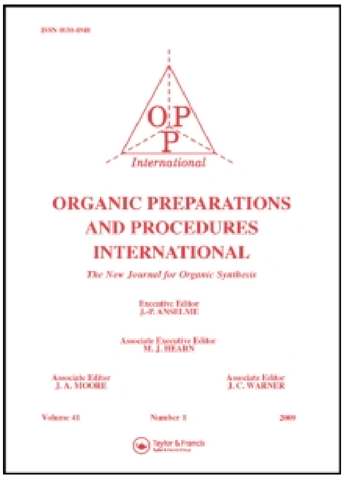

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A CONVENIENT METHOD FOR PREPARATION OF TRIAZOLINEDIONES

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A CONVENIENT METHOD FOR PREPARATION OF TRIAZOLINEDIONES

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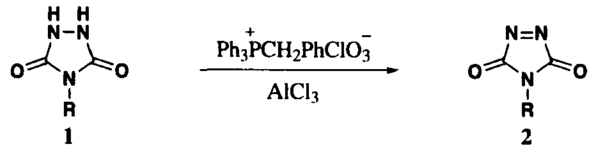
4-Substituted-1,2,4-triazoline-3,5-diones are very important because of their ability to participate in concerted and stepwise reactions.[1-4] These compounds have been used in electrophilic aromatic substitution,[5] as dehydrogenation agents[6] and in the oxidation of alcohols to aldehydes and ketones.[7] Since they are very reactive and sensitive to heat and to the oxidizing agents used to generate them, the preparation of these compounds is difficult. Most of the reported reagents for the oxidation of urazoles to the corresponding triazolinediones lead to the formation of by-products, which either are difficult to remove or can destroy the sensitive triazolinediones. Another major problem is the use of oxidizing reagents which are highly toxic and expensive or which present serious disposal problems.[8-11]

Readily prepared benzyltriphenylphosphonium chlorate ($Ph_3\overset{+}{P}CH_2Ph\ Cl\overset{-}{O_3}$, **BTPPC**) is a mild, efficient, stable and inexpensive reagent has been used for the oxidation of alcohols and oxidative deprotection of trimethylsilyl and tetrahydropyranyl ethers.[12-13] In continuation of our previous studies,[11] we now report the oxidation of urazoles to the corresponding triazolinediones with **BTPPC** in the presence of $AlCl_3$ at room temperature. Initially, we investigated the oxidation of 4-phenylurazole (**1a**) with this reagent under non-aqueous conditions at room temperature without catalyst; the reaction failed to proceed at all, even with a higher molar ratio of the oxidant (1.5 mmol). Thus the catalytic effects of several Lewis acids such as $ZnCl_2$, $FeCl_6{\bullet}6H_2O$, $BiCl_3$ and $AlCl_3$ were studied and surprisingly, only $AlCl_3$ was found to be effective. The role of CH_3CN and CH_2Cl_2 on the oxidation of urazoles with **BTPPC** in the presence of $AlCl_3$ was examined. Methylene chloride was found to be a better solvent because acetonitrile may interact with the triazolinediones. The reaction was performed by mixing a solution of **BTPPC** and the urazole in methylene chloride in the presence of $AlCl_3$ (0.3 molar ratio) and stirring for the time specified at room temperature (*Table*). In continuation of our program to develop environmentally benign methods using solid supports,[14] we also used **BTPPC** to oxidize urazoles to the corresponding triazolinediones in the presence of $AlCl_3$ under solvent-free conditions.The process involves simple mixing of **BTPPC** and urazoles in the presence of $AlCl_3$ (0.3 molar ratio) in a mortar and grinding the mixture for the time specified in the *Table* at room temperature. In comparison with the oxidation of urazoles under non-aqueous conditions, the oxidation of urazoles under solvent-free conditions does not employ any solvent except for extraction and the reaction time is shorter. Compared to reported methods;[8-11] this reagent has the advantages of producing high yields with straightforward isolation of products and short reaction times the reaction is very clean without the formation of by-products.

Table. Oxidation of Urazoles to Triazolinediones with **BTPPC/$AlCl_3$**[a,b]

Cmpd	mp. (°C)	*lit.* mp. (°C)	In CH_2Cl_2 time (min)	Yield[c] (%)	Solvent-free time (min)	Yield[c] (%)
1a	170-174	170-178[10]	15	97	10	94
1b	94-96	95-96[8]	15	95	10	92
1c	43-45	44-45[15]	15	95	10	90
1d	111-113	113-115[15]	20	92	15	93
1e	126-128	128-129[15]	30	90	8	96

a) Substrate/Oxidant/ $AlCl_3$(1:1:.3); b) Confirmed by comparison with authentic samples;[8-11]
c) Yield of isolated pure products as red compounds.



a) R = C_6H_5; b) R = c-C_6H_{11}; c) R = n-C_4H_9; d) R = 3,4-$Cl_2C_6H_3$; e) R = 4-$NO_2C_6H_4$

Scheme 1

EXPERIMENTAL SECTION

Urazoles were synthesized according to reported procedures.[1,4,5,10,11] The reagent (**BTPPC**) was synthesized by described method.[12,13] Yields refer to isolated pure products. The oxidation products were characterized by comparison of their spectral (IR, UV, ^{1}H NMR) and physical data with the authentic samples.[8-11] All ^{1}H NMR spectra were recorded on EM390 and Varian 500 spectrometers at 90 or 500 MHz in $CDCl_3$ relative to TMS and IR spectra were obtained on a Shimadzu 435 IR spectrometer. Although we never experienced any explosion in the preparation and use of this reagent, from the safety standpoint all reactions under solvent-free conditions and in CH_2Cl_2 at room temperature were performed in a hood with strong ventilation. The reagent (**BTPPC**) was prepared according to the described procedure.[12,13]

Oxidation of Urazoles with BTPPC/AlCl$_3$ in CH$_2$Cl$_2$ at Room Temperature. General Procedure.- A solution of the urazole (1 mmol), **BTPPC** (1 mmol, 0.43 g, 1 mmol) and $AlCl_3$ (0.04 g, 0.3 mmol) in dichloromethane in a round-bottom flask was stirred for 20-30 min. When TLC (CH_2Cl_2, silica gel) showed the complete disappearance of urazole, the mixture was filtered and the filtrate was purified by column chromatography on silica gel with dichloromethane as eluent. Evaporation of the solvent gave pure triazolinediones in 90-97% yield.

Oxidation of Urazoles with BTPPC/AlCl$_3$ under Solvent-free Conditions.- A mixture of the urazole (1mmol), **BTPPC** (0.43 g, 1 mmol) and $AlCl_3$ (0.04 g, 0.3 mmol) in a mortar was ground with a pestle for 8-15 min. When TLC showed complete disappearance of the urazole, the mixture was extracted with CH_2Cl_2. Evaporation of the solvent gave pure triazolinediones in 92-96% yield.

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