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Arynes in green solvent: employing *o*-silylaryl triflates with propylene carbonate†

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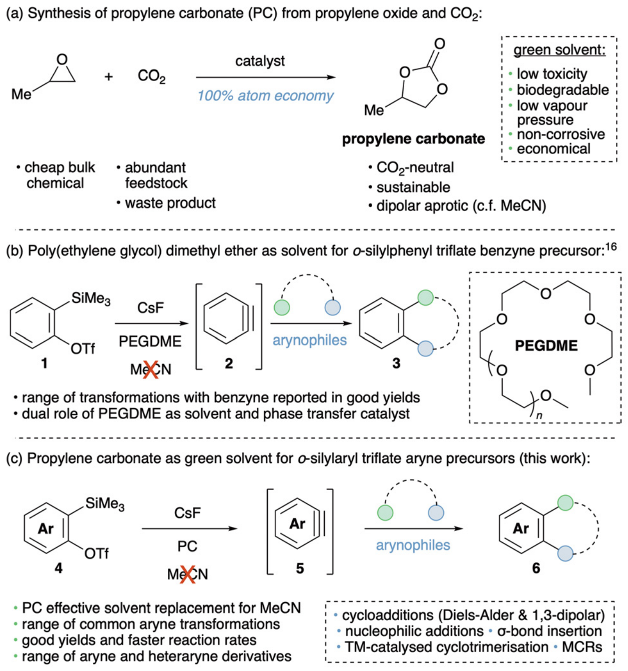
Arynes generated from *o*-silylaryl triflate precursors are shown to engage with a range of arynophiles in propylene carbonate solvent. Possessing similar physicochemical properties to acetonitrile, propylene carbonate is found to be an effective direct solvent replacement, affording similar yields and promoting increased reaction rates. This is the first time that arynes have been used in conjunction with green and sustainable cyclic carbonate solvents.

Introduction

Solvents are the major component of chemical reactions. As traditional organic solvents are often volatile and toxic liquids, the large volumes used renders them one of the foremost chemical products harmful to health and the environment.[1] In the pharmaceutical sector, organic solvents can comprise up to 56% of the entire mass involved in the preparation of a typical active pharmaceutical ingredient.[2] Reducing the overall volume of solvent used, as well as finding safer and more sustainable alternatives to traditional options are key actions that align with the principles of green chemistry.[3] Desirable characteristics for green solvent alternatives include low toxicity, low cost, biodegradability, simple handling and good chemical yields. To this end, many different solvents possessing a range of physicochemical properties have been investigated and several guides produced by industrial and academic consortia aimed at providing chemists with tools for alternative solvent selection.[4]

Cyclic carbonates are receiving growing interest as green solvents in both academia and industry.[5] Amongst this class, propylene carbonate (PC) scores highly in the GSK Solvent Sustainability Guide and is one of the most widely used organic carbonates.[6] PC is a non-corrosive liquid with low toxicity, high boiling point and low vapour pressure. It is also biodegradable and economical to produce, making it favourable to applications in large-scale industrial settings. The most common approach to synthesise PC is *via* cycloaddition of propylene oxide and CO_2 (Scheme 1a), with cheap and effective methods reported for industrial-scale production.[5–8] The process is 100% atom economical and makes use of an abundant non-toxic and renewable source of carbon. Given the continued rise in global CO_2 emissions, fixation of this waste greenhouse gas affords additional environmental and sustain-



Scheme 1 (a) Propylene carbonate as a green and sustainable dipolar aprotic solvent. (b) Application of PEGDME as solvent in benzyne reactions. (c) Use of propylene carbonate as green solvent replacement for acetonitrile in aryne reactions.

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ability benefits.[9] The physicochemical properties of PC, such as dipole moment and Hansen solubility parameters (van der Waals forces, polarity and hydrogen bonding) are very similar to acetonitrile.[4f,10] With comparable solvating ability to traditional dipolar aprotic solvents and featuring in several selection guides, PC is being used for an increasing range of synthetic transformations. These include hydrogenation,[11a] aldol[11b] and cyanohydrin[11c] reactions, hydrosilylation,[11d] metal-catalysed cross couplings,[11e–g] proline-catalysed aminations,[11h] bisindole synthesis,[11i] hydroacylation of alkynes,[11j] enzymatic kinetic resolution,[11k] Povarov cycloaddition[11l] and oxidations under continuous flow.[11m]

Aryne chemistry is an area of synthesis that relies heavily on the use of dipolar aprotic solvents. These versatile reactive intermediates rapidly generate valuable benzenoid and heterocyclic frameworks commonly found in pharmaceuticals, agrochemicals and organic materials.[12] They have experienced a recent resurgence in interest due to the advent of precursors that act under mild conditions, such as the *o*-trimethylsilylaryl triflates (*o*SATs),[13] hexadehydro-Diels–Alder reaction of polyalkynes[14] and the development of arenes bearing onium ion leaving groups.[15] Most of the contemporary precursors, including *o*SAT and onium ion species, employ acetonitrile or ethereal solvents. However, very little has been documented regarding the replacement of these traditional solvents with greener and more sustainable alternatives. To the best of our knowledge, just one study exists in this area. Chandrasekhar and coworkers reported that a variety of benzyne reactions proceeded with good yields in poly(ethylene glycol) dimethyl ether (PEGDME), an environmentally benign and recyclable high boiling point solvent (Scheme 1b).[16] The PEGDME was proposed to operate as both solvent and phase transfer catalyst to help solubilise the inorganic fluoride salt. Whilst these are very encouraging results, substituted aryne derivatives were not reported. Furthermore, PEGDME does not feature in major solvent selection guides (*e.g.* GSK solvent sustainability guide, Pfizer solvent selection tool, CHEM21 selection guide)[4] which is likely to hinder uptake in the near future.

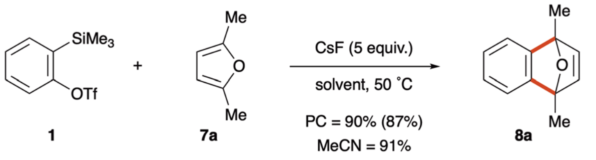
Given our interests in the chemistry of arynes,[17] we postulated whether PC would be a viable alternative to the use of acetonitrile in transformations involving *o*SAT precursors (Scheme 1c). As the two solvents share very similar Hansen solubility parameters and PC scores highly in the GSK solvent guide,[4e,f] this could favour potential future adoption by the synthetic community. Such a replacement would provide a greener and more sustainable alternative to the conventional dipolar aprotic solvents currently used with *o*SAT precursors and would expand the options available to synthetic chemists when developing new aryne-based methodologies.

Results and discussion

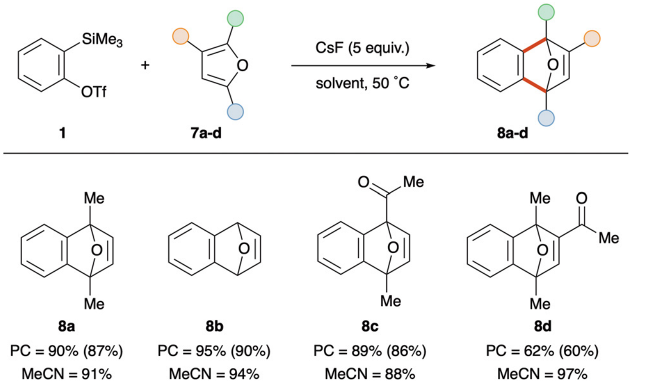
To test our hypothesis, examples of well-known aryne transformations were selected that have been previously optimised for acetonitrile. The reactions were conducted in both PC and acetonitrile, to benchmark the literature processes in our hands and to enable a direct comparison of outcomes. Aryne Diels–Alder cycloadditions have been extensively studied over the years, so this transformation was chosen for the initial investigations. Following the procedure described by Garg and co-workers for the preparation of benzonorbornadiene units used for subsequent polymerisation, 2-trimethylsilylphenyl triflate **1** was heated to 50 °C in the presence of 2,5-dimethyl furan **7a** and CsF (Scheme 2).[18] Excitingly, when the reaction was conducted in PC the desired product **8a** was isolated in an excellent 87% yield, which compared well with the literature. To directly assess the reaction efficiencies of PC and acetonitrile in our hands, addition of an internal standard (dibromomethane) to each crude mixture enabled swift quantification *via* ^{1}H NMR spectroscopy. Herein PC and acetonitrile were found to perform equally well, affording 90% and 91% NMR yields respectively. Attempts to reduce the amount of CsF employed in the process to 3 equivalents, from the 5 equivalents reported by Garg and co-workers,[18] afforded only trace amounts of the Diels–Alder adduct in both solvents.

Next, we investigated the rate of reaction in the two different solvents. To this end, aliquots were taken from each reaction mixture at fixed intervals and both the consumption of precursor **1** and formation of Diels–Alder adduct **8a** were monitored by ^{1}H NMR spectroscopy. Interestingly, the process conducted in PC was found to proceed at twice the rate of acetonitrile (see ESI† for details). Although the two solvents share many similar physicochemical properties, the observed difference in rates could be attributed to the marked variation in dielectric constants (PC = 64.9 *cf.* MeCN = 35.9 at 25 °C).[4f] It follows that greater solvation of CsF by PC should increase the rate at which the *o*SAT precursor is converted to aryne. This difference in aryne generation could be a valuable new tool for future methodology development involving *o*SATs.

Having confirmed that PC compares favourably to acetonitrile as a solvent for the Diels–Alder reaction between **1** and **7a**, attention turned to investigating the substrate scope of the transformation. First, *o*SAT **1** was exposed to a selection of furans (**7a–d**) under the same reaction conditions (Scheme 3). Pleasingly, a comparison of the yields obtained in PC and acetonitrile revealed analogous reaction efficiencies to deliver adducts **8a–c**. A slight decrease in yield was observed when furan derivative **7d** was run in PC as opposed to acetonitrile (62% and 97% yields respectively).

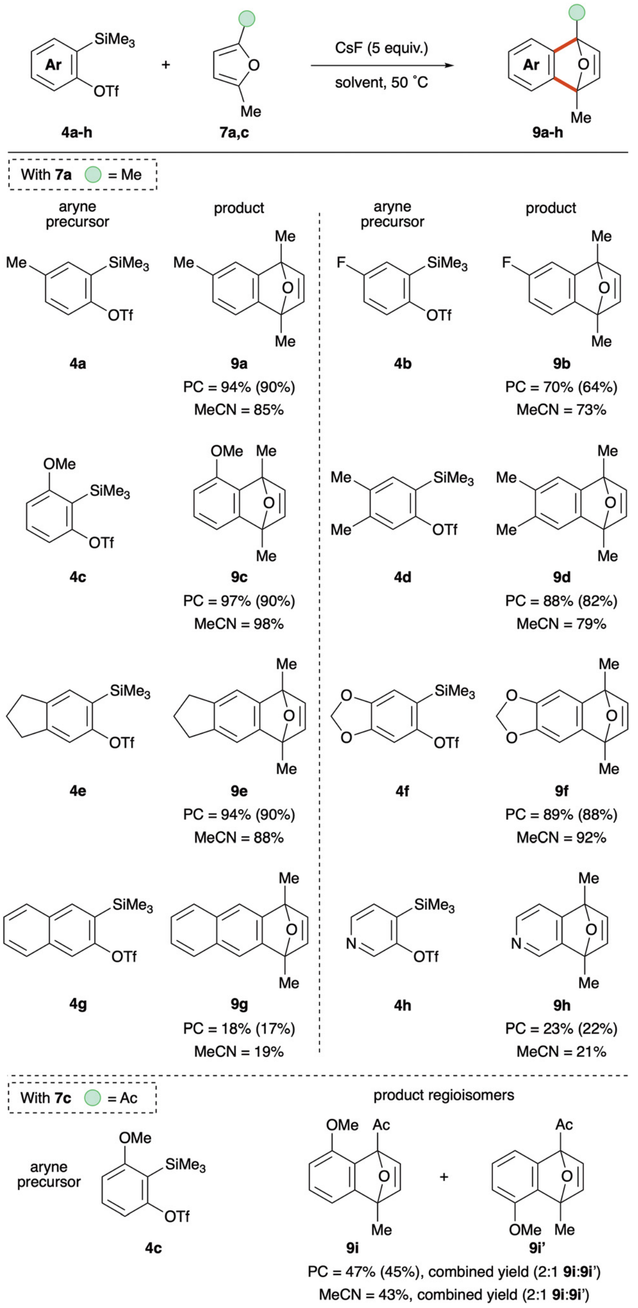


Scheme 2 Diels–Alder cycloaddition reactions of benzyne and 2,5-dimethyl furan conducted in propylene carbonate and acetonitrile solvents. ^{1}H NMR yields *vs.* dibromomethane internal standard, isolated yield in parentheses.



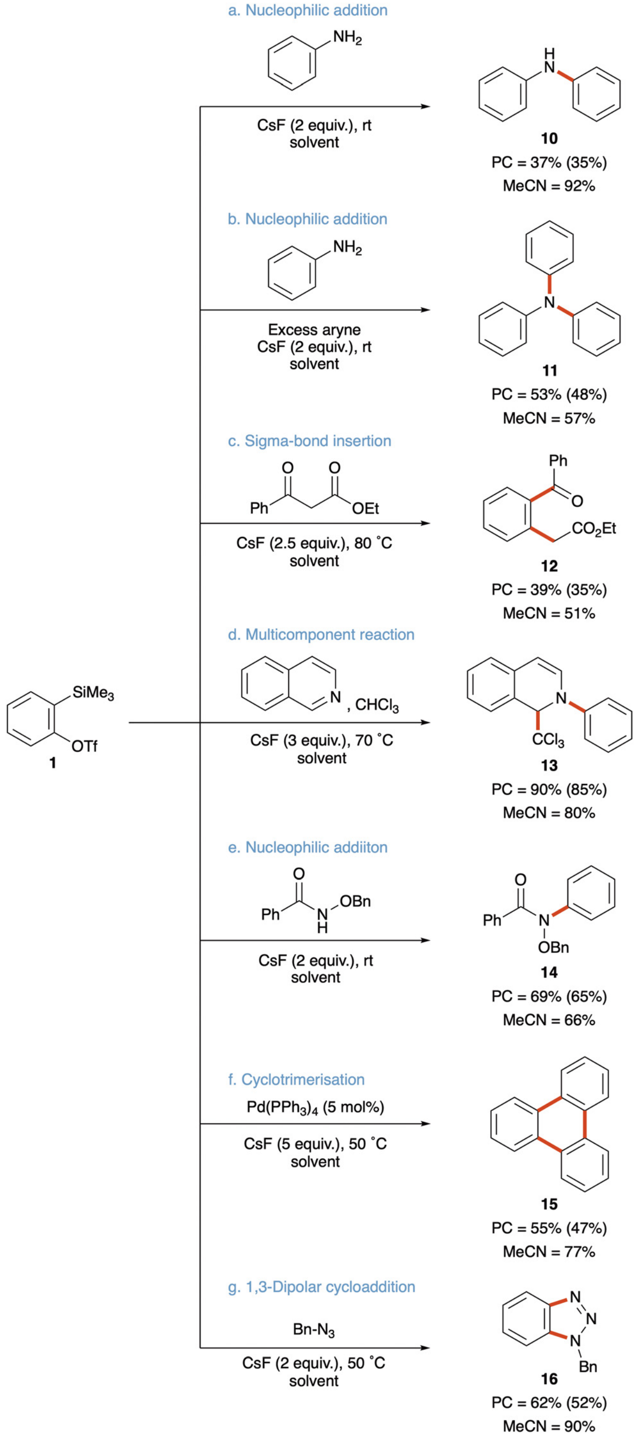
Scheme 3 Diels–Alder cycloaddition reactions of benzyne and various furan derivatives conducted in propylene carbonate and acetonitrile solvents. ^{1}H NMR yields *vs.* dibromomethane internal standard, isolated yields in parentheses.

Next, the Diels–Alder cycloaddition of furan **7a** was performed with a range of substituted aryne derivatives **4a–h** (Scheme 4). Encouragingly, there were no significant differences in reaction efficiencies between PC and acetonitrile in all examples. The cycloaddition worked very well with *o*SATs that possessed electron-donating or electron-withdrawing substituents, as well as moderate steric congestion around the aryne (**4a–f**). As such, adducts **9a–f** were all furnished in very good to excellent yields and with no sizeable variation between the outcomes in both solvents. Interestingly, cycloadducts **9g** and **9h** were obtained in considerably lower yields; however, it is notable that the reaction efficiency in PC still matched that seen in acetonitrile (18% PC *vs.* 19% MeCN for **9g** and 23% *vs.* 21% for **9h**). These two compounds are generated *via* cycloaddition with the more reactive 2,3-naphthyne and 3,4-pyridyne intermediates, which might explain the lower yields attained. Finally, *o*-methoxy aryne precursor **4c** was exposed to an unsymmetrical furan (**7c**). The reaction performed equally well in both solvents, with an analogous regioisomeric mixture of products afforded (2 : 1, **9i** : **9i′**). It is noteworthy that no further reaction optimisation was attempted with any substrate in PC, as the primary focus of this investigation was the direct comparison of PC and acetonitrile. Importantly, this is the first time that substituted *o*SAT precursors have been used in a green solvent, whilst the successful inclusion of a heteroaryne (**4h**) is particularly interesting with regards to substrate diversification in methodology development.



Scheme 4 Diels–Alder cycloaddition reactions of various aryne derivatives and 2,5-dimethyl furan conducted in propylene carbonate and acetonitrile solvents. ^{1}H NMR yields *vs.* dibromomethane internal standard, isolated yields in parentheses.

With the suitability of PC fully established as a solvent for the aryne Diels–Alder reaction, the final objective was to investigate whether it is a viable green alternative for acetonitrile across all the main classes of aryne reactivity. To this end, examples of nucleophilic addition, sigma bond insertion, multicomponent reactions, metal-catalysed cyclotrimerization and 1,3-dipolar cycloaddition were selected from the literature; all transformations having been optimised for acetonitrile.[19–24] Following the procedures reported by Larock and co-workers,[19] aniline was successfully mono- and di-arylated in both solvents to afford diphenylamine **10** and triphenylamine **11**, respectively (Scheme 5a & b). However, whilst triphenylamine **11** was furnished in analogous yields across the two solvents, monoarylation was much less effective in PC (37% *vs.* 92% yield in MeCN). Interestingly, analysis of the ^{1}H NMR spectrum of the crude material from the PC reaction revealed the presence of triphenylamine **11**. It is postulated that the faster rate of aryne generation in PC, as previously observed in the Diels–Alder cycloaddition, could lead to deleterious consumption of the



Scheme 5 Common aryne transformations conducted in propylene carbonate and acetonitrile solvents. ^{1}H NMR yields *vs.* dibromomethane internal standard, isolated yields in parentheses.

target diphenylamine **10** during the mono-arylation process. Next, a formal aryne insertion into the central C–C sigma bond of ethyl 3-phenylpropionate was achieved without a major variation in reaction efficiency between the two solvents (39% PC and 51% MeCN, Scheme 5c).[20] Encouragingly, a multicomponent reaction described by Tan and co-workers involving benzyne, isoquinoline and chloroform proceeded better in PC than acetonitrile (affording 90% *vs.* 80% respective NMR yields of dearomatized product **13**) (Scheme 5d).[21] PC was equally effective as a solvent in the transition metal free *N*-arylation of *O*-benzyl hydroxamate reported by Jin and co-workers, affording **14** in 69% NMR yield compared to 66% in acetonitrile (Scheme 5e).[22] A more sizeable difference (*i.e.* >20% yield) was observed in the final two transformations studied, the palladium-catalysed cyclotrimerisation of benzyne reported by Pérez, Guitián and co-workers (Scheme 5f)[23] and a 1,3-dipolar cycloaddition of benzyl azide described by Larock and co-workers (Scheme 5g).[24] Importantly, PC still proved to be a suitable solvent for both reactions, leading to good amounts of the desired products, triphenylene **15** (55%) and benzotriazole **16** (62%). However, in these cases a more significant decrease was observed compared to acetonitrile (77% and 90% yields for **15** and **16** respectively). As previously noted in the Diels–Alder studies, none of the literature reactions were further optimised when PC was used as the solvent, so it is possible that the yields of these two processes, plus the mono-arylation of aniline, could be improved in the future if desired.

Conclusions

It has been shown that PC can be used as a direct replacement for acetonitrile in a range of aryne transformations involving *o*SAT precursors. There is little compromise on reaction efficiency, as the two solvents typically give analogous yields in reactions previously optimised for acetonitrile. PC was also found to promote reaction rate, potentially due to increased solubility of the inorganic fluoride salt. Reaction protocols involving PC are operationally simple, although it is noted that the high boiling point (242 °C) does require extraction of the reaction mixture with a small volume of hexane. Nevertheless, replacement of the reaction solvent with a green alternative, as well as reducing the volume of organic solvent required during work-up are notable advances with regards to applying green chemistry principles to chemical synthesis involving arynes. This study provides organic chemists with a viable greener and more sustainable solvent option to explore during future aryne methodology development.

Author contributions

Synthetic work was conducted by HF, KS, NA, RK and LAS. KS also supervised synthetic studies and contributed to paper writing. CJ conceived and led the project and wrote the paper.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

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