

Glycolic Acid-Based Natural Deep Eutectic Solvents (NADESs) as Catalytic Reaction Media for the Synthesis of β -Nitro Ketones

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β -nitro ketones represent highly significant compounds for their simultaneous nucleophilic and electrophilic reactive sites in 1,3-related positions. These molecules are commonly obtained via nitration of enones in aprotic apolar organic solvents (such as THF and CPME) with large excesses of nitrating agents and acetic acid. In this work the use of weakly acidic natural deep eutectic solvents (NADESs) – glycolic acid based-ones – is proposed as both green and catalytic reaction media for

the nitration of enones giving β -nitro ketones. The NADESs mixtures employed were the ones formed by mixing glycolic acid with trimethylglycine, with choline chloride and with water. The reaction proceeded with stoichiometric amounts of nitration agents and taking advantage from the catalytic behavior of the NADESs solvents; the scope was explored giving satisfactory yields.

1. Introduction

The solvent is the most abundant part in any chemical transformation; its toxicity, recyclability and the control of its dispersion in the environment represent important matters to be faced whenever a transformation should be considered environmentally friendly or not.^[1–4] These aspects nowadays are fundamental to contribute to the reduction of the human-sourced pollution of the planet.^[5]

In this topic, in recent years many solutions to these issues were proposed in the literature with both advantages and disadvantages. Bio-based solvents, ionic liquids, and more recently deep eutectic solvents (DESs) represent relevant examples in the scientific research to face off to these matters.^[6–9] DESs nowadays represent a step-ahead for the development of green and also innovative chemical procedures for their environmentally friendly features, their structural characteristics as well as their catalytic capabilities.^[10–12]

DESs are mixtures of two or more substances in which weak interactions, mainly H—bonds, occur between a hydrogen bond donor specie and a hydrogen bond acceptor specie. In principle,

the increase of interactions between two species could lead to an increase of the melting (or boiling) points of the systems but as well as these HBD-HBA adducts, also HBD-HBD and HBA-HBA ones occur as reported in literature; this leads to an impossible regular crystal lattice formation, therefore to liquids.^[13] Therefore there is a balance in terms of enthalpic contributes, determined by the weak interactions, and entropic ones, determined by the impossibility of crystallization of the substances, that are the driving forces leading to liquid status of these systems.^[14,15] Many different molecules capable of H—bonds or weak interactions can act as DESs' components, therefore the number of novel liquids reported in the literature is rapidly increasing with wide different characteristics.^[16–18]

The green features of DESs rely on their low or absent vapor pressure, their low or absent toxicity, their recycle capabilities.^[19,20] Surely not all the DESs mixtures have the same green features, because their properties are related to the molecules forming them. However, all the DESs share an important green aspect represented by their realization, that do not need any other solvent, no purification procedure, and proceeds with 100% yields and atom economy from the starting molecules.^[21] This is a great advantage compared to ionic liquids and bio-based solvents so far.^[22,23] If the molecules forming the liquids are natural-sourced ones, this increases by much their green features in terms of biocompatibility and sustainability, and the liquids are named as NADESs: Natural Deep Eutectic Solvents.^[24] DESs can exhibit also catalytic features that are linked and related to their structural features. DESs can show in fact acidic, basic, reducing and also organocatalytic activities whenever formed by acid, basic, reducing and organocatalyst molecules, respectively.^[11,25–28] In this topic, the activity of the DESs mixtures to act as catalysts, and as reactant/reagents as well, was demonstrated to be related to the intimacy of the DESs couples, in terms of availability of a molecule to act in another way rather than simply DES' component.^[29,30] Therefore, the structural features of the DESs act as important factors to be considered in order to study their catalytic properties; a relevant

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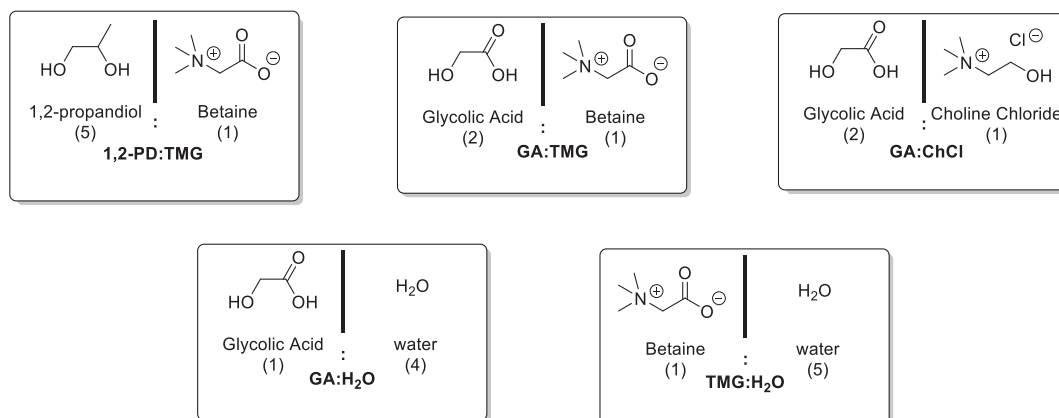


Figure 1. Tested DESs Solvents.

Table 1. Screening of glycolic acid-based DESs Solvents.^{a)}

Entry	DES	Yield ^{b)}
1	1,2-PD:TMG (5:1)	-
2	GA:TMG (2:1)	60%
3	GA:ChCl (2:1)	52%
4	GA:H ₂ O (1:4)	45%
5	TMG:H ₂ O (1:5)	23%

^{a)} Typical reaction conditions: Ethyl vinyl ketone (1 mmol), NaNO₂ (1.5 mmol), DES solvent (500 mg/mmol), r.t., 16h, closed vial. ^{b)} Chromatographic yield.

example of this concept was shown by acid-based liquid DESs acting as weak base catalysts, because of the involvement of the acid protons of the reactants inside the H-bond networks of the DESs.^[31]

DESs are widely applied as substitutes to common volatile organic compounds (VOCs) in many different topics, such as extractions from food and waste matrixes, nanotechnologies, analytical chemistry, electrochemistry, biocatalysis and so on.^[32–34] One of the most studied is their use as reaction media for chemical transformations, in which DESs can act as “innocent” liquids, whenever they simply act as green solvents, or “active” ones in the cases where they can participate to the reaction as reactant/reagents or catalysts.^[11,35]

In this work, following our ongoing studies on DES applications,^[36,37] the acidic catalytic effect of a set of weak acid based NADESs, glycolic acid-based ones, was evaluated in the reaction of nitration of enones affording β -nitro ketones. This class of compounds is highly significant in organic synthesis due to the simultaneous presence of nucleophilic and electrophilic carbons in 1,3-related positions. In fact, over the years, this feature has rendered β -nitro ketones, particularly their more stable keto-protected forms, valuable precursors for the synthesis of highly functionalized materials and heterocyclic

systems.^[38–40] However, despite their importance, procedures for enone nitration remain mainly limited to a couple of methods reported by Miyakoshi in 1981, and more recently by us.^[41,42] Although the latter method addressed some sustainability concerns, both approaches suffer from significant drawbacks, such as the use of volatile organic solvents (THF and CPME, respectively) and the requirement for large excesses of acetic acid and the nitrating reagent.

Herein, we report the use of DESs as superior reaction media for promoting the nitration of enones under acetic acid-free conditions and in the presence of a stoichiometric amount of nitrating agent.

2. Results and Discussion

2.1. Screening of Glycolic Acid-Based DESs Solvents

The first step of this work was a screening of a set of glycolic acid (GA) -based DESs in a model-type reaction, in order to take advantage of the weakly acidic catalytic behavior of GA-based DESs. In this set of experiments ethyl vinyl ketone **1** was used as starting material and NaNO₂ as source of nitrite

anion. GA can form DESs whenever mixed with a wide set of molecules; choline chloride (ChCl) and betaine (or trimethylglycine, TMG) molecules were used to form DESs with it.^[43,44] Over these two counterparts, also water was used as DES couple with GA as the GA:H₂O mixture was demonstrated to be a DES thanks to the theoretical/experimental melting curves comparison approach.^[45] In order to demonstrate the catalytic role of the GA in this transformation, also other mixtures containing the same counterparts without GA were tested: 1,2-propanediol:betaine DES as well as betaine:water mixture.^[45,46] Except for the 1,2-propanediol-based DES, all the other liquids are NADESs and this increases their green properties for the natural occurrence of the molecules forming them.^[19,47–49] In Figure 1 the set of the DESs and mixtures used, the chemical structures of the forming components, the molar ratios of them in the liquids, their acronyms are reported; the results of their catalytic use in the nitration of ethyl vinyl ketone with NaNO₂ are reported in Table 1.

1,2-propanediol:betaine DES (1,2-PD:TMG (5:1), Entry 1 Table 1), even if it was proficiently used in other chemical transformations,^[36] didn't show any product formation, due to the absence of acidic molecules in its components. The GA-based DES resulted in good yields: 60% yield after chromatographic purification was observed with GA:TMG DES (Entry 2 Table 1), without detecting any starting enone and without detecting sideproducts (neither investigated). Additionally, when switching the DES counterpart and using GA:ChCl DES solvent, a comparable outcome was obtained, with a yield of 52% (Entry 3 Table 1). On the other hand, *aquo*DESs did not prove efficacy in this model reaction, as the nature of the counterpart to water significantly influenced the reaction trend: GA:H₂O *aquo*DES (Entry 4 Table 1) afforded a 45% yield, while the TMG:H₂O (Entry 5 Table 1) produced a complex mixture of products from which it was possible to isolate the target product with a yield of 23%. Therefore, the glycolic acid:trimethylglycine NADES (GA:TMG) resulted the best of the set, so it was used in the optimization of the reaction conditions as well as for the scope expansion of the studied reaction.

2.2. Optimization of Reaction Conditions

After the best GA-based DES solvent for the nitration reaction was found, different reaction conditions were tested in order to optimize the reaction. In this set of experiments, the amount of NaNO₂, the reaction times, the reactants concentrations, the temperatures and alternative sources of nitrite were tested in a set of experiments involving again ethyl vinyl ketone as starting material. All the performed experiments are reported in Table 2.

Comparing to the results obtained with 1.5 equivalents of sodium nitrite (Entry 1 Table 2), the increase of the amount of NaNO₂ to three equivalents (Entry 2, Table 2) led to a decreased yield, likely due to the limited solubility of the nitrite salt in this DES solvent. In fact, upon addition of the salt, a lumpy mixture was formed, which partially hindered the stirring efficiency. On the other hand, a reaction time of 5 h (Entry 3 Table 2) was not sufficient to obtain the product in satisfactory yield. In order

to improve the solubility of the salt, the reaction was carried out with a higher dilution (1000 mg/mmol, Entry 4, Table 2), but the yield remained unchanged. Performing the reaction at 40 °C afforded the product in 42% yield (Entry 5, Table 2). Reactions using 3.0 or 4.0 equivalents of NaNO₂, or a higher dilution of 2000 mg/mmol, resulted in lower yields (Entries 5–7 Table 2). Finally, we tested two alternative sources of nitrite: AgNO₂ and tetrabutylammonium nitrite (TBAN). Surprisingly, the ammonium salt proved to be the most effective. After a brief screening of conditions in terms of changing the times to 5 h and also by using GA:H₂O DES (Entries 9–13 Table 2), the desired product was obtained in a satisfactory 71% yield using 1.0 equivalent of TBAN and a dilution of 500 mg/mmol in GA:TMG DES (Entry 12 Table 2). This improved yield may be attributed to the better solubility of TBAN in the DES solvent, which remained a homogeneous solution—unlike the heterogeneous mixture observed with NaNO₂. The reduced concentration may have also contributed positively to the reaction outcome. Furthermore, it is important to underline how our methodology with the nitrite anion allows us to overcome the serious drawback that accompanies many other methods, namely the presence of a mixture of two products, difficult to purify, of the desired nitro compound together with the undesired nitrite compound.^[50] Indeed, the NMR spectra of the crude reaction mixtures show that by our conditions no traces of the nitrite by-product are present.

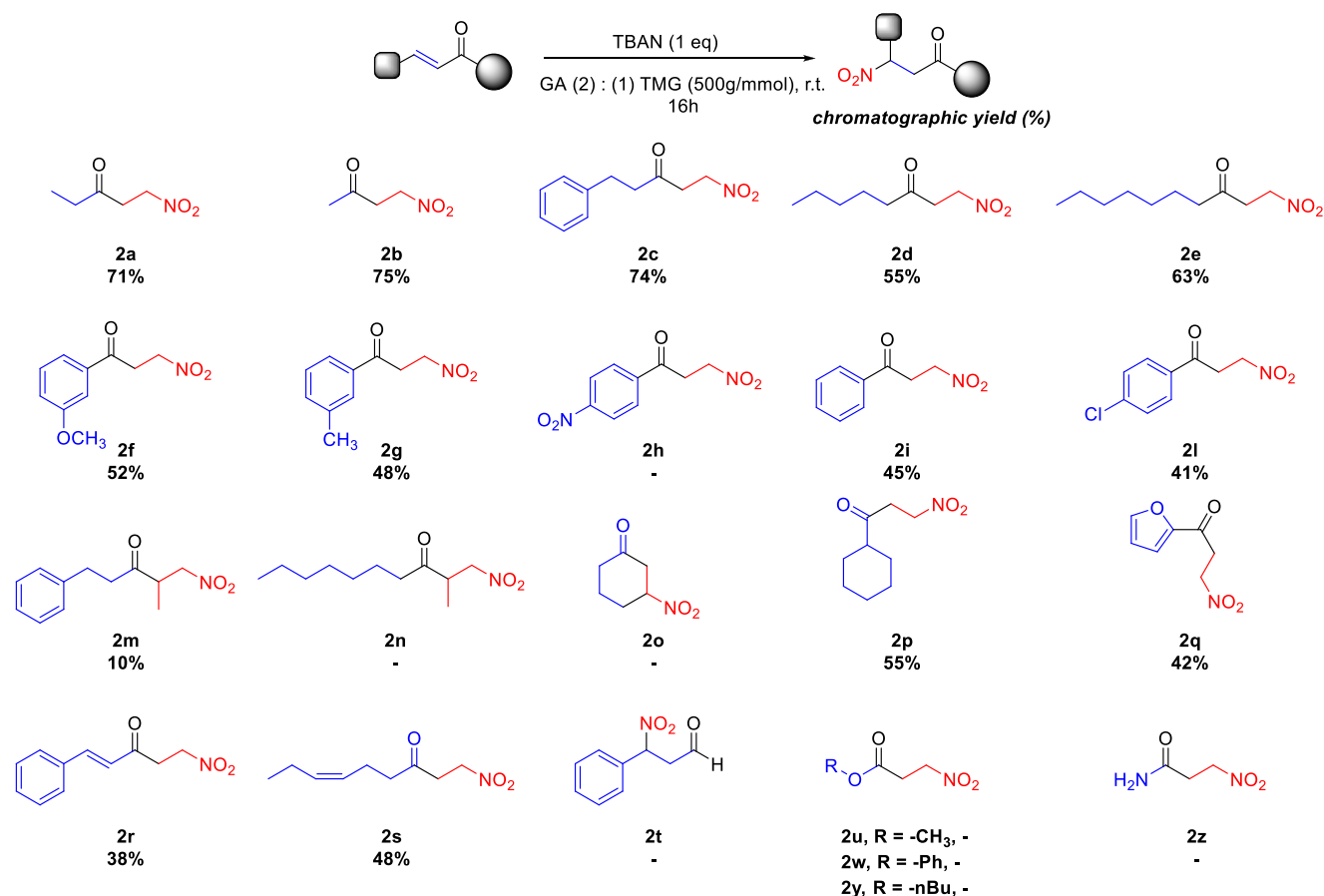
2.3. Validation of the Method

Once the optimal reaction conditions were established (Entry 12 Table 2), the performance of various substrates under this protocol was evaluated. As shown in Scheme 1, a clear difference in reactivity can be observed between aliphatic and aromatic enones. In particular, aliphatic vinyl ketones such as ethyl (2a), methyl (2b), 2-phenylethyl (2c), hexyl (2d), and butyl (2e) derivatives gave the desired products in satisfactory yields, ranging from 55% to 75%. These promising results are likely due to the good solubility of both TBAN and the corresponding starting materials in the DES medium. In the cases of 2a, 2b, and 2c, the starting materials were fully consumed, although it was not possible to identify potential side products formed during the reactions. Notably, cyclohexyl vinyl ketone (2p) also performed well, affording the product in 55% yield. In contrast, aromatic enones showed lower efficiencies. Both unsubstituted and substituted phenyl vinyl ketones led to moderate yields, generally around 40%–50%. The reaction with unsubstituted phenyl vinyl ketone (2i) provided a 45% yield, with partial recovery of starting material and formation of undefined side products. Electron-donating group (EDG)-substituted derivatives, such as compounds 2f and 2g, gave acceptable yields, likely because increased electron density within the conjugated system promotes reactivity. Conversely, electron-withdrawing group (EWG) substituents reduced reactivity significantly. For example, (4'-nitrophenyl) vinyl ketone (2h) failed to afford any desired product, instead forming a complex mixture. Compound 2l, bearing an EWG, was isolated in only 41% yield. Interestingly, the

Table 2. Screening of DES Solvents.^{a)}

Entry	Source of -NO ₂ (eq.)	Yield ^{b)}
1	NaNO ₂ (1.5 eq.)	60%
2	NaNO ₂ (3.0 eq.)	55%
3 ^{d)}	NaNO ₂ (3.0 eq.)	40%
4 ^{d)}	NaNO ₂ (3.0 eq.)	47%
5 ^{e)}	NaNO ₂ (3.0 eq.)	42%
6 ^{d)}	NaNO ₂ (4.0 eq.)	23%
7 ^{f)}	NaNO ₂ (3.0 eq.)	35%
8 ^{f)}	NaNO ₂ (4.0 eq.)	40%
9 ^{d)}	AgNO ₂ (3.0 eq.)	48%
10 ^{c)}	TBAN (3.0 eq.)	58%
11 ^{c)}	TBAN (1.0 eq.)	61%
12	TBAN (1.0 eq.)	71%
13 ^{g)}	TBAN (1.0 eq.)	51%

^{a)} Typical reaction conditions: Ethyl vinyl ketone (1 mmol), DES solvent (500 mg/mmol), r.t., 16h, closed vial. ^{b)} Chromatographic yield. ^{c)} Reaction stopped after 5h. ^{d)} Reaction performed with 1000 mg/mmol of DES. ^{e)} Reaction performed at 40 °C. ^{f)} The reaction was performed involving 2000 mg/mmol of DES. ^{g)} The reaction was performed using GA:H₂O (1:4) DES (500 mg/mmol)



Scheme 1. Validation of the method.

nature of the enone's double bond also strongly influenced the reaction outcome. Substrates bearing substituents on the double bond, such as **2m** and **2n**, displayed drastically reduced reactivity, and the products were not formed; only starting material was recovered. Similarly, 2-cyclohexenone (**2o**) did not afford the desired product. Remarkably, in the case of (E)-1-phenylpenta-1,4-dien-3-one (**2r**), the reaction showed high regioselectivity, targeting the terminal double bond rather than the internal one. The product was isolated in 38% yield, with recovery of the starting material, and no trace of the regioisomer was detected. This result is in line with what was observed for substrates **2m**, **2n**, and **2o**, and was further confirmed by reactions involving cinnamaldehyde. Another interesting observation is that the intrinsic acidity of the DES is not strong enough to induce isomerization of internal double bonds (confirmed by ^1H - ^1H NOESY NMR, see [supporting information](#)), but it appears to act as a mild catalyst, allowing product formation in good yield as demonstrated in the case of compound **2s**. Finally, we explored the reactivity of other conjugated systems, such as acrylates and acrylamides, but no product formation was observed, and only the starting materials were recovered.

Unfortunately, attempts to recover the DES solvent were only partially successful. While it was possible to reuse the solvent for one cycle, during the second cycle, evaporation of water left behind a slightly yellow solid. ^1H NMR analysis revealed that some tetrabutylammonium salt remained dissolved in the DES and/or the aqueous phase, likely interacting with the DES network, and once evaporated the water, the DES network was destroyed and it was no more possible to use the DES solvent.

3. Conclusion

In conclusion in this paper β -nitro ketones were successfully synthesised from enones with the use of glycolic acid-based NADESs as solvents. In this relevant transformation the NADESs acted as both green and catalytic reaction media, avoiding the use of catalytic acetic acid, and furthermore, promoting the reaction development by using smaller amounts of nitration agents, that can be used in stoichiometric ratio with the reactants. In the set of the explored NADESs (GA:ChCl, GA:water, GA:TMG, TMG:water), the glycolic acid:betaine mixture showed the best results and it was also employed for the synthesis of differently structured products, showing satisfactory yields in many entries. These products are commonly synthesised in aprotic apolar solvents, while these NADESs are on the contrary actually protic polar reaction media; this underlines their peculiar structural features that are worth to be explored in many relevant reactions such as the one studied in this work

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that supports the findings of this study are available in the supplementary material of this article

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