

SHORT
COMMUNICATIONS

Calcium Hypochlorite as an Efficient Reagent for Oxidation of Urazoles under Mild Heterogeneous Conditions*

M. A. Zolfigol¹, Sh. Mallakpour², A. Khazaiae¹, R. G. Vaghaie¹, and M. Torabi¹

¹ Chemistry Department, College of Science, Bu-Ali Sina University, Hamadan, 65174 Iran
e-mail: zolfi@basu.ac.ir

² Organic Polymer Chemistry Research Laboratory, College of Chemistry, Isfahan University of Technology, Isfahan, 84156 Iran

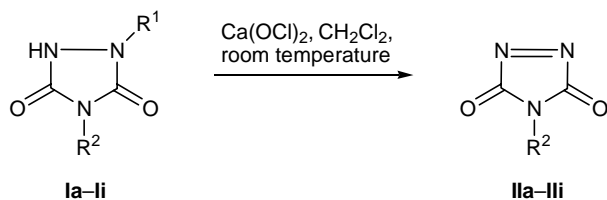
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4-Substituted 4,5-dihydro-3*H*-1,2,4-triazole-3,5-diones attract interest due to their versatile reactivity and ability to participate in such reactions as [4+2]- [1, 2] and [2+2]-cycloadditions [3], ene reactions [4], electrophilic aromatic substitution [5], dehydrogenation [6], and oxidation of alcohols to aldehydes and ketones [7]. On the other hand, their unusual reactivity makes them difficult to prepare and purify. For example, 4-phenyl-4,5-dihydro-3*H*-1,2,4-triazole-3,5-dione (**IIe**) is an extremely reactive dienophile and enophile which is at least 1000 times more reactive than tetracyanoethylene in the Diels–Alder reaction with 2-chlorobutadiene and 2000 times more reactive than maleic anhydride [1]. All known methods of synthesis of these compounds require oxidation of the corresponding 1,2,4-triazolidine-3,5-diones **I** and **III** which are more commonly known as urazoles.

Although a wide variety of reagents are capable of effecting oxidation of urazoles [8–18], this transformation remains capricious because the initial compounds are very sensitive to the oxidant and reaction

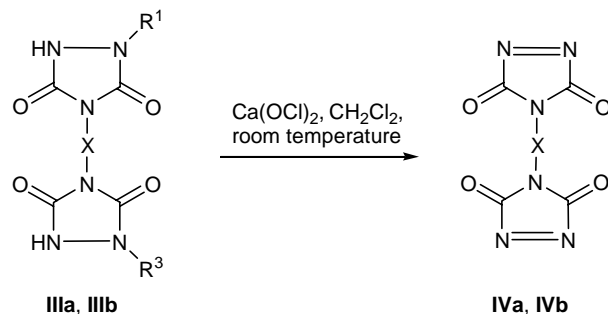
conditions. Moreover, most of the reported reagents produce by-products which either initiate decomposition of the sensitive dihydrotriazole-diones or are difficult to remove from the latter. Another significant drawback of the old procedures is the use of reagents which either are highly toxic or produce serious disposal problems (or both) [8]. We recently demonstrated the remarkable convenience of using gaseous N₂O₄ generated *in situ* as a clean and efficient oxidant for the above purpose [1, 10, 11]. It is known that gaseous N₂O₄ is corrosive and highly toxic and that it must be generated under an effective hood with caution. Therefore, we decided to develop a new reagent or reagent system to overcome the above limitations and provide a clean and easy work-up. Heterogeneous reagent systems [19] offer many advantages such as simple experimental procedure, mild reaction conditions, and minimization of chemical wastes as compared to reactions in solution. We have examined a number of heterogeneous reagent systems based on generation *in situ* of HNO₂ (NO⁺) [12] or

Scheme 1.



I, II, R¹ = H, R² = Me (**a**), Et (**b**), Bu (**d**), cyclohexyl (**e**), Ph (**f**), 4-ClC₆H₄ (**g**), 4-O₂NC₆H₄ (**h**), 3,4-Cl₂C₆H₄ (**i**); R¹ = Na, R² = Pr (**c**).

Scheme 2.



III, IV, R¹ = R³ = Na; X = (CH₂)₆ (**a**); R¹ = R³ = H, X = 4-C₆H₄CH₂C₆H₄-4 (**b**).

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Oxidation of urazoles **I** and bis-urazoles **III** to the corresponding dihydrotriazolediones **II** and **IV** with $\text{Ca}(\text{OCl})_2$ in methylene chloride at room temperature.

Initial comp. no.	Product ^a	Oxidant-to-substrate ratio, mmol	Time, min	Yield, ^b %	mp, °C	
					found	reported
Ia	IIa [8]	2	15	100 ^c	97–99	98–98.5 [8]
Ib	IIb [15]	2	15	100 ^c	54–56	53 [15]
Ic	IIc [11, 15]	2	15	82	42–44	44 [11]
Id	IIId [8]	2	15	85	42–45	44–44.5 [8]
Ie	IIe [8]	2	15	95	97–98	95–96 [8]
If	IIIf [8, 10]	2	15	92	168–175	170–178 [10]
Ig	IIg [8]	2	15	98	134–135	130–132 [8]
Ih	IIh [8,17]	4	45	70	125–126	128–129 [17]
Ii	IIi [14]	2	15	90	110–113	113–115 [14]
IIIa	IVa [17]	2	20	98	145–150	146–149 [17]
IIIb	IVb [17]	2	30	75	182–185 ^d	185 ^d [17]

^a All the isolated products are known compounds; their spectral parameters and physical constants have been reported in the literature.

^b Yields of the isolated products.

^c Conversion.

^d With decomposition.

H_2O_2 (Cl^+) [13]. As a result, we have developed a simple, cheap, and convenient method for effective conversion of urazoles **I** and bis-urazoles **III** to the corresponding dihydrotriazolediones **II** and **IV** using calcium hypochlorite under heterogeneous conditions (Schemes 1, 2).

Different urazoles and bis-urazoles were subjected to oxidation in the presence of $\text{Ca}(\text{OCl})_2$ in methylene chloride. The reactions were performed under mild conditions at room temperature with excellent yields. The products, dihydrotriazolediones **II** or bis-dihydrotriazolediones **IV** can be isolated by simple filtration of the reaction mixture, followed by removal of the solvent from the filtrate. The results and reaction conditions are given in table.

Oxidation of 4-cyclohexylurazole (Ie) to 4-cyclohexyl-4,5-dihydro-3H-1,2,4-triazole-3,5-dione (IIe) with $\text{Ca}(\text{ClO})_2$. A mixture of 0.366 g (2.0 mmol) of compound **Ie** and 0.568 g (4 mmol) of $\text{Ca}(\text{ClO})_2$ in 20 ml of methylene chloride was stirred for 15 min at room temperature. The mixture was filtered, and the solvent was distilled off from the filtrate on a water bath (40–50°C). Yield 0.290 g (95%); red crystals, mp 95–98°C; published data [8]: mp 95–96°C. ^1H NMR spectrum (90 MHz, CDCl_3 , TMS), δ , ppm: 3.90 quint (1H), 1.82–1.26 m (10H). ^{13}C NMR spectrum (CDCl_3 , TMS), δ_{C} , ppm: 158.77, 53.93, 28.72, 24.96, 24.28. Compounds **IIa–IIId** and **IIIf–IIi** were synthesized in a similar way. The products were

identified by comparing their spectral parameters (IR, UV, and ^1H and ^{13}C NMR) and physical constants with those of authentic samples. 4,5-Dihydro-3H-1,2,4-triazole-3,5-diones are sensitive to light, heat, alcohols, ethers, transition metals, and any nucleophiles. In addition, they are very volatile; therefore, the solvent must be removed at a temperature not exceeding 50°C to avoid loss of the target product. From this viewpoint, methylene chloride is the best solvent.

Chemicals were purchased from Fluka, Merck, Riedel–Dehaen AG, and Aldrich chemical companies. All urazoles and bis-urazoles were synthesized by the procedures reported previously [1, 4, 5, 10, 11].

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