

# REACTIONS OF AZIDOHETEROCYCLIC COMPOUNDS WITH C - H ACIDS

## IV.\* REACTION OF 1-PHENYL-4-AZIDO-5-CHLORO-6-PYRIDAZONE WITH SOME $\beta$ -DICARBONYL COMPOUNDS

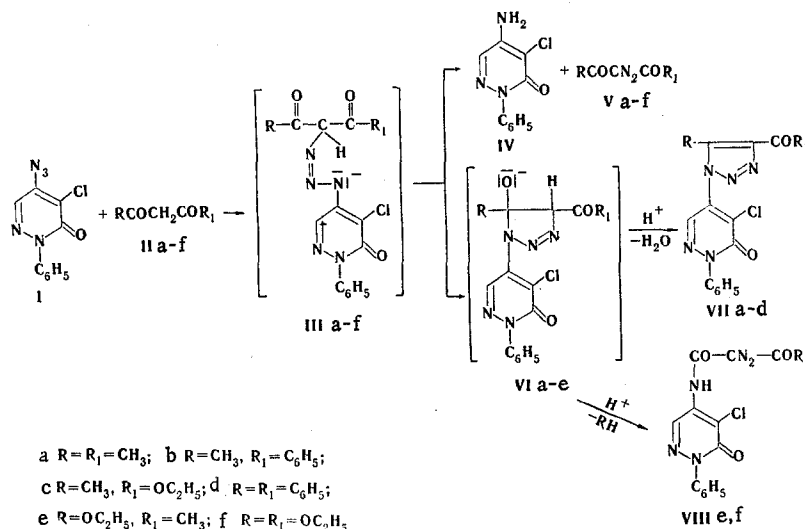
V. V. Solov'eva and É. Yu. Gudriniece

UDC 547.852.2.3'791

1-Phenyl-4-azido-5-chloro-6-pyridazone (I) reacts with acetylacetone, benzoylacetone, dibenzoylmethane, and acetoacetic ester in the presence of triethylamine to give 1,2,3-triazolyl-6-pyridazones. Diazodicarbonyl derivatives were obtained with diethyl malonate and acetoacetic ester in the presence of sodium ethoxide. Dimedone and indane-1,3-dione react with I to give 1-phenyl-4-amino-5-chloro-6-pyridazone and 2-diazodimedone and 2-diazoindane-1,3-dione, respectively.

In a continuation of our investigations of reactions of azido-heterocyclic compounds with C-H acids [1], we have studied the reactions of 1-phenyl-4-azido-5-chloro-6-pyridazone (I) with some  $\beta$ -dicarbonyl compounds. Judging from [2-6], the formation of derivatives of 1,2,3-triazole [2,3], primary amines, and diazodicarbonyl compounds [4-6] is possible in these reactions.

Primarily 1,2,3-triazolyl-6-pyridazones (VIIa-d) were obtained in the reactions of I with acetylacetone, benzoylacetone, dibenzoylmethane, and acetoacetic ester in the presence of an equimolar amount of triethylamine. Small amounts of 1-phenyl-4-amino-5-chloro-6-pyridazone (IV), the presence of which in the reaction mixture can be explained by decomposition of intermediate triazene III [4], are also isolated. The formation of triazoline VI is apparently less likely as the acidity of the  $\beta$ -diketone decreases, and the yields of VIIa-d therefore decrease, while the yields of IV, respectively, increase.



\*See [1] for communication III.

Riga Polytechnic Institute. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 2, pp. 256-258, February, 1973. Original article submitted January 13, 1972.

© 1975 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for \$15.00.

TABLE 1. 6-Pyridazone Derivatives (VII)

Comp.*	R	R <sub>1</sub>	mp, °C	Empirical formula	Found, %				Calc., %				IR spectra cm <sup>-1</sup> (C=O)	Yield, %
					C	H	Cl	N	C	H	Cl	N		
VIIa	CH <sub>3</sub>	CH <sub>3</sub>	212— 213	C <sub>15</sub> H <sub>12</sub> ClN <sub>5</sub> O <sub>2</sub>	54,2	3,5	10,9	21,1	54,6	3,7	10,7	21,2	1672, 1651	89,5
VIIb	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	187— 188	C <sub>20</sub> H <sub>14</sub> ClN <sub>5</sub> O <sub>2</sub>	61,0	3,5	—	17,9	61,3	3,6	—	17,9	1682, 1661	66,4
VIIc	CH <sub>3</sub>	OC <sub>2</sub> H <sub>5</sub>	207— 208	C <sub>15</sub> H <sub>14</sub> ClN <sub>5</sub> O <sub>3</sub>	52,2	3,8	10,2	19,9	51,8	4,06	10,2	20,1	1703, 1669	63,1
VIIId	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	127— 128	C <sub>25</sub> H <sub>16</sub> ClN <sub>5</sub> O <sub>2</sub>	65,7	3,4	7,9	15,4	65,1	3,5	7,8	15,4	1691, 1650	44,5

\*The yields of IV, with mp 200–201°, were 3.3, 3.3, 24.5, and 27.9%, respectively.

In the presence of an equimolar amount of sodium ethoxide, I reacts with acetoacetic ester to give 1-phenyl-4-( $\alpha$ -oxo- $\beta$ -diazoo- $\beta$ -acetylethylamino)-5-chloro-6-pyridazone (VIIIe), ethyl diazoacetoacetate (Vc), and amine IV. The formation of VIIIe can be explained by the instability of intermediate anion VIe, which is cleaved to VIIIe in acidic media [7]. The reaction of I with diethyl malonate in the presence of sodium ethoxide proceeds similarly, while only amine IV and diazomalonic ester are isolated in the presence of triethylamine. Compound VI (R = R<sub>1</sub> = OC<sub>2</sub>H<sub>5</sub>) apparently does not form under these conditions.

In the presence of both sodium ethoxide and triethylamine, I reacts with dimedone and indane-1,3-dione to give amine IV, 2-diazodimedone, and 2-diazoindane-1,3-dione, respectively. Bindone [5] apparently forms in the reaction of I with indane-1,3-dione as a result of self-condensation of the latter, for we were able to isolate a small amount of diazobindone.

#### EXPERIMENTAL

The purities of the substances obtained were checked by thin-layer chromatography on activity II aluminum oxide. A hexane–chloroform–ethyl acetate (1:1:1) system was used. The IR spectra of paraffin oil and hexachlorobutadiene suspensions were obtained with a UR-20 spectrophotometer.

1-Phenyl-4-(4'-acetyl-5'-methyl-1',2',3'-triazol-1'-yl)-5-chloro-6-pyridazone (VIIa). A mixture of 0.4 ml (4 mmole) of acetylacetone and 0.4 ml (4 mmole) of triethylamine was cooled to 5°, and a solution of 1.0 g (4 mmole) of I in 5 ml of absolute dioxane was added to it slowly with stirring. The mixture was then held at 5° for 1 h. The precipitate was recrystallized from ethanol and dioxane (5:1) to give 1.2 g (89.5%) of colorless crystals of VIIa (Table 1). The product was quite soluble in alcohols, dioxane, acetone, tetrahydrofuran, and dimethylformamide.

The filtrate remaining after separation of VIIa was diluted to 100 ml with water, and the mixture was acidified to pH ~ 2 with hydrochloric acid. The acidic mixture was extracted with diethyl ether (five 20-ml portions), and the ether extracts were dried with anhydrous sodium sulfate. The ether was removed by vacuum distillation with a water aspirator to give 0.03 g (3.3%) of IV with mp 200–201° [8] (from ethanol).

The remaining compounds (VIIb–c) were similarly obtained (Table 1).

1-Phenyl-4-( $\alpha$ -oxo- $\beta$ -diazoo- $\beta$ -acetylethylamino)-5-chloro-6-pyridazone (VIIIe). A solution of 1.0 g (4 mmole) of I in 5 ml of absolute dioxane was added with stirring to 0.5 ml (4 mmole) of acetoacetic ester in 4 ml of a 1 M solution of sodium ethoxide. After 1 h, the precipitate was crystallized from ethanol to give 0.6 g (64.6%) of IV.

The filtrate remaining after separation of IV was diluted to 100 ml with water, and the mixture was acidified to pH ~ 2 with hydrochloric acid. The precipitate was removed by filtration and crystallized from ethanol to give 0.4 g (22.8%) of colorless crystals of VIIIe with mp 185–186° (dec.). IR spectrum, cm<sup>-1</sup>: 1675, 1659, 1631 (C=O), 2148 (=N<sub>2</sub>); 3140 (NH). Found, %: C 50.6; H 3.0; Cl 11.1; N 21.1. C<sub>14</sub>H<sub>10</sub>ClN<sub>5</sub>O<sub>3</sub>. Calculated, %: C 50.7; H 3.0; Cl 10.7; N 21.0.

Compound VIIIe decomposes with nitrogen evolution at its melting point and under the influence of concentrated mineral acids. The aqueous solution remaining after separation of VIIIe was extracted with diethyl ether (five 20-ml portions), and the ether extracts were dried with anhydrous sodium sulfate to give 0.1 g (16%) of ethyl diazoacetoacetate (Vc) as a yellowish oil. IR spectrum, cm<sup>-1</sup>: 1660, 1713 (C=O); 2154 (=N<sub>2</sub>).

Compound VIII<sub>f</sub> with mp 150-151° was similarly obtained in 39.4% yield. Found, %: C 49.8; H 3.3; N 19.4. C<sub>15</sub>H<sub>12</sub>ClN<sub>5</sub>O<sub>4</sub>. Calculated, %: C 49.8; H 3.3; N 19.4. IR spectrum, cm<sup>-1</sup>: 1711, 1683 (CO); 2139, 2152 (=N<sub>2</sub>); 3205 (NH). The yield of IV was 52.4%.

Reaction of I with Dimedone. A solution of 1.0 g (4 mmole) of I in 5 ml of absolute dioxane was added to 0.6 g (4 mmole) of dimedone and 0.4 ml (4 mmole) of triethylamine in 5 ml of absolute dioxane, and the mixture was stirred for 4 h. The precipitate was crystallized from ethanol to give 0.6 g (69.2%) of IV.

The dioxane was removed by vacuum distillation with a water aspirator, and the dry residue was washed with diethyl ether. The ether was removed by distillation to dryness, and the residue was crystallized from diethyl ether-petroleum ether (1:1) to give 0.3 g (48.3%) of 2-diazodimedone with mp 106-108° [6]. IR spectrum, cm<sup>-1</sup>: 1638, 1657 (C=O); 2134, 2184 (=N<sub>2</sub>). Found, %: N 17.1. C<sub>8</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>. Calculated, %: N 16.8.

Reaction of I with Indane-1,3-dione. This reaction proceeded similarly to give 59.2% of IV; the yield of 2-diazoindane-1,3-dione, with mp 149° [5] was 18.4%; the yield of diazodindone, with mp 208° [5], was 0.1 g (8.4%).

#### LITERATURE CITED

1. V. V. Solov'eva and É. Yu. Gudriniece, *Izv. Akad. Nauk Latv. SSR, Ser. Khim.*, 572 (1972).
2. O. Dimroth, *Ber.*, 35, 1029 (1902).
3. L. Gattermann and H. Rolfes, *Ann.*, 425, 135 (1921).
4. M. Regitz, *Ber.*, 99, 3128 (1966).
5. M. Regitz and G. Heck, *Ber.*, 97, 1482 (1964).
6. M. Regitz, *Ann.*, 676, 101 (1964).
7. A. Kh. Karklin' and É. Yu. Gudriniece, *Izv. Akad. Nauk Latv. SSR, Ser. Khim.*, 449 (1970).
8. L. Ya. Avota, N. Ya. Ozolin', and S. A. Giller, *Izv. Akad. Nauk Latv. SSR, Ser. Khim.*, 347 (1967).