Oxidation of Bis-semicarbazones of α-Dicarbonyl Compounds with Lead(IV) Acetate. A One-step Synthesis of 1-(*N*-Ureido)-1,2,3-triazoles

N. E. Alexandrou*, S. Adamopoulos[1]

Laboratory of Organic Chemistry, University of Thessaloniki, Greece

In connection with our previous work on the oxidation of bis-aroylhydrazones of α-dicarbonyl compounds, which leads to the formation of 1-(α-aroyloxyarylideneamino)-1,2,3-triazoles[2,3] (1,2,3-triazolyl-isoimides), we have tried to oxidise bis-semicarbazones (**1**) with lead(IV) acetate. Although lead(IV) acetate has been used for the oxidation of a great variety of organic nitrogen compounds[4], no data have been reported on the oxidation of bis-semicarbazones. It should be noticed, however, that the oxidation of aldehyde semicarbazones gives 2-amino-1,3,4-oxadiazoles[5], whereas ketone semicarbazones are finally oxidized to Δ^3-1,3,4-oxadiazolin-2-ones[6].

The bis-semicarbazones of α-dicarbonyl compounds (**1**) undergo cyclisation on treatment with lead(IV) acetate to give ureido-1,2,3-triazoles (**3**), which are thus obtained for the first time in a yield of 30–40% (Table). The products

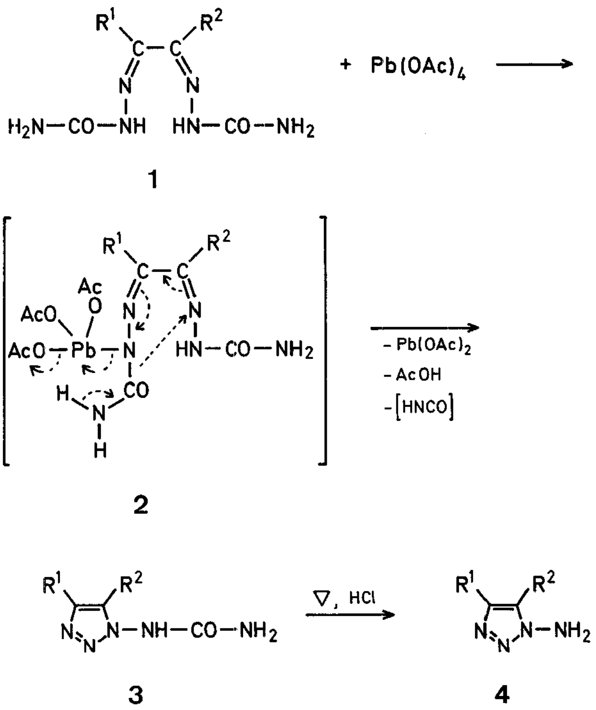

Table. Synthesis of 1-(*N*-Ureido)-1,2,3-triazoles (**3**) by Oxidation of Bis-semicarbazones (**1**)

	Products[a] (**3**)				Amino-triazoles (**4**)	
	R^1	R^2	m.p.	Yield (%)	m.p.	Yield (%)
a	CH_3	CH_3	225–226°	30	89–91°	65
b	C_6H_5	C_6H_5	209–211°	40	126–128°	55
c	C_6H_5	CH_3	207–208°	34	142–144°	55
d	$4\text{-}H_3C\text{—}C_6H_4$	CH_3	203–204°	40	164–165°	58
e	$4\text{-Br—}C_6H_4$	CH_3	204–205°	38	169–171°	50
f	$4\text{-}H_3C\text{—}C_6H_4$	H	224–226°	32	123–124°	52

[a] All products **3** and **4** had satisfactory elemental analyses ($C \pm 0.3\%$, $H \pm 0.15\%$, $N \pm 0.4\%$) and spectroscopic data (I.R., N.M.R., M.S.) in agreement with proposed structures.

3 were obtained by reacting in dichloromethane solution equimolecular amounts of **1** and lead(IV) acetate for 3h at room temperature. They exhibit in the I.R. spectra characteristic absorptions at 3385–3200 (NH) and 1685–1670 (CO) cm^{-1} and main peaks in their mass spectra at $M^{\oplus}$, $[M-28]^{\oplus}$ and $[M-58]^{\oplus}$, the last peak corresponding to loss of the $NCONH_2$ fragment.

The structure of ureidotriazoles **3c–f** derived from the oxidation of unsymmetric bis-semicarbazones has been proved by acid hydrolysis with concentrated hydrochloric acid to give the corresponding 1-amino-1,2,3-triazoles (**4**). It has been shown that these amino-triazoles were identical with those obtained by hydrolysis of the analogously 4,5-substituted triazolyl-isoimides.

Concerning the reaction mechanism, it is suggested that the intermediate **2** upon elimination of lead(II) acetate, isocyanic acid, and acetic acid undergoes cyclisation to give the ureido-product **3**.

Preparation of 1-(*N*-Ureido)-1,2,3-triazoles (3); General Procedure: To a suspension of bis-semicarbazone **1** (0.02 mol) – prepared according to a general procedure[7] – in dichloromethane (100 ml) is added lead(IV) acetate (0.021 mol) and the mixture is stirred for 3h at room temperature. The reaction mixture is filtered and the precipitate is treated with methanol. The methanolic solution upon evaporation gives the ureido-triazole (**3**), which is recrystallised from methanol or ethanol; yields: 30–40% (Table). The yield is not increased by longer reaction times or by a slight heating.

Hydrolysis of Ureido-triazoles (2) to 1-Amino-1,2,3-triazoles (4): A mixture of ureido-triazole (0.5 mmol) and concentrated hydrochloric acid (5 ml) is refluxed for 2 h. The reaction mixture is neutralised with sodium hydroxide solution and extracted with chloroform. Evaporation of the solvent afforded the crude 1-amino-1,2,3-triazole in 60% yield; the product was recrystallized from a mixture of petroleum ether/chloroform. These aminotriazoles (Table) were identical with those obtained by hydrolysis of the corresponding triazolyl-isoimides.

We thank the National Hellenic Research Foundation for financial support and Professor A. R. Katritzky for helpful discussions.

Received: April 12, 1976

---

[1] S. Adamopoulos, *Ph. D. Thesis*, to be submitted to the University of Thessaloniki.

[2] N. E. Alexandrou and E. D. Micromastoras, *J. Org. Chem.* **37**, 2345 (1972).

[3] H. Bauer, A. J. Boulton, W. Fedeli, A. R. Katritzky, A. Majid-Hamid, F. Mazza and A. Vaciago, *J. Chem. Soc. Perkin Trans. 2* **1972**, 663.

[4] J. B. Aylward, *Q. Rev. Chem. Soc.* **25**, 407 (1971).

[5] F. L. Scott, T. M. Lambe, R. N. Butler, *J. Chem. Soc. Perkin Trans. 1* **1972**, 1918.

[6] P. Knittel, S. L. Lee, J. Werkentin, *Can. J. Chem.* **50**, 3248 (1972).

[7] K. V. Auwers, H. Ludewig, *Justus Liebigs Ann. Chem.* **526**, 130 (1936).