CLEAVAGE OF THE FURAN NUCLEUS IN SOME 2-FURYLBENZIMIDAZOLES

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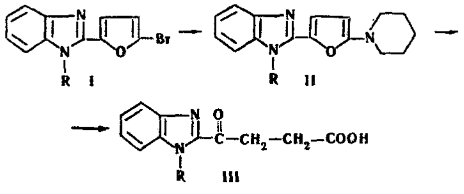
We have found that the furan nucleus, which is fairly stable in 1-alkyl-2-[5'-halo-2-furyl) benzimidazoles (I) [1], becomes unstable to the action of mineral acids after the halogen atom has been replaced by a secondary amine residue.

When 1-alkyl-2-(5'-piperidino-2'-furyl)benzimidazoles (II), prepared by heating I with piperidine in a sealed tube at 125°–130° C, were treated with boiling concentrated HCl, the furan nucleus was opened with the formation of γ-(1-alkyl-2-benzimidazolyl)-γ-oxobutyric acids (III).



$R = a)\ CH_3;\ b)\ CH_2C_6H_5$

The structure of III was shown by the independent synthesis of IIIa from 2-lithio-1-methylbenzimidazole and diethyl succinate, and also by a study of IR spectra.

The spectrum of IIIb has an absorption band at 1696 cm^{-1} which in an ester is split into bands at 1694 and 1733 cm^{-1}. The IR spectrum of the sodium salt of the acid IIIb has the characteristic frequencies of a carbonyl group (1685 cm^{-1}) and an ionized carboxy group (1581 cm^{-1}).

γ-(1-Methyl-2-benzimidazolyl)-γ-oxobutyric acid (IIIa). Mp 193.5° C (from aqueous ethanol). Yield 20%: Found, %: C 62.05; H 5.01; N 12.26. Calculated for $C_{12}H_{12}N_2O_3$, %: C 62.06; H 5.21; N 12.06.

γ-(1-Benzyl-2-benzimidazolyl)-γ-oxobutyric acid (IIIb). Mp 171°–172° C (from aqueous ethanol). Yield 37%. Found, %: C 70.03; H 5.29; N 9.38. Calculated for $C_{18}H_{16}N_2O_3$, %: C 70.06; H 5.19; N 9.08.

The methyl ester of the acid IIIb was obtained by the action of diazomethane on the acid. Mp 77°–79° C (from hexane). Yield 70%. Found, %: C 70.68; H 5.63. Calculated for $C_{19}H_{18}N_2O_3$, %: C 70.82; H 5.62.

REFERENCE

1. F. T. Posharskii, V. Ts. Bukhaeva, and A. M. Siminov, KhGS [Chemistry of Heterocyclic Compounds], 910, 1967.

THE CRYSTALLINE STRUCTURE OF 1-ETHYLGERMATRAN

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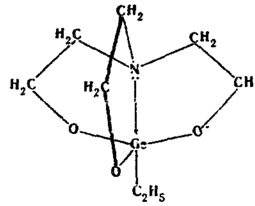
Ethylgermatran (I) was synthesized by M. G. Voronkov and G. I. Zelčans [1, 2] and courteously given to us for study of the X-ray diffraction. The experimental X-ray diffraction data were obtained by Cu-emission and are represented as a collection of Weisenberg diagrams of hk0–hk6 and 0kl–3kl.



The following crystallographic data were obtained for the crystals I:

$a = 9.34 \pm 0.02$ Å $\quad M = 247.832$

$b = 16.75 \pm 0.04$ Å $\quad d_n = 1.591$ g/cm^3

$c = 6.72 \pm 0.02$ Å $\quad d_p = 1.561$ g/cm^3

$V = 1051.3$ Å^3 $\quad \mu(CuK_\alpha) = 41.6$ cm^{-1}

$F_{(000)} = 512$ $\quad Z = 4$

The space group was $P2_12_12_1$.

The structure was determined by the heavy atom method. The Ge atom was detected from the three-dimensional dispersion of the Patterson function. By means of successive calculation of the electron density, a model was obtained of the structure of ethylgermatran. The uncertainty on all nonzero images at this stage of the structural determination was 13.5%.

The structural study showed that the Ge atom in I possesses the configuration of the trigonal bipyramid, in the apices of which the N and C atoms (of the ethyl group) are found. The Ge atom is displaced from its plane by 0.23 Å on the side of the C atom from the ethyl group. In this stage of our research $l_{Ge \leftarrow N} = 2.25$ Å, ∠N–Ge–C = 176°. The isomerism of 1-ethylgermatran and ethylsilatran was established experimentally [3].