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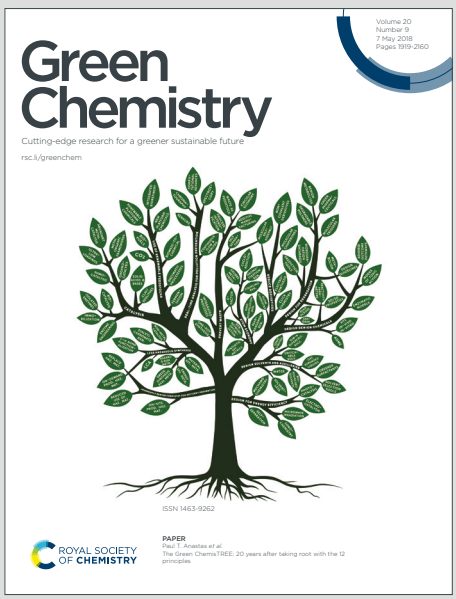

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ARTICLE

Multicomponent Synthesis of Sulfonamides from Triarylbismuthines, Nitro Compounds and Sodium Metabisulfite in Deep Eutectic Solvents

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A sustainable synthesis of sulfonamides using a copper-catalysed process starting from triarylbismuthines, $Na_2S_2O_5$ and nitro compounds is described, in a Deep Eutectic Solvent (DES) as reaction medium. Thus, triarylbismuthines are used as reagents for the incorporation of SO_2 into organic motifs. The bismuth salts formed as by-product can be easily removed from the crude reaction mixture by precipitation with water, while the use of volatile organic compounds (VOCs) as solvents can be avoided in the entire process. The eutectic mixture employed as solvent is fully characterised, with the preliminary results proving its low toxicity. The designed DES also allows for a novel multicomponent reaction which saves time, reduces purification steps, energy and cost.

Introduction

The manufacturing of active pharmaceutical ingredients (APIs) generates more waste than any other process within the existing chemical industries.[1] The sulfonamide functional group is widely present in pharmacologically active compounds,[2] which include those related to new research[3] on anticancer active molecules.[4] Despite its undeniable interest, traditional methods for its synthesis are still prevailing.[5] For more than a century, sulfonamides have been mostly prepared from amines and activated sulfonyl derivatives,[6] usually sulfonyl chlorides. This method is efficient but relies entirely on the use of stoichiometric sulfonyl chlorides, which are not stable or commercially affordable and generate stoichiometric amounts of corrosive HCl. For this reason, new methodologies avoiding the use of unstable and toxic reagents, harsh reaction conditions or dry volatile organic compounds (VOCs) as solvents are demanded.

Multicomponent methods[7] have also been explored using SO_2 surrogates under transition metal catalysis.[8] Recently, we reported the efficient multicomponent synthesis of sulfones from aryl boronic acids, sodium metabisulfite (a food additive) and electrophiles as alkylating reagents catalysed by Pd nanoparticles.[9] The use of sodium metabisulfite possess some advantages, since it is an inexpensive reagent used in food industry. It is known to yield SO_2 under heating or in the presence of water,[10] generating only Na_2SO_3 as waste, thus avoiding the generation of toxic organic by-products. In this case, a DES was used as green reaction medium to carry out the sulfone synthesis, benefitting from the enhanced SO_2 solubility in this type of medium.[11]

DESs are solvents formed by combining a hydrogen-bond donor and an acceptor, affording a mixture with strong interactions. As a consequence, a depression of the melting point of the mixture is observed.[12] Since its discovery, hundreds of mixtures have been found to form a eutectic phase, with more than ten million low-transition-temperature mixtures being available.[13] Changing one of the DES components can modify dramatically its properties. Thus, DESs can be designed for each reaction by choosing carefully the eutectic components. In addition, most of the components are naturally-occurring, bio-renewable, biodegradable or can be bio-assimilated, which makes these solvents an interesting alternative to traditional hazardous organic solvents.[14]

Despite the obvious sustainable advantages of DESs as reaction media, there is still controversy about their potential toxicity; several reports support the theory that DESs are non-toxic, eco-friendly, biodegradable and benign solvents, whilst other similar studies demonstrate exactly the opposite.[15] For this reason, a rigorous analysis of the real toxicity of each new mixture must be performed.

In this study, a new multicomponent reaction using triarylbismuth reagents as starting materials to generate sulfonamides was planned. Triarylbismuthines are non-toxic,[16] and unlike other organometallic reagents (such as boron or tin derivatives) can react with 3 equivalents of an electrophilic reagent (in this case SO_2), increasing the atom economy of the

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process. As the Bi-C bond energy is quite low, the reactivity displayed by these reagents would be enhanced.[17] The reaction of triarylbismuth reagents with $Na_2S_2O_5$ as SO_2 source, would provide aryl sulfinates that could react in situ with nitro compounds.[18] The Na_2SO_3 by-product formed during the first sulfonylation step, reacts with hydrogen donor compounds giving $NaHSO_3$, a potential reductant.[19] The corresponding reaction intermediate would afford, after reduction, a sulfonamide as product. This strategy reduces the by-product formation, meeting the Green Chemistry criteria.[20]

Results and discussion

The study was started by optimising the reaction conditions to yield *N*-phenylbenzenesulfonamide (**4a**), using triphenylbismuthine (**1a**), $Na_2S_2O_5$ (**2**), and nitrobenzene (**3a**) as the model reaction (Table S1). Using choline chloride (ChCl):acetamide (1:2) as solvent, different copper sources were analysed. The use of just 1 mol% of CuCl yielded the desired product in 43% yield without the need of any external ligand or base. Next, different DESs and conventional organic solvents were tested. However, none of them afforded better results. The reaction did not take place in organic solvents or water. Although the reaction did not proceed in ChCl:Urea (1:2) or chlorocholine chloride (ClChCl):Urea (1:2), yields around 50% were obtained both, in ChCl:Acetamide (1:2) and acetyl choline chloride (AcChCl):Urea (1:2). Therefore a new mixture, AcChCl:Acetamide (1:2), was deemed the most suitable reaction medium. These components were found to form a eutectic mixture in a 1:2 molar ratio (according to DSC analysis, Fig. 1). To the best of our knowledge, this mixture has not been described previously in the literature.

By using this novel DES as medium, 99% yield was obtained, proving that both components of the DES mixture have an important effect in the reaction course (Fig 2).

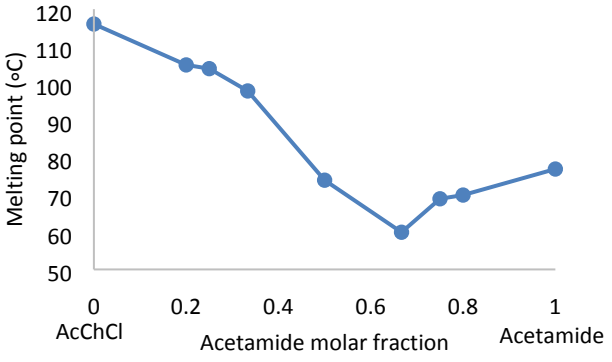

Figure 1. Phase diagram of the mixture acetylcholine chloride:Acetamide.

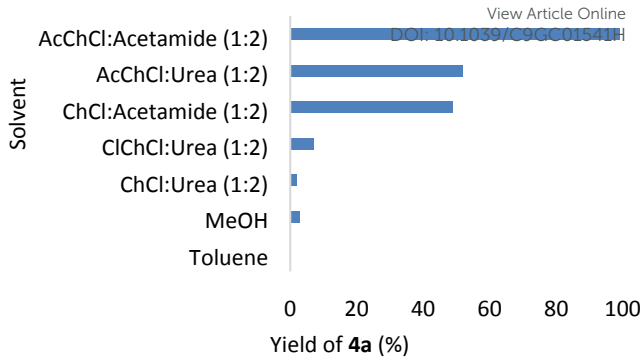

Figure 2. Solvent optimisation.

With these optimised conditions in hand, the scope of nitro compounds was evaluated (Chart 1). No effect on the electronic properties of the substituents of the nitro arene was observed.

Good to excellent yields were obtained for nitro arenes bearing neutral, electron-donating or electron-withdrawing groups. The reaction was chemoselective, as no Suzuki-type by-product was observed.[21] This transformation was also compatible with nitro alkanes, although the product was obtained in lower yield (**4m**). The reaction could also take place twice in the same substrate by using 1,3-dinitrobenzene as starting material (**4i**).

Then, the scope of Ar_3Bi was evaluated (Table 1). The reaction exhibited good to excellent yields for triarylbismuth reagents bearing neutral or electron donating groups (**5a-5e**) and lower yields were obtained with electron-withdrawing groups (**5f-5i**). The use of more complex structures and functional groups is also compatible, making the synthesis of biologically active compounds in a single step possible (Scheme 1).[22]

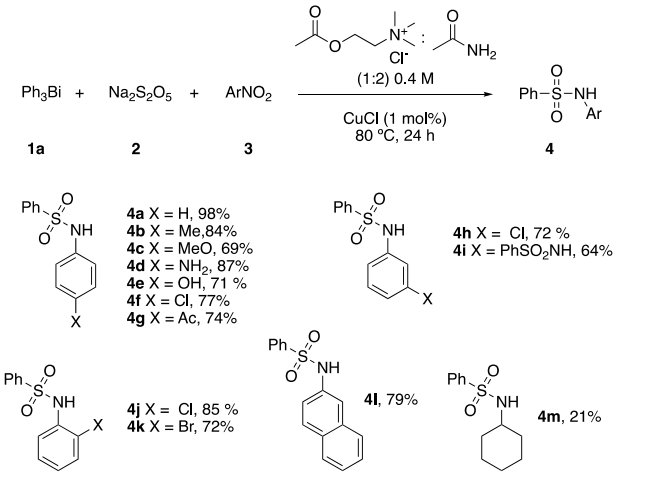

Chart 1. Scope of nitro compounds. Reaction conditions: Ph_3Bi (0.2 mmol), $Na_2S_2O_5$ (1.32 mmol, 251 mg), CuCl (0.59 mg, 1 mol%) and $ArNO_2$ (1.2 mmol) in 1.5 mL of DES were stirred at 80 °C for 24 h. Isolated yields are based on the consumption of the three phenyl groups attached to Bi.

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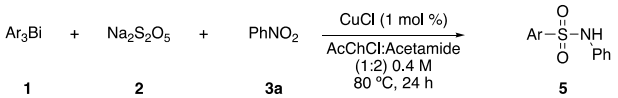
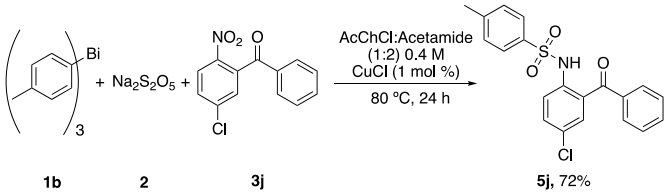
Table 1. Scope of triarylbismuthines.[a]



Entry	Ar	Product	Yield[b]
1	4-MeC_6H_4	**5a**	82%
2	1-naphtyl	**5b**	75%
3	4-MeOC_6H_4	**5c**	71%
4	3,4,5-MeOC_6H_2	**5d**	72%
5	4-$Me_2NC_6H_4$	**5e**	78%
6	4-FC_6H_4	**5f**	49%
7	4-BrC_6H_4	**5g**	62%
8	2-$CF_3C_6H_4$	**5h**	28%
9	3-$CF_3C_6H_2$	**5i**	48%

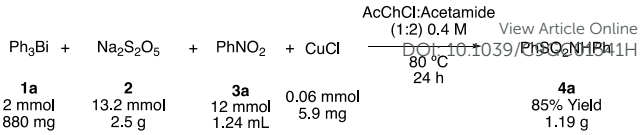
[a] Reaction conditions: Ar_3Bi (0.2 mmol), $Na_2S_2O_5$ (1.32 mmol, 251 mg), CuCl (0.59 mg, 1 mol%) and $PhNO_2$ (1.2 mmol, 123 μL) in 1.5 mL of DES were stirred at 80 °C for 24 h. [b] Isolated yields based on the consumption of the three aryl groups attached to Bi.



Scheme 1. Synthesis of anti-leprosy compound **5j**.

The recycling of the DES and catalyst was attempted by the extraction of the product using immiscible organic solvents, and subsequent addition of fresh reagents to perform a new reaction cycle.[23] However, the use of 2-MeTHF as extraction solvent for this purpose was unsuccessful, since the reaction yield dropped from 98% to 27% in the second cycle. This was probably due to the salts formed during the process affecting the DES structure and therefore limiting its recyclability. Alternatively, in order to avoid the use of VOC solvents in the process, a gram-scale reaction was performed. At the end of the reaction process, a solution of HCl (0.5 M) was added in order to remove the bismuth-waste, obtaining product **4a** as a precipitate which was filtered and rinsed with water. In this case, the use of VOC solvents was completely avoided during the whole process, obtaining 1.19 g of compound **4a** with high purity (85% yield, see Fig S1 for ^{1}H NMR). A similar result was obtained through VOC extraction using EtOAc as solvent (Scheme 2). When the reaction was quenched with only water and the organic products were extracted with EtOAc, the formation of a precipitate containing bismuth salts was observed. After removal of the precipitate, an ICP-mass analyses of both, the organic and aqueous layer, showed only a presence of 0.02% and 2.3% of bismuth, respectively.

To have some insights in the reaction mechanism, several control experiments were performed (see supporting information).



Scheme 2. Gram-scale reaction without using VOC solvents.

In view of the obtained results, a possible mechanism has been proposed. The first step involved the disaggregation of $Na_2S_2O_5$ through a homolytic cleavage of the S-S bond. This step includes the formation of radical intermediates,[24] in accordance with our radical-trapping experiments. Running the reaction in the presence of TEMPO (2,2,6,6-etramethylpiperidine 1-oxyl) completely inhibits the product formation. However, when TEMPO was added to the pre-formed sodium sulfinate, CuCl, nitrobenzene and $NaHSO_3$, the reaction proceeded, although with lower yields. These radical intermediates suffer a disproportionation to afford electrophilic SO_2 and the by-product Na_2SO_3. Next, SO_2 undergoes insertion between C-Bi bond.[25] Given that a large excess of chloride anions is present in the medium, $BiCl_3$ may be released, alongside the corresponding sulfinate. Finally, the sulfinate reacts with the nitro arene, being reduced by $NaHSO_3$[19d] (generated from Na_2SO_3 and moisture) to yield sulfonamide, in a process catalysed by copper (Scheme 3).

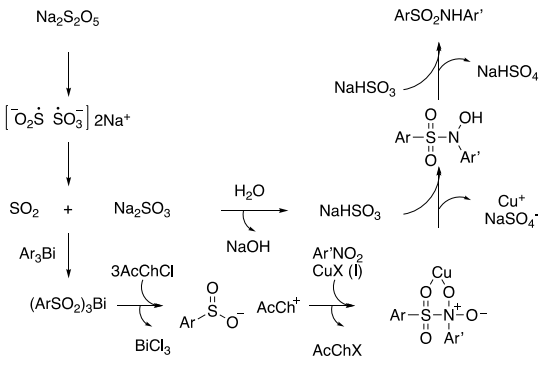
DES physicochemical characterisation.

Since the eutectic mixture employed in this study has not been described previously, a complete physicochemical characterisation was performed. First, the density was measured employing a 50 mL pycnometer (equation 1).

$$\rho_{DES} = \frac{m_{DES}}{m_{water}}\rho_{water} = 1.09\ g/mL\ (28\ ^{\circ}C)$$

Equation 1. Density of DES.

The pH value is a very important parameter to be measured for a new solvent. It can be crucial for the corrosion, catalytic or dissolution properties of the solvent, limiting its industrial applicability. In non-aqueous solutions, pH depends on temperature and on the chemical potential of hydrogen.



Scheme 3. Plausible reaction mechanism.

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The chemical potential depends on the presence of ions and hydrogen-bonding with other species.[26] It was observed that the pH value decreased linearly with the acetamide molar fraction (Fig. 3); meaning that the more hydrogen bonds available, the lower the chemical potential of hydrogen was and the lower pH value was obtained. The phase diagram (Fig 1) was plotted using the individual differential scanning calorimetry analyses of several mixtures containing different proportions of the two DES components (Fig S4).

Finally, the potential toxicity of this novel eutectic mixture was studied. Preliminary studies carried out with strains of mesophilic bacteria showed that the DES is non-toxic for concentrations below 300 mM. Nevertheless, further studies will be carried out in order to completely assess the DES toxicity.

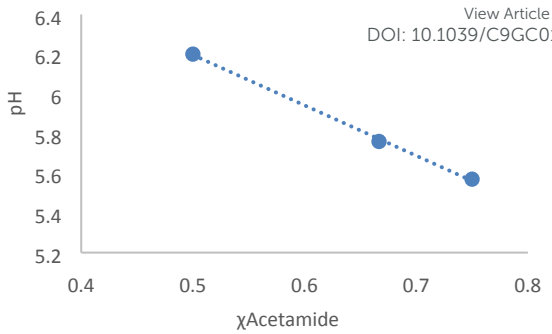

Figure 3. pH values depending on the acetamide molar fraction.

Experimental

General

Melting points were obtained with a Reichert Thermovar apparatus. NMR spectra were recorded on a Bruker AC-300 (300 MHz for ^{1}H and 75 MHz for ^{13}C) using $CDCl_3$ as a solvent and TMS as internal standard for ^{1}H and ^{13}C; chemical shifts are given in δ (parts per million) and coupling constants (*J*) in Hertz. FT-IR spectra were obtained on a JASCO 4100LE (Pike Miracle ATR) spectrophotometer. Mass spectra (EI) were obtained at 70 eV on a Himazdu QP-5000 spectrometer, giving fragment ions in m/z with relative intensities (%) in parentheses. The mass spectrometry analyses of high resolution (HRMS) were performed in the unit of Mass Spectrometry of the Technical Services Research at the University of Alicante with a spectrometer Finnigan MAT95-S. DIP analyses were performed using an Agilent mass spectrometer, model Network 5973 Mass Selective with direct sample introduction to the ion source through the SIS (Scientific Instrument Services) probe Direct Insertion Probe (73DIP-1).The chromatographic analyses (GLC) were determined with a Hewlett Packard HP-5890 instrument equipped with a flame ionization detector and 12 m HP-1 capillary column (0.2 mm diam, 0.33 mm film thickness, OV-1 stationary phase), using nitrogen (2 mL/min) as a carrier gas, $T_{injector}$ = 275 °C, $T_{detector}$ = 300 °C, T_{column} = 60 °C (3 min) and 60-270 °C (15 °C/min), P = 40 kPa. Thin layer chromatography (TLC) was carried out on Schleicher&Schuell F1400/LS 254 plates coated with a 0.2 mm layer of silica gel; detection by UV_{254} light. DSC analysis were carried out on a METTLER TOLEDO equipment, model TGA/SDTA851e/LF/1600, and EM analysis on a PFEIFFER VACUUM, model THERMOSTAR GSD301T. pH measurements were performed using a Mettler Toledo SevenEasy S20 pH-meter. Reactions carried out under microwave irradiation were performed on a MW CEM Discovery 908010 apparatus. Column chromatography was performed using silica gel 60 of 40-63 mesh. All reagents were commercially available (Acros, Aldrich, Fluorochem) and were used as received.

Synthesis of Ar_3Bi.

For commercially available organomagnesium reagents: a solution of the $BiCl_3$ in dry THF (1M) was added dropwise over a solution of ArMgBr in THF or Et_2O (1M) under argon atmosphere with magnetic stirring. Once the addition was completed, the solution was heated to reflux for 12 h. Then, the reaction was allowed to reach room temperature and poured slowly over a cold saturated aqueous solution of NH_4Cl. Product was extracted 3 times with Et_2O. The combined organic phases were dried over $MgSO_4$ and the solvent was removed under reduced pressure.[27]

For non-commercially available organomagnesium reagents: the corresponding aryl iodide (6.2 mmol) was dissolved in dry THF and cooled to -78 °C in an acetone bath. A *n*-butyllithium solution (2.5 M, 6.2 mmol) was added dropwise and the mixture was stirred at that temperature for 1 h. Then, a solution of $BiCl_3$ (2 mmol) in dry THF was added dropwise and the mixture was slowly allowed to reach room temperature. The corresponding mixture was stirred overnight at rt and then quenched with sat. aq. $NaHCO_3$. The aqueous layer was extracted with EtOAc (15 mL x 3) and the combined organic layers washed with H_2O and brine. The organic layer was dried over $MgSO_4$, filtered and reduced under reduced pressure. Ar_3Bi were usually purified by recrystallization from hot EtOH or by flash chromatography using a mixture of EtOAc and hexanes.[30]

Synthesis of sulfonamides.

A solution of Ar_3Bi (0.2 mmol), sodium metabisulfite (1.32 mmol), CuCl (0.006 mmol) and the corresponding nitro compound (1.2 mmol) in 1.5 mL of DES was stirred for 24 h at 80 °C in a reaction vessel opened to air. Once the reaction was completed, water was added to dissolve the DES phase. A precipitate containing the bismuth waste was formed. The bismuth by-product was only soluble in acidic aqueous solutions. The aqueous suspension was extracted three times with EtOAc. The sulfonamide product and the excess of nitro compound were dissolved in EtOAc. The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. Products were usually purified by

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chromatography on silica gel (hexane/ethyl acetate) and/or distillation to give the corresponding products **4/5**.

Alternatively, product could be isolated by quenching the reaction mixture with HCl (0.5 M) and filtering the suspension. The filtrate was rinsed with distilled water to afford products **4/5** in high purity, although with lower yields than in the previous method due to the slight solubility of sulfonamides in water. Isolated yields are based on the consumption of the three aryl groups attached to Bi.

Conclusions

In summary, an efficient one-pot, one-step synthesis of sulfonamides is described in this study; starting from unactivated reagents such as nitro compounds and triarylbismuthines, with $Na_2S_2O_5$ as SO_2 source and reductant. This process, catalysed by copper chloride in a ligand-free fashion has been demonstrated to be chemoselective, simple, and air and moisture insensitive. In addition, in this study non-toxic reagents are used, and the excess of by-product formation is reduced, following most of the Green Chemistry principles. The resulting bismuth salts are easily removed from the reaction crude mixture by precipitation with water. The eutectic mixture here described has been characterised, with preliminary analyses showing low toxicity.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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