

Ca(OCl)₂ as an Efficient Oxidizing Agent for the Oxidation of Urazoles under Mild and Heterogeneous Conditions

Mohammad Ali Zolfigol,^{*} Shadpour Mallakpour,^{†,§} Ardashir Khazaie, Ramin Ghorbani Vaghaie, and Mehdi Torabi

Chemistry Department, College of Science, Bu-Ali Sina University, Hamadan 65174, Iran

[†]Organic Polymer Chemistry Research Laboratory, College of Chemistry, Isfahan University of Technology, Isfahan 84156, Iran

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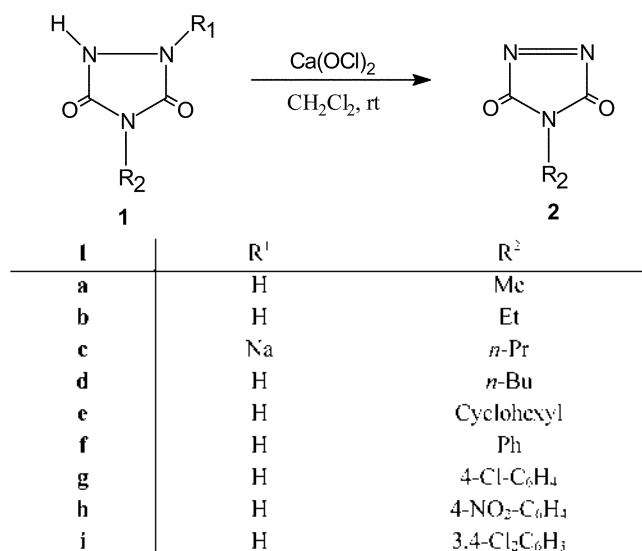
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4-Substituted-1,2,4-triazole-3,5-diones (TADs) are notable for their ability to participate in a wide range of reactivity and reaction types, e.g. [4+2]^{1,2} and [2-2]³ cycloadditions, ene reactions,⁴ electrophilic aromatic substitution,⁵ dehydrogenating properties⁶ and oxidation of alcohols to aldehydes and ketones.⁷ However, the unusual reactivity which makes 1,2,4-triazole-3,5-diones (**2**, **4**) of interest, to organic chemists makes them difficult to prepare and purify as well. For example: 4-phenyl-1,2,3-triazoline-3,5-dione (**2e**) is an extremely reactive dienophile and enophile which is at least 1000 times more reactive than tetracyanoethylene (TCNE) 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 (**1**, **3**), more commonly known as urazoles.

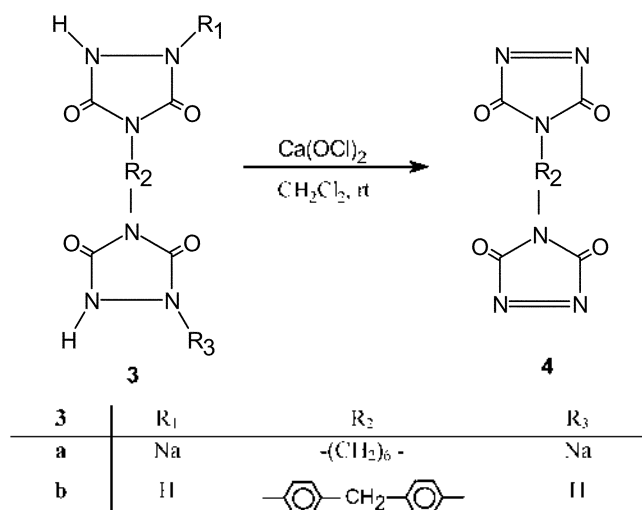
Although a wide variety of reagents are capable of effecting the urazoles oxidations⁸⁻¹⁸ this transformation remains capricious because these compounds are very sensitive to the oxidizing agents and reaction conditions. Moreover, most of the reported reagents produce some by-products, which either destroy, or are difficult to remove from the sensitive triazolinediones. Another major drawback to the older procedures is their use of reagents which are either highly toxic or produce serious disposal problems (or both).⁸ Recently, we have demonstrated the remarkably practical use of *in situ* generated N₂O₄ gas as a clean and efficient oxidant for this purposes.^{1,10,11} It is known that gaseous N₂O₄ is corrosive and highly toxic and 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. Since heterogeneous reagent systems¹⁹ have many advantages such as simple experimental procedures, mild reaction conditions and minimization of chemical wastes as compared to the solution phase counterparts. Therefore, we were interested to find a heterogeneous system for urazole oxidation and we have investigated a number of different reaction conditions based upon the *in situ* generation of HNO₂(NO⁻)¹² or H₂O₂ (Cl⁻).¹³ Therefore, we wish to report a simple, cheap and convenient method for the effective

conversion of urazoles and as well as bis-urazoles to their corresponding triazolinediones (**2**, **4**) by using Ca(OCl)₂ under heterogeneous conditions (Schemes 1 and 2).

Different kinds of urazoles and bis-urazoles were subjected to oxidation reaction in the presence of Ca(OCl)₂ in



Scheme 1



Scheme 2

^{*}Corresponding Author. e-mail: Zolfigol@basu.ac.ir

[§]Previous Name: Shadpour E. Mallakpour

Table 1. Oxidation of urazoles (**1**) and bis-urazoles (**3**) to their corresponding triazolinediones (**2**, **4**) with Ca(OCl)₂ in dichloromethane at room temperature

Urazole or (bis)	Product ^a	(Reagent/Substrate) (mmol)	Time (min.)	Yield ^b %	mp °C	
					Found	Reported
1a	2a ⁸	2	15	100 ^c	97-99	98-98.5 ⁸
1b	2b ¹⁵	2	15	100 ^c	54-56	53 ¹⁵
1c	2c ^{11,15}	2	15	82	42-44	44 ¹¹
1d	2d ⁸	2	15	85	42-45	44-44.5 ⁸
1e	2e ⁸	2	15	95	97-98	95-96 ⁸
1f	2f ^{6,10}	2	15	92	168-175	170-178 ¹⁰
1g	2g ⁸	2	15	98	134-135	130-132 ⁸
1h	2h ^{8,17}	4	45	70	125-126	128-129 ¹⁷
1i	2i ¹⁴	2	15	90	110-113	113-115 ¹⁴
3a	4a ¹⁷	2	20	98	145-150	146-149 ¹⁷
3b	4b ¹⁷	2	30	75	182-185 (dec.)	185 (dec.) ¹⁷

^aAll of the isolated products are known compounds and their spectra and physical data have been reported in the literature. ^bIsolated yields. ^cConversion.

dichloromethane (Schemes 1 and 2). The oxidation reactions were performed under mild conditions at room temperature with excellent yields. The triazolinedione (**2**) or bis-triazolinedione (**4**) can be obtained by simple filtration and evaporation of the solvent.²⁰⁻²² The results and reaction conditions are given in the Table 1.

In conclusion, practical and efficient oxidations of urazoles and bis-urazoles have been achieved by the new methodology described. Thus this reagent could be used for the oxidation of a wide variety of urazole derivatives under mild condition.

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- Chemicals were purchased from Fluka, Merck, Riedel-dehaen AG and Aldrich chemical companies. Yields refer to isolated pure products. The oxidation products were characterized by comparison of their spectral (IR, UV, ¹H-NMR, and ¹³C-NMR) and physical data with the authentic samples. All urazoles and bis-urazoles were synthesized according to our previously reported procedures.^{1,4,5,10,11,21}
- Oxidation of 4-cyclohexyl urazole (**1e**) to 4-cyclohexyl-1,2,4-triazoline-3,5-dione (**2e**) with Ca(OCl)₂: A typical procedure. A mixture of compound **1e** (0.366 g, 2.0 mmol) and Ca(OCl)₂ (0.568 g, 4 mmol) in dichloromethane (20 mL) was stirred at room temperature for 15 minutes. Then the reaction mixture was filtered. Dichloromethane was removed by water bath (40-50 °C)²² under simple distillation. The yield was 0.290 g (95%) of crystalline red solid (**2e**), mp 95-98 °C [Lit⁸ mp 95-96 °C]. ¹H-NMR (FT-90 MHz, CDCl₃/TMS): δ 3.90 (quintet, 1H), 1.82-1.26 (m, 10H). ¹³C-NMR (FT-90 MHz, CDCl₃/TMS): δ 158.77, 53.93, 28.72, 24.96, 24.28.
- These compounds are sensitive to the light, heat, alcohols, ethers, transition metals and any nucleophiles. Also they are very volatile so that, if temperature rises over than 50 °C in the course of removing of CH₂Cl₂, some of **TADs** are removed with solvent simultaneously. Therefore, the temperature must be controlled and dichloromethane is the best solvent for this purpose.