# 3-[ω-(2-BENZIMIDAZOLYL)ALKYL]BENZOXAZOLONES

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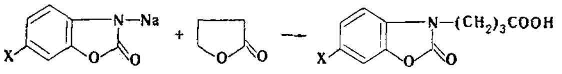
UDC 547.787.3'785.5

A new method for the preparation of γ-(3-benzoxazolonyl)butyric acids from sodium salts of benzoxazolones and γ-butyrolactone was developed. 3-[ω-(2-benzimidazolyl)alkyl]benzoxazolones were synthesized by the reaction of these acids and also (3-benzoxazolonyl)acetic and β-(3-benzoxazolonyl)propionic acids with o-phenylenediamine.

Among the benzoxazolones there are natural fungicides that are present in plants that are resistant to some diseases [1].

Ring-substituted γ-(3-benzoxazolonyl)butyric acids have not been described in the literature except for γ-(3-benzoxazolonyl)butyric acid itself, which was obtained by the Arndt–Eistert reaction [1] or by alkylation of benzoxazolone with methyl γ-chlorobutyrate [1].

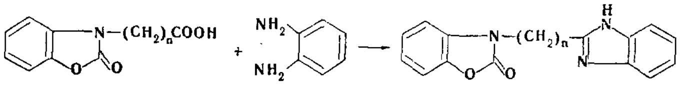
We have developed a one-step method for the preparation of substituted γ-(3-benzoxazolonyl)butyric acid (Table 1) by reaction of the sodium or potassium salt of the appropriate benzoxazolone with butyrolactone.



I a-d

a X=H; b X=Cl; c X=Br; d X=$NO_2$

It seemed of interest to synthesize new heterocyclic compounds – 3-[ω-(2-benzimidazolyl)alkyl]benzoxazolone (II) (Table 2) – from the γ-(3-benzoxazolonyl)butyric, β-(3-benzoxazolonyl)propionic, and (3-benzoxazolonyl)acetic acids and to study their biological activity.



II a-c

a $n=1$; b $n=2$; c $n=3$

TABLE 1. Substituted γ-(3-Benzoxazolonyl)butyric Acids (Ia-d)

| Compound | mp, °C | Empirical formula | N, % |  | Yield, % |
|---|---|---|---|---|---|
|  |  |  | found | calc. |  |
| Ia | 135–136* | $C_{11}H_{11}NO_4$ | 6,2; 6,2 | 6,3 | 70 |
| Ib | 139–140 | $C_{11}H_{10}ClNO_4$ | 5,6; 5.6 | 5,5 | 60 |
| Ic | 147–148 | $C_{11}H_{10}BrNO_4$ | 4,5; 4,5 | 4.7 | 59 |
| Id | 150–152 | $C_{11}H_{10}N_2O_6$ | 10,5; 9,9 | 10,5 | 45 |

*According to [1], this compound has mp 137°.

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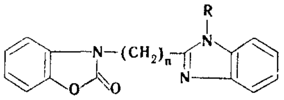
Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 464-466, April, 1973. Original article submitted February 28, 1972.

TABLE 2



| Compound | R | $n$ | mp, °C | Empirical formula | Found |  | Calc. |  | Yield, % |
|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  | $M^a$ | N, % | $M$ | N, % |  |
| IIa | H | 1 | 226—228$^b$ | $C_{15}H_{11}N_3O_2$ | 265 | 15,4; 15,3 | 265 | 15,8 | 66 |
| IIb | H | 2 | 168—170$^d$ | $C_{16}H_{13}N_3O_2$ | 279 | 14,9; 14,8 | 279 | 15,0 | 56 |
| IIc | H | 3 | 156—158$^e$ | $C_{17}H_{15}N_3O_2$ | 293 | 14,0; 14,1 | 293 | 14,3 | 60 |
| III | $CH_3OCO$ | 1 | 174—176$^f$ | $C_{17}H_{13}N_3O_4$ | 323 | 13,6; 13,6 | 323 | 13,3 | 70 |

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[a] From the mass-spectral data. [b] From alcohol. [c] Found: C 67.7, 67.6; H 4.1, 4.0%. Calculated: C 67.9; H 4.2%. [d] From benzene. [e] From acetone. [f] From aqueous alcohol.

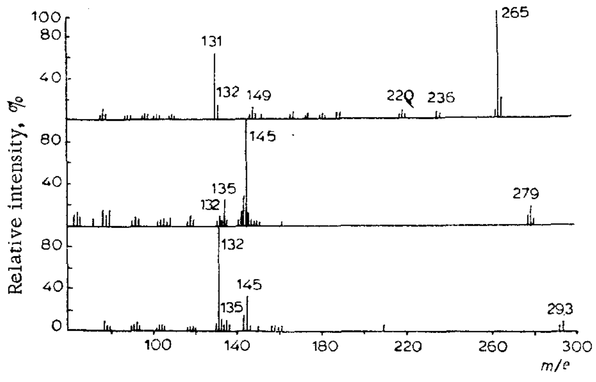
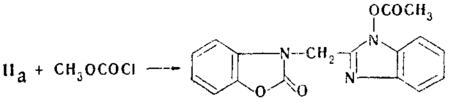


Fig. 1. Mass spectra of 3-[ω-(2'-benzimidazolyl)-alkyl]benzoxazolones.

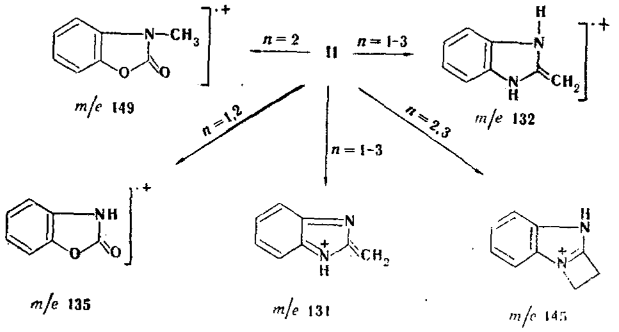
3-[1-(1-Carbomethoxy-2-benzimidazolyl)methyl]benzoxazolone (III) (Table 2) was synthesized from IIa and methyl chlorocarbonate.



III

The synthesized compounds were studied by mass spectrometry. Their mass spectra are characterized by the presence of molecular-ion peaks, the m/e values and paths of disintegration of which are in complete agreement with the proposed structures. As the number of bridge methylene links increases, the stability of the molecular ions decreases; this is reflected in a decrease in the intensities of their peaks in the spectra. On the other hand, a decrease in the intensity of the $M^+$ ions leads to an increase in the intensities of the peaks of the fragment ions (see Fig. 1). The disintegration of the molecular ions proceeds primarily to favor the formation of fragments that contain benzoxazolone (ion peaks with m/e 135 and 149) and benzimidazole (ion peaks with m/e 131, 132, 144, and 145) portions of the molecule. The formation of ions with m/e 131 and 145 occurs through cleavage of the C—C bond, and in the development of fragments with m/e 131, 133, and 149 cleavage is accompanied by the migration of hydrogen atoms to the charged portion of $M^+$. (See scheme on next page.)

A characteristic feature of the spectra is the high intensity of the ion peaks with m/e 131, 132, and 145, which contain the benzimidazole portion of $M^+$, and the low intensity of the ion peaks with m/e 135 and 149, which contain the benzoxazolone portion of $M^+$ (see Fig. 1). This is evidence that the positive charge is primarily localized in the benzimidazole portion of the molecular ions of these substances. The low degree of localization of the positive charge in the benzoxazolone fragment of $M^+$ is apparently associated with the reduced basicity of the nitrogen atom under the influence of the lactam carbonyl group.



## EXPERIMENTAL

γ-(3-Benzoxazolonyl)butyric Acid (Ia). A mixture of 0.05 mole of the dry finely ground sodium salt of benzoxazolone, 0.055 mole of freshly distilled γ-butyrolactone, and 7-10 ml of dry dimethylformamide was stirred and heated at 150-155° for 2 h, after which it was decomposed with an equal volume of hot water. It was then cooled and acidified with hydrochloric acid, and the acidic mixture was extracted with ether. The extract was washed with water and treated with saturated sodium bicarbonate solution. The alkaline extracts were combined and acidified with hydrochloric acid. The liberated reaction product was filtered, dried, and recrystallized from benzene–hexane to give acid Ia with mp 135-136° (mp 137° [1]) in 70% yield.

The other γ-(3-benzoxazolonyl)butyric acids (Table 1) were similarly synthesized.

3-[(2-Benzimidazolyl)methyl]benzoxazolone (IIa). A mixture of 0.1 mole of (3-benzoxazolonyl)acetic acid [2] and 0.1 mole of o-phenylenediamine was heated at 180-200° for 6 h in a flask equipped with a Dean–Stark trap. The resulting solid mass was washed successively with a 2% sodium bicarbonate solution and water, dried, and recrystallized from alcohol to give IIa with mp 226-228° in 66% yield.

Benzoxazolones IIb,c (see Table 2) were similarly obtained.

3-[(1-Carbomethoxy-2-benzimidazolyl)methyl]benzoxazolone (III). A 0.1-mole sample of methyl chlorocarbonate was added with vigorous stirring to a solution of 0.1 mole of IIa and 0.1 mole of dimethylaniline in 100 ml of acetone. The mixture was heated on a boiling-water bath for 2 h, after which the solvent was removed by distillation, and the residue was crystallized from aqueous alcohol (see Table 2).

## LITERATURE CITED

1. H. Zinner, T. Randow, and H. Wigert, J. Prakt. Chem., 33, 130 (1966).
2. C. Lespagnol, Comptes Rend., 237, 1164 (1953); Ref. Zh. Khim., 39,501 (1954).