Formation of Two Novel Heterocycles

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During studies on 2-aminobenzothiazole (I), we have synthesised 2- $(\omega$ -chloroacylamino)benzothiazoles (II), so that the pharmacological properties of the products of the reaction of these chloroacylamino-derivatives (II) with various amines can be examined.¹ While the reaction of 2-aminobenzo-

$$\begin{array}{c|c}
N & N \\
S & NH \cdot CO \cdot [CH_2]_n CI \\
\hline
(II) & (III)
\end{array}$$

$$\begin{array}{c|c}
N & N \\
\hline
(III) & (IV)
\end{array}$$

thiazole with chloroacetyl chloride proceeds normally, leading exclusively to the corresponding 2-(2-chloroacetamido)benzothiazole (II, n=1), the reaction with β -chloropropionyl and γ -chlorobutyryl chloride shows certain peculiarities.

Reaction of equimolar quantities (chloroform solution) of 2-aminobenzothiazole and β -chloropropionyl chloride in alkaline medium (Na₂CO₃) gives 2-(3-chloropropionylamino)benzothiazole (II, n=2, 45—50% yield) and a halogen-free product (C₁₀H₈N₂OS, m.p. 214—217°, 18—20% yield). We assign to this product the structure (III), which is confirmed by elemental analysis, mass-spectral

determination of the molecular weight and spectra† $[\lambda_{\max} 218 \text{ m}\mu \ (\epsilon 27,000) \text{ and } 310 \text{ m}\mu \ (\epsilon 25,500); \nu_{\max} (\text{KBr}) \ 6.05 \ \mu]$. The corresponding chloroacyl compound (II) (n=2) presents a λ_{\max} at 275 m μ of moderate intensity and ν_{\max} (KBr) at 5.92 μ . Compound (III) being too insoluble in the usual solvents, it was not possible to obtain its n.m.r. spectrum.

Reaction of 2-aminobenzothiazole with γ chlorobutyryl chloride under the same experimental conditions leads to the corresponding chloroamide (II, n = 3, 80% yield). This, on reaction with certain amines, e.g., diethylamine and piperidine, gives a compound C₁₁H₁₀N₂OS, m.p. 177—178°, instead of the desired alkylaminoacylamino-derivative. Again, the structure (IV) assigned to this product is confirmed by elemental analysis and spectral data. Of considerable value for this assignation is the n.m.r. spectrum obtained in CDCl₃—CCl₄ solution at 60 Mc./sec. (Me₄Si as internal standard); signals appear at δ 2.0-2.8 p.p.m. as a multiplet (4H), δ 4·21 p.p.m. as a triplet (2H, $-CO-CH_2-$) and $\delta 7\cdot 2-7\cdot 9$ p.p.m. as a multiplet (4H, aromatic).

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- † All new compounds gave satisfactory elemental analyses. U.v. spectra were measured in absolute ethanol solution.
 - ¹ G. Tsatsas and N. Vassiliadou, Bull. Soc. chim. France, 1962, 736.