Trichloroisocyanuric Acid as a Novel Oxidizing Agent for the Oxidation of Urazoles Under Both Heterogeneous and Solvent Free Conditions

Mohammad Ali Zolfigol,*[a] Elaheh Madrakian,[a] Ezat Ghaemi,[a] Shadpour Mallakpour[b]

[a] Chemistry Department, College of Science, Bu-Ali Sina University, Hamadan, 65174, Iran.
E-mail: Zolfi@basu.ac.ir

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

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Abstract: Trichloroisocyanuric acid was used as an effective oxidizing agent for the oxidation of urazoles and bis-urazoles to their corresponding triazolinediones under both heterogeneous and also solvent free conditions with excellent yields at room temperature.

Keywords: trichloroisocyanuric, urazoles, bis-urazoles, triazolinediones, solvent free conditions

4-Substituted-1,2,4-triazole-3,5-diones (**TAD**s) 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 properties[6] and oxidation of alcohols to aldehydes and ketones.[7] However, the unusual reactivity which makes 1,2,4-triazoline-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 oxidation[8–11] 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 N_2O_4 gas as a clean and efficient oxidant for this purpose.[1,10,11] It is known that gaseous N_2O_4 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. Heterogeneous reagent systems[12] or solvent free reactions[13] 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 $HNO_2(NO^+)$[14] or H_2O_2 (Cl^+).[15] In continuation of our studies in this regard,[16] we have found that trichloroisocyanuric acid a cheap commercially available reagent used primarily as a disinfectant and deodorant, has found little application in organic chemistry.[17] 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 trichloroisocyanuric acid both under heterogeneous and also solvent free conditions (Scheme 1 and Scheme 2).

Different kinds of urazoles and bis-urazoles were subjected to oxidation reaction in the presence of trichloroisocyanuric acid in dichloromethane (Scheme 1 and Scheme 2) or solvent free conditions. 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.[23–26] The results and reaction conditions are given in Table 1.

The synthesis of Diels–Alder adducts of triazolinediones specially 4-(4′-aminophenyl)triazolinedione are our main interest for some mechanistic studies of halogenation reactions on its double bond of cyclopentadiene moieties.[1b-c] It is interesting to note that, we have had problems for the oxidation of urazoles containing of functional groups sensetive to the oxidizing agents during our previous work.[14,15,22c] For example, we have tried to oxidized the compound 4-(4′-aminophenyl)urazole with different oxidizing agent, but we failed. Here for the first time we wish to report that, we were able to oxidize this compound successfully by oxidation with trichloroisocyanuric acid. Since the triazolinedione from this compound is not stable due to the presence of amino group or its salt, we first generated this triazolinedione in dichloromethane and then we added cyclopentadiene and sodium carbonate to the reaction mixture. Thus the Diels–Alder adduct of the above mentioned compound was prepared in one pot (Scheme 3). The resulting Diels–Alder adduct was isolated in high yield. The structure of this adduct was con-

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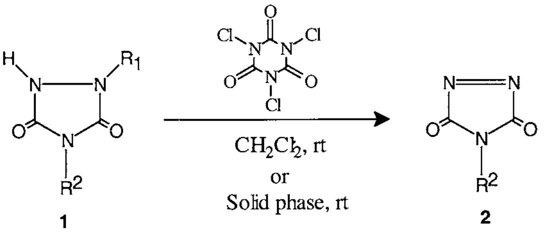
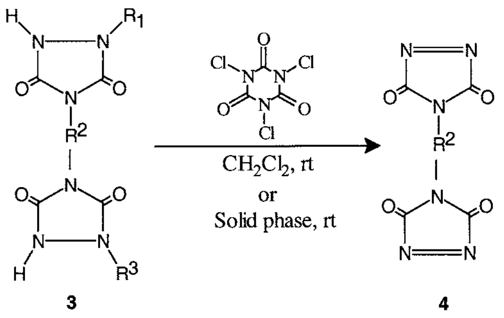


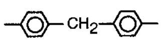
1	R^1	R^2
a	H	Me
b	H	Et
c	Na	*n*-Pr
d	H	*n*-Bu
e	H	Cyclohexyl
f	H	Ph
g	H	4-Cl-C_6H_4
h	H	4-NO_2-C_6H_4
i	H	3,4-$Cl_2C_6H_3$

Scheme 1

firmed by high resolution mass spectroscopy and elemental analysis.

This new reagent e.g. trichloroisocyanuric acid is an effective source for the in situ generation Cl^+ which behaves like HNO_2,[14] H_2O_2/MCl_n[15] and N_2O_4 ($N_2O_4 \Leftrightarrow NO^+NO_3^-$).[22] Therefore, on the basis of our results and, the products which were obtained, the following mechanism may be proposed (Scheme 4).



3	R^1	R^2	R^3
a	Na	-$(CH_2)_6$ -	Na
b	H		H

Scheme 2

We have also used a combination of cyanuric chloride (**5**, Figure 1) and $NaNO_2$ in the presence of wet SiO_2 for the oxidation of urazoles. The reaction proceeded via in situ generation of HNO_2 and NO^+ respectively.[14] Although the oxidation reaction worked well, but during of work up the resulting triazolidiones (**2** and **4**) were contaminated with some of the cyanuric chloride and it was difficult to isolate it, even we have tried to purified them with sublimation technique, but it was unsuccessful.

In conclusion, practical and efficient oxidations of urazoles and bis-urazoles have been achieved by the new methodology described. The chemoselectivity of the

Table 1 Oxidation of Urazoles (**1**) and bis-Urazoles (**3**) to their Corresponding Triazolinediones (**2**, **4**) with Trichloroisocyanuric Acid Both in Dichloromethane (**I**) and Solvent Free Conditions (**II**) at Room Temperature

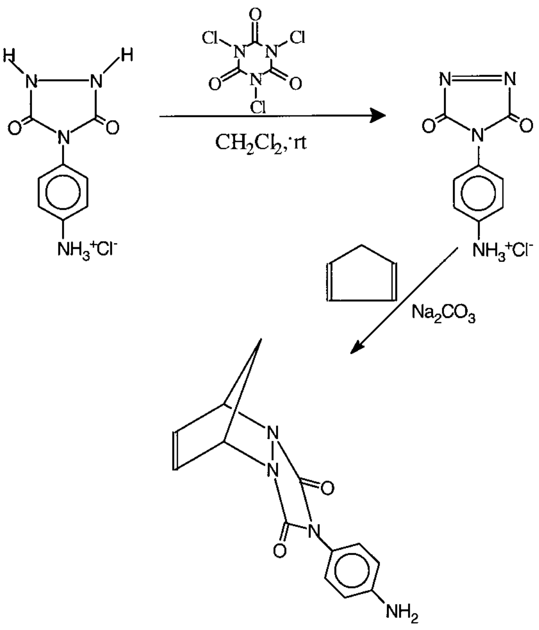
Urazole or (bis)	Product[a]	Reagent/Substrate[b]		Time (h) I (II)	Yield[c] (%) I (II)	Mp °C	
		I	II			Found	Reportet
1a	**2a**[8]	1	1	0.50 (0.50)	100[d] (100[d])	97–99	98–98.5[8]
1b	**2b**[19]	1	1	0.50 (0.50)	100[d] (100[d])	54–56	53[19]
1c	**2c**[11,19]	1	1	0.50 (0.25)	98 (94)	42–44	44[11]
1d	**2d**[8]	1	1	0.50 (0.25)	100 (97)	42–45	44–44.5[8]
1e	**2e**[8]	4	2	0.50 (0.25)	99 (98)	97–98	95–96[8]
1f	**2f**[8,10]	1	1	0.50 (0.25)	74 (70)	168–175	170–178[10]
1g	**2g**[8]	1	1	0.50 (0.25)	96 (90)	134–135	130–132[8]
1h	**2h**[8,21]	1	1	0.50 (0.25)	63 (63)	125–126	128–129[21]
1i	**2i**[18]	1	1	0.50 (0.25)	98 (98)	110–113	113–115[18]
3a	**4a**[21]	2	2	0.50 (0.25)	90 (72)	145–150	146–149[21]
3b	**4b**[21]	2	2	0.50 (0.25)	90 (72)	182–185 (dec.)	185 (dec.)[21]

[a] All of the isolated products are known compounds and their spectra and physical data have been reported in the literature.

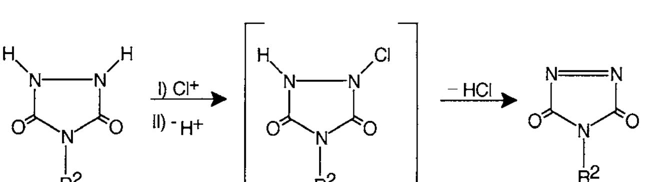
[b] Molar ratio of trichloroisocyanuric acid in CH_2Cl_2 (**I**) mmol and under solvent free conditions (**II**) mmol.

[c] Isolated yields.

[d] Conversion.



Scheme 3



Scheme 4

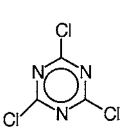


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Figure 1

trichloroisocyanuric acid is very interesting for urazole compounds containing highly reactive functional group towards oxidation reaction. Thus this reagent could be used for the oxidation of a wide variety of urazole derivatives under safe condition.

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(23) Chemicals were purchased from Fluka, Merck, Riedel-deHaën AG and Aldrich chemical companies. Yields refer to isolated pure products. The oxidation products were characterized by comparison of their spectral (IR, UV, ^{1}H NMR, and ^{13}C 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]

(24) Oxidation of 4-cyclohexyl urazole(**1e**) to 4-cyclohexyl-1,2,4-triazoline-3,5-dione(**2e**) with trichloroisocyanuric acid, a typical procedure. A mixture of compound **1e** (0.366 g, 2.0 mmol) and trichloroisocyanuric acid (0.232 g, 1.0 mmol) was shaken at r.t. for 0.25 h and dichloromethane (20 mL) was added to the resulting mixture then filtered. Dichloromethane was removed by water bath (40–50 °C)[25] under simple distillation. The yield was 0.35 g (98%) of crystalline red solid (**2e**), mp 95–98 °C [Lit[8] mp 95–96 °C]. ^{1}H NMR (FT-90 MHz, $CDCl_3$/TMS): $\delta = 3.90$ (quintet, 1 H, $J = 12$ Hz), 1.82–1.26 (m, 10 H). ^{13}C NMR (FT-22.5 MHz, $CDCl_3$/TMS): $\delta = 158.77$, 53.93, 28.72, 24.96, 24.28.

(25) 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 CH_2Cl_2, some of **TADs** are removed with solvent simultaneously. Therefore, the temperature must be controlled and dichloromethane is the best solvent for this purpose.

(26) For running the oxidation reaction under heterogeneous conditions please see ref. 14.