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An efficient method for the oxidation of urazoles with $[NO^+ \cdot crown \cdot H(NO_3)_2^-]$

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Abstract—An ionic complex has been obtained from N_2O_4 in the presence of the macrocyclic polyether 18-crown-6. This crystalline compound was used as an effective oxidizing agent for the oxidation of urazoles to their corresponding triazolinediones at room temperature with excellent yields. © 2001 Elsevier Science Ltd. All rights reserved.

4-Substituted-1,2,4-triazole-3,5-diones (TADs) are notable for their ability to participate in a wide range of concerted and stepwise reactions.[1–7] Considerable attention has been paid to their additions to activated alkenes,[1–4] electrophilic aromatic substitution,[5] dehydrogenating properties[6] and oxidation of alcohols to aldehydes and ketones.[7] The unusual reactivity which makes TADs (**2**, **4**) of interest also makes them hard to prepare and purify.

Although a variety of reagents are capable of effecting these oxidations,[8–11] this transformation is not easy because these compounds are very sensitive to the oxidizing agents and reaction conditions.

However, most of the reported reagents produce by-products which either destroy, or are difficult to remove from, the sensitive triazolinedione. Another major drawback to the older procedures is their use of reagents which are either highly toxic or impart serious disposal problems (or both).[8] Very recently we, among many others, have demonstrated that heterogeneous reagent systems have many advantages such as simple experimental procedures, mild reaction conditions and the minimization of chemical wastes as compared to their liquid phase counterparts.[12] We were interested in finding a new form of heterogeneous system for urazole oxidation and thus, we have investigated a number of different reaction conditions based upon the in situ generation of NO^+. In continuation of our studies on the application of N_2O_4,[1,11] metal nitrate dinitrogen tetroxide complexes[13] and complexation of transition metals with macrocyclic ethers,[14] we found that 18-crown-6 gives an ionic complex $[NO^+ \cdot crown \cdot H(NO_3)_2^-]$ in quantitative yields with N_2O_4 gas. By using this new reagent, we report in this article a simple and convenient method for the effective conversion of urazoles (**1** and **3**) to their corresponding triazolinediones (**2** or **4**) under mild and heterogeneous conditions.

Different types of urazoles (**1** and **3**) were subjected to oxidation reaction in the presence of $[NO^+ \cdot crown \cdot H(NO_3)_2^-]$ in dichloromethane (Schemes 1 and 2). The oxidation reactions were performed under mild and completely heterogeneous conditions at room temperature with quantitative yields. As mentioned above, the oxidation reactions are heterogeneous because urazoles and bis-urazoles [(**1**, **3**) white solids] are insoluble in dichloromethane whereas, all the triazolinediones and bis-triazolinediones [(**2**, **4**) red and pink, respectively] are very soluble in dichloromethane. As might be expected, the oxidation products (**2**, **4**) migrate to the liquid phase (CH_2Cl_2) immediately after oxidation.

This oxidation reaction can be readily carried out only by placing $[NO^+ \cdot crown \cdot H(NO_3)_2^-]$, **1** or **3**, SiO_2 (for the adsorption of HNO_3 and H_2O) with dichloromethane as solvent in a reaction vessel, and efficiently stirring the resulting heterogeneous mixture at room temperature. The reactions were completed immediately. The solvent was evaporated and the extra pure triazolinediones (**2** or **4**) were obtained by sublimation of the residue.

In conclusion, practical and efficient oxidation of urazoles was achieved using the present methodology. The $[NO^+ \cdot crown \cdot H(NO_3)_2^-]$ complex, with easy preparation and handling, can act as a relatively stable and efficient

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Keywords: oxidation; triazolinedione; urazole; $[NO^+ \cdot crown \cdot H(NO_3)_2^-]$.

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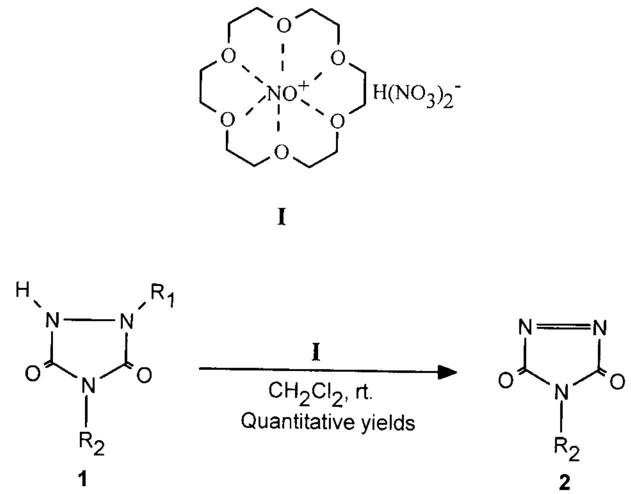
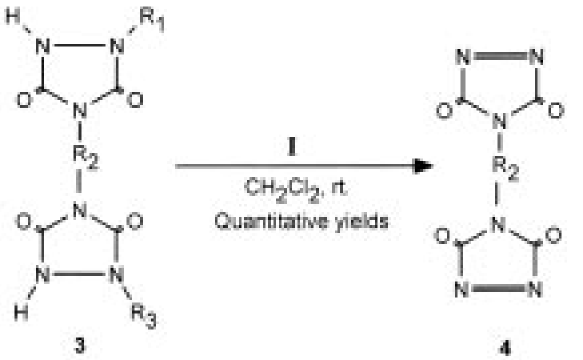


1	R_1	R_2
a	H	Me
b	H	Et
c	Na	*n*-Pr
d	H	*n*-Bu
e	H	Cyclohexyl
f	H	Ph
g	H	4-Cl-C_6H_4
h	H	4-NO_2-C_6H_4

Scheme 1.

reagent as a source for the delivery of nitrosonium ion (NO^+) under mild and homogeneous conditions. Meanwhile, 18-crown-6 can be recycled and reused. The [NO^+·crown·$H(NO_3)_2^-$] is completely soluble in dichloromethane and also more reactive than those reagents which were reported previously.[1–9] We believe that the present methodology is an important addition to existing methodologies.



3	R_1	R_2	R_3
a	Na	-$(CH_2)_6$-	Na
b	H		H

Scheme 2.

1. Experimental

1.1. General

Chemicals were purchased from Fluka, Merck, Riedel-dehaen AG and Aldrich chemical companies. The oxidation products were characterized by comparison of their spectral (IR, UV, ^1H NMR, and ^{13}C NMR) and physical data with literature [**2a**,[8] **2b**,[15] **2c**,[11] **2d**,[10] **2e**,[8] **2f**,[8] **2g**,[16] **2h**,[8] **4a**,[5] **4b**[5]]. All urazoles and bis-urazoles were synthesized according to our previously reported procedures.[1,4,5,10,11] The [NO^+·crown·$H(NO_3)_2^-$] was synthesized according to the reported procedure,[17] with a slight modification. Here, we used N_2O_4 gas instead of liquid N_2O_4. Dinitrogen tetroxide (N_2O_4) gas was generated in situ according to the previously reported procedure as follows.[1,10,11]

1.1.1. Generation of NO_2–N_2O_4 gas[1,10,11]. Lead(II) nitrate (50 g) was crushed into a powder and was dried in an oven at 120°C for three days. The resulting powder was transferred into a one-necked round-bottomed flask (250 ml) which was equipped with an air condenser and a gas trap containing P_2O_5. The flask was heated by a Bunsen burner to generate a brownish-red NO_2–N_2O_4 gas, which was used immediately for the subsequent preparation of [NO^+·crown·$H(NO_3)_2^-$].

1.1.2. Preparation of [NO^+·crown·$H(NO_3)_2^-$]. A solution of 18-crown-6 (5.286 g, 0.02 mol) in CH_2Cl_2 (10 ml) was prepared in a three-necked round-bottomed flask (50 ml) equipped with a magnetic stirrer, a gas inlet tube, a thermometer and a drying tube, and cooled to −10°C with an ice–salt bath while being stirred. Generated NO_2–N_2O_4 gas was bubbled through this solution for 30 min. The solvent was evaporated under vacuum at 20°C to give the [NO^+·crown·$H(NO_3)_2^-$] complex, as a pale yellow deliquescent solid compound **I** [8.380 g, 0.02 mol (~100%)], mp 50–55°C [Lit.[17] mp 53–55°C]. ^1H NMR (FT-90 MHz, $CDCl_3$/TMS): 3.536 (s, 24H), 11.464 (s, 1H).

1.1.3. Oxidation of urazole (1c) to substituted triazolinedione (2c)—a typical procedure. A solution of compound **1c** (0.164 g, 1 mmol), [NO^+·crown·$H(NO_3)_2^-$, 0.419 g, 1 mmol] and SiO_2 (0.3 g) in dichloromethane (3 ml) was stirred at room temperature (the reaction was complete immediately) and then filtered. Dichloromethane was removed by water bath (40–50°C),[18] and simple distillation. The residue was sublimed at 50°C. The yield was 0.135 g (95%) of crystalline pale red solid (**2c**), mp 44°C [Lit. mp 44°C]. ^1H NMR (FT-90 MHz, $CDCl_3$/TMS): δ 3.63 (t, 2H, $J=9.02$ Hz), 1.68 (sextet, 2H, $J=7.55$ Hz), 0.94 (t, 3H, $J=9.02$), [Lit.[5]]. ^{13}C NMR (FT-90 MHz, $CDCl_3$/TMS): δ 159.33, 42.88, 20.59, 10.66.

Acknowledgements

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18. These compounds are sensitive to light, heat, alcohols, ethers, transition metals and any nucleophiles. Also they are very volatile so that, if temperature rises above 50°C in the course of removing of CH_2Cl_2, some of TADs are simultaneously removed with solvent. Therefore, the temperature must be controlled; dichloromethane is the best solvent for this purpose.