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A HIGHLY EFFICIENT AND ECO-FRIENDLY APPROACH FOR THE SYNTHESIS OF TRIARYLPYRIDINE AND NOVEL TRIARYL-[1,3]THIAZEPINE DERIVATIVES VIA RING TRANSFORMATION AND EXPANSION OF TRIARYLTHIOPYRYLIUM SALTS

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GRAPHICAL ABSTRACT



Abstract The paper reports, for the first time, thermally induced ring transformation and expansion of triarylthiopyrylium salts using a novel task-specific dicationic ionic liquid [1,1'-(butane-1,4-diyl)-bis(3-methylimidazolium)] diazide as a nucleophile source. This method furnished a straightforward route for the synthesis of valuable 2,4,6-triarylpyridine and 2,5,7-triaryl-[1,3]thiazepine derivatives, which are widely present as motifs in an assortment of biologically active molecules.

Keywords Task-specific dicationic ionic liquid; ring transformation and expansion of thiopyrylium salts; bioactive heterocyclic compound; triarylpyridine; triaryl-[1,3]thiazepine

INTRODUCTION

Reducing the use of hazardous and toxic solvents, reagents, and catalysts in chemical synthesis and avoiding the generation of waste is one of the most important challenges presented by the effort to minimize pollution and risks associated with the production of chemicals.¹ Accordingly, organic reactions in ionic liquid have attracted a great deal of interest in both academic and industrial research because of their synthetic efficiency and

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environmental friendliness.² In the last decade, dicationic ionic liquids have appeared as promising and innovative media due to improved and unique properties such as higher thermal stability, lower volatility, and more flexibility in tuning the physicochemical properties compared with corresponding monocationic ionic liquid.³ Modification of the cation and/or anion with the appropriate functional groups often leads to a pronounced change in the properties of the ionic liquid. Therefore, ionic liquids often are referred to as tailor-made or tunable materials and are now expected to be designer liquids with controllable physical and chemical properties or even specific function liquids such as catalyst and reagent. Functionalized ionic liquids as organic reagents are very important areas of green chemistry where current methods can lead to major environmental problems due to the use of highly toxic reagents. Task-specific nitrite and azide ionic liquids were used for the efficient one-pot synthesis of 1,2,3-triazoles from aniline derivatives, the use of these organic reagents and procedure provides a fascinating potent and practical strategy for the eco and efficient preparation of desired products without handling of highly toxic chemicals.⁴

The synthesis of heterocyclic moieties has attracted tremendous attention due to the utilization of heterocyclic compounds in biological, biochemical, pharmaceutical, and asymmetric chemical investigations. In this context, six- and seven-membered rings containing nitrogen and/or sulfur atoms are essential constituents of a range of products from pharmacologically active substances to various materials.

Among this class of compounds, the pyridine ring system is one of the most prominent six-membered heterocycles present in various natural products and exhibit a board range of biological activities.⁵

Moreover, organic compounds containing thiazepine, as seven-membered molecular scaffold, broadly applied to cure many kinds of diseases. Thiazepine scaffolds can also act as intermediates for preparing clotiapine and quetiapine, which are atypical antipsychotics approved for the treatment of depressive disorder, psychosis and bipolar disorder, and schizophrenia.⁶

On the one hand, due to the unique position of 2,4,6-triarylpyridine derivatives in pharmacological chemistry, a great deal of efforts have been drawn to develop new and efficient synthetic routes for their generation in recent years.⁷ However, many of these methods suffer from one or more drawbacks such as expensive catalyst, long reaction times,^{7a-e} and special care in handling and storing the reagents.^{7a-e}

On the other hand, in spite of aforementioned advances in the synthesis and application of thiazepine derivatives, there have been no or few reports on the synthesis of triaryl substituted of these compounds so far. Hence, it is still of significant interest to explore novel and efficient synthetic approaches for the preparation of these molecules.

A possible route for the synthesis of triarylpyridine and triarylthiazepine derivatives is the nucleophilic reaction of triarylthiopyrylium salts with azide anion.⁸

Previous studies have revealed that the reactivity of azide anion with thiopyrylium cations at room temperature depends on the substitution of heterocyclic cation. Only sterically hindered thiopyrylium cations lead to the formation of a covalent azide, and tri-substituted examples give only a donor-acceptor complex.⁸ The formation of this complex constitutes a dead-end reaction on normal pathway to covalent azide. In this vein and in continuation of our success in the development of simple and environment-friendly experimental procedure for various important reactions and transformations,⁹ besides our new interest in the synthesis of biologically important heterocyclic compounds,¹⁰ herein we report, for the first time, the synthesis of triarylpyridine and triaryl-[1,3]thiazepine derivatives

via ring transformation and expansion of tri-substituted thiopyrylium salts using dicationic ionic liquid as an efficient reaction media, promoter, and reagent.

RESULTS AND DISCUSSION

It was decided in the present work to investigate an expedient route for the synthesis of triarylpyridine and novel triaryl-[1,3]thiazepine derivatives through the nucleophilic reaction of triarylthiopyrylium salts with azide anion.

Initially, the reaction of triphenylthiopyrylium perchlorate (**1A**) with sodium azide was selected as the model reaction to optimize the requisite reaction condition. The effect of different protic and aprotic solvents such as ethanol, methanol, dichloromethane, chloroform, acetonitrile, xylene, and tetrahydrofuran was investigated in model reaction at room temperature. It was observed that all media remained inactive for the reaction after prolonged stirring (24 h). Next, in order to evaluate the influence of temperature, the model reaction was performed in different solvents under reflux condition for 24 h. The reaction of model compound with sodium azide in boiling acetonitrile gave 2,5,7-triphenyl-[1,3]thiazepine (**3A**) and 2,4,6-triphenylpyridine (**4A**) in low yield (5 and 8%, respectively) along with considerable amount of starting material **1A** and byproduct **2A**. To determine the appropriate concentration of reagent, the reaction of model compound with varying amounts of sodium azide was investigated. The best result was obtained using two equivalents of NaN_3 per triphenylthiopyrylium perchlorate (**1A**).

As stated earlier, the formation of charge transfer complex constitutes a dead-end reaction on the normal pathway to covalent azide and prevents the formation of desired products.⁸ It is believed that the byproduct produced as a consequence of the competing side reaction (I) occurs in parallel to the intended reaction (II). The two pathways are summarized in Scheme 1.

For environmental concerns and due to the need for green solvent besides the significant properties of compounds of type **3** and **4**, continuation of the present work was encouraged to synthesize these privileged compounds in a more efficient method with the aim to prevent any concentration of the starting material **1A** and the byproduct **2A**. In view of this, it was decided to modify the strategy and find suitable alternatives to conventional organic solvents. Also, considering green credentials of ionic liquid and in view of the remarkable ability of ionic liquids to efficiently promote a wide range of conventional reactions, the exploration was started again by synthesizing [1,1'-(butane-1,4-diyl)-bis(3-methylimidazolium)] dibromide as a highly polar and recyclable dicationic ionic liquid and unambiguous structural elucidation, accomplished by spectroscopic data. Following the characterization, the reaction of model compound with sodium azide in the dicationic ionic liquid as a sustainable medium at different temperature was investigated. Interestingly, the use of ionic liquid gave encouraging results at 130°C. As illustrated in Table 1, the reaction time was dramatically reduced and the yields of desired products were considerably increased without any unreacted starting material **1A** and byproduct **2A** (entry 5). This is probably due to the good solubility of triphenylthiopyrylium salt and sodium azide in the ionic liquid compared with organic solvent. Moreover, the capacity of ionic environments to generate internal pressure and to promote the association of reactants in solvent cavities renders them excellent media for this reaction. Thereby the ionic liquid not only acts as a favorable reaction medium but also as a promoter of the reaction.

Table 1 The reaction of model compound with sodium azide in dicationic ionic liquid at different temperatures

Entry	Temperature (°C)	Time	Yield (%) (3A , 4A)
1	80	24 h	5, 8
2	100	24 h	9, 11
3	110	24 h	10, 11
4	120	24 h	12, 14
5	130	40 min	30, 35
6	140	40 min	30, 35

It was found that increasing the temperature did not improve the reaction rate (Table 1, entry 6), while reducing the temperature led to lower yield due to the formation of byproduct **2A** (Table 1, entry 1–4).

It is noteworthy that owing to the high toxicity of sodium azide, this method is not very environment-friendly.

To circumvent this dilemma and reduce the toxicity of azide ion, the attention was shifted to the design, synthesis, and use of novel azide source that not only possesses high activity and selectivity, but is also simultaneously benign to the environment. Accordingly, a new synthetic strategy commenced with the synthesis of novel task-specific dicationic ionic liquid was carried out. Task-specific ionic liquid [1,1'-(butane-1,4-diyl)-bis(3-methylimidazolium)] diazide was prepared by the anion exchange of [1,1'-(butane-1,4-diyl)-bis(3-methylimidazolium)] dibromide with NaN_3 in the absence of organic solvents at room temperature.

The use of this novel task-specific dicationic ionic liquid as reagent decreases the reaction time (Table 2, entry 2). A weak interaction between azide anion and imidazolium cations, which increases the nucleophilicity of azide anion, might contribute to the suppression of byproduct formation and to the rapid progress of nucleophilic reaction.

To the best of our knowledge, this is the first synthetic utility of a task-specific dicationic ionic liquid as a nucleophile source for the green synthesis of heterocyclic compounds.

These extraordinary results promoted us to demonstrate the efficiency and the applicability of the present method. Therefore, the reaction was performed for a variety of triarylthiopyrylium salts containing electron-withdrawing groups (such as halide and nitro groups) or electron-donating groups (such as alkyl and methoxy groups) with azide anion under optimized reaction conditions (Table 3).

As is evident from Table 3, for series of **1B–D**, the thiopyrylium ring containing electron-donating groups reacted well with azide anion to give the corresponding products **3** and **4**. It is interesting that the reaction of these substrates (**1B–D**) was more sluggish than reaction of model compound (**1A**). This may be ascribed to the fact that these groups

Table 2 Reaction of the model compound **1A** with two different types of reagents

Entry	Solvent	Nucleophile source	Time (min)
1	Dicationic ionic liquid	NaN_3	40
2	Dicationic ionic liquid	Task-specific ionic liquid	20

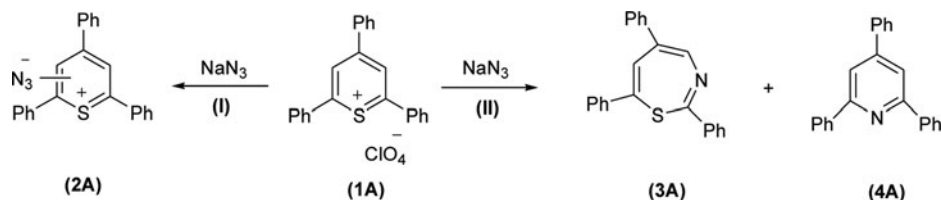
Table 3 The conversion of various triarylthiopyrylium salts (**1**) into the corresponding 2,5,7-triaryl-[1,3]thiazepine (**3**) and 2,4,6-triarylpyridine derivatives (**4**) using task-specific ionic liquid as reagent under optimized condition

No.	Substrate (1)	Product (3)	Product (4)	Yield (%) (3)/(4)	Time (min)
A				30/35	20
B				15/40	30
C				30/35	22
D				30/35	85

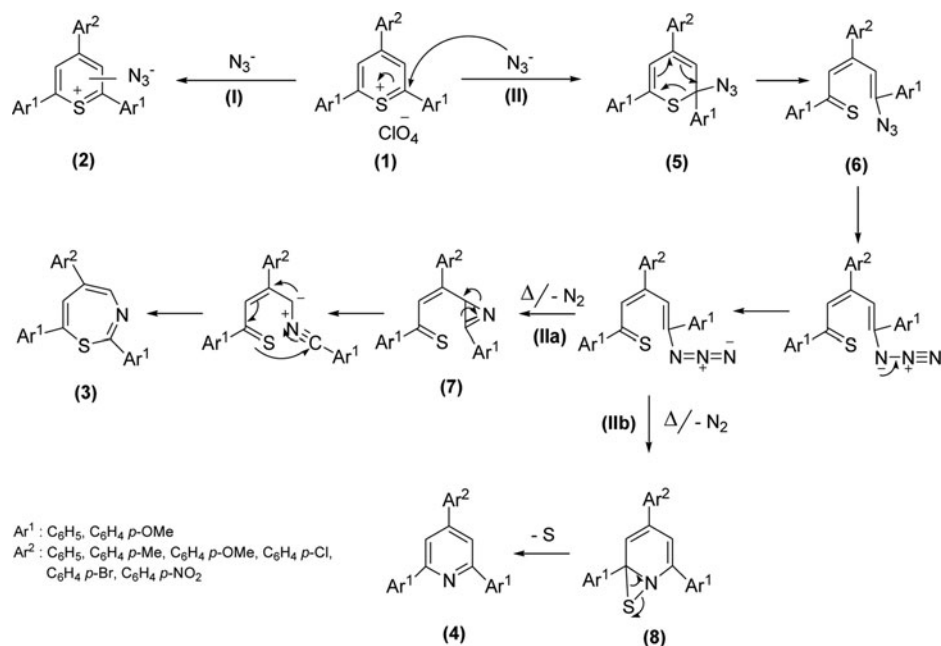
decrease the positive charge at the α -position of heterocyclic ring. The effect of electron-withdrawing groups was also viewed clearly. The reaction of these substrates with azide anion gave the corresponding charge transfer complex (**2**) as the sole product. This can be rationalized by considering the fact that these groups increase the positive charge of the heterocyclic ring, thereby increase its tendency for the formation of the charge-transfer complex (**2**).

These results confirm that these reactions occur competitively by two pathways involving the formation of the charge transfer complex **I** and the nucleophilic attack of azide anion **II**. As shown in Scheme 2, the complex formation path is the main route for the thiopyrylium ring containing electron-withdrawing groups, while the nucleophilic attack path is the main route for the thiopyrylium ring containing electron-donating groups.

A conceivable mechanism for the synthesis of triaryl-[1,3]thiazepine (**3**) and triarylpyridine (**4**) derivatives via a nucleophilic attack route (**II**) is outlined in Scheme 2. The first step of the reaction affords 2-azidothiopyran (**5**), which undergoes ring opening, leading to acyclic valence tautomer **6**. Subsequently, thermal elimination of N_2 molecule from compound **6** followed by intramolecular nitrogen insertion into C-C double bond (**IIa**) yields azirine **7**, which readily rearranged to the stable 2,5,7-triaryl-[1,3]thiazepine (**3**). Another plausible pathway that can occur after the release of N_2 molecule from compound **6** is the insertion of nitrogen atom into the C-S double bond (**IIb**), which affords



Scheme 1 Two pathways for the reaction of model compound with sodium azide in boiling acetonitrile.



Scheme 2 Plausible mechanism for the reaction of triarylthiopyrylium salts (1) with azide nucleophile.

bicyclic thiaziridine **8**. Eventually, extrusion of the sulfur atom from compound **8** leads to the formation of 2,4,6-triarylpyridine (**4**).

The proposed mechanism is in agreement with the previously reported mechanism for the nucleophilic attack of azide anion to the sterically hindered thiopyrylium salts.⁸

The structure of all the products was settled from their physical and spectroscopic data (¹H **nuclear magnetic resonance** (NMR), ¹³C NMR and mass spectrum (MS); see Supplementary Materials, available online).

It is worthy to note that compounds **3** and **4** are of considerable interest since it is for the first time that the synthesis of these privileged heterocyclics via ring expansion and transformation of triarylthiopyrylium salts using a task-specific dicationic ionic liquid was reported.

To confirm the stability of compound **3** under reaction conditions, the isolated product was heated in the dicationic ionic liquid at 130°C for a prolonged period. According to thin-layer chromatography (TLC) analysis, there was no evidence for the transformation of compound **3**.

Table 4 Comparison of the present method with literature methods for the synthesis of 2,4,6-Triphenyl-pyridine via ring expansion

Entry	Reagent	Catalyst	Time	Ref.
1	NH ₄ OAc	Bi(OTf) ₃	2 h	7a
2	NH ₄ OAc	AcOH	4 h	7b
3	NH ₄ OAc	Pentafluorophenylammonium triflate	2 h	7c
4	NH ₄ OAc	H ₁₄ [NaP ₅ W ₃₀ O ₁₁₀]	3.5 h	7d
5	NH ₄ OAc	HClO ₄ -SiO ₂	4 h	7e
6	NaN ₃	—	48 h	8
7	Ionic liquid bearing azide anion	—	20 min	Present work

Table 4 confirms that this method presents the best currently available method in terms of yield and time for the preparation of the 2,4,6-Triphenyl-pyridine.

CONCLUSIONS

As a conclusion from the present study, a convenient method was reported for the preparation of valuable six- and seven-membered ring heterocycles (triarylpyridine and triaryl-[1,3]thiazepine derivatives) using the new azide source in ionic solvent. To the best of our knowledge, this is the first reported example for the formation of 2,4,6-triarylpyridine and 2,5,7-triaryl-[1,3]thiazepine derivatives starting from thiopyrylium salts, as a simple and readily available starting materials, in the green solvent. Further studies on the applications of these compounds, which concluded from the heterocyclic structure, are currently under way in our laboratory.

EXPERIMENTAL

General

Chemicals were purchased from Fluka, Merck, and Aldrich chemical companies. Monitoring of the reactions was accomplished by TLC. Infrared (IR) spectra were obtained on a Bomen MB:102 FT-IR spectrophotometer. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker spectrometer at 400 and 100 MHz, respectively, in CDCl₃ or D₂O with tetramethylsilane as an internal standard. MS spectra were measured on an Agilent 5975 Mass Spectrophotometer. The Supplemental Materials contain the complete characterization and sample spectra for 3A–3D (Figures S1–S12). (All supplemental materials, including Figures S1–S12, are available online under “Supplemental Materials.”)

Synthesis

Synthesis of Triarylthiopyrylium Perchlorates. All triarylthiopyrylium perchlorates were synthesized by the method described previously.¹¹

Synthesis of [1,1'-(butane-1,4-diyl)-bis(3-methylimidazolium)] dibromide. [1,1'-(butane-1,4-diyl)-bis(3-methylimidazolium)] dibromide was synthesized by the method described previously.¹²

Synthesis of [1,1'-(butane-1,4-diyl)-bis(3-methylimidazolium)] diazide. [1,1'-(butane-1,4-diyl)-bis(3-methylimidazolium)] diazide was synthesized by the method described previously for the synthesis of azide monocationic ionic liquid.⁴ Briefly, freshly prepared [1,1'-(butane-1,4-diyl)-bis(3-methylimidazolium)]dibromide (1 mmol) and NaN₃ (2 mmol) were added into deionized water (2 mL), and the mixture was stirred for 24 h at room temperature. The solvent was removed under reduced pressure at 50°C to obtain the crude product containing azide ionic liquid and NaBr, which was washed with acetonitrile (3 × 10 mL). The remaining acetonitrile was removed under high vacuum to give diazide as a white solid product. IR spectrum revealed that the ionic liquid conveniently loaded with the desired azide anion (see Supplemental Materials).

General procedure for the synthesis of 2,5,7-triaryl[1,3]thiazepine (3A-D) and 2,4,6-triarylpyridine (4A-D) derivatives. A mixture of triarylthiopyrylium perchlorates (1 mmol), [1,1'-(butane-1,4-diyl)-bis(3-methylimidazolium)] diazide 1 mmol containing azide anion (2 mmol) in [1,1'-(butane-1,4-diyl)-bis(3-methylimidazolium)]dibromide (1 g) as a solvent was heated to 130°C. After the completion of the reaction, as indicated by TLC (*n*-hexane/ether, 4/1), the products were extracted from a quenched reaction mixture with dichloromethane (10 mL), the solvent was evaporated under vacuum and the residue was adsorbed on silica, transferred to a silica column, and eluted with a 4/1 mixture of *n*-hexane/ether. Therefore, the first solid and the second oil parts containing 2,4,6-triarylpyridine and 2,5,7-triaryl[1,3]thiazepine were obtained, respectively. The sampled parts were concentrated and analyzed by NMR spectroscopy and MS.

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SUPPLEMENTAL MATERIAL

Supplemental data for this article can be accessed on the publisher's website at <http://dx.doi.org/10.1080/10426507.2015.1054482>.

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