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Synthesis of Highly Labile SG1-Based Alkoxyamines under Photochemical Conditions

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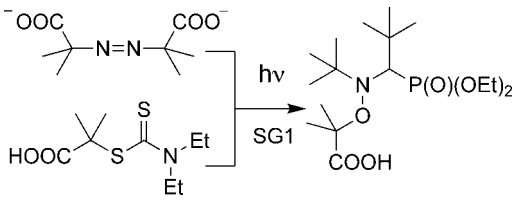
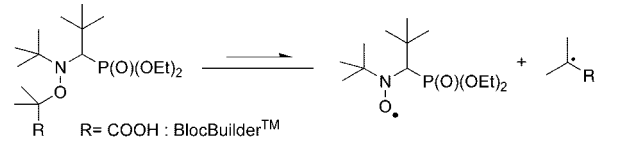


Highly labile SG1-based alkoxyamines were synthesized using the photodecomposition of both azo compounds and dithiocarbamates. The former method was a straightforward procedure to obtain the alkoxyamines, but a high [azo]/[nitroxide] ratio is needed. The latter method required only a stoichiometric amount of dithiocarbamate and allowed the recovery of the disulfide after irradiation. This enabled combination of the two methods in a process where only 0.75 equiv of azo compound is needed and where sulfurous compounds acted only as intermediates.

During the past few years, the radical reactivity of alkoxyamines has attracted a particular interest for its use in nitroxide mediated polymerization[1–3] (NMP) and in organic synthesis.[4] Indeed, numerous studies have shown that the thermal reversible alkoxyamine dissociation is a highly efficient method for the clean generation of carbon-centered radicals.[5,6] For instance, this method has been successfully applied for metal-free cyclization[7,8] and intermolecular radical addition.[9,10] In the field of NMP, numerous works have proven that alkoxyamine-based initiators could exert an efficient control, on the radical polymerization of various monomers,[3,11] on chain end functionalization,[3,12,13] and on macromolecular architecture.[3,13,14] Recently, we showed[15,16] that owing to a very high dissociation rate constant, the alkoxyamine BlocBuilder (based on the 1-carboxy-1-methylethyl radical and the nitroxide *N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) or SG1) was up to now one of the most potent alkoxyamines reported in NMP. Moreover, due to the carboxylic acid group being allowed to work in aqueous media[17] and to perform coupling reactions,[18] this alkoxyamine has been chosen by ARKEMA to be synthesized in a large scale.[19] The industrial requirements for its commercialization involve developing a new synthetic approach taking into account special criteria such as large scale production, economic viability, environmental friendliness, etc.

SCHEME 1. SG1 and SG1-Based Alkoxyamines



Although many routes have been developed to synthesize alkoxyamines,[20] these compounds are mainly prepared through two pathways: via nucleophilic substitution reaction or via coupling reaction between alkyl and nitroxyl radicals. The nucleophilic substitution of an alkyl halide by the hydroxylamine anion is scarcely employed when SG1 nitroxide is used because of the relative instability of the corresponding hydroxyaminate anion.[21] The coupling of radicals is therefore the most developed and used approach. The coupling between alkyl and nitroxide has been extensively used, and all common methods to prepare alkyl radical have been employed: addition of a radical on an

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activated olefin,[22] abstraction of a labile hydrogen atom on a substrate by an alkoxyl radical,[22] carbanion oxidation,[23] use of Jacobsen catalyst,[24] thermal decomposition of azo compounds,[25] etc. A few years ago, Matyjaszewski applied the concept of atom transfer radical polymerization[26] (ATRP) to generate readily alkyl radicals. The technique called atom transfer radical addition[27] (ATRA) affords high yield and purity. Nevertheless, the use of transition-metal complexes such as copper complexes is a major drawback for the scale-up of this technique due to the production of toxic effluents.

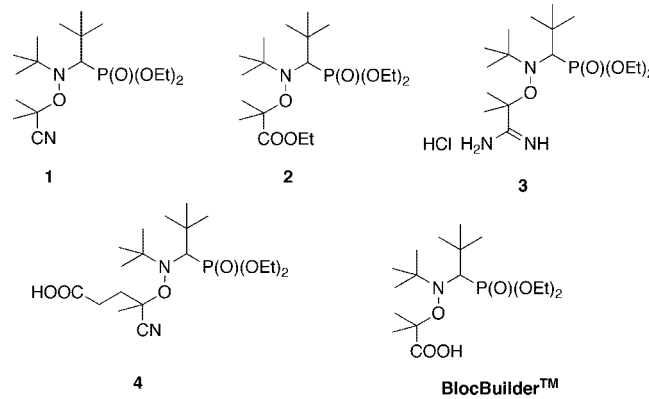
To overcome the above-mentioned drawback, this work presents a convenient metal-free synthesis with high yield and purity of tertiary SG1-based alkoxyamines, especially BlocBuilder. Since the tertiary SG1-based alkoxyamines exhibit particularly low dissociation temperature (cleavage temperature close to 30 °C),[28] the alkyl radicals have to be generated at room temperature or below. Except for the elegant work of Braslau et al.,[29] only photochemistry could allow working using these mild conditions. Usually, the alkoxyamines are stable under UV irradiation and to induce homolytic cleavage, sensitizers, or chromophore groups linked to the nitroxide moiety have to be used.[30]

The preparation of TEMPO-based alkoxyamines under photochemical conditions has been already reported. This method is based on benzylic H-atom abstraction by photoinduced alkoxyl radicals.[31] The extent of this technique for the synthesis of tertiary crowded SG1-based alkoxyamines was, however, not successful.[21] Two other photochemical routes have been developed, a first one by Scaiano et al.[31] in which the authors used the photoinduced cleavage of the C−Br bond to generate alkyl radicals. In a second one, Engel et al.[32] have reported the use of TEMPO as a spin-trap of alkyl radical generated by azo compounds in order to study the cage effect but in this case the alkoxyamines have not been isolated. In the same manner, Rizzardo et al.[1] have synthesized 4-cyano-4-(di-*tert*-butylaminyloxy)pentanol by photodecomposing the 4,4′-azobis(4-cyano-*n*-pentanol) in presence of di-*tert*-butyl nitroxide DBNO. The yield obtained in this experiment was quite low (40%).

Attracted by these results, we investigated the preparation of crowded tertiary SG1-based alkoxyamines **1**−**4** by irradiation of commercially available azo compounds (azobisisobutyronitrile AIBN, 4,4′-azobiscyanopentanoic acid ACPA, ethyl 2,2′-azobisisobutyrate DEAB, 2,2′-azobis(2-methylpropionamidine) dihydrochloride V50). The purpose of these experiments was not only to validate the photolytic synthetic route but also to prepare functional highly labile alkoxyamines.

TABLE 1. Synthesis of Alkoxyamines Using Photodecomposition of Azo Compounds

alkoxyamine	solvent	isolated yield (%)	[Azo]/[NO•] ratio
1	acetonitrile	93	2.8
2	THF	75	3.0
3	H_2O/EtOH	60	2.85
4	H_2O/EtOH	70	2.8



Irradiations were performed at 10 °C in a 100 mL double-jacketed reactor equipped at the top with a specific optic fiber (320−400 nm) linked to a Lumatec SuperLite SUV-DC-P lamp (200 W high-pressure mercury lamp, 6 $W \cdot cm^{-2}$ at the end of the fiber).

Following this procedure, we prepared (Table 1) the targeted alkoxyamines in moderate to high yields. However, it can be noted that such results needed a large excess of the azo compound ($[azo]_0/[SG1]_0$ ratio = 2.8−3.0). We investigated the effect of the reactants concentration (with a constant $[azo]_0/[SG1]_0$ ratio), and no influence was observed in the range of $1.0-1.0 \times 10^{-3}$ $mol \cdot L^{-1}$. These results confirmed that the recombination between alkyl radicals occurred only in the cage of solvent. Usually, the efficiency of azo compounds is close to 0.8, that is a ratio of 0.625 should be sufficient to have a quantitative yield. The high $[azo]_0/[SG1]_0$ ratio in our case (efficiency of 0.18) could be due to the nonoptimal geometry of irradiation, and mostly to the temperature in the medium. The cage effect is indeed known to drastically decrease the efficiency when decreasing temperature (0.9 to 0.45 when T decreases from 98 to 60 °C).[33] The increase of cage effect to rationalize our result seems awfully large. We therefore investigated the temperature dependence of the cage effect using the modeling developed by Russell and Buback[34] (see the Supporting Information for more details) and found good agreement (calculated 84%, experimental 82%) with our experimental results.

Nevertheless, it can be noticed that the reaction yield is always quantitative with respect to SG1 provided that there is enough radicals to react with the nitroxide. The conditions used and results are given in Table 1.

As the major side product, which was the dimer formed by the recombination between two alkyl radicals, was inert for the

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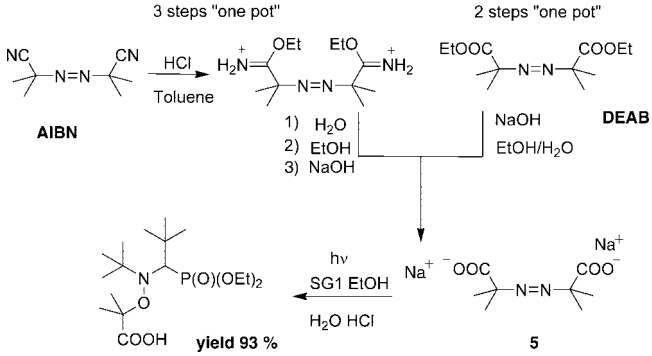
SCHEME 2. One-Pot Synthesis of the BlocBuilder Alkoxyamine



polymerization, no further purification was required. However, if necessary, the dimer can be easily removed by column chromatography. In addition, alkoxyamine **3** and **4** are very interesting because purification can be also made by selective precipitation in an appropriate solvent (dichloromethane for the alkoxyamine **3**, acidic water for alkoxyamine **4**).

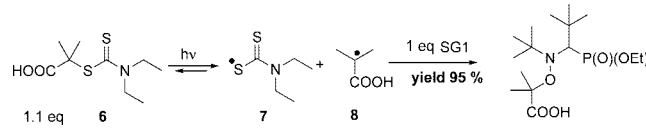
After showing that the photodecomposition of azo was a efficient route to prepare SG1-based alkoxyamines, we decided to use this strategy to prepare the alkoxyamine BlocBuilder. Since the azo precursor corresponding to this alkoxyamine is not commercially available, the 2,2′-azobisisobutyric acid sodium salt was prepared by hydrolysis of azoesters (i.e., DEAB). The neutralization of this product to prepare 2,2′-azobisisobutyric acid only conducted to a strong exothermic degradation. The sodium salt exhibits a higher stability: an aqueous DSC measurement showed no thermal dissociation before the thermal degradation which occurred at 210 °C (see the Supporting Information for details).

A two- or three-step (depending of the starting materials AIBN or DEAB, see Scheme 2), one-pot synthesis has been developed to produce the BlocBuilder.[35] The first step, which is not compulsory, was the preparation of azoesters from AIBN according to the procedure of Gritsenko.[36] During this step, an iminoether derivative was reacted with water and can be isolated or kept to be used for the next step. The second step consisted in the hydrolysis of the azoester in a H_2O/EtOH mixture by adding 3 equiv of NaOH. The nitroxide in solution in EtOH was added, and then the mixture was photolyzed until the the medium was bleached. The alkoxyamine BlocBuilder was then purified very easily by precipitation in cold acidic water (93% yield by the two-step process).

The photodecomposition of azo compounds enabled the preparation in one pot of the desired alkoxyamine with high yield and purity in a metal-free process. Nevertheless, from an industrial point of view, the inherent loss of radicals due to the cage effect during the decomposition of azo compound at low or moderate temperature involved to use a large excess of azo initiator compared to the nitroxide.

To develop an alternative but sustainable metal-free synthesis of BlocBuilder, we studied the photodecomposition of dithio compounds and in particular dithiocarbamate compounds, known to undergo homolytic cleavage of the sulfur−carbon bond under UV irradiation.[37] This property has been extensively

SCHEME 3. Synthesis of BlocBuilder by the Photodecomposition of Dithiocarbamate



used in polymerization where dithiocarbamate could act as iniferters and control the polymerization of styrene, acrylate, and methacrylate derivatives.[38] The spin-trapping technique has been used to understand the mechanism of decomposition[39] and the results showed that if the alkyl R group linked to the sulfur is stable enough, the dissociation occurred exclusively between the R and dithiocarbamyl group. In this system, we avoid the irreversible termination in the solvent cage, since the nondiffusion of the alkyl radical only led to the reformation of the dithiocarbamate.

The first step of this sequence (Scheme 3) consists of the synthesis of the corresponding dithiocarbamate, i.e., the *S*-(1-methyl-1-carboxyethyl)-*N,N*-diethyl dithiocarbamate **6**. Three different methods are available in the literature to prepare this compound: the nucleophilic substitution between the dithiocarbamate sodium salt and the 2-bromoisobutyric acid,[40] the radical addition of an azo compound and a disulfide[41] followed by an hydrolysis and the haloform reaction between acetone, chloroform, and the dithiocarbamate sodium salt.[42]

These three methods have been used (see the Supporting Information), and we chose the nucleophilic substitution for the easily purification process regardless of the moderate yield.

The photolysis of **6** in the presence of SG1 was carried out in ethanol. We observed by ^{31}P NMR only the peak of the targeted alkoxyamine. It can be noticed that the side product issued from the cross recombination between SG1 and the dithiocarbamyl radical **7** was not detected. We investigated the effect of the $[\text{dithiocarbamate}]_0/[\text{nitroxide}]_0$ ratio and we observed that a ratio of 1.1 is sufficient to obtain a quantitative yield in BlocBuilder. This result shows that no alkyl self-termination occurred in this system compared to the photolysis of azo compounds. This procedure was extended to secondary dithiocarbamate, i.e., *S*-(1-carboxyethyl)-*N,N*-diethyl dithiocarbamate with success even if the alkoxyamine has not been isolated (^{31}P NMR spectrum, see the Supporting Information for details).

The purification procedure in this method is as follows: after the aqueous acidic precipitation, we obtained a mixture of BlocBuilder and tetraethylthiuram disulfide (TEDS) coming from the dimerization of dithiocarbamyl radicals. In order to remove the disulfide, a NaOH solution was added to the medium until pH 10 to solubilize the alkoxyamine, and then the mixture was filtrated off to remove the side product as a yellow powder (more than 80% recovery). A further acidification/precipitation step enabled us to obtain the desired alkoxyamine (95% yield) as a white powder after filtration.[43] Elemental analysis showed

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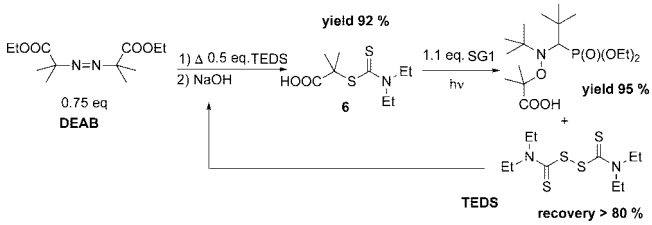
SCHEME 4. New Synthetic Procedure Used To Prepare the BlocBuilder



no trace of sulfur in the final product. One extra advantage of this method lies on the recovery of the tetraethylthiuram disulfide. This product could indeed be recycled as a value-added product but could also be one of the reactants used to prepare the dithiocarbamate **6** by the radical addition method (92% yield, see the Supporting Information).[41] From an economic point of view, we developed an experimental procedure to prepare the BlocBuilder using the recycled disulfide and combining the photodecomposition of DEAB and dithiocarbamate **6** (Scheme 4).

As the intermediate **6** is thermally stable, this procedure allowed us to avoid the low efficiency of azo compounds (thermal or photo) decomposition at low temperature. Indeed, the first step has been carried out in refluxing ethyl acetate. Interestingly, the dithiocarbamate acts only as an intermediate and does not appear in the overall reaction scheme.

In conclusion, two alternative routes to the ATRA method for the synthesis of alkoxyamines have been developed in order to avoid any metal in both products and effluents. The two methods are based on the photodecomposition of either azo compounds or dithiocarbamates and led to quantitative yields with respect to the nitroxide. The first method was easier to handle but needed an excess of reactant. The second one required only a stoichiometric amount of reactant but used sulfurous compounds. The two methods could be combined to prepare highly labile alkoxyamines with only a slight excess of reactant and sulfurous compounds as intermediates.

Experimental Section

Ethyl 2-Methyl-2-[*N*-*tert*-butyl-*N*-(1-diethoxyphosphoryl-2,2-dimethylpropyl)aminoxy]propionoate (DEAB-SG1) Alkoxyamine 2. A N_2-bubbled solution of ethyl 2,2′-azobisisobutyrate DEAB (6.5 g, 24 mmol) and SG1 (2.8 g, 8.1 mmol) in THF (100 mL) was irradiated in a 100 mL double-jacketed reactor equipped at the top with a specific optic fiber (320−400 nm) linked to a Lumatec SuperLite SUV-DC-P lamp (200 W high-pressure mercury lamp, 6 W·cm^{-2} at the end of the fiber) at 365 nm for 4.5 h at 10 °C. The solvent was removed to yield a pale yellow oil, which was purified by silica gel column chromatography using pentane/diethyl ether 1:1 as eluent. The product (2.48 g, 6.1 mmol, yield 75%) was obtained as a pale yellow oil. ^{31}P NMR ($CDCl_3$, 121.49 MHz): δ 25.48 (s). ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ 1.00 (s, 9 H); 1.09 (s, 9 H); 1.21 (m, 9 H); 1.50 (s, 3 H); 1.60 (s, 3 H); 3.13 (d, $^1J_{H-P}$ = 25.88 Hz, 1 H); 3.90−4.10 (m, 4 H); 4.26 (t, $^1J_{H-H}$ = 6.8 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 75.47 MHz): δ 13.6 (CH_3); 15.7 ($^3J_{C-P}$ = 6.59 Hz)-16.1 ($^3J_{C-P}$ = 6.04 Hz) (CH_3); 22.0−27.6 (CH_3); 27.7 (CH_3); 29.5 ($^3J_{C-P}$ = 5.49 Hz) (CH_3); 35.5 ($^2J_{C-P}$ = 6.04 Hz) (C_q); 58.0 ($^2J_{C-P}$ = 7.69 Hz) (CH_2); 60.2 (CH_2); 61.2 ($^2J_{C-P}$ = 6.04 Hz) (CH_2); 61.7 (C_q); 68.7 ($^1J_{C-P}$ = 137.22 Hz) (CH); 83.2 (C_q); 174.6 (C_q). ESI-HRMS: calcd for $C_{19}H_{40}NO_6P$ [M + H]$^+$ 410.2666, found 410.2663.

2-Methyl-2-[*N*-*tert*-butyl-*N*-(1-diethoxyphosphoryl-2,2-dimethylpropyl)aminoxy]propionic Acid (BlocBuilder) Alkoxyamine. A N_2-bubbled solution of *S*-(1-methyl-1-carboxyethyl)-*N,N*-diethyl dithiocarbamate **6** (4.8 g, 2.0 × 10^{-2} mol) and SG1 (6.28 g, 1.82 × 10^{-2} mol) in 350 mL of ethanol was irradiated at 365 nm using the previously described optic fiber for 4.5 h at 10 °C. After the solution bleached, the resulting mixture was precipitated in acid−water (200 mL + 3 mL of 33% HCl solution), filtered, and dried under vacuum. This pale yellow powder was then diluted in 200 mL of water at pH 9. The yellow precipitate is removed by filtration (TEDS, > 80% recovery), and the filtrate was acidified by addition of HCl. After filtration and drying under vacuum, the product (6.58 g, 17.2 mmol, yield 95%) was obtained as a white powder. Mp: 122−125 °C. ^{31}P NMR ($CDCl_3$, 121.49 MHz): δ 27.63 (s). ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ 1.13 (s, 9 H); 1.22 (s, 9 H); 1.30 (t, $^1J_{H-H}$ = 7 Hz, 6 H); 1.58 (s, 3 H); 1.76 (s, 3 H); 3.34 (d, $^1J_{H-P}$ = 27.22 Hz, 1 H); 3.90−4.30 (m, 4 H). ^{13}C NMR ($CDCl_3$, 75,47 MHz): δ 6.1−16.5 (CH_3); 24.1 (CH_3); 28.8 (CH_3); 29.8 (CH_3); 36.1 (CH); 60.2−60.4 (CH_2); 63.3 (C_q); 69.0−70.8 (CH); 84.9 (C_q); 176.8 (C_q). Anal. Calcd for $C_{17}H_{36}O_6N$: C, 53.53; H, 9.51; N, 3.67. Found: C, 53.78; H, 9.57; N, 3.69.

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Supporting Information Available: Characterization of the alkoxyamines **1**, **3**, **4**, BlocBuilder, and the intermediates used such as dithiocarbamate **6** and 2,2′-azobisisobutyric acid sodium salt **5**. Copies of the NMR spectra for new products. Cage effect modeling. This material is available free of charge via the Internet at http://pubs.acs.org.

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