9	13,8	43
IV	Cl	H	Cl	—	240—242	$C_{10}H_8Cl_2N_2O$	49,0	3,0	12,1	49,3	3,3	11,5	57
V	H	Cl	Cl	—	220—222	$C_{10}H_8Cl_2N_2O$	50,3	3,6	11,5	49,3	3,3	11,5	52
VI	H	Cl	H	CH_3	190—192	$C_8H_7ClN_2O$			15,7			15,3	69
VII	H	Cl	H	C_2H_5	184—185[5]	$C_9H_9ClN_2O$							68
VIII	H	Cl	H	C_3H_7	180—182	$C_{10}H_{12}ClN_2O$			13,3			13,3	60
IX	H	Cl	H	C_4H_9	120—121	$C_{11}H_{14}ClN_2O$			12,6			12,4	53
X	H	Cl	H	$CH_2CH{=}CH_2$	172—173[5]	$C_{10}H_{10}ClN_2O$							61
XI	H	H	H	$(CH_2)_3COOH$	84—86	$C_{14}H_{16}N_2O_3$	64,0	5,9	10,1	64,6	6,1	10,7	50

The establishment of the structure of unknown compounds II-V showed that in the case of monosubstituted o-phenylenediamine, the reaction proceeds at the more basic amino group through an intermediate arylaminocrotonate, which is cyclized to the corresponding 1-isopropenylbenzimidazolone under the reaction conditions. The reaction proceeds at the less basic amino group for 3,5-disubstituted compounds, probably because of steric hindrance created by the substituent adjacent to the more basic amino group. The absence of dihydrobenzodiazepinones is possibly explained by direct cyclization of the arylaminocrotonate to 1-isopropenylbenzimidazolone without isomerization to the amide of acetoacetic acid.

6-Chloro-1-alkylbenzimidazolones VI-X (Table 1) were obtained by alkylation of benzimidazolone II with alkyl halides, as in [5].

We were able to isolate 1-isopropenyl-3-(3-carboxypropyl)benzimidazolone (XI) by reaction of 1-isopropenylbenzimidazolone with γ-butyrolactone in dry dimethylformamide (DMF):



XI

Absorption bands of the C=O group of the imidazolone ring (1680-1725 cm^{-1}) and absorption bands of 1,2,4- (810-820 cm^{-1}), 1,2,4,5- (850-855 cm^{-1}), and 1,2,3,5-substituted (840 cm^{-1}) benzene rings are observed in the IR spectra of I-XI and the 3-acyl derivatives.

Some of the synthesized compounds have selective herbicidal action [7, 8].

EXPERIMENTAL

The PMR spectra of chloroform (I-III, XI) and deuteropyridine (IV, V) solutions were recorded with a JNM-4H-100 spectrometer with tetramethylsilane as the internal standard.

5-Chloro-1-isopropenylbenzimidazolone (II). A solution of 1.52 ml (0.012 mole) of acetoacetic ester (purified by the method in [9]) in 1 ml of xylene was added dropwise to a refluxing solution of 1.42 g (0.01 mole) of 4-chloro-1,2-phenylenediamine in 12 ml of xylene, and the mixture was heated until the water had been completely removed by distillation (2 h, with a Dean–Stark trap), after which it was cooled to 35-40° and treated with 15 ml of 10% aqueous potassium hydroxide solution. The sodium salt of the condensation product precipitated on standing. The precipitate was separated and dissolved in water, and the solution was acidified to give 1.13 g (41%) of benzimidazolone II with mp 186-189° (from benzene). Acidification of the alkaline filtrate gave an additional 0.1-0.15 g of II.

Compounds I and III-V were similarly obtained (Table 1).

6-Chloro-1-methylbenzimidazolone (VI). A 2.08 g (0.01 mole) sample of dry benzimidazolone II was added to a solution of sodium ethoxide, prepared from 0.23 g (0.01 g-atom) of sodium and 10 ml of absolute ethanol, after which 7.6 ml (0.12 mole) of methyl iodide was added dropwise with stirring. The mixture was then refluxed for 4 h, cooled, treated with 20 N sulfuric acid (1.4 ml), and allowed to stand at room temperature for 3 h. An equal volume of water was added, and the mixture was evaporated to half its volume on a water bath to precipitate 1.2 g (60%) of benzimidazolone VI with mp 190° (from aqueous alcohol).

Compounds VII-X were similarly obtained (Table 1).

1-Isopropenyl-3-(3-carboxypropyl)benzimidazolone (XI). A mixture of 9.8 g (0.05 mole) of dry, finely ground sodium salt of 1-isopropenylbenzimidazolone, 4.75 g (0.055 mole) of freshly distilled γ-butyrolactone, and 7-10 ml of dry dimethylformamide was heated with stirring at 150-155° for 2 h, after which it was cooled to about 100° and decomposed with an equal volume of hot water. The solution was cooled and made weakly acidic with hydrochloric acid, and the reaction product was extracted with ether. The extract was washed with water and treated three times with saturated sodium bicarbonate solution. The alkaline extracts were combined and acidified with hydrochloric acid to give 6 g (50%) of benzimidazolone XI with mp 84-86° (from aqueous alcohol). PMR spectrum: δ 3.91 (triplet, J = 6 Hz, α-CH_2), 2.33 (triplet, J = 6 Hz, γ-CH_2), 2.00 (multiplet, β-CH_2), 10.54 ppm (singlet, COOH).

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