

I is also obtained by treating the diethylacetal of benzimidazolyl-2-mercaptoacetic aldehyde with  $\text{H}_2\text{SO}_4$  or by heating with  $\text{POCl}_3$ , followed by the action of  $\text{H}_2\text{SO}_4$  on the 3-ethoxythiazolino [3,2-a] benzimidazole. I forms a picrate, salts with mineral acids, and quaternary salts with alkyl halides.

Thiazolo [3,2-a] benzimidazole (I), colorless needles, mp 141.5–142.5 (ex aqueous EtOH). Found: C 61.83; H 3.27; N 16.28; S 16.28%. Calculated for  $\text{C}_9\text{H}_6\text{N}_2\text{S}$ : C 62.04; H 3.47; N 16.08; S 18.41%.

#### REFERENCES

1. A. R. Todd, F. Bergel and Karimullah, Ber., 69, 217, 1936.
2. H. Andersag and H. Westphal, Ber., 70, 2035, 1937.
4. B. Rudner, U.S. Patent no. 279 0172; C.A., 51, 13934, 1957.
5. J. J. D'Amico, R. H. Campbell, and E. C. Guinn, J. Org. Chem., 29, 865, 1964.
6. I. I. Iwai and T. Hiracka, C. A., 61, 9487, 1964.

3 January 1966

Ordzhonikidze All-Union Scientific Research  
Chemical and Pharmaceutical Institute,  
Zaporozh'e Pharmaceutical Institute

UDC 547.823

#### SYNTHESIS OF DERIVATIVES OF 3-( $\delta$ -BUTOXYCARBONYL) PYRIDAZIN-6-ONE

R. G. Kitner and N. V. Savitskaya

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 2, No. 6, pp. 946, 1966

It is known that the action of hydrazine hydrate on  $\gamma$ -oxopimelic acid or its ethyl ester gives 3-( $\beta$ -ethoxycarbonyl) pyridazin-6-one (called in the literature pyridazin-6-one-3-propionic acid), or its derivatives [1].

We have investigated the action of hydrazine hydrate on  $\gamma$ -ketoazelaic acid and its ethyl ester. Reaction of the latter with 1 mole of hydrazine hydrate gives the ethyl ester of 3- $\delta$ -(butoxycarbonyl) pyridazin-6-one. The same compound was obtained by prolonged boiling of the ethyl ester of 3-( $\delta$ -butoxycarbonyl) pyridazin-6-one with hydrazine hydrate. However the hydrazide could be isolated only as the hydrazone with anisaldehyde. Treatment of  $\gamma$ -ketoazelaic acid with 1 mole of hydrazine hydrate led to the isolation of 3-( $\delta$ -butoxycarbonyl) pyridazin-6-one. The diethylamide of 3-( $\delta$ -butoxycarbonyl) pyridazin-6-one could not be obtained either by prolonged heating of the ester of this acid under ordinary conditions, or under pressure.

Ethyl ester of 3-( $\delta$ -butoxycarbonyl) pyridazin-6-one was prepared by reacting 5 g diethyl  $\gamma$ -ketoazelaate, 1 ml hydrazine hydrate (99.7%), 5 ml dry EtOH, and 2 drops of AcOH, together by refluxing the mixture for 3 hr 30 min. After removing solvent, the residue (4 g, mp 55–58° C) was twice recrystallized from ether, to give colorless needles, mp 61–63° C. Found: C 58.23; H 7.76; N 12.62%. Calculated for  $\text{C}_{11}\text{H}_{18}\text{O}_3\text{N}_2$ : C 58.38; H 8.01; N 12.37%; C 58.38, H 8.01; N 12.37%.

3-( $\delta$ -Butoxycarbonyl) pyridazin-6-one was prepared by refluxing together for 1 hr a mixture of 4 g  $\gamma$ -ketoazelaic acid, 1 ml hydrazine hydrate, and 20 ml dry EtOH, yield 2.5 g, mp 123–125° C (ex EtOAc). Found: C 54.15; H 7.19; N 14.37%. Calculated for  $\text{C}_9\text{H}_{14}\text{O}_3\text{N}_2$ : C 54.53; H 7.12; N 14.14%.

Amide of 3-( $\delta$ -butoxycarbonyl) pyridazin-6-one. This was prepared from the ethyl ester of 3-( $\delta$ -butoxycarbonyl) pyridazin-6-one and concentrated aqueous ammonia, mp 152–154.5° C (ex absolute EtOH). Found: C 54.46; H 7.64; N 21.21%. Calculated for  $\text{C}_9\text{H}_{15}\text{N}_3\text{O}_2$ : C 54.80; H 7.67; N 21.31%.

Anisylhydrazone hydrazide of 3-( $\delta$ -butoxycarbonyl) pyridazin-6-one. 1.1 g diethyl  $\gamma$ -ketoazelaate, and 1.2 ml hydrazine hydrate in 5 ml dry EtOH were refluxed together for 4 hr, then left overnight. The material remaining after removing the solvent crystallized, and had mp 78–98° C; it was dissolved in ethanol and treated with 0.6 g anisaldehyde. Yield 0.6 g anisylhydrazone, colorless crystals, mp 176–177° C. Found: C 61.50; H 6.63; N 17.07%. Calculated for  $\text{C}_{17}\text{H}_{22}\text{N}_4\text{O}_2$ : C 61.80; H 6.71; N 16.96%.

#### REFERENCES

1. N. H. Beaugeard and M. J. Matti, *Bull. soc. chim. Fr.*, 1612, 1956.
2. B. Camerino and B. Patelli, *Farmaco (Pavia) Ed. Sci.*, 11, 446, 1956; *C. A.*, 53, 11220, 1959.

9 January 1966

Ordzhonikidze All-Union Scientific Research  
Chemical and Pharmaceutical Institute, Moscow