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# Photoacid generators (PAGs) based on *N*-acyl-*N*-phenylhydroxylamines for carboxylic and sulfonic acids

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ABSTRACT

Simple and efficient photoacid generators (PAGs) for carboxylic and sulfonic acids based on *N*-acyl-*N*-phenylhydroxylamines have been demonstrated. Irradiation of *o*-carboxylates and thermally rearranged *o*-arenesulfonates of *N*-acyl-*N*-phenylhydroxylamines using UV light (≥254 nm) in aqueous methanolic solution resulted in efficient generation of carboxylic and sulfonic acids, respectively. The carboxylic acid generation ability of *N*-acyl-*N*-phenylhydroxylamines was found to be dependent on their *N*-acyl substituents. Further, polymer bearing *o*-arenesulfonates of *N*-acyl-*N*-phenylhydroxylamine was synthesized and demonstrated as PAG for sulfonic acids.

## 1. Introduction

The growing demand to generate photoresist materials with high resolution[1] and high sensitivity[2] for lithography have sparkled the interest in photoacid generators (PAGs).[3,4] PAGs can be classified into two group's namely ionic and non-ionic type.[5] Non-ionic PAGs have gained much attention over ionic type due to its wide range of solubility in organic solvents and in polymer films.[6] A variety of non-ionic PAGs have been reported for the generation of sulfonic acids,[7,8] carboxylic acids,[9] phosphoric acids[10] and hydrogen halides.[11,12]

In the past years, significant progress has been made in the field of photoinduced cleavage of N–O bond due to its potential applications in the areas like radical generation,[13] protecting groups for biological molecules,[14] photopolymerisation[15] and also for the synthesis of several biologically important heterocyclic compounds.[16] In recent times, homolytic cleavage of the weak N–O bond by direct or sensitized photolysis shows growing interest in the area of PAGs. So far, only certain sulfonate esters derived from *N*-hydroxyamides,[17] *N*-hydroxyimides[3] and few imino sulfonates[18] were reported to generate sulfonic acids on photolysis via homolytic N–O bond cleavage. Hence, in search of simple organic molecules, which can act as efficient PAGs for both carboxylic and sulfonic acids by photoinduced homolytic N–O bond cleavage led us to explore *N*,*O*-diacyl-*N*-phenylhydroxylamines.

Considerable research has been undertaken to understand the mechanistic mode of N–O bond cleavage of *N*,*O*-diacyl-*N*-phenylhydroxylamines in connection to its photoaroyloxy rearrangement.[19] Sakurai and his co-workers[19] showed that direct photolysis of *N*,*O*-diacyl-*N*-phenylhydroxylamines undergoes efficient homolytic N–O bond cleavage from its singlet excited state to form 1,3 and 1,5 aroyloxy rearranged products via 'in-cage' reaction of aroyloxyl and amido radicals, along with fragmentation products, such as arenecarboxanilide, carboxylic acid and hydrocarbons through 'cage-escape' reaction of the above said radicals. Interestingly, the same group further showed that photolysis of *N*,*O*-diacyl-*N*-phenylhydroxylamines in hydrogen donor solvents produced largely fragmentation products (carboxylic acid and carboxanilide) via efficient hydrogen atom abstractions by aroyloxyl and amido radicals from the solvent by cage escape mechanism.[19,20] Considering the above result to produce carboxylic acids as a major product in hydrogen donor solvents, together with our recent research interest on exploring the applications of homolytic N–O bond cleavage of *N*,*O*-diacyl-*N*-phenylhydroxylamines,[21] made us to investigate *N*,*O*-diacyl-*N*-phenylhydroxylamines as PAGs.

Herein, we report *o*-carboxylates and thermally rearranged *o*-arenesulfonates of *N*-acyl-*N*-phenylhydroxylamines as simple and efficient PAGs for carboxylic and sulfonic acids, respectively. The synthesis and the characterization of the PAGs were discussed. The generation of carboxylic and sulfonic acids was achieved by irradiating their corresponding PAGs using UV light (≥254 nm). The

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effect of different *N*-acyl substituents on the acid generation ability of the PAGs was investigated. Further, we also synthesized polymers bearing *o*-arenesulfonyloxyanilide and showed that irradiation of these polymers in thin films resulted in the generation of sulfonic acids.

## 2. Results and discussion

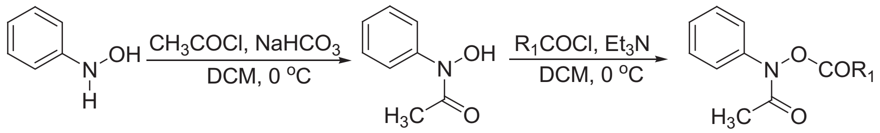
### 2.1. Carboxylates of *N*-acyl-*N*-phenylhydroxylamines as PAGs for carboxylic acids

*2.1.1. Synthesis of carboxylates of N-acetyl-N-phenylhydroxylamine (**3a–h**).* We have synthesized carboxylate esters of *N*-acetyl-*N*-phenylhydroxylamine (**3a–h**) as outlined in Scheme 1. The carboxylates were synthesized, initially by carrying out N-acetylation of *N*-phenylhydroxylamine (**1**) with acetyl chloride in presence of $NaHCO_3$ in dry DCM at 0 °C to yield *N*-acetyl-*N*-phenylhydroxylamine (**2**).[22]Treatment of **2** with various acid chlorides in presence of triethylamine in dry DCM resulted in quantative yield of carboxylates of *N*-acetyl-*N*-phenylhydroxylamine (**3a–h**, Table 2). All the carboxylates were characterized by $^1H$, $^{13}C$ NMR, IR and mass spectral analysis.

**Table 2**
Synthetic yield, UV/vis and photolysis data of the carboxylate esters of *N*-acetyl-*N*-phenylhydroxylamine (**3a–h**)

| Entry | Carboxylate | Synthetic yield[a] (%) | UV/vis | | Photogeneration of carboxylic acids | | |
|---|---|---|---|---|---|---|---|
| | | | λ (nm)[b] | log ε[c] | Time (min.)[d] | Yield[e] ($RCO_2H$) | Quantum yield (φ)[f] |
| 1 | **3a**[g] | 90 | 230 | 4.17 | 60 | 91 | 0.042 |
| 2 | **3b** | 91 | 277 | 4.31 | 90 | 90 | 0.028 |
| 3 | **3c**[g] | 90 | 246 | 4.27 | 120 | 95 | 0.022 |
| 4 | **3d**[g] | 92 | 243 | 4.29 | 100 | 95 | 0.026 |
| 5 | **3e**[g] | 90 | 261 | 4.24 | 50 | 93 | 0.051 |
| 6 | **3f** | 95 | 298 | 4.57 | 30 | 95 | 0.088 |
| 7 | **3g**[g] | 90 | 243 | 4.20 | 110 | 92 | 0.023 |
| 8 | **3h**[g] | 93 | 246 | 4.22 | 140 | 85 | 0.017 |

[a] Based on isolated yield.
[b] Maximum absorption wavelength.
[c] Molar absorption coefficient.
[d] Time for photolysis.
[e] Photolysis yield based on HPLC.
[f] Quantum yield for the generation of various carboxylic acids at room temperature (error limit within ±5%).
[g] Carboxylates for which the photoproducts were isolated and compared with authentic samples.



**1** **2** **3a-h**

$R_1$ = $CH_2C_6H_5$ (**3a**), $C_2H_2C_6H_5$ (**3b**), $C_6H_5$ (**3c**), *p*-$MeC_6H_4$ (**3d**), *p*-$MeOC_6H_4$ (**3e**), *p*-EtO(*m*-MeO)$C_6H_3$ (**3f**), *p*-$ClC_6H_4$ (**3g**), *p*-$NO_2C_6H_4$ (**3h**).

**Scheme 1.** Synthesis of carboxylate esters of *N*-acetyl-*N*-phenylhydroxylamine.

### 2.2. Photolysis of carboxylate esters of *N*-acetyl-*N*-phenylhydroxylamine (3a–h) to form carboxylic acids

Initially, we investigated the photolysis of carboxylate (**3c**) in methanolic solution using a 125-W medium pressure Hg lamp with quartz sleeve and we found homolytic N–O bond cleavage occurred to produce benzoic acid and acetanilide in good yields. This observation encouraged us to find the best solvent system for the efficient generation of carboxylic acids in high yield. We carried out the photolysis of **3c** (0.05 mM) in various solvents including methanol (MeOH), acetonitrile (ACN), tetrahydrofuran (THF), MeOH/$H_2O$ (9:1) and ACN/$H_2O$ (9:1) for 2 h and the results are tabulated in Table 1.

**Table 1**
Photolysis of carboxylate (**3c**) in various solvents

| Entry | Solvent system | % of Acid generated[a] | Quantum yield (φ)[b] |
|---|---|---|---|
| 1 | MeOH | 80 | 0.019 |
| 2 | ACN | 70 | 0.016 |
| 3 | THF | 75 | 0.017 |
| 4 | ACN/$H_2O$ (9:1) | 75 | 0.017 |
| 5 | MeOH/$H_2O$ (9:1) | 95 | 0.022 |

[a] Photolysis yield based on HPLC.
[b] Quantum yield for the generation of benzoic acid at room temperature (error limit within ±5%).

Among the above solvents, we found carboxylate (**3c**) generated benzoic acid in relatively high quantum yield and chemical yield in MeOH/$H_2O$ (9:1) compared to other solvents used for the study.

Hence, we irradiated the carboxylate esters of *N*-acetyl-*N*-phenylhydroxylamine (**3a–h**) in MeOH/$H_2O$ (9:1) solution and we found the corresponding carboxylic acids to be generated in nearly quantative yield as summarized in Table 2. In each case the photolysis was stopped when conversion reached at least 95% (as indicated by HPLC). For the carboxylates indicated in Table 2, their photoproducts (carboxylic acid and acetanilide) were isolated and characterized by $^1H$ NMR spectra with corresponding authentic samples. Quantum yield for the generation of various carboxylic acids were found to be in the range of 0.017–0.088 using valerophenone as an actinometer.[23]

As a representative example, we have shown in Fig. 1a HPLC analysis of photolyzed **3d**. The HPLC data clearly shows the depletion of the peak at $t_R$ 17.48 min with increase in irradiation time, indicating the photodecomposition of the carboxylate (**3d**). On the other hand, we noticed gradual increase of two new major peaks at $t_R$ 5.76 min and $t_R$ 10.03 min corresponding to the photoproducts *p*-toluic acid and acetanilide, respectively.

In order to compare the efficiency of photorelease from various solutions of carboxylates, The compound **3a**, **3c**, **3e**, and **3h** (0.05 mM) in MeOH/$H_2O$ (9:1) were irradiated using light above 254 nm and the course of the reaction was monitored by HPLC at regular interval of time. The Fig. 1b shows appearance of the carboxylic acids with respect to irradiation time. We notice that these carboxylates generates the corresponding carboxylic acids (≥85%) within 140 min of irradiation. In particular, aromatic carboxylic acids with electron donating substituent were generated more efficiently compared to aromatic carboxylic acids with electron withdrawing substituent (for example, *p*-methoxy benzoic acid was formed almost three times more efficiently compared to *p*-nitro benzoic acid).