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Visible photons for the regioselective nucleophilic ring opening of epoxides†

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Arylazo sulfones were used as Photoacid Generators (PAGs) for the visible-light photorelease of strong sulfonic acids to promote the ring opening of epoxides in benign media (DMC/water mixtures) or under neat conditions. Water, alcohols, azide and thiocyanate anions, as well as electron-rich aromatics were used in the role of the nucleophile. The resulting 1,2-disubstituted adducts were formed mostly in >99% yield in a high regioselective fashion.

Introduction

Epoxides are key building blocks in organic synthesis[1] exploited for the construction of natural bioactive chemical frameworks,[2] of benzo-fused heterocycles,[3] of polycyclic ethers *via* a cascade-ring opening reaction,[4] as well as in the preparation of 1,2-difunctionalized compounds.[5] As an example, the ring opening of epoxides with alcohols[6] provides access to β-alkoxyalcohols which structural motif has found wide applications in immunosuppressive and anti-tumoral pharmaceuticals.[7] Moreover, the hydrolysis of epoxides is adopted to synthesize 1,2-diols, which in turn find applications as coolants and as co-monomers in the production of polyester fibres and resins.[8] In particular, the synthesis of ethylene glycol from ethylene oxide is performed industrially in the presence of high excess of water, for the sake of chemoselectivity,[9] and the final product must be recovered from the aqueous crude mixture by distillation. In this context, the use of metal-based Lewis acids, such as cobalt[10] or tin[11] can be helpful to lower the water/ethylene oxide ratio in the procedure. At any rate, the ring opening of epoxides by weak nucleophiles preferably takes place under catalytic conditions, and metal catalysis is the preferred option[12] (even making use of expensive catalysts with a rather limited availability, such as molybdenum,[12i,j] erbium[12k] and gallium derivatives[12l]), along with the use of metal porphyrins[12m] or other organometallic species[12n–p] (Scheme 1). A particular case is the homolytic ring opening of epoxides by the Nugent–RajanBabu Reagent (Cp_2TiCl).[13] Nonetheless, chemists have proposed several metal-free approaches to trigger the ring-opening reaction of epoxides,[14] including, among others, the use of cyclodextrins,[15] metal-free boron-based frustrated Lewis pairs,[16] N-heterocyclic carbenes[17] or graphene oxide as the catalysts[18] (Scheme 1). The procedures have been performed in different media, including ionic liquids,[19] hot water[20] or under continuous flow conditions.[21] Given the impressive range of chemical structures accessible from epoxides, the design and the development of increasingly sustainable, versatile and efficient approaches for their opening is still a challenge.

Recently, there is a growing interest in the development of PhotoAcid Generators (PAG) known to release an acid species upon irradiation. These derivatives (whether non-ionic or ionic) may be used as an acid surrogate since their slow release in solution could be beneficial for the reaction to catalyze.[22] We recently used arylazo sulfones due to their sulfonic acid photorelease (under aerated conditions) to promote the protection of alcohols,[23a] ketones[23b] and the functionalization of indoles.[23c,d] We then envisaged that the visible light photoreactivity of these sulfones,[24,25] may be helpful to induce the mild ring opening of epoxides (Scheme 1).

Results and discussion

The feasibility of our proposal was tested on the ring opening of styrene oxide **2a** (1 mmol) by using methanol (2.5 mmol, 2.5 equiv.) in the presence of arylazo sulfone **1a** (5 mol%, precursor of methanesulfonic acid, MSA) in an air-equilibrated neat conditions upon visible light irradiation (for the spectrum in the visible range of **1a** see Fig. S2†). To our delight, methoxy

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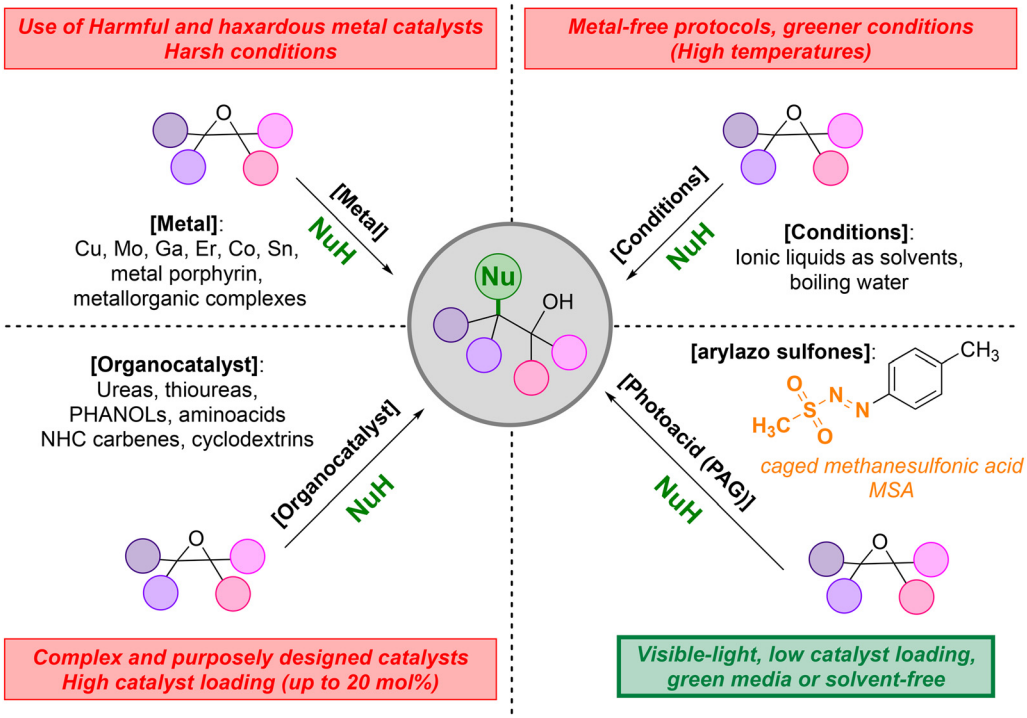
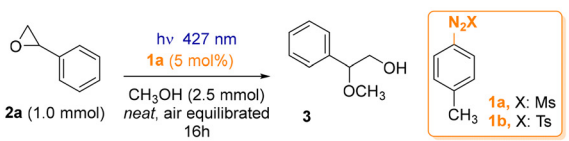


Scheme 1 Different protocols for the nucleophilic ring-opening reaction of epoxides.

alcohol **3** was obtained quantitatively with a complete regioselectivity by irradiation with a 427 nm lamp for 16 h (Table 1, entry 1). Several conditions were tested (for instance nucleophile-epoxide ratio, solvents, irradiation wavelengths *etc.*, see Table S1† for further details). Decreasing the amount of **1a** (2.5 mol%) or of MeOH (1.5 equiv.) caused a yield drop (entries 2 and 3). The effect of a cosolvent (mandatory when the nucleophile is not soluble in the reaction mixture) was tested. Thus, the presence of MeCN affected the outcome of the reaction (46% yield, entry 4), contrary to DMC (a benign cosolvent[26]) where compound **3** was again formed in quantitative yield (entry 5). When arylazo sulfone **1b** (5 mol%) was tested as alternative PAG (as a photochemical precursor of PTSA) by maintaining DMC as the solvent, compound **3** was obtained in a slightly lower yield (81%, entry 6). Finally, some control experiments were carried out (entries 7–10). The presence of an inorganic ($NaHCO_3$, 0.15 equiv., entry 7) or an organic base (pyridine, 0.15 equiv., entry 8) completely sup-

Table 1 Conditions chosen for the photoinduced nucleophilic ring opening of **2a**



Entry	Deviation from standard conditions	Yield[a]
1	None	>99%
2	**2a** (1 mmol), **1a** (2.5 mol%), CH_3OH (2.5 mmol, 2.5 equiv.), *hν* 427 nm	72%
3	**2a** (1 mmol), **1a** (5 mol%), CH_3OH (1.5 mmol, 1.5 equiv.), *hν* 427 nm	92%
4	**2a** (1 mmol, 2 M), **1a** (5 mol%), CH_3OH (2.5 mmol, 2.5 equiv.), CH_3CN, *hν* 427 nm	46%
5	**2a** (1 mmol, 2 M), **1a** (5 mol%), CH_3OH (2.5 mmol, 2.5 equiv.), DMC, *hν* 427 nm	99%
6	**2a** (1 mmol, 2 M). **1b** (5 mol%), CH_3OH (2.5 mmol, 2.5 equiv.), DMC, *hν* 427 nm	81%
7	**2a** (1 mmol, 2 M), **1a** (5 mol%), CH_3OH (2.5 mmol, 2.5 equiv.), $NaHCO_3$ (0.15 mmol, 0.15 equiv.), *hν* 427 nm	0%
8	**2a** (1 mmol, 2 M), **1a** (5 mol%). CH_3OH (2.5 mmol, 2.5 equiv.), pyridine (0.15 mmol, 0.15 equiv.), *hν* 427 nm	0%
9	**2a** (1 mmol), CH_3OH (2.5 mmol, 2.5 equiv.), *hν* 427 nm	0%
10	Solution covered with an aluminum foil	0%
11	**2a** (1 mmol, 2 M), MSA (5 mol%), CH_3OH (2.5 mmol, 2.5 equiv.), DMC	24%

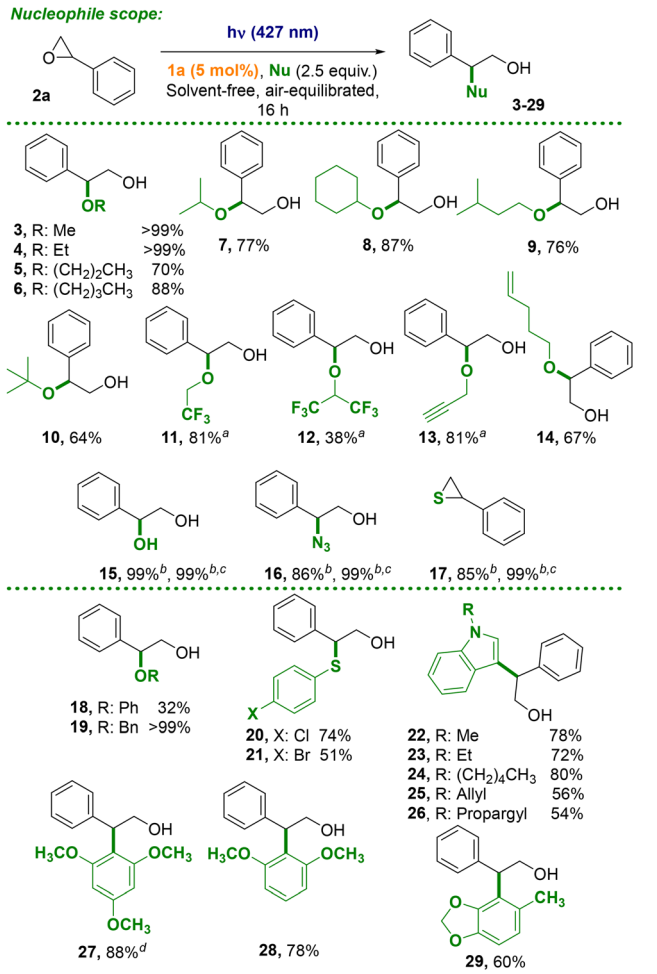
[a] Yields determined by GC analysis.

pressed the reaction (the epoxide was recovered unaltered). The presence of an arylazo sulfone (entry 9), as well as of the light (entry 10), was required to promote the ring opening. Moreover, the addition of MSA (5 mol%) in one time to the starting reaction mixture again formed **3**, but unsatisfactorily (*ca.* 24% yield, entry 11). Kinetic analysis of the reaction (Fig. S7†) showed that the product was formed very fast at the initial stage of the reaction (60% yield after 1 h), but the complete conversion of the epoxide required 16 h irradiation. With the optimised conditions in our hand, we explored the scope of the protocol by using a series of alcohols in the role of the nucleophile (Scheme 2). The reaction has been performed mostly under neat conditions or, in alternative, by adopting DMC or in DMC/water mixtures as reaction media. The reaction with unbranched primary alcohols such as ethanol, propanol or butanol afforded the desired products **4–6** in satisfactory yields (>70%). Branched alcohols, such as iso-propanol, cyclohexanol, iso-pentanol or even *tert*-butanol served likewise as suitable nucleophiles (>64% yield, compounds **7–10**). Less nucleophilic fluorinated alcohols gave, however, products **11** (81% yield) and **12** (38% yield) from 2,2,2-trifluoroethanol (TFE) and hexafluoroisopropanol (HFIP), respectively. Unsaturated alcohols (propargyl alcohol and pent-4-en-1-ol) yielded **13** and **14** in a satisfying yield (81% and 67%).

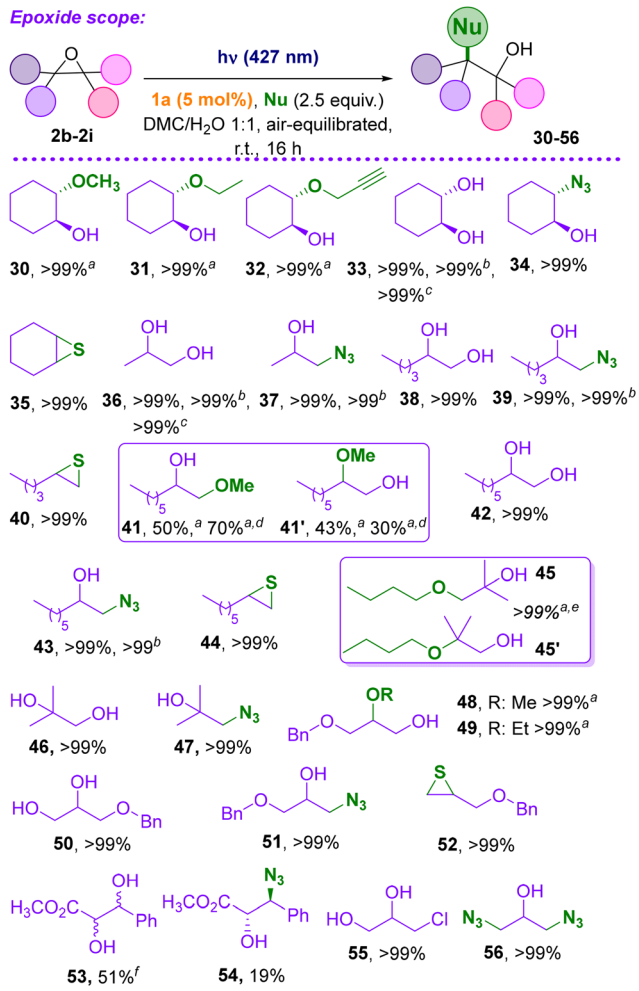
Testing other types of nucleophiles (*e.g.* water, sodium azide or potassium thiocyanate) led to the quantitative formation of the corresponding glycol **15**, the azido alcohol **16**, or the thiirane **17** (Scheme 2). The latter reactions were carried out in DMC/water 1 : 1 and have been repeated on a 5 mmol scale maintaining the same excellent results (Fig. S4†).

More complex nucleophiles having an aromatic ring were then investigated and the reaction with phenol, benzylic alcohol, and substituted thiols gave the 1,2-disubstituted products **18–21** in variable yields. Finally, some electron-rich aromatics were explored to mimic a Friedel Crafts-like reaction. To our pleasure, our protocol proved to be robust and afforded the regioselective arylation of *N*-substituted indoles (products **22–26**) and of electron-rich benzenes (products **27–29**) in good yields (Scheme 2).

Other epoxides were employed to investigate the versatility of this protocol, starting from cyclohexene oxide (**2b**, Scheme 3). The organocatalyzed reaction of **2b** with selected alcohols gave *trans*-derivatives **30–32** in almost quantitative yields. The formation of glycol **33** was quantitative in batch, as well even on a 5 mmol scale **2b** and under flow conditions (Fig. S5 and S6†), where 20 mmol of epoxide were processed after 6 h reaction, reaching a 9.3 g day^{-1} productivity of **33** (see ESI, section 4†). Compound **2b** was found an excellent starting material for the conversion into azido alcohol **34** and thiirane **35**. We then tested related epoxides of terminal alkenes. Propylene glycol **36** (extensively used as solvent carrier in e-cigarettes liquids and in various industrial applications[27]) was easily formed from propylene oxide **2c** in up to 5 mmol scale in batch or in 20 mmol scale in flow (productivity of 6.1 g day^{-1}). The reaction of **2c** with azide anion led to the regioselective formation of **37** (>99% yields on 5 mmol scale). Good results have been obtained from 1,2-hexene oxide **2d**, (compounds **38–40**). The reaction is still regioselective, leading to the more substituted alcohol (*e.g.* in compound **39**). In the ring-opening of 1,2-octene oxide **2e**, a single product was obtained, except from the reaction with MeOH that afforded two regioisomers (**41** and **41′**) in a 93% overall yield. Interestingly, when the irradiation was carried out by using **1b** (a caged PTSA), the yield increased to quantitative, along with the change of the regioisomeric ratio (**41** became by far the more abundant isomer, 70% instead of 50%). The ring opening reaction was also performed using isobutene oxide **2f**. The addition of *n*-butanol onto this epoxide caused the quantitative formation of the 1,2-adducts **45** and **45′** in a 1 : 1 ratio. A single product was however formed, when using water and azide anion as the nucleophiles (compounds **46** and **47**, quantitative yield) by using a DMC/water mixture as the reaction media. 2-((Benzyloxy)methyl)oxirane **2g** was next investigated



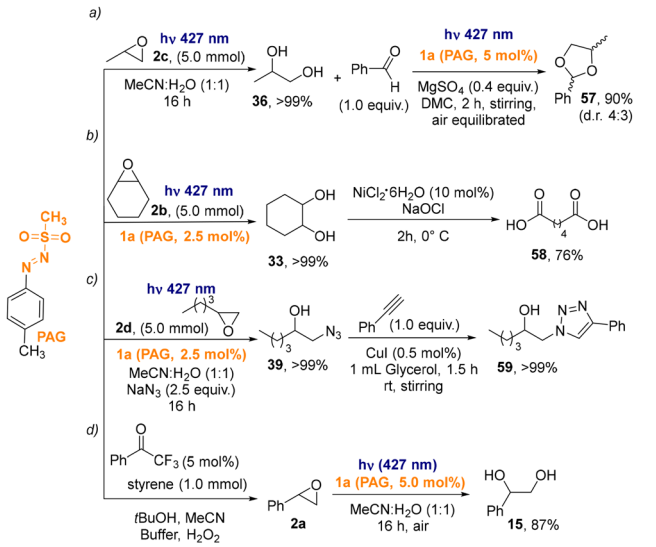
Scheme 2 Nucleophile scope on the visible-light ring-opening reaction of **2a** catalyzed by **1a**. Reaction conditions: **2a** (0.5–1 mmol, 1 equiv.), the chosen nucleophile (2.5 equiv.), **1a** (5 mol%) irradiated at 427 nm for 16 h under air-equilibrated conditions. Isolated yields. [a] NMR analyses revealed the presence (≤5%) of a minor regioisomer. [b] Reaction performed in DMC/water 1 : 1. [c] Reaction performed on a 5 mmol scale. [d] Reaction performed in DMC.



Scheme 3 Epoxide scope of the nucleophilic ring-opening reaction catalyzed by **1a** as PAG and triggered by visible-light. Reaction conditions: **2b–2i** (0.5–1 mmol, 1 equiv.), the chosen nucleophile (2.5 equiv.), **1a** (5 mol%) irradiated in DMC/water 1 : 1 at 427 nm for 16 h under air-equilibrated conditions. [a] Neat conditions. [b] Reaction performed on a 5 mmol scale. [c] Flow conditions (20 mmol, 6 h irradiation). [d] Reaction performed by using **1b** in place of **1a**. [e] Compounds **45** and **45′** formed in a 1 : 1 ratio. [f] 1 : 1 mixture of diastereomers.

and the functionalization with methanol and ethanol afforded **48** and **49** quantitatively, as in the synthesis of glycol **50**, azido alcohol **51** and thiirane **52** (Scheme 3). The reaction on electron-poor epoxides such as methyl 3-phenyloxirane-2-carboxylate **2h**, proved to be less efficient. Glycol **53** was obtained as a mixture of diastereoisomers (1 : 1 ratio) with an overall yield of 51%, meanwhile the azido alcohol **54** was obtained in only 19% yield as the *trans* isomer.

Finally, the reactivity on epichlorohydrin **2i** was tested making use of water and sodium azide as nucleophiles. In the first case, chlorine containing glycol **55** was formed, whereas in the latter 1,3-diazidopropan-2-ol **56** (resulting from the nucleophilic substitution on the C–Cl bond and by the nucleophilic ring opening reaction) was prepared both in quantitative fashion.



Scheme 4 Telescopic post-transformations.

The appeal of our protocol was further highlighted by performing selected telescopic reactions involving the present ring opening procedure. Propylene oxide **2c** (5.0 mmol) was opened to form the corresponding glycol **36** that it was converted into acetal **57** by reaction with benzaldehyde, exploiting again arylazo sulfone **1a** as PAG (90% yield, dr 4 : 3) (Scheme 4a).[23b] In another case, adipic acid **58** was obtained in two steps, starting from cyclohexene oxide by the Ni(II)-catalyzed oxidation of glycol **33** (Scheme 4b).[28] The adduct formed between **2d** and sodium azide was successfully converted into 1,2,3-triazole **59**, following a green procedure in glycerol in just 1.5 h (Scheme 4c).[29] Noteworthy, all of these telescopic reactions were carried out with no need to purify the ring-opened products and diacid **58** was isolated upon a simple recrystallization of the crude product. Finally, epoxide **2a** was prepared starting from styrene[30] and then photochemically opened to diol **15**.

The mild ring-opening of epoxides described herein occurs at room temperature under neat conditions or in an eco-sustainable solvent mixture (DMC/water or neat DMC[26]). The protocol exploits the tuneable release of methanesulfonic acid from a readily prepared PAG (compound **1a**) that leaves only traces of toluene as byproduct in the reaction mixture.[23] In some cases, a simple work-up consisting in the addition of $MgSO_4$, removal of the drying agent and the solvent afforded the desired product in high yield and satisfactory purity. The low values of PMI calculated for the preparation of compounds **16** and **33** (2.86 and 3.53 kg kg^{-1}, respectively) is an indication of the tiny amounts of waste produced in the reaction (see ESI, section 4† for further details). In the synthesis of **33**, a further reduction of the PMI value (from 3.53 to 1.86 kg kg^{-1}) resulted, when the process was scaled up to a 20 mmol scale in flow (irradiation time 6 h *vs.* 16 h). With our method, uncharged weak nucleophiles, such as water and alcohols, were easily added to epoxides. In the first case, 1,2-diols, including the

wide used propylene glycol **36**, were formed, while in the latter case valuable 1,2-alkoxyalcohols are accessed, despite a low regioselectivity was observed in selected cases (see for instance products **41** and **41′**). The addition of SCN^- to epoxide is efficiently catalyzed by **1a** (see compounds **17**, **35**, **40**, **44**, **52** in Schemes 2 and 3). This reaction led to the formation of the corresponding thiiranes *via* the oxathiolan-2-imine intermediate[31] as previously observed under catalyzed conditions[12a,32a,b] and under catalyst-free conditions[32c] using PEG[32d] or ionic liquids[32e] as the reaction media.

Conclusions

Summing up, we would point out that the simplicity of the method presented herein well met most of the photo-click chemistry criteria,[33] since it allows a process with a significantly high thermodynamic driving force,[34] it is wide in scope and affords the desired products in very high yields. Furthermore, in several cases, isolation of the end products took place with no need of separation upon column chromatography and products were obtained (at least starting from **2b** and **2h**) in a satisfactory diasteroselectivity.[33] The ring-opening of epoxides may be easily included in telescopic transformations as illustrated in Scheme 4. Noteworthy, the synthesis of **57** was carried out by two consecutive acid catalyzed reactions promoted by the same arylazo sulfone as PAG.

Author contributions

Beatrice Bernardoni: Investigation; Lorenzo Di Terlizzi: conceptualization, investigation and writing – original draft; Eirini M. Galathri: investigation. Christoforos G. Kokotos: funding acquisition, writing – review and editing. Maurizio Fagnoni: conceptualization, supervision, writing – original draft, writing – review and editing. Stefano Protti: funding acquisition, writing – review and editing.

Data availability

The authors confirm that the data supporting the findings of this study are available within the article and its ESI.†

Conflicts of interest

There are no conflicts to declare.

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