Abstract: The one-pot synthesis of a series of sulfonium salts containing transferable diazy methyl groups is described, and the structure of these compounds is elucidated by X-ray crystallography. Under photochemical conditions, reaction of these salts with N,N-dialkyl hydrazones affords 1-(diazykylami no)-1,2,3-triazoles via diazomethyl radical addition to the azomethine carbon followed by intramolecular ring closure. The straightforward transformation of the structures thus obtained into mesoionic carbene–metal complexes is also reported and the donor properties of these new ligands characterized.

Sulfonium ions are defined as positively charged organosulfur species of general formula [R₂S]⁺, in which a central sulfur(IV) atom is attached to three organic rests while keeping a non-shared electron pair.[1] The reactivity of these salts is dominated by the positive charge that they bear, mainly located at sulfur.[2] Thus, on treatment with bases, α-CH deprotonation occurs on alkyl sulfonium salts leading to the formation of sulfur ylides; a class of compounds of demonstrated utility for the synthesis of three-membered rings such as cyclopropanes, epoxides and aziridines.[3] Also as consequence of their positive charge, the RS fragment in aryl sulfonium salts behaves as an excellent leaving group making possible the direct attack of nucleophiles to form Nu-R coupling products,[4] or the oxidative addition of low oxidation-state metals into the Ar-S bond. This reactivity makes sulfonium salts suitable electrophilic partners for typical Pd- or Ni-catalyzed coupling reactions.[5] One electron reduction is also a relatively facile process in sulfonium salts; it leads to a fast mesolytic scission of one of the C–S bonds, generating thiourea and organic radicals,[6] being the latter able to further engage in synthetically useful transformations such as cross coupling, oxidation, amination or fluorination reactions among others (Figure 1a).[7]

The reactivity pattern just described shows clear overlaps between the chemistry of sulfonium salts and that of hypervalent I(III) reagents.[8] The selection of one or the other for a determined transformation often depends on factors such as the ease of synthesis of the necessary reagent, their relative stability, and the balancing between the levels of reactivity and selectivity that they provide for the specific process under study.[9,10] Considering these precedents and being aware that α-diazo iodonium salts such as A,[11] and B have been used as diazo transfer reagents under thermal[12] and photochemical conditions,[13] we questioned ourselves whether sulfonium equivalents of these reagents could be efficiently prepared, and if so, what kind of reactivity would they exhibit.[14]

Herein, the one pot synthesis of a series of such reagents from sulfoxides and diazo compounds is described, and their ability to transfer the diazo moity to hydrazones under photochemical conditions is preliminary evaluated (Figure 1b).

Our initial efforts were focused on the synthesis of the parent sulfonium salt 1a, derived from the dibenzo thiophene platform and containing an ethyldiazoacetate substituent. Sulfonium salts of related structure have been previously reported; however, they were prepared without exception by reaction of dialkyl sulfides with iodonium salt A.[15–18] Hence, alternative routes which avoid the use of that I(III)-reagent were explored. Considering the natural nucleophilicity of diazo compounds at the carbon adjacent to the dinitrogen moiety, we hypothesized that ethyldiazoacetate might directly react with sulfoxide 2 after its activation with triflic acid anhydride. Gratifyingly, the desired reaction took place in acceptable yield (61%), and compound 1a was isolated as a pale yellow crystalline solid (Scheme 1a). Moreover, the reaction could be scaled up to 30 mmol without drop in the isolated yield.
(see the Supporting Information). This simple protocol also allowed the preparation of 1b starting from trifluoromethyl diazomethane; or 1c, 1d and 1e, which are based on the thianthrene, phenoxathiine and tetrahydrothiophene platforms, respectively (Scheme 1b).

Monocrystals suitable for X-ray diffraction analysis were grown by slow diffusion of Et₂O into saturated CH₂Cl₂ solutions of 1a–d. The thus obtained molecular diagrams confirmed the expected connectivity (Figure 2 and the Supporting Information). In 1a the sulfur atom remains at the plane defined by the dibenzothiophene skeleton and adopts a trigonal-pyramidal coordination environment, being the sum of the bond angles around S1 303.8(1)°. The S1–C1 bond distance of 1.7357(12) Å falls within the range for S-C(sp²) single bonds, while the C1–N1 and N1–N2 lengths (1.3367(15) Å and 1.1111(2) Å) are identical, within the experimental error, to those found in non-charged diazo compounds. Very similar parameters are found in the structures of 1b–d; the only difference of note is the increase in the sum of bond angles around S1 in 1c (306.4(1)°) and 1d (311.5(1)°), which is a consequence of the geometry imposed by the heterocyclic skeleton. It is also worth noting that all compounds 1a–d are found to form dimeric aggregates in the solid state where two triflate anions bridge simultaneously the sulfur atoms of two sulfonium moieties. In all cases the S⋯O distances are definitely shorter than the sum of the van der Waals radii of both elements (3.32 Å), revealing a remarkable electrophilicity at S1.

Differential scanning calorimetry (DSC) analysis for 1a shows decomposition starting at 130 °C that leads to an energy release of 384 J g⁻¹ (Figure 3a). Similar values were obtained for 1c.
(396 J g⁻¹) and 1d (348 J g⁻¹), all significantly lower than those reported for III analogues (549 J g⁻¹). On the basis of these results, the use of the sulfonium salts herein described should be safer; we carefully recommend however not to expose multigram quantities 1a–e to temperatures above 80°C.

At this stage we evaluated the possibility to generate diazomethyl radicals through single electron reduction of 1a–e; specifically, via photoredox catalysis. An experiment often used to determine the feasibility of the desired activation consists in the evaluation of fluorescence intensity quenching of the photoexcited state of a photocatalyst in the presence of the reaction substrate (Stern Volmer relation). In fact, this analysis revealed an effective oxidative quenching of the photoexcited [Ru(bipy)₃][PF₆]₂ catalyst (E°(II*/III) = −0.81 V vs. SCE) in the presence of 1a (E_red = −0.50 V vs. SCE). The formation of the envisaged diazomethyl radical was subsequently evidenced by testing 1a in the benchmark C–H diazomethylation of arenes recently reported by Suero. Gratifying, irradiation of 1a in the presence of [Ru(bpy)₃][PF₆]₂ (1 mol%) and 1,3,5-trimethylbenzene (2 equiv) afforded the diazomethylated arene product 3a in 73% isolated yield (Figure 3). Under identical conditions salts 1c and 1d also promoted the formation of 3a, albeit with lower isolated yields; when employing reagent 1e not even traces of 3a were detected.

Having confirmed that possibility, we set about determining the potential of the photocatalytic system just developed on the C(sp²)-H diazomethylation of aldehyde-derived hydrazones 4. It was reasoned at that stage that in case of a successful transfer of the diazo group, the initially obtained α-diazohydrazones 5 should tautomerize to the corresponding 1,2,3-triazoles 5 providing not only a synthetically useful entry to N-dialkylamino triazoles of potential pharmacological interest, but also easy to handle precursors for α-imino metal carbenoids in case a ring to chain equilibrium between 5 and 5 could be established.

We were pleased to observe that under slightly modified reaction conditions to those employed for the obtention of 3a, the triazole products 5–v were formed in good to excellent yields from the corresponding N,N-dibenzyl hydrazones, being those slightly better for hydrazone substrates derived from electron poor aldehydes. The cyclic nature of the products isolated was unambiguously assigned from the single-crystal structures of 5i and 5s (Scheme 2 and the Supporting Information).

Interestingly, in these structures the dialkylamino nitrogen is pyramidal. As illustrative example, the sum of angles around N(4) is 329.4° in 5i; therefore, at least in the solid state the exo-amino group is not conjugated with the heterocyclic ring. Morpholine derived hydrazones also get involved in this transformation; yields however are slightly lower, 5w–5an. Scheme 2 also depicts compound 5a derived from 1,1-dimethylamino hydrazine, which has been included in our product scope table for completeness.

Note that the most commonly used route to prepare 1,2,3-triazoles precursors is a [2+3] dipolar cycloaddition of alkynes and alkyl/aryl azides. This synthetic approach however, is not suitable for the preparation of the corresponding 1-(dialkylamino) derivatives due to the unavali-

ability of di(alkylamino)azides, which are known to be explosive compounds.

A plausible reaction pathway for the formation of 5 from 1a/b and 4 is depicted in Scheme 3. Initially, irradiation of [Ru(bpy)₃]⁺ generates photo exited ([Ru(bpy)₃]²⁺), which reduces reagent 1a/b via single-electron transfer and generates the transient diazomethyl radical (Int-I) via homolytic S–
C bond cleavage. Addition of the latter intermediate to the azomethine carbon of 4 delivers an aminal radical intermediate (Int-II), which is subsequently oxidized by [Ru(bpy)3]2+ (E1/2(ox/re) = 1.29 V vs. SCE).[22] Deprotonation would re-establish the C-N double bond of the hydrazone moiety leading to 5′, which ultimately cyclizes to the observed 1,2,3-triazole 5. Alternatively, deprotonation of Int-II may occur first leading to the corresponding radical anion, which would undergo oxidation to 5′.[23] A light on/off experiment confirmed the necessity of continuous irradiation for the reaction to proceed; moreover, measurement of the quantum yield of the reaction to form 5c (Φ = 0.18) suggests that a radical chain process cannot be a predominant path.[24]

Finally, the plausible utility of the triazole products obtained as precursors for mesoionic 1-(dialkylamino)-1,2,3-triazol-4-ylidene ligands was evaluated.[25] Hence, 5a,d,w,x were submitted to reaction with one equivalent of methyl triflate, affording triazolium salts 6a,d,w,x. Methylation selectively occurs at position 3- of the heterocycle (Scheme 4). Subsequent saponification of these species in the presence of LiOH took place with concomitant loss of CO2 delivering azolium salts 7a,d,w,x. The connectivity of 7w and 7x was additionally confirmed by X-ray analysis. This opened the stage to the reaction with [RhCl(COD)]2 in the presence of KHMDS to afford the desired carbene-metal complexes 8a,d,w,x as air stable yellow solids. Compounds 8w and 8x were also crystallized and their structures in the solid state are depicted in Scheme 4 and the Supporting Information.

Rhodium dicarbonyl complexes 9a and 9x were synthesized by reaction of precursors 8a and 8x with CO, respectively, and their CO stretching vibrations (υ(CO) = 2029 cm⁻¹, 9a and υ(CO) = 2032 cm⁻¹, 9x) compared with that of 1-alkyl analogues (υ(CO) = 2027 cm⁻¹).[26] This analysis suggests that the introduction of the dialkylamino group at N(1) slightly reduces the donor ability exhibited by the original 1,2,3-triazol-4-ylidene probably due to the inductive effect of a dialkylamino moiety, which is not conjugated with the ring.[27] Both carbene ligands remain anyway stronger donors than conventional NHCs (υ(CO) = 2039–2041 cm⁻¹).[28]

In conclusion, diazomethyl radicals can be efficiently generated under photochemical conditions from α-diazo sulfonylum triflates, whose synthesis is described along this paper. Addition of these species to hydrazones followed by intramolecular cyclization affords 1-(dialkylamino)-1,2,3-triazoles in moderate to excellent yields. Finally, these heterocyclic compounds were further elaborated into mesoionic carbene ligands having an unprecedented dialkylamino rest at position 1. The development of additional synthetic applications of sulfonium salts is an active area of investigation in our laboratory and further progress on the topic will be reported in due course.

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Conflict of interest

The authors declare no conflict of interest.

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