Characterization of novel sulfonium photoacid generators and their microwave-assisted synthesis†

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Received (in Berkeley, CA, USA) 10th September 2008, Accepted 4th December 2008
First published as an Advance Article on the web 7th January 2009
DOI: 10.1039/b815831b

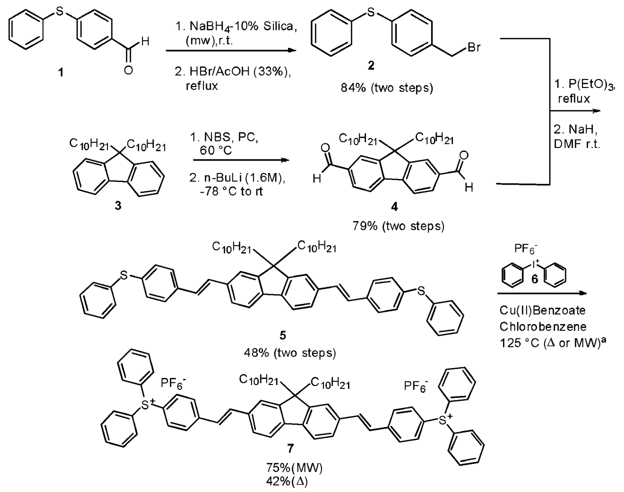
Microwave-assisted synthesis of triarylsulfonium salt photoacid generators (PAGs) afforded reaction times 90 to 420 times faster than conventional thermal conditions, with photoacid quantum yields of new sulfonium PAGs ranging from 0.01 to 0.4.

Since their discovery, the use of photoacid generators, PAGs, have been widely adopted by the polymer industry in coatings, paints, anticorrosives, photoresists, and microelectronics,[1] and 2D and 3D lithographic patterning.[2,3]

Two-photon absorption (2PA) has been reported for a number of applications, exploiting the fact that the 2PA probability is directly proportional to the square of the incident light intensity ($dw/dt \propto I^2$)[4] (while one-photon absorption bears a linear relation to the incident light intensity, $dw/dt \propto I$). This intrinsic property of 2PA leads to 3D spatial localization, important in fields such as optical data storage,[5–7] fluorescence microscopy,[8,9] and 3D microfabrication.[10,11] There have been demonstrations of successful two-photon microfabrication using commercial PAGs,[11,12] even though the 2PA cross-section of these initiators is low.[13] Two-photon 3D microfabrication with a novel PAG was reported to fabricate MEMs structures.[14] To further advance a number of emerging technologies, there is a great need for PAGs with higher 2PA cross-sections.

Microwave-facilitated synthesis has been the subject of substantial interest over the last decade.[15,16] Seipel *et al.* recently reported microwave-assisted reaction times 80 times faster than conventional heating reaction times,[17] and that these reactions are potentially more energy-efficient than those that use conventional heating. To our knowledge, there are no reports of the microwave-assisted synthesis of sulfonium salts.

The synthesis of triarylsulfonium salts by thermolysis of the diphenyliodonium counterpart in the presence of a diphenylsulfide was originally reported by Crivello and Lam[18,19] Herein, we report the microwave-assisted synthesis of triarylsulfonium salt PAGs. Several of the PAGs are novel and have potential for use as 2PA photoinitiators in negative resists for 3D microfabrication or in optical data storage. Furthermore, the efficiency of forming these sulfonium salts by the microwave-assisted process was evaluated relative to the conventional thermal reaction of diphenylsulfides in the presence diphenyliodonium salts. Finally, photoacid quantum yields were determined for several of the novel PAGs.



Scheme 1 Synthesis of PAG **7**. [a]Reactions were carried out both by conventional methods, Δ, and microwave heating, MW.

The new PAGs were designed to exhibit high 2PA cross-sections. Because of its high thermal and photochemical stability, fluorene was chosen as the core structure of the PAGs.[20] Quite advantageously, fluorene lends itself to ready substitution in its 2-, 7-, and 9-positions. Stilbene or thiophene motifs were introduced (2- and 7-positions) in order to extend the π-conjugation. Ultimately, two acceptor groups (triarylsulfonium and nitro) were introduced.

In order to enhance the photoacid quantum yield per molecule, the first approach was to incorporate two sulfonium salt motifs onto the fluorenyl scaffold, such as **7** in Scheme 1. However, this molecule exhibited high fluorescence quantum yield (0.80), limiting the photoacid quantum yield to (0.03) when excited at 400 nm. The direct photolysis of triarylsulfonium salts has been reported to occur primarily from the first excited singlet state. However, sensitization studies have shown that triplet triarylsulfonium salts are also labile.[21] Consequently, we proceeded to incorporate a nitro group in the structures to induce intersystem crossing.

As a result of this strategy, the fluorescence quantum yield of precursors **10** and **12**, and sulfonium salts **11** and **13**, were significantly decreased (Table 1), thereby reducing the radiative decay pathway. Nitro-containing sulfonium salt **11** exhibited an increased photoacid quantum yield (Table 1). The photoacid quantum yields were determined by a steady-state method in which solutions of the PAGs in acetonitrile were selectively irradiated at the desired wavelength with

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† Electronic supplementary information (ESI) available: Detailed synthetic procedures, microwave conditions, and characterization of the compounds. See DOI: 10.1039/b815831b

Table 1 Fluorescence quantum yields and photoacid quantum yields of sulfide precursors and PAGs

Compound	Φ_F	Φ_{H+}
5	1.0	—
7	0.8	0.03[a]
10	0.0	—
11	0.0	0.16[a]; 0.30[b]
12	0.0	—
13	0.0	0.01[b]; 0.04[d]
20	—	0.53[c]

[a] 400 nm irradiation. [b] 350 nm irradiation. [c] Literature value.[22] [d] 270 nm irradiation.

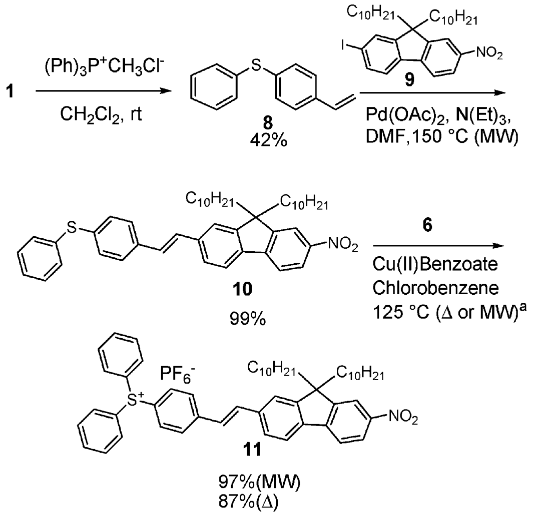
an excitation source and monochromator of a spectrofluorimeter. Rhodamine B was used as a sensor for photoacid generation, as reported by Scaiano *et al.*[23] Special care was taken to record the photodecomposition conversion no greater than 5% in order keep secondary photoproduct generation to a minimum. Previously, we determined a number of photochemical quantum yields under one- and two-photon excitation, and found no significant difference relative to the excitation mode. Hence, the values of Table 1 are good estimates under 2PA.[24]

Precursor **5** was prepared by a convergent synthesis (Scheme 1) of benzyl bromide **2** and bis-diformylfluorene **4**. The phosphonate was obtained from 4-(phenylthio)benzaldehyde, which was first reduced with $NaBH_4$ (10% in silica) aided by conventional, multimode microwave radiation.[25] Since hydrogen is extruded during the reaction when carried out on scales larger than 0.500 g, safety concerns lead us to run the reaction at room temperature for 24 h.

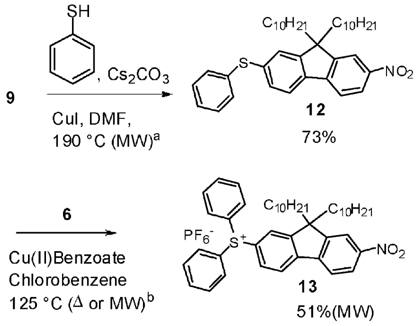
The resulting alcohol was refluxed in HBr (33% in AcOH) to obtain the benzylic bromide intermediate, subsequently used to obtain the bisphosphonate. The second branch of the synthesis started from fluorene, alkylation of the 9-position with bromodecane imparted the desired solubility to the molecule (**3**).[26] Bromination with NBS at the 2- and 7-positions of the alkylated fluorene was followed by introduction of the formyl group. Bisformyl fluorene **4** and the bisphosphonate were coupled *via* a Wadsworth–Horner–Emmons reaction, yielding exclusively the *trans*-isomer **5**. Bis-sulfide **5** was the precursor for bis-sulfonium salt **7** under both conventional and microwave-assisted conditions.

The versatile 2-iodo-7-nitro-9,9-didecylfluorene **9** was used as a precursor in the synthesis sulfonium salts **11** and **13** (Schemes 2 and 3). It was prepared as reported by Belfield *et al.*[26] Interestingly, stilbenyl sulfide **10** was obtained quantitatively *via* a microwave-assisted palladium acetate-catalyzed Heck reaction, coupling vinyl sulfide **8** and precursor **9**. The yields for both conventional and microwave-assisted methods were the highest for PAG **11** of the entire series. Fluorenylphenylsulfide **12** was prepared from Cu-catalyzed S-arylation of **9** and thiophenol.

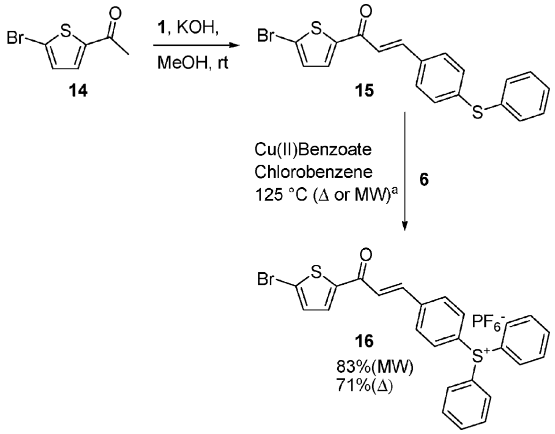
Diphenyl sulfide **15** was prepared to evaluate how the thiophene and chalcone functionalities would withstand the rapid heating conditions of the microwave-assisted method, further demonstrating the versatility of the microwave-assisted-method. Precursor **15** resulted from a straightforward Claisen condensation of 5-bromo-2-acetylthiophene **14** and formylphenylsulfide **1** (Scheme 4). Both functionalities were intact after the microwave-assisted reaction was carried out.



Scheme 2 Synthesis of PAG **11**, [a]Δ: 125 °C; MW: 100 W, closed vessel, standard mode; 40 psi; 125 °C.

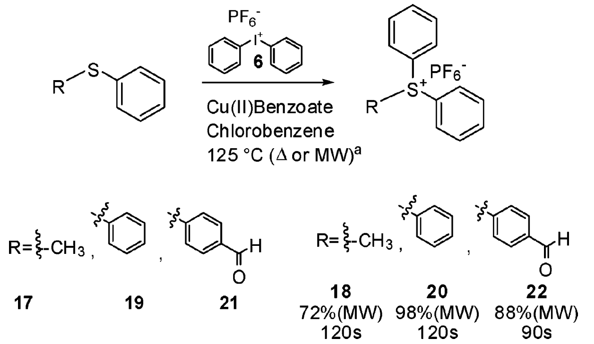


Scheme 3 Synthesis of PAG **13**, [a]150 W, closed vessel, standard mode; 100 psi; 190 °C, [b]Δ, 125 °C; MW: 100 W, closed vessel, standard mode; 40 psi; 125 °C.



Scheme 4 Synthesis of PAG **16**, [a]Δ: 125 °C; MW: 100 W, closed vessel, standard mode; 40 psi; 125 °C.

Furthermore, we sought to compare the effectiveness of this method when performed on less conjugated sulfides that may be more relevant in UV or deep UV lithographic applications (Scheme 5). The yields of **18** and **20** were comparable to those



Scheme 5 Synthesis of PAGs 18, 20 and 22, [a]Δ: 125 °C; MW: 100 W, closed vessel, standard mode; 40 psi; 125 °C.

Table 2 Microwave-assisted *vs.* conventional heating reaction times for sulfonium salt PAG formation

Reagent	Product	MW Time (yield)	Δ Time (yield)
5	**7**	6 min (75%)	29 h (42%)
10	**11**	8 min (97%)	8 h (87%)
12	**13**	10 min (51%)	70 h (10%)
15	**16**	14 min (83%)	24 h (71%)
17	**18**	120 s (72%)	3 h (100%)[a]
19	**20**	120 s (98%)	3 h (97%)[b]
21	**22**	90 s (88%)	3 h (83%)

[a] Literature value.[27] [b] Literature value.[19]

reported in the literature. As in the previous precursors, microwave heating significantly reduced reactions times for the formation of these sulfonium salts when compared to conventional heating times performed by us, **21**, or reported in the literature, **20** and **22** (Table 2).

The reactions that were carried out under conventional conditions were performed in an oil bath heated to 125 °C at atmospheric pressure; whereas the microwave-assisted reactions were run at the same temperature in closed vessel mode, reaching pressures no higher than 30 psi.

In every case, the reactions that were heated conventionally took significantly longer than the analogous microwave reactions, and microwave-assisted reaction yields were higher.

In conclusion, we have developed a new, more favorable methodology for the formation of sulfonium salts *via* microwave-assisted decomposition of diphenyliodonium salts in the presence of diphenylsulfides. Microwave-assisted reaction times were 90 to 420 times faster, resulting in generally higher yields. We have also shown that the introduction of groups that favor intersystem crossing is a viable means for increasing the photoacid quantum yield of novel triarylsulfonium salt PAGs.

The National Science Foundation (ECS-0621715 and ECS-0524533) is acknowledged for support of this work.

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