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Oxidation of urazoles to their corresponding triazolinediones using benzyltriphenylphosphonium nitrate

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Benzyltriphenylphosphonium nitrate in the presence of $AlCl_3$ oxidised 1,2,4-triazolidine-3,5-diones to the corresponding 4-substituted-1,2,4-triazole-3,5-diones.

Keywords: 1,2,4-triazole-3,5-diones, 1,2,4-triazolidine-3,5-diones, urazoles, benzyltriphenylphosphonium nitrate

4-Substituted-1,2,4-triazole-3,5-diones (TADs) are involved in various organic reactions. For example, they have been used in electrophilic aromatic substitution, ene or [2+2] cycloadditions, dehydrogenation reactions, condensation of dicarbonyl compounds, Diels–Alder reactions, polymerisation and oxidation of organic compounds.[1–10] 4-Substituted-1,2,4-triazole-3,5-diones have also been used as a derivatisation reagent for the analysis of 25-hydroxyvitamin D_3,(a major curculating metabolitein humans).[11]

All known methods of synthesis of 4-substituted-1,2,4-triazole-3,5-diones require oxidation of the corresponding 1,2,4-triazolidine-3,5-diones **1** and **3** which are more commonly known as urazoles.[1–11] Although various reagents are capable of effecting the oxidation of urazoles, this transformation remains difficult because the initial compounds are very sensitive to the oxidant, and the preparation and purification of these compounds are problematical due to their unusual reactivity and sensitivity to reaction conditions.[12–30]

Some new oxidising reagents have been prepared, and several techniques have been used. Most of them suffer at least from one of the following disadvantages: (1) high costs of preparations, (2) long reaction times, (3) hygroscopicity, (4) no selectivity, (5) photosensitivity, (6) dangerous procedures for their preparation, and (7) tedious work-up procedures.[21–32]

In continuation of our previous works, on oxidation and synthesis of heterocyclic compounds,[33–39] we now introduce an efficient, mild and rapid method for the oxidation of urazoles to their corresponding 4-substituted-1,2,4-triazole-3,5-diones (TADs), by using benzyltriphenylphosphonium nitrate (**I**, BTPPN) as a mild and novel oxidising reagent which is readily prepared by reaction of an aqueous solution of benzyltriphenylphosphonium chloride with $NaNO_3$ solution at room temperature (Scheme 1).

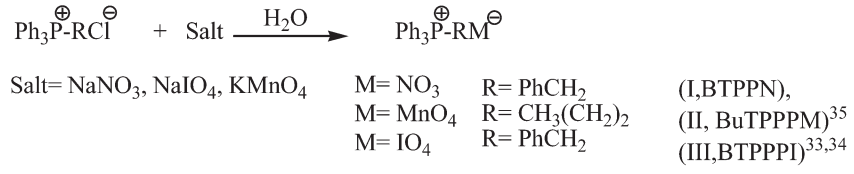
Benzyltriphenylphosphonium nitrate (BTPPN, I) was prepared by the dropwise addition of an aqueous solution of $NaNO_3$ to an aqueous solution of benzyltriphenylphosphonium chloride at room temperature. Filtration and drying of the precipitate produced a white powder, which can be stored for months without loss of its reactivity, and is soluble in acetone, dimethylformamide, acetonitrile, chloroform, ethyl acetate and dichloromethane.

Although a variety of alcohols were converted to their corresponding carbonyl compounds by using butyltriphenylphosphonium permanganate (**II**) and benzyltriphenylphosphonium periodate (**III**) under non-aqueous conditions,[32–34] benzyltriphenylphosphonium nitrate (**I**) could not convert alcohols to their corresponding carbonyl compounds (Scheme 2).

Oxidation of 4-phenyl-1,2,4-triazolidine-3,5-diones (**1a**) to its corresponding 4-phenyl-1,2,4-triazole-3,5-diones (**2a**) with reagents such as **I**, **II**, **III** in the presence of various Lewis acids such as $ZnCl_2$, $FeCl_3$, $BiCl_3$, $AlCl_3$ and $InCl_3$, were also examined in dichloromethane (Scheme 3, Table 1). Our observations showed that the rate of oxidation of urazoles is affected by the nature of the Lewis acids and reagents. BTPPN in the presence of $AlCl_3$ was shown to be an effective catalyst for the preparation of 4-phenyl-1,2,4-triazole-3,5-diones (**2a**) from the corresponding 4-phenyl-1,2,4-triazolidine-3,5-diones (**1a**). $AlCl_3$ in comparison with the other Lewis acids is more effective.

We also tried the oxidation of 4-phenyl-1,2,4-triazolidine-3,5-diones with $NaIO_4$, $NaNO_3$, $KMnO_4$ in refluxing dichloromethane as well as in a mixture of water and dichloromethane (50:50) by using $AlCl_3$. In the case of the reaction with $NaIO_4$, $NaNO_3$ and $KMnO_4$ in dichloromethane under refluxing conditions, the reaction does not give good yield neither after 30min nor in a mixture of water in dichloromethane in the presence of $AlCl_3$.

4-Substituted-1,2,4-triazolidine-3,5-diones **(1, 3)** are oxidised to the corresponding 4-substituted-1,2,4-triazole-3,5-diones **(2,4)** in dichloromethane under refluxing conditions in the presence of $AlCl_3$ in good yields (Scheme 4, Table 2).

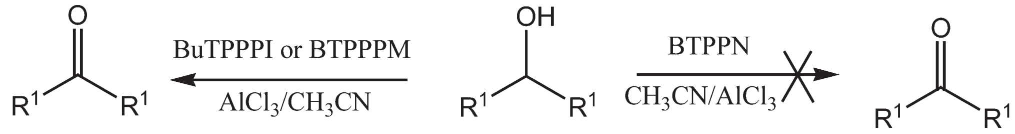


$$Ph_3\overset{\oplus}{P}\text{-}R\overset{\ominus}{Cl} + \text{Salt} \xrightarrow{H_2O} Ph_3\overset{\oplus}{P}\text{-}R\overset{\ominus}{M}$$

Salt= $NaNO_3$, $NaIO_4$, $KMnO_4$

M= NO_3 R= $PhCH_2$ (I,BTPPN),
M= MnO_4 R= $CH_3(CH_2)_2$ (II, BuTPPPM)[35]
M= IO_4 R= $PhCH_2$ (III,BTPPPI)[33,34]

Scheme 1



Scheme 2

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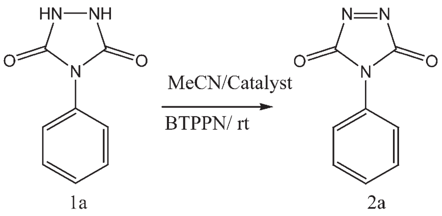


Scheme 3

Table 1 Oxidation of **1a** with reagents such **as I,II,III** with different Lewis acids in dichloromethane after 30 min[a]

Entry	Lewis acid	Reagent	Yield/%
1	$ZnCl_2$	**I**	64
		II	58
		III	40
2	$FeCl_3$	**I**	52
		II	30
		III	45
3	$BiCl_3$	**I**	64
		II	64
		III	57
4	$AlCl_3$	**I**	96
		II	78
		III	71
5	$InCl_3$	**I**	64
		II	55
		III	42

[a] Oxidant/urazole/Lewis acid (1:1:0.5).

Table 2 Synthesis of 4-substituted-1,2,4-triazole-3,5-diones in dichloromethane in the precence of $AlCl_3$ and BTPPN after 30 min

Entry	R[1]	Yield/%[a]	M.p./°C[24]	M.p./°C[b]
1a	C_6H_5-	96	174–175	173–175
1b	CH_3CH_2-	95	52–55	52–54
1c	Bu-	89	42–44	40–43
1d	Cyclohexyl	91	95–97	95–97
1e	4-$NO_2C_6H_4$-	85	126–128	125–127
1f	4-$MeOC_6H_5$- -	93	90–93	90–93
1g	4-ClC_6H_4	73	143–145	143–144
1h	$CH_3CH_2CH_2$-	94	42–44	42–45
1i	Me-	81	97–98	96–98
3a	-$C_6H_4CH_2C_6H_4$-	93	183–185	182–184

[a] Isolated yield after purification. [b].experemental melting point found

Table 3 Comparison between the different methods used for the oxidation of 4-phenylurazole

Entry	Reagent	Time /min	Yield/% [Ref.][a]
1	$AlCl_3$/ $Ph_3PCH_2PhNO_3$	30	96
2	HNO_3/$NaNO_3$	90	86[18]
3	Oxalic acid/ $NaNO_2$	60	80[22]
4	Wet silica/$NaNO_2$	180	98[23]
5	$9H_2O$:SiO_2–OSO_3H/$Al(NO_3)_3$.	120	98[25]
6	$KHSO_4$.wet SiO_2/$NaNO_2$	90	94[19]
7	Trichloromelamine	180	87[24]
8	$Ca(ClO)_2$	15	95[25]
9	1.3-Dichloro-5,5-dimethylhydantoin	120	80[26]
10	1,4-Diazabicyclo[2.2.2]octane-bromine	120	80[15]
11	Oxone/KBr	25	95[20]

[a] Isolated yields.

To show the efficiency of this reagent in comparison with previously reported procedures, we compared our results obtained for oxidation of 4-phenylurazole (as a typical example) with the best of the literature data as shown in Table 3.

In entry 1–6 *in situ* generation of NO^+ or NO_2^+ oxidised 4-phenyl-1,2,4-triazolidine-3,5-diones to the corresponding 4-phenyl-1,2,4-triazole-3,5-diones.

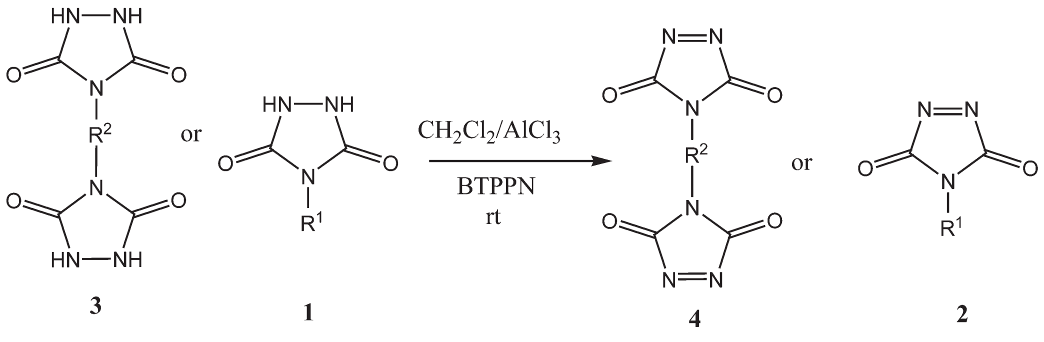
A plausible mechanism of urazole oxidation in the reported urazoles oxidation is outlined in Scheme 5 which proposes that the oxidation reaction occurs via *in situ* generation of cation species (Z^+). We propose the oxididation of urazoles in the presence of BTPPN and $AlCl_3$ proceeds via *in situ* generation of NO_2^+ like some other reagents that have nitrate or nitrite (entries 1–6, Table 3).

In this study we have introduced a new and mild reagent for the oxidation of different types of urazoles in dichloromethane in the presence of $AlCl_3$. The stability, easy preparation, mildness of the reagent, reaction conditions, easy work up and the high yields of the products under non-aqueous conditions make this method useful for the oxidation of different urazoles to afford the corresponding 4-substituted-1,2,4-triazole-3,5-diones.

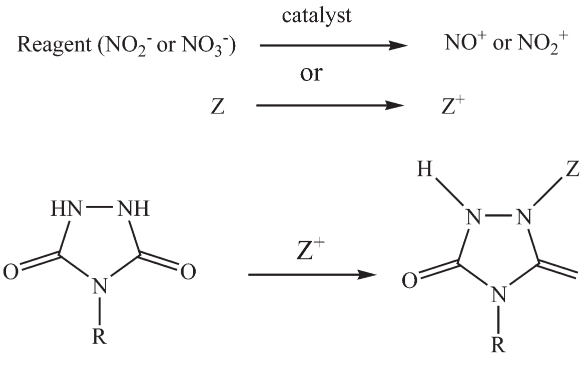
Experimental

^1H NMR spectra were obtained on a Bruker DRX-500 and those of ^{13}C NMR spectra on a Bruker DRX-125 Avance spectrometer. FTIR spectra were recorded on a Shimadzu FTIR- 8400S spectrometer. Chemical shifts of 1H and ^{13}C NMR spectra are expressed in ppm downfield from tetramethylsilane. Melting points were measured on a Buchi melting point B-540 instrument and are uncorrected. Elemental analyses were done by a Carlo-Erba EA1110CNNO-S analyser and agreed with the calculated values. All the chemicals were purchased from Merck and used without further purification.

Benzyltriphenylphosphonium nitrate **(1a):** A solution of benzyltriphenylphosphonium chloride (7.8 g, 0.02mol) in 50 mL of water was prepared, then $NaNO_3$ (2.02 g, 0.02mol) in water (50 mL) was added dropwise to the above solution and stirred for 20 min at room temperеture. The resulting white precipitate was filtered and washed with cooled distilled H_2O (50 mL) and dried in a desiccator under vacuum



Scheme 4



Scheme 5

over calcium chloride to afford a white powder (8.13 g, 98% yield, 203–205 °C). 1H NMR: 7.74–6.90 (m, 20 H), 4.93(d, $J = 25.7$ Hz, 2H). ^{13}C NMR: 135.2, 134. 99, 134.1, 134.30, 134.22, 134.09, 134.02, 131.36, 131.28, 130.26, 130.16, 130.07, 128.51, 127.12, 127.05, 117.99, 117.30, 29.89 (d, $J = 193$ Hz, C-P). IR (KBr): 3050, 2985, 1600, 1495, 1410, 1200-1400, 1120, 960, 750, 670, 610. cm–1. Anal. Calcd for $C_{25}H_{22}NO_3P$ (415.1): C, 72.28; H, 5.34; N, 3.37; O, 11.55; P, 7.46. Found: C, 72.50; H, 5.30; N, 3.37; O, 11.8%.

Triazolinediones(**1a–i, 3a**): A suspension of (1mmol), urazole, $AlCl_3$ (0.5mmol) and BTPPN (1mmol) were added to dichloromethane (10 mL) and the suspension was vigorously stirred for 30 min (Table 2). The residue was washed with CH_2Cl_2 (2 × 10 cm^3) and filtered. The filtrate was dried over anhydrous Na_2SO_4, which was filtered off after the appropriate time. Then the filtrate was passed through a short pad of silica gel for removing any remaining of reagent residue. Dichloromethane was removed by using a distillation apparatus and a water-bath (40–50 °C). A crystalline or powder solid is obtained in good yields.

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