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FULL PAPER

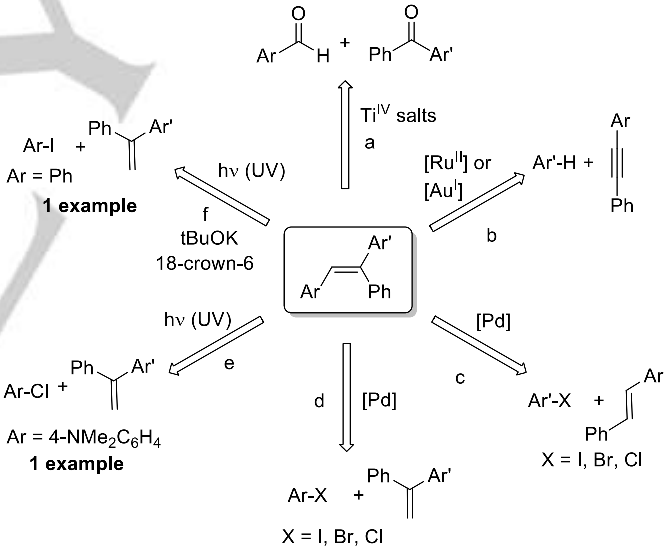
Sunlight-driven synthesis of triarylethylenes (TAEs) via metal-free Mizoroki–Heck-type coupling

Louis Onuigbo,[a] § Carlotta Raviola,[a] § Andrea Di Fonzo,[b] Stefao Protti[a]* and Maurizio Fagnoni[a]

Abstract: A protocol for the preparation of substituted triarylethylenes (TAEs) was developed by using arylazo sulfones as substrates in the presence of 1,1-diarylethylenes. The process took place efficiently in the absence of any (photo)catalyst upon exposure of the reaction mixture to (simulated) sunlight .

Introduction

Compounds bearing the triarylethylene (TAE) core mimic the effect of natural estrogen by binding to the Estrogen Receptor (ER) and produce either an agonist or an antagonist effect. These so-called *selective estrogen receptor modulators* (SERM) find application in the treatment of estrogen-dependent disorders,[1] namely breast cancer (tamoxifen[2] and its analogue toremifene[3]), osteoporosis (raloxifene)[4] and cyclical mastalgia (afimoxifene).[5] Other bioactive TAEs are clomifene, that is currently employed for fertility induction,[6] and ormeloxifene (also known as centchroman) a non-hormonal, nonsteroidal oral contraceptive.[7] Furthermore, substituted triarylethylenes exhibiting aggregation-induced emission (AIE) have been recently considered for the preparation of Organic Light Emitting Diodes (OLEDs).[8] For this aim, a large number of protocols having the TAE moiety as synthetic target have been reported in the literature, including, among others, the McMurry coupling between two ketones occurring in the presence of a low-valent titanium salt,[9] (Scheme 1, path a) and the transition-metal catalyzed hydro(hetero)arylation of diarylalkynes (path b).[10] On the other hand, the poor regioselectivity of such processes, along with the formation in the former example of homocoupling products, limited seriously their synthetic application.[9] Another strategy relies on the formation of an Aryl-C$_{sp2}$ bond and, among the different approaches proposed,[11-13] the Mizoroki–Heck reaction involving the coupling of a 1,2- (path c)[14,15a,b] or a 1,1- (path d)[15a,c] disubstituted alkene with an aryl halide is the most attractive since no previous activation of the olefin is needed. Recently several efforts have been devoted to improve the Heck reaction in terms of sustainability and safety[16,17] but only little attention has been given to the development of metal-free protocols,[18] most of them exploiting photochemical conditions.[19-21] However, despite the formation of a triarylethylene from 1,1-diphenylethylene and aryl halides (iodides, chlorides) has been described to occur via the photogeneration of a triplet aryl cation (path e)[20] or an aryl radical[21] (path f), the scope of such proposals is rather limited, and, a high energy demanding UV-light source is required to activate the aromatic substrates.[20,21] Thus, currently, to the best of our knowledge, a versatile metal-free Heck protocol for the preparation of TAEs is still lacking.



Scheme 1. Synthetic approaches to the triarylethylene core proposed in the literature.

We recently exploited the peculiar photochemical properties of arylazo sulfones **I** in organic synthesis.[22-25] Such bench-stable derivatives of anilines bear a -N$_2$SO$_2$CH$_3$ moiety[22] that imparts both color and photoreactivity to the molecule and for this reason, has been dubbed as *dyedauxiliary group*.[24] Indeed, aryl radicals (Ar$^•$, obtained via homolysis of the N-S bond occurring from the $^1n\pi^*$ state and loss of a N$_2$ molecule) and triplet aryl cations (^{3}Ar$^+$, in turn generated upon heterolysis from the $^3\pi\pi^*$ state and loss of N$_2$) were smoothly generated from **I** in a wavelength-selective fashion by irradiation with visible and UV-light sources, respectively.[22] Obviously, upon solar light exposition both

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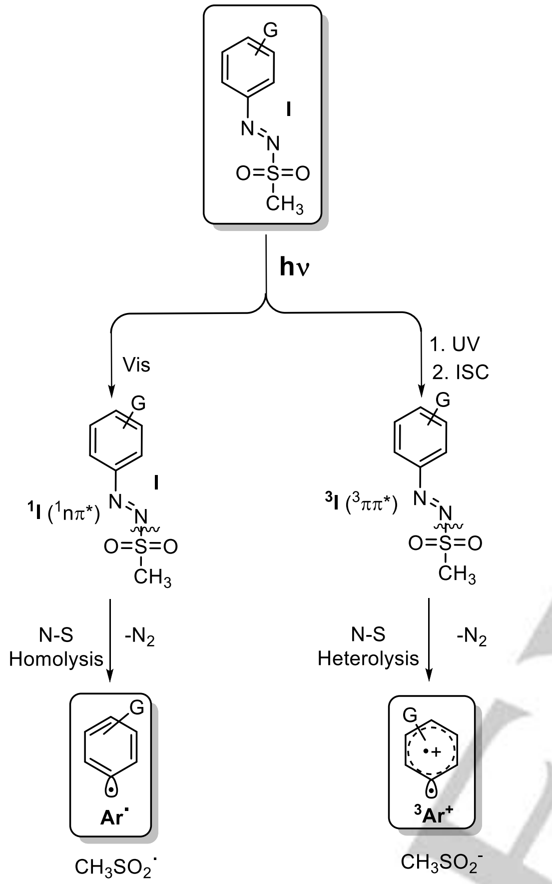
species were released.[22] These substrates have been employed in different photocatalyst- and metal-free arylation protocols, for the preparation of (hetero)biaryls,[22] allyl arenes[23] and aromatic amides.24



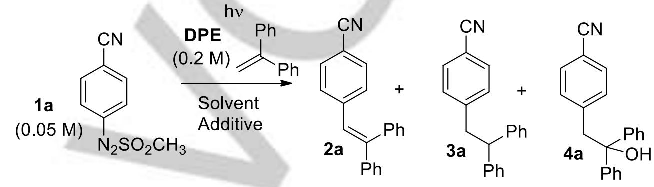
Scheme 2. Wavelength-selective generation of aryl radicals and aryl cations from arylazo sulfones (**I**).

In the aim of investigating the scope of arylazo sulfones as photoactivated substrates in metal-free arylation procedures we thus decided to explore the reactivity of such compounds in the presence of 1,1-diarylethylenes, being capable to trap various chemical intermediates.[20,21]

Results and Discussion

At the beginning, we investigated the photolysis of 4-cyanophenylazo sulfone **1a** (0.05 M) in the presence of 1,1-diphenylethylene (**DPE**, 0.2 M) as the coupling partner (Table 1). Reactions were performed by means of a solar simulator equipped with a 1500 W Xenon lamp. The reaction mixture was deareated by means of three freeze pump thaw cycles. Gratifyingly, irradiation in dichloromethane resulted in the formation of triarylethylene **2a** in 65% yield, along with a low amount of 1,1,2-triarylethane **3a** (7%, entry 1). The use of ethyl acetate as the solvent was detrimental for the process (entry 2), whereas in acetone the efficiency of the arylation increased, and a 5:1 mixture of **2a** and **3a** was obtained (entry 3). Notably, when moving to dry acetonitrile, **2a** was the only product observed (80%, entry 4). Arylation remained the exclusive path also in the presence of a halved concentration of **DPE**, but the efficiency of the reaction significantly dropped. Replacing part of the organic solvent with water resulted in a decrease of the amount of **2a** along with the formation of carbinol **4a** (entry 5).

Table 1. Optimization of the reaction protocol. [a]



Entry	Conditions	Light source, t_{irr} (h)	Products (% yield)
1	dry CH_2Cl_2	Solarbox,[b] 4h	**2a**, 65; **3a**, 7
2	dry CH_3COOEt	Solarbox,[b] 4h	**2a**, 50; **3a**, 7
3	dry Acetone	Solarbox,[b] 4h	**2a**, 81; **3a**, 16
4	dry MeCN	Solarbox,[b] 4h	**2a**, 80, (55)[c]
5	MeCN-H_2O (9:1)	Solarbox,[b] 4h	**2a**, 46; **4a**, 6
6	$K_2S_2O_8$ (1 equiv.), MeCN/H_2O (9:1)	Solarbox,[b] 4h	**2a**, 69; **4a**, 6
7	dry MeCN	366 nm,[d] 4h	**2a**, 22
8	dry MeCN	410 nm,[e] 16 h	**2a**, 82
9	dry MeCN	450 nm,[f] 16 h	**2a**, 80
10	dry MeCN	Natural Sunlight, 2 days [g]	**2a**, 83
11[h]	dry MeCN	-	- [i]

[a] The reaction mixture was deareated by means of three freeze-pump-thaw cycles. Irradiations have been carried out until the complete consumption of **1a**. [b] A solar simulator equipped with a 1500 W Xe lamp (500 W/m^2). [c] 0.1 M **DPE** used. [d] 10 x 15 W Phosphor coated Hg lamp. [e] 1 W LED (410 nm). [f] 1 W LED (450 nm). [g] The reaction vessel was exposed to sunlight for 2 days (6 h per day). [h] Blank experiment carried out in the absence of light. [i] No arylation observed.

External oxidants such as $K_2S_2O_8$ did not alter improve significantly the selectivity of the process (entry 6). We finally investigated the role of different light sources, finding that the reaction was inefficient under UV-light irradiation (366 nm, 22% yield of **2a**, entry 7). On the other hand, visible LEDs (entries 8,9) gave results comparable to that observed in entry 4. To our delight, a 83% yield of **2a** was also obtained when exposing the reaction vessel to natural sunlight for two sunny days in Pavia, September

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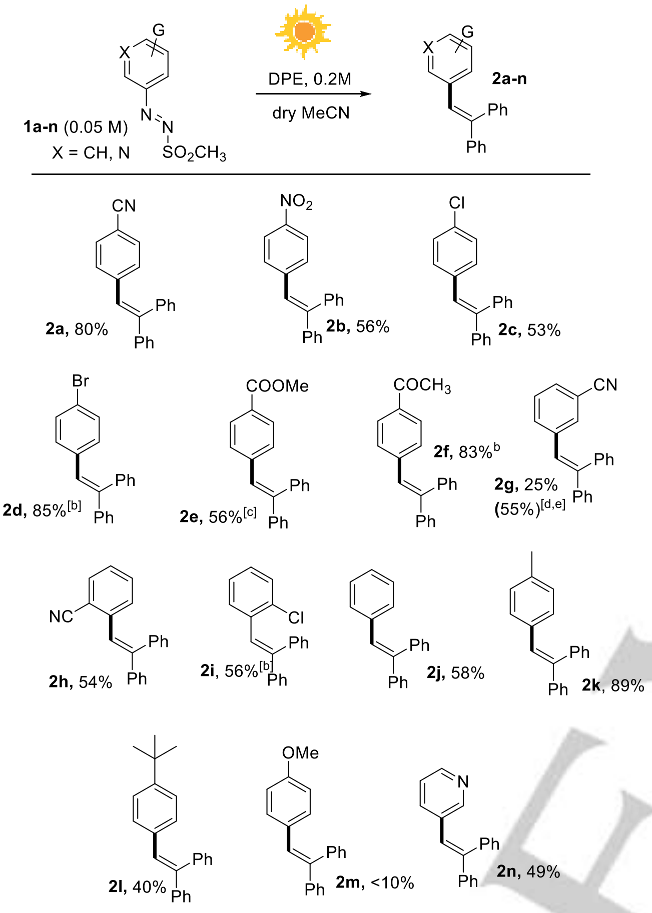
2017 (6 h of exposition per day, entry 10, see also ESI). Finally, no reaction took place when storing the reaction vessel covered by an aluminium foil in the solar simulator (entry 11).



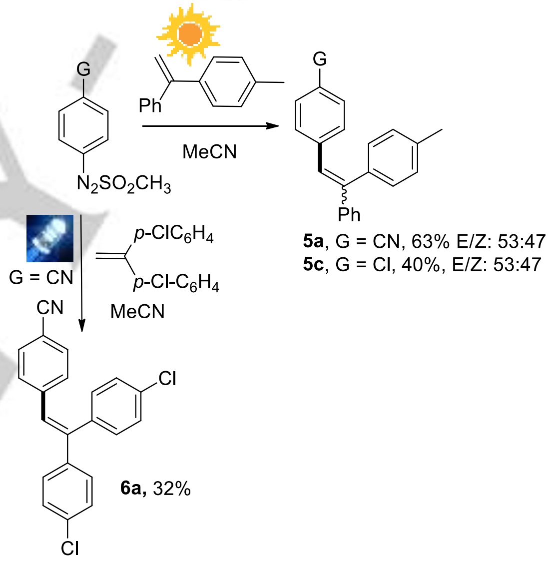
[a] The reaction mixture was deareated by means of three freeze-pump-thaw cycles. Irradiations have been carried out until the complete consumption of **1** in a solar simulator equipped with a 1500 W Xe lamp (500W/m^2).
[b] 90% of the unreacted **DPE** recovered during the isolation step
[c] 15% of carbinol **4e** was also isolated.
[d] Irradiation was carried out in MeCN/H_2O 9:1 mixture.
[e] Traces (<5%) of compound **3g** were observed.

Scheme 2. Preparation of triarylethylenes **2a-n**

With these preliminary results in hand, we thus adopted the reaction conditions described in entry 4 in order to extend the scope of such arylation protocol.

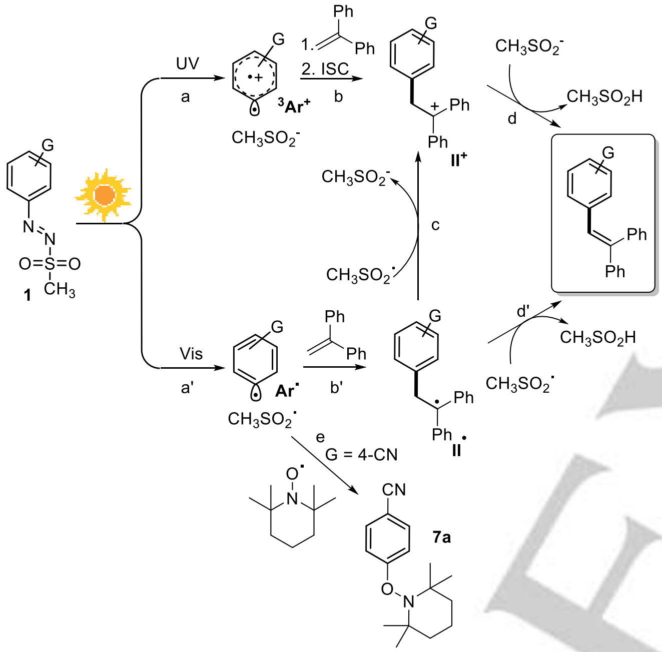
As depicted in Scheme 2, the reaction took place efficiently with substrates bearing electron-withdrawing substituents in para-position and compounds **2a-f** were isolated in up to 85% yield (see the case of *p*-bromoderivative **2d**). Good yields (around 55%) were also obtained in the synthesis of 3- and 2-vinylbenzonitriles **2g** and **2h** as well as in the preparation of the 2- chloroderivative **2i**. Interestingly, in the case of **2g** the yield was strongly improved when carrying out the reaction in MeCN-H_2O 5:1 mixture. Analogously, irradiation of phenylazo- and *p*-tolylazo sulfone **1j** and **1k** afforded the corresponding 1,2,2-triarylethylenes **2j,k** in 58 and 89% yield, respectively. The results were not satisfactory starting from **2l** (40% of the 4-*t*butyl-substituted product isolated), whereas with **1m** the reaction failed, since a mixture of **2m** and **3m** was formed in a very low overall yield. The process was applied also to nitrogen-containing heterocycles, and 3-pyridyl derivative **2n** was obtained in a moderate yield (49%). Furthermore, in selected case we demonstrated that the excess of the employed diphenylethylene can be recovered almost quantitatively (ca. 90%).

The developed protocol worked to some extent also in the case of substituted diphenylethylenes, as depicted in Scheme 3. Thus, arylated **5a** and **5c** were obtained from 1-methyl-4-(1-phenylvinyl)benzene as a mixture of diasteroisomers, in discrete yields (up to 60%), whereas in the case of 1,1'-(ethenylidene)-bis(4-chlorobenzene), trapping of the photogenerated intermediates took place unsatisfactorily and only a 28% yield of **6a** was formed under simulated sunlight exposition (32% yield when a 450 nm LED was employed).



Scheme 3. Synthesis of substituted triarylethylenes **5** and **6**.

As hinted above, the photoreactivity of arylazo sulfones **1** has been the subject of a detailed investigation by our research group. Thus, a triplet aryl cation (Scheme 4, path a) and an aryl radical/$CH_3SO_2^•$ pair (path a') are both generated upon solar exposition. According to the reported literature[19,20] such intermediates can be easily trapped by diarylethylenes to afford the cation **II$^+$** and the radical adduct **II$^•$**, respectively. Whereas deprotonation by the methanesulfinate anion ($CH_3SO_2^-$) is the most feasible pathway occurring to **II$^+$** (path d), the methanesulfonyl radical ($CH_3SO_2^•$) was found able to act as a monoelectronic oxidant for different radical intermediates including imidoyl radicals.[24] Thus, oxidation of **II$^•$** to **II$^+$** (path c) and ensuing deprotonation (path d) afforded the desired products **2**, **5-6**. However, a hydrogen atom abstraction from **II$^•$** by $CH_3SO_2^•$ to give directly the triarylethylene can not be so far excluded. With the aim of further investigating the mechanism of the reaction, and confirming the intermediacy of an aryl radical, we carried out the irradiation at 450 nm of **1a** in dry acetonitrile in the presence of **DPE** and of the radical trap 2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO).[26] In this case, arylation of **DPE** was almost suppressed (5% yield of **2a**) and we isolated only a small amount of adduct **7a** (23% yield). On the other hand, the formation of **2a** observed also during the irradiation at 366 nm (where, according to literature, a triplet aryl cation is exclusively generated)[22] confirmed likewise the capability of the diarylethylene to act as a phenyl cation trap. Finally, the formation of a reactive Electron Donor-Acceptor complex between the arylazo sulfones and the diarylethylenes was excluded on the basis of spectroscopic analyses (see ESI files for further details).



Scheme 4. Proposed mechanism for the photoinduced synthesis of triarylethylenes

As concerning the influence of the aromatic substituent of arylazo sulfones **1** on the efficiency of the arylation, and in particular, on the unsatisfactory results obtained in the case of substrates bearing electron-donating groups (see for instance compounds. **2l,m**) it should be noticed that a similar behaviour have been already observed in our previous works[22,24] and in recent arylation procedures where an aryl radical is involved.[27]

Conclusions

As hinted above, the development of a metal-free Mirozoki-Heck coupling has been documented in literature[18-21] and such protocols were sometimes applied to the building of a triarylethylene core.[19,20] However, whereas the previous examples showed a limited scope, the present proposal can be efficiently applied to a wide range of substrates (including heteroaromatics), with the only exception of compounds bearing strong electron-donating substituents such as **2m** (which already gave unsatisfactory results in previous investigations). [23]
The obtained results pointed out the potentialities of our approach as a sustainable and versatile route to TAE derivatives.
This metal- and (photo)catalyst-free arylation procedure combines the peculiar photoreactivity of arylazo sulfones and the impressive reactivity of the 1,1-diarylethylene moiety towards photogenerated intermediates such as aryl radicals and triplet aryl cations. The process occurs under mild conditions, since simulated or natural sunlight are exclusively employed to activate the substrates, and the reaction was applied, to some extent, also to substituted diarylethylenes. Finally, a large part of the unreacted diphenylethylene employed can be easily recovered during the purification step.

Experimental Section

Experimental

General. ^{1}H and ^{13}C NMR spectra were recorded on a 300 MHz spectrometer, chemical shifts were reported in ppm downfield from TMS, and the attributions were made on the basis of ^{1}H and ^{13}C signals, as well as DEPT-135 experiments; chemical shifts are reported in ppm downfield from TMS. GC-MS analyses were carried out by using a GC-DSQ single quadrupole GC/MS system. A Rtx-5MS (30 m × 0.25 mm × 0.25 μm) capillary column was used for analytes separation with helium as carrier gas at 1 mL min^{-1}. The injection in the GC system was performed in split mode and the injector temperature was 250 °C. The GC oven temperature was held at 80°C for 5 min, increased to 250 °C by a temperature ramp of 10 °C min^{-1} and held for five min. The transfer line temperature was 250 °C and the ion source temperature 250 °C. Mass spectral analyses were carried out in full scan mode. The reaction course was followed by GC and TLC analyses. Solvent of HPLC purity were employed in the photochemical reactions. 1,1-diphenylethylene is commercially available and was purified by column chromatography before using. Arylazo sulfones **1a-n** were previously synthesized and fully characterized in our lab.[24]

Photochemical synthesis of triarylethylenes 2, 5-6.
A solution (8 mL) of arylazo sulfone **1a-n** (0.05 M, 0.4 mmol, except where otherwise reported), the chosen diarylethylene (0.2 M, 1.6 mmol, except where otherwise reported) in dry acetonitrile was divided in four portions and poured into four Pyrex vials (2 mL each one). The vials were sealed with a septum, degassed three times by “pump-freeze-thaw” cycles (×3) via a syringe needle and the reaction mixture was irradiated in a solar simulator equipped with a 1.5 kW Xenon lamp (conditions: 500W with outdoor + IR filter) for 4 h. The photolyzed solution was then concentrated under vacuo and purified by flash chromatography (eluant: petroleum ether:AcOEt mixture).

4-(2,2-diphenylvinyl)benzonitrile (2a). From 84 mg of 4-((methylsulfonyl)diazenyl)benzonitrile (**1a**, 0.05 M, 0.4 mmol) and 282 μL (0.2 M, 1.6 mmol) of 1,1-diphenylethylene (**DPE**) in 8 mL

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of dry MeCN, irradiated for 4 h. Purification by flash chromatography afforded 90 mg of **2a** (white solid, mp: 104-105°C, lit.[27a] 110°C, 80% yield). Spectroscopic data of **2a** were in accordance with the literature.[28] The same process was carried out by exposing the reaction mixture to natural sunlight for 2 days (6 hours/day). Under these conditions, **2a** was isolated in 83% yield. When the reaction was carried out in acetone, the GC-MS analysis pointed out the presence of **3a** (81%) along with minor amounts of 4-(2,2-diphenylethyl)benzonitrile[29] (**3a**, 16% yield, m/z: 167 (M^+, 100)). On contrast, when a MeCN-H_2O 5:1 mixture was used as the solvent, 4-(1-hydroxy-2,2-diphenylethyl)benzonitrile[30] (**4a**, 6% yield, m/z:183 (100), 116 (5)) was obtained as the byproduct.

1-(2-(4-nitrophenyl)-1-phenylvinyl)benzene (2b). From 92 mg of 1-(methylsulfonyl)-2-(4-nitrophenyl)diazene (**1b**, 0.05 M, 0.4 mmol) and 282 μL (0.2 M, 1.6 mmol) of **DPE** in 8 mL of dry MeCN. Purification by flash chromatography afforded 68 mg of **2b** (yellow solid, mp: 146-148°C, lit·[31a] 148-150°C), 56% yield). Spectroscopic data of **2b** were in accordance with the literature.[31a,b]

2-(4-chlorophenyl)-1,1-diphenylethylene (2c). From 88 mg of 1-(methylsulfonyl)-2-(4-chlorophenyl)diazene (**1c**, 0.05 M, 0.4 mmol) and 282 μL (0.2 M, 1.6 mmol) of **DPE** in 8 mL of dry MeCN. Purification by flash chromatography afforded 62 mg of **2c** (colorless oil, 53% yield). Spectroscopic data of **2c** were in accordance with the literature.[32]

2-(4-bromophenyl)-1,1-diphenylethylene (2d). From 105 mg of 1-(methylsulfonyl)-2-(4-bromophenyl)diazene (**1d**, 0.05 M, 0.4 mmol) and 282 μL (0.2 M, 1.6 mmol) of **DPE** in 8 mL of dry MeCN. Purification by flash chromatography afforded 114 mg of **2d** (colorless solid, 85% yield, mp: 72.9-74°C, lit[33a] 77°C). Spectroscopic data of **2d** were in accordance with the literature.[33b] Furthermore, 90% of the the unreacted DPE was recovered during the isolation step.

Methyl 4-(2,2-diphenylvinyl)benzoate (2e). From 98 mg of methyl 4-((methylsulfonyl)diazenyl)benzoate (**1d**, 0.05 M, 0.4 mmol) and 282 μL (0.2 M, 1.6 mmol) of **DPE** in 8 mL of dry MeCN. Purification by flash chromatography afforded 70 mg of **2e** (colourless oil, 56% yield) along with a minor amount of methyl 4-(2-hydroxy-2,2-diphenylethyl)benzoate (**4e**, 20 mg, 15% colourless solid, mp: 147-150°C).

2e: ^{1}H NMR ($CDCl_3$), δ; 3.90 (s, 3H), 7.00 (s, 1H), 7.10-7.15 (d, 2H, J = 8.3 Hz), 7.20-7.25 (m, 2H), 7.36 (s, 1H), 7.80-7.85 (d, 2H, J = 8.3 Hz). ^{13}C NMR ($CDCl_3$) δ 51.9 (CH_3), 127 (CH), 127.6, 127.7 (CH), 127.9 (CH), 128.2 (CH), 128.6 (CH), 129.1 (CH), 129.3 (CH), 129.9, 130.2 (CH), 132.3 (CH), 139.7, 142.1, 142.8, 144.9, 166.8. IR (NaCl, ν/cm^{-1}) 2926, 2844, 1706, 1212, 755. Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C,84.1; H, 5.8.

4e: ^{1}H NMR ($CDCl_3$), δ: 3.70 (s, 2H), 3.90 (s, 3H), 6.95-7.00 (m, 2H), 7.25-7.40 (m, 10 H), 7.80-7.85 (m, 2H). ^{13}C NMR ($CDCl_3$) δ: 48.1 (CH_2), 52 (CH_3),78.1, 126.1 (CH), 127.1 (CH), 127.8 (CH), 128.4, 129 (CH), 130, 130.8 (CH), 141.8, 146.1, 166.6. IR (NaCl, ν/cm^{-1}) 2954, 1706, 1120, 755. Anal. Calcd for $C_{22}H_{20}O_3$: C, 79.50; H, 6.06. Found: C,79.5; H, 6.1.

1-(4-acetyl)phenyl-2,2-diphenylethylene (2f). From 91 mg of 1-(4-((methylsulfonyl)diazenyl)phenyl)ethanone (**1f**, 0.05 M, 0.4 mmol) and 282 μL (0.2 M, 1.6 mmol) of **DPE** in 8 mL of dry MeCN. Purification by flash chromatography afforded 99 mg of **2f** (white solid, mp: 121-123°C, lit.[34] 125°C), 83% yield). Spectroscopic data of **2f** were in accordance with the literature·35 IR (NaCl, ν/cm^{-1}): 2935, 2846, 17501, 956, 894. Furthermore, 90% of the the unreacted DPE was recovered during the isolation step.

3-(2,2-diphenylethenil)benzonitrile (2g). From 84 mg of 2-((methylsulfonyl)diazenyl)benzonitrile (**1h**, 0.05 M, 0.4 mmol) and 282 μL (0.2 M, 1.6 mmol) of **DPE** in 8 mL of dry MeCN. Purification by flash chromatography afforded 28 mg of **2h** (colorless oil, 25% yield). Spectroscopic data of **2h** were in accordance with the literature[36] IR (NaCl, ν/cm^{-1}) 3059, 2923, 2853, 2116, 1491,1027, 942, 885. When the same reaction is carried out in MeCN-H_2O 9-1 mixture instead of dry MeCN, **2h** was isolated in 55% yield.

2-(2,2-diphenylvinyl)benzonitrile (2h). From 84 mg of 3-((methylsulfonyl)diazenyl)benzonitrile (**1g**, 0.05 M, 0.4 mmol) and 282 μL (0.2 M, 1.6 mmol) of **DPE** in 8 mL of dry MeCN. Purification by flash chromatography afforded 61 mg of **2g** (colorless solid, mp: 120-121°C, lit 124-125°C,37 54% yield). Spectroscopic data of **2g** were in accordance with the literature.[37]

2-(2-chlorophenyl)-1,1-diphenylethylene (2i). From 88 mg of 1-(methylsulfonyl)-2-(2-chlorophenyl)diazene (**1i**, 0.05 M, 0.4 mmol) and 282 μL (0.2 M, 1.6 mmol) of **DPE** in 8 mL of dry MeCN. Purification by flash chromatography afforded 65 mg of 2i (colorless solid, 56% yield, mp: 110-111°C). Spectroscopic data of **2i** were in accordance with the literature.[38] A 90% of the the unreacted DPE was recovered during the isolation step.

1,1,2-Triphenylethylene (2j). From 74 mg of 1-(methylsulfonyl)-2-phenyldiazene (**1j**, 0.05 M, 0.4 mmol) and 282 μL (0.2 M, 1.6 mmol) of **DPE** in 8 mL of dry MeCN. Purification by flash chromatography afforded 59 mg of **2j** (colourless solid, mp: 70-72°C, lit.[39] 71-73°C, 58% yield). Spectroscopic data of **2j** were in accordance with the literature.[39]

1,1-diphenyl-2-(4-methylphenyl)ethylene (2k). From 79 mg of 1-(methylsulfonyl)-2-(4-methylphenyl)diazene (**1k**, 0.05 M, 0.4 mmol) 282 μL (0.2 M, 1.6 mmol) of **DPE** in 8 mL of dry MeCN. Purification by flash chromatography afforded 96 mg of **2k**. (colourless oil, 89% yield). Spectroscopic data of **2k** were in accordance with the literature.[31]

1,1-Diphenyl-2-(4-*tert*-butylphenyl)ethylene (2l). From 96 mg of 1-(methylsulfonyl)-2-(4-tert-butylphenyl)diazene (**1l,** 0.05 M, 0.4 mmol) and 282 μL (0.2 M, 1.6 mmol) of **DPE** in 8 mL of dry MeCN. Purification by flash chromatography afforded 50 mg of **2l** (white solid, mp: 71-73°C, lit.[40] 74-76°C, 40% yield). ^{1}H NMR data of **2l** were in accordance with the literature.[36] ^{13}C NMR ($CDCl_3$) δ 31.1 (CH_3), 34.4, 124,8 (CH), 127.2 (CH), 127.3 (CH), 127.9 (CH), 128.0(CH), 128.1 (CH), 128.6 (CH), 129.12 (CH), 130.1 (CH), 134.3, 140.5, 141.5, 143.5, 149.8. Anal. Calcd for $C_{24}H_{14}$: C, 92.26; H, 7.74. Found: C, 92.3; H, 7.7.

Irradiation of 1m in MeCN in the presence of DPE. A solution of 86 mg of 1-(methylsulfonyl)-2-(4-methoxyphenyl)diazene (**1m**, 0.05 M, 0.4 mmol) and 282 μL (0.2 M, 1.6 mmol) of **DPE** in dry MeCN (8 mL) was irradiated in a Solarbox for 4 hours. GC -MS analyses of the photolysed pointed out the presence of low amount (<10% overall) of 1,1-diphenyl-2-(4-methoxyphenyl)ethylene[41a] (**2m**, m/z: 286 (M^+, 100), 165 (40)) and 1,1-diphenyl-2-(4-methoxyphenyl)ethane[41b] (**3m**, m/z: 167 (30), 120 (100)).

1,1-diphenyl-2-(3-pyridyl)ethylene (2n). From 74 mg of 3-((methylsulfonyl)diazenyl)pyridine (**1n**, 0.05 M, 0.4 mmol) and 282 μL (0.2 M, 1.6 mmol) of **DPE** in 8 mL of dry MeCN. Purification by flash chromatography afforded 50 mg of **2n** (oil, 49% yield). Spectroscopic data of **2n** were in accordance with the literature.[16d]

4-(2-phenyl-2-(p-tolyl)vinyl)benzonitrile (5a). From 84 mg (0.05 M, 0.4 mmol) of **1a** and 317 μL (0.2 M, 1.6 mmol) of 1-methyl-4-(1-phenylvinyl)benzene in dry MeCN (8 mL). Purification by flash chromatography afforded 74 mg of **5a** (colouless oil, 63%, dr 53:47).

5a:^{1}H NMR ($CDCl_3$) δ: 2.40 (s, 3H), 2.45 (s, 3H), 6.90-6.95 (m, 2H), 7.05-7.10 (m, 5H), 7.15-7.20 (m, 7H), 7.25-7.30 (m, 2H), 7.35-7.45 (m, 12H); ^{13}C NMR ($CDCl_3$) δ: 21.1 (CH_3), 21.2 (CH_3),109.4, 109.5, 118.9, 119, 125.2 (CH), 125.7 (CH), 127.5 (CH), 127.8 (CH), 127.9 (CH), 128.1 (CH), 128.2 (CH), 128.7 (CH), 128.8 (CH), 129 (CH), 129.5 (CH), 129.7 (CH), 129.8 (CH), 129.9 (CH), 130 CH), 131.5 (CH), 131.6 (CH), 136.2, 137.9, 138.2, 139.4, 139.6, 142.2, 142.3, 142.7, 146.1, 146.2. IR (NaCl, ν/cm^{-1}) 3020, 2220, 1595, 1070, 890. Anal. Calcd for $C_{22}H_{17}N$: C, 89.46; H, 5.80; N, 4.74. Found: C, 88.5; H, 5.9; N, 4.6.

1-chloro-4-(2-phenyl-2-(p-tolyl)vinyl)benzene (5c). From 88 mg (0.05 M, 0.4 mmol) of **1c** and 317 μL (0.2 M, 1.6 mmol) of 1-methyl-4-(1-phenylvinyl)benzene in dry MeCN (8 mL). Purification by flash chromatography afforded 48 mg of **5c** (colouless oil, 40% yield, dr 53:47).

5c:^{1}H NMR ($CDCl_3$) δ: 2.35 (s, 3H), 2.40 (s, 3H), 6.85-6.90 (m, 2H), 6.95-7.00 (m, 4H), 7.05-7.24 (m, 13H), 7.30-7.35 (m, 9H). ^{13}C NMR ($CDCl_3$) δ: 21.0 (CH_3), 21.2 (CH_3), 125.8 (CH), 126.4 (CH), 127.5 (CH), 127.4 (CH), 127.95(CH), 128.0 (CH), 128.1 (CH), 128.6 (CH), 128.9 (CH), 129.3 (CH), 130 (CH), 130.1 (CH), 130.5 (CH), 130.6 (CH), 132.03, 132.08, 135.9, 136, 136.8 (CH), 137.2, 137.5, 140, 140.1, 140.3, 143.1, 143.2, 143.4. IR (NaCl, ν/cm^{-1}) 3060, 2918, 1595, 1012, 907, 822. Anal. Calcd for $C_{21}H_{17}Cl$: C, 82.75; H, 5.62. Found: C, 82.7; H, 5.6.

4-[2,2-bis-(4-chloro-phenyl)-vinyl]-benzonitrile (6a). From 50 mg (0.03 M, 0.24 mmol) of 1a, 239mg (0.12 M, 0.96 mmol) of 1,1'-(ethenylidene)-bis(4-chlorobenzene) in dry MeCN (8 mL). Purification by flash chromatography afforded 32 mg of **6a** (white solid, 28% yield, mp: 115-116°C, lit.[42] 117-118°C).

6a:^{1}H NMR (CD_3COCD_3) δ 7.20-7.30 (m, 5H), 7.35-7.50 (m, 6H), 7.60-7.65 (m, 2H); ^{13}C NMR (CD_3COCD_3) δ 111.5, 119.7, 128.7 (CH), 129.8 (CH), 130.4 (CH), 130.5 (CH), 131.4 (CH), 133.1 (CH), 134.9, 135, 139.1, 142.2, 143, 144.5. IR (NaCl, ν/cm^{-1}) 2914, 2125, 1585, 1114, 1036, 955. Anal. Calcd for $C_{21}H_{13}Cl_2N$: C, 72.01; H, 3.74; N, 4.00. Found: C, 72.1; H, 3.7; N, 4.1.

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Keywords: Metal-free Arylation • Photogenerated intermediates • Triarylethylenes • Sunlight-driven processes • Photochemistry.

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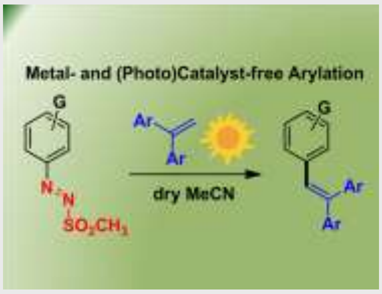
FULL PAPER

The preparation of substituted triarylethylenes (TAEs) was achieved under metal- and (photo)catalyst-free conditions, starting from photoactivated arylazo sulfones.



L. Onuigbo, C. Raviola, A. Di Fonzo, S. Protti and M. Fagnoni*

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Sunlight-driven synthesis of triarylethylenes (TAEs) via metal-free Mizoroki–Heck-type coupling