# SYNTHESIS OF 5-AMINO-1-(AMINOTHIOFORMYL)-1,2,4-TRIAZOLES

G. I. Chipen, R. P. Bokaldere, and V. Ya. Grinshtein

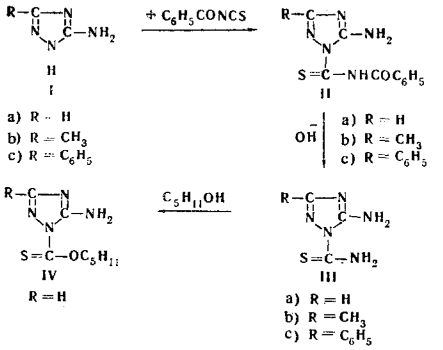
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 4, No. 4, pp. 743–745, 1968

UDC 547.792

By the reaction of 5-amino-1,2,4-triazoles with benzoyl isothiocyanate we have synthesized 5-amino-1-(benzoylaminothioformyl)-1,2,4-triazoles, which form 5-amino-1-(aminothioformyl)-1,2,4-triazoles on alkaline hydrolysis.

Of the N-aminothioformyl derivatives of 5-amino-1,2,4-triazoles, only some 5-amino-N-(alkyl- and arylaminothioformyl)-1,2,4-triazoles, obtained from the corresponding aminotriazoles and alkyl and aryl isothiocyanates, are described in the literature [1,2]. In order to synthesize 5-amino-N-(aminothioformyl)-1,2,4-triazoles we have studied the reaction of the aminotriazoles with benzoyl isothiocyanate, since attempts to obtain these compounds by the reaction of the aminotriazoles with potassium thiocyanate in analogy with the synthesis of 5-amino(1-aminoformyl)-1,2,4-triazoles [3] were unsuccessful.

The reaction of the aminotriazoles with benzoyl isothiocyanate forms 5-amino-1-(benzoylaminothioformyl)-1,2,4-triazoles (IIa, b, c). By analogy with reactions of aminotriazoles with some electrophilic reagents — the reactions with KCNO and methyl isocyanate [3] and acylation and alkylation [4]— we assumed that the benzoylaminothioformyl group was located on the first nitrogen atom of the triazole ring.



The reactions of a, b, and c with benzoyl isothiocyanate were carried out in a mixture of anhydrous acetone and dimethylformamide, since in the presence of water benzoyl isothiocyanate undergoes hydrolysis [5] and 5-amino-1-benzoyl-1,2,4-triazoles are formed as by-products, which lowers the yield of the main reaction.

On being boiled with 10% alkali, compounds IIa, b, and c are readily hydrolyzed, forming the corresponding aminothioformyl derivatives IIIa, b, and c and benzoic acid. Compounds IIa, b, and c and IIIa, b, and c are crystalline substances; IIa, b, and c and IIIc are insoluble in water, while IIIa and b are soluble in water. Compounds IIa and b and IIIa, b, and c decompose at the melting point, which excludes the possibility of obtaining the corresponding triazolylthiourea derivatives by thermal isomerization. The triazolylthioureas were not formed, either, when IIa, b, and c were boiled in propanol and pentanol — in contrast to 5-amino-N-(alkyl- or arylaminothioformyl)-1,2,4-triazoles which form N-(alkyl or aryl)-N'-(1,2,4-triazol-5-yl)thioureas under similar conditions [6].

When IIIa was boiled in pentanol, 5-amino-1-(pentyloxythioformyl)-1,2,4-triazole (IV) was formed. Compounds IIIb and c underwent no change under similar conditions.

## EXPERIMENTAL

**5-Amino-1-(benzoylaminothioformyl)-1,2,4-triazoles (IIa, b, c).** A solution of benzoyl isothiocyanate in acetone prepared from 10 g of ammonium thiocyanate and 10 ml of benzoyl chloride by the method described in [7] was added to a solution of the appropriate aminotriazole (0.075 mole) in the minimum amount of anhydrous dimethylformamide (20–40 ml). The solution was boiled in the water bath for 2 hr, the acetone was distilled off in vacuum, and the residue was poured into 500 ml of water. IIa, b, c deposited. In the case of **Ib**, even during boiling compound IIb crystallized out; after the boiling process this was filtered off and the filtrate was treated as described above. The physical constants and analytical data of the compounds IIa, b, and c synthesized are given in Table 1.

**5-Amino-1-(aminothioformyl)-1,2,4-triazoles (IIIa, b, c).** These were obtained by boiling IIa, b, c, respectively, in 10% caustic soda solution for 5 min. After cooling, the solution was acidified with concentrated HCl to pH ~2. Mixtures of IIIa, b, and c with benzoic acid were obtained, and the latter was eliminated by washing the dry pro-

Table 1

5-Amino-1-(benzoylaminothioformyl)-1,2,4-triazoles

| Compound | Solvent for crystallization | Mp, °C | Empirical formula | Found, % | | | | Calculated, % | | | | Yield, % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | C | H | N | S | C | H | N | S | |
| IIa | Water-ethanol | 176 (Decomp.) | $C_{10}H_9N_5OS$ | 48.57 | 3.72 | 28.67 | 12.86 | 48.57 | 3.67 | 28.32 | 12.96 | 42 |
| IIb | Dimethylformamide-water | 202 (Decomp.) | $C_{11}H_{11}N_5OS$ | 50.15 | 4.12 | 26.52 | 12.08 | 50.56 | 4.24 | 26.80 | 12.27 | 45 |
| IIc | Dimethylformamide-water | 197 | $C_{16}H_{13}N_5OS$ | 59.92 | 4.07 | 21.67 | 9.56 | 59.42 | 4.05 | 21.65 | 9.91 | 37 |

Table 2

5-Amino-1-(aminothioformyl)-1, 2, 4-triazoles

| Compound | Solvent for crystallization | Mp, ° C | Empirical formula | Found, % | | | | Calculated, % | | | | Yield, % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | C | H | N | S | C | H | N | S | |
| IIIa | Water | 230 (Decomp.) | $C_3H_5N_5S$ | 25.92 | 3.62 | 48.71 | 22.87 | 25.16 | 3.52 | 48.91 | 22.39 | 87 |
| IIIb | Water | 236 (Decomp.) | $C_4H_7N_5S$ | 30.73 | 4.36 | 43.71 | 20.47 | 30.56 | 4.48 | 44.55 | 20.39 | 89 |
| IIIc | Dimethylformamide-water | 244 (Decomp.) | $C_9H_9N_5S$ | 48.73 | 4.10 | 31.92 | 15.04 | 49.29 | 4.14 | 31.94 | 14.62 | 91 |

duct with ether. The physical constants and analytical data are given in Table 2.

**5-Amino-1-(pentyloxythioformyl)-1, 2, 4-triazole (IV).** A mixture of 0.45 g of IIIa in 15 ml of pentanol was boiled for 2 hr. After cooling, 0.3 g (44%) of IV crystallized out. Mp 170° C (from a mixture of water and ethanol). Found, %: C 44.59; H 6.24; N 26.10; S 15.00. Calculated for $C_8H_{14}N_4OS$, %: C 44.83; H 6.58; N 26.14; S 14.93.

## REFERENCES

1. P. Fantl and H. Silbermann, Ann. 467, 247, 1928.
2. British patent no. 919458, 1963; C. A., 59, 8759, 1963.
3. E. C. Taylor and R. W. Hendess, J. Am. Chem. Soc., 87, 1980, 1965.
4. G. I. Chipen, Ya. A. Eidus, Ya. S. Bobovich, and V. Ya. Grinshtein, ZhSKh, 6, 53, 1965.
5. D. T. Elmore and I. R. Ogle, J. Chem. Soc., 1141, 1958.
6. G. I. Chipen, R. P. Bokaldere, and V. Ya. Grinshtein, KhGS [Chemistry of Heterocyclic Compounds], 2, 110, 1966.
7. Organic Synthesis [Russian translation], IL, Moscow, 4, 512, 1963.

21 June 1966

Institute of Organic Synthesis AS
Latvian SSR