SATURATED AMINE FLUORESCENCE QUENCHING IN NON-POLAR SOLUTION BY VARIOUS ORGANIC MOLECULES

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Summary

The fluorescence quenching of a prototype saturated amine N,N-diethyl-methylamine (DEMA) was examined in n-hexane solution at 25 °C by measuring the quencher concentration dependence of the DEMA fluorescence lifetime. The quenchers studied included N,N-dimethylformamide (DMF), acetic acid, ethyl acetate, acetonitrile, 2-butyne, dimethyl sulfoxide (DMSO), tetramethylethylene, perfluorocyclohexane, n-propyl bromide and oxygen. In all cases, within the respective quencher concentration ranges studied, no evidence of exciplex fluorescence was obtained; moreover, with the exception of oxygen, linear Stern–Volmer kinetics were observed. DEMA fluorescence quenching by these molecules is generally discussed in terms of possible energy transfer and electron (or charge) transfer mechanisms, although hydrogen bonding is considered for the acetic acid system. It was found that, even for those molecules for which energy transfer is highly improbable, efficient quenching is observed if the quencher molecule is polar (*e.g.* DMF, acetonitrile, DMSO and n-propyl bromide). In general, non-polar molecules having high-lying S_1 states are inefficient quenchers, perfluorocyclohexane being an exception. Finally, quenching by molecular oxygen and by a secondary amine is mentioned. Complications arising from the ground state association between the amine and oxygen are discussed. The intermolecular quenching by a secondary amine is used to rationalize the very weak emissivity of N-methylpiperazine.

1. Introduction

Saturated tertiary amines (*e.g.* triethylamine) are known to have very large fluorescence quantum efficiencies ϕ_f, both in the vapor phase [1] where ϕ_f is nearly unity and in non-polar (n-hexane) solution [2] where ϕ_f is 0.69. Because of the high emissivity of the tertiary saturated amines and the potential use of this fundamental chromophore as a fluorescent probe for analytical and biological applications, it is important to know the conditions under which the amines retain their high fluorescence efficiency. The only

other conventional solvent media in which the saturated tertiary amines retain reasonably high fluorescence quantum efficiencies are saturated ethers (diethyl ether, tetrahydrofuran (THF) etc.). As first reported by Muto *et al.* [3] and more recently by Vanderauweraer *et al.* [4], the fluorescence spectra of the amines are considerably red shifted in the ether solvents relative to the saturated hydrocarbon solvents. For example, the fluorescence spectrum of diethylmethylamine (DEMA) in *n*-hexane has a maximum at a wavelength of 292 nm; in diethyl ether and THF solution the maxima appear at 308 nm and 340 nm respectively. In addition to these spectral changes the fluorescence quantum efficiency decreases while the lifetime increases. These phenomena were recently discussed by Halpern [5] who considered the possible role of an amine–ether exciplex as the origin of these observations. The conclusion, based on the fluorescence properties of model aminoethers, was that a 1:1 exciplex could not be invoked and that either higher order photoassociation takes place between the photoexcited amine and the solvent molecules or the ether solvents, having larger dielectric constants relative to the hydrocarbons, stabilize the Rydberg (or Rydberg-like) lowest excited state of the amine [3, 6].

In an attempt to identify other common solvent media in which the amines were appreciably fluorescent, the quenching efficiencies of many different organic molecules were measured. DEMA was used as a prototypal tertiary amine and *n*-hexane was chosen as the working solvent medium. The results show that the (lowest) excited state of DEMA is quite susceptible to quenching reactions with a wide variety of organic molecules, and it appears that accordingly a number of different fluorescence quenching mechanisms may operate (either separately or in combination) in depleting the DEMA excited state.

2. Results and discussion

The fluorescence quenching rate constants were determined by measuring the fluorescent lifetime of a 3×10^{-4} M solution of DEMA in *n*-hexane (measured at a wavelength of 290 nm) as a function of the quencher concentration. The excitation wavelength varied between 230 and 250 nm depending on the nature of the quencher. In all cases except one (ethanol) linear Stern–Volmer kinetics were followed; thus the quenching constant k_Q was obtained from the simple relation

$$1/\tau_f = k_A^0 + k_Q[Q] \qquad (1)$$

where k_A^0 is the fluorescent lifetime of the DEMA solution in the absence of quencher and [Q] is the molar concentration of quencher. In all cases reported here the DEMA fluorescence decay curves were observed to follow simple (one component) exponential decay (for at least 2 - 3 decades of fluorescence intensity). In addition, plots of eqn. (1) for the various quenchers provided, within experimental error, the same intercept ($k_A^0 =$

3.8×10^7 s^{-1}). Moreover, no evidence of exciplex emission was obtained with the quenchers studied; thus, up to the limits of the quencher concentrations used in the respective studies, there were no discernible changes in the DEMA fluorescence spectrum. The kinetic results are summarized in Table 1 which also contains certain relevant properties of the quenchers such as the ionization potential (IP), the lowest singlet state energy $E(S_1)$ and the dipole moment μ. The data contained in Table 1 are arranged in groups of quenchers having similar structures. The first group contains carboxyl compounds: an amide (N,N-dimethylformamide (DMF)), a carboxylic acid (acetic acid) and a carboxylic acid ester (ethyl acetate). Other carbonyl compounds such as the aliphatic ketones and aldehydes are not included in this study because the ketones have already been shown to quench saturated tertiary amine fluorescence via (at least) energy transfer with high efficiency [7, 8]. To wit, sensitized ketone fluorescence was observed (both intramolecularly and intermolecularly) consequent to photoexcitation of the amine. It is straightforward to rationalize the high efficiency of this process on the basis of the fact that the lowest excited $^1(n,\pi^*)$ state of the ketones lies lower than that of the amine; in fact the amine fluorescence is nearly resonant with the $^1(n,\pi^*)$ absorption of ketones [8]. The same spectroscopic situation also holds for the aldehydes, although these compounds have not been examined in this respect.

TABLE 1

The quenchers used in this study along with their dipole moments, S_1-S_0 energy levels, IPs and the measured quenching constants

Quencher	μ(debye)	$E(S_1)$ ($\times 10^3$ cm^{-1})	IP (eV)	k_Q[a] ($\times 10^{10}$ M^{-1} s^{-1})
N,N-Dimethyl- formamide	3.86	41 - 42	9.24	4.9
Acetic acid	1.74	(42)	10.87	1.8
Ethyl acetate	1.78	(42)	10.36	0.65
Acetonitrile	3.94	55	12.2	2.4
2-Butyne	(0)	55	—	0.014
Dimethyl sulfoxide	3.96	—	—	2.4
Acetone	2.9	(31)	9.70	3.2
Tetramethylethylene	(0)	43	—	0.001
Benzene	(0)	37.1	9.25	2.1
Perfluorocyclohexane	(0)	67.2	12.75	0.13
n-Propyl bromide	2.0	56.	10.3	2.9

[a]Measured at 25 °C from the slope of $1/\tau_f$ vs. [Q] (see text).

The role (or roles) of the three carbonyl compounds studied in the fluorescence quenching of DEMA is considered in terms of the following simple mechanisms.

(1) The first mechanism is that of energy transfer. Unlike the situation with the aliphatic ketones, in which sensitized fluorescence was observed, these molecules have fluorescence efficiencies which are too low to enable such a probe to be made. (Fluorescence has not been reported for these compounds.) On purely energetic grounds, however, the question of (singlet–singlet (S–S)) energy transfer can be discussed. It is interesting to note that the quenchers in this class have nearly equivalent S_1 energies, namely $(41 - 42) \times 10^3$ cm^{-1} (adiabatic or 0–0 energies) (these values are estimated from the absorption spectra [9]) and about $(45 - 47) \times 10^3$ cm^{-1} (vertical) (this is assigned as the (n_0, π^*) transition or W band; see for example ref. 10). The S_1 energy levels of DEMA can only be estimated from available spectroscopic data for other amines and are about 39×10^3 cm^{-1} (adiabatic) (based on the observed vapor phase 0–0 transition for 1-azabicyclo[2.2.2]octane [11]) and about 44×10^3 cm^{-1} (vertical) (based on the observed vapor phase transition of trimethylamine). Thus, if S–S energy transfer is considered as a potential quenching mode an (endothermic) gap of about 2×10^3 cm^{-1} is involved and, assuming a simple collisional model of energy transfer, an energy transfer rate constant of about 1×10^9 M^{-1} s^{-1} is calculated (based on a value of 3.3×10^{10} M^{-1} s^{-1} at 25 °C for the diffusion-limited rate constant in n-hexane; see ref. 12). This value is nearly an order of magnitude smaller than the quenching rate constant measured for ethyl acetate, the weakest of the three quenchers in this class. Thus, based on these simple considerations we would not expect S–S energy transfer to play an important role in the fluorescence quenching of saturated amines.

(2) The second mechanism is that of proton transfer. Because of the relatively high efficiency with which acetic acid quenches the DEMA fluorescence (*vis-à-vis* ethyl acetate — see Table 1), we would tend to consider proton transfer as a quenching route. While direct proton transfer cannot be rigorously discounted at this time, it seems doubtful that this process is important here. Firstly, the solvent medium (n-hexane) has a low dielectric constant and is incapable of solvating the ions (or ion pair) produced subsequent to proton transfer and thus the energies of the ions (or the ion pair) would lie too high to be accessible as a quenching channel. Secondly, because of the tendency of the acetic acid molecules to dimerize ($K = 2 \times 10^3$ in carbon tetrachloride [13]), a substantial fraction of the acetic acid exists as dimers under the experimental conditions employed here. Hence the opening up of the cyclic dimer to produce a Brønsted acid site would represent another energy barrier pursuant to the eventual proton transfer by the acyclic dimer.

(3) The third mechanism is that of hydrogen bonding. With respect to the acetic acid system this is a plausible quenching process, especially because of the non-polarity of the medium. Indeed, it is known that acetic acid and its dimer both undergo hydrogen bonding with (ground state) amines such as

triethylamine (TEA). Recently, Nakanishi *et al.* [14] have examined the acetic acid–TEA system, both in *n*-heptane and in the vapor phase using UV spectroscopy to determine the equilibrium constants of the hydrogen-bonded complexes. They report that in *n*-heptane, in which the dimer predominates at the acetic acid concentrations used, the equilibrium constant for the hydrogen bonding of the opened (acyclic) dimer with TEA is about 117, while in the vapor phase, where the monomer predominates, the equilibrium constant is about 2.8×10^4. With respect to the fluorescence quenching experiments, however, the presence of excited hydrogen-bonded complexes of dimer (or monomer) with the amine can in all likelihood be discounted. This stems from the fact that, as shown by Nakanishi *et al.* [14], the absorption spectrum of the amine (in that case TEA) is significantly blue shifted as a consequence of the hydrogen bonding with the acetic acid. Hence, it can be presumed that much of the complexed DEMA is not photoexcited in these experiments (where λ_{exc} is 230 nm).

The monomer–dimer equilibrium of acetic acid must be taken into account, however, in considering the actual nature of the quenching species present. The equilibrium constant for this dimerization is about 2×10^3 and the (formal) concentration range used in the quenching experiments is 1.0×10^{-3} - 1.0×10^{-2} M. Thus the fraction of acetic acid dimer which is expected to be present is from 0.5 to 0.8 over this concentration range. Notwithstanding the changing composition (the entire system also consists of the amine–monomer and the amine–dimer complexes [14]) of the quenching species with respect to the formal acetic acid concentration, a plot of $1/\tau_f$ *versus* the formal acetic acid concentration reveals a reasonably straight line for DEMA having a slope of 1.8×10^{10} M^{-1} s^{-1}. No curvature can be detected in the Stern–Volmer plot for an acetic acid concentration ranging between 1×10^{-3} and 1×10^{-2} M.

Thus the acetic acid system quenches the DEMA fluorescence at about the diffusion-controlled rate in *n*-hexane. The lack of curvature in the Stern–Volmer plot (which would be expected if it is presumed that the dimer would have a smaller quenching efficiency relative to the monomer) can be rationalized by assuming that the potent quenching species, presumably the acetic acid monomer, is engaged in fast multiple equilibria with the other members of the system: the acetic acid dimer, the monomer–amine ground state complex and the dimer–amine ground state complex. Thus the rapid depletion of the monomer via DEMA fluorescence quenching would result in fast monomer regeneration from the other monomer-containing species present in solution.

(4) The fourth mechanism is that of electron transfer. Because of the fundamentally electron-donating nature of the amines in the ground state, and especially because of the nature of photoexcitation in these compounds (*i.e.* in producing Rydberg or Rydberg-like states), we would certainly anticipate electron transfer from the photoexcited amine to be an important and general pathway for deactivation. Technically, we should consider (or refer to this quenching process as) charge transfer interaction because in the non-

polar medium used in these studies the states appropriate to a full charge transfer would lie too high in energy to be expected to play an important role in the quenching process; see ref. 15. The carbonyl compounds in this class of quenchers are known to undergo electrochemical reduction processes. Thus we may envisage the following prototype reaction for the quenching of DEMA fluorescence:

The decrease in the quenching efficiency of ethyl acetate *vis-à-vis* the acetic acid system may signify that the type of electron transfer reaction depicted here is operative in this class of compounds but at a lower overall efficiency because of the elimination of the hydrogen-bonding channel.

By far the most efficient quencher in this group is DMF for which k_Q is measured to be 4.9×10^{10} M^{-1} s^{-1}. This value is roughly twice that expected for a simple diffusion-controlled process and may be a consequence of the rather large dipole moment associated with DMF (see Table 1). Thus, a somewhat longer range electron transfer step may be envisaged in which an electron from the photoexcited DEMA is "harpooned" by the electropositive end of the DMF dipole (*i.e.* the carbon-atom-bearing portion of the molecule). (For a discussion of long-range effects in charge transfer processes see ref. 16.)

In the next group of quenchers we encounter two triple-bonded species: acetonitrile and 2-butyne. These quenchers obviously have disparate efficiencies and this may be attributed to their respective polar and non-polar properties. The high efficiency of acetonitrile is reminiscent of that of DMF, another polar molecule for which energy transfer appears to be an inaccessible quenching route. A valence shell band lies at 60×10^3 cm^{-1} and a Rydberg band is assigned at 77.374×10^3 cm^{-1} [17].

The low quenching of the alkyne may be attributed both to its non-polarity and to its relatively high (adiabatic) singlet state (see Table 1). In fact, S–S energy transfer from the photoexcited amine to the quencher involves a substantial endothermic gap (about 15×10^3 cm^{-1}) and, assuming a simple S–S transfer mechanism, this mode can be reasonably discounted. (A low quenching efficiency may imply, of course, that a weakly bound (highly reversible) exciplex between the amine and the quencher may be

formed. By necessity, such an exciplex must be (1) highly dissociative and/or (2) very unstable with respect to the products or the original ground state species.) It is significant to point out in this regard that, for both bis-1,4-(N,N-dimethylamino)-2-butyne and 1-dimethylamino-2-butyne, no fluorescence could be detected $(\phi_f < 10^{-5})$. The absorption spectra of these compounds are consistent with amine-like transitions near 200 nm. These observations imply that (1) the presence of the triple bond causes intra-molecular amine fluorescence quenching or (2) there is a mixed transition (i.e. n,π^*) which results in (presumably) internal conversion.

In the group of quenchers containing double bonds we encounter di-methyl sulfoxide (DMSO), acetone and tetramethylethylene. The very high efficiency of acetone can be viewed, as mentioned earlier, in the context of exothermic energy transfer. The (n,π^*) singlet state of acetone, which lies at about 31×10^3 cm^{-1} (compared with about 39×10^3 cm^{-1} for the amine), is nearly on resonance with the Stokes-shifted amine fluorescence. Both intermolecular and intramolecular energy transfer from amines to ketones have previously been described [7, 8].

DMSO also quenches DEMA fluorescence with a high efficiency in n-hexane solution. While it seems plausible that the relatively high polarity of the molecule is an important factor in this process, the role of S–S energy transfer can be reasonably neglected. The excited electronic states of DMSO have apparently not been fully identified or assigned to date, but Clark and Simpson [18] imply that there might be (vertical) states at 45×10^3 and 49×10^3 cm^{-1}. If this were the case, energy transfer from DEMA to DMSO would indeed be expected to be relatively unimportant (with an efficiency of about $10^{-4} - 10^{-5}$).

Tetramethylethylene is a non-polar molecule which has a relatively high-lying (lowest) excited singlet state. This state is at about 43×10^3 cm^{-1} (the transition is assigned as a $\pi \rightarrow 3s$ Rydberg transition [19]). Based on a simple collisional model of energy transfer, a rate constant of about 4×10^7 M^{-1} s^{-1} is estimated. Assuming that energy transfer is an operative mecha-nism in the quenching process, the fact that the observed k_Q value is some-what smaller than this estimate may be a consequence of the large geometry change which the olefins (and presumably also tetramethylethylene) undergo consequent to electronic excitation [20]. The earlier remarks about exciplex formation may also hold here.

Benzene, the only aromatic molecule contained in Table 1, is an effi-cient quencher of DEMA fluorescence. (Higher members of the series of aromatic compounds are not included because their role as quenchers of saturated amine fluorescence cannot be evaluated in view of their strong competitive optical absorptivities.) The mechanism of this reaction has been shown by Halpern [5] to be S–S energy transfer and may involve an exciplex intermediate [4, 21]. (Although non-exponential fluorescence decay curves were observed in the amine–benzene system in n-hexane solution, this was shown to be a result of overlapping DEMA and benzene fluorescence in the wavelength region studied.) Thus sensitized benzene fluorescence is observed consequent to DEMA photoexcitation.

Two halogenated hydrocarbons were studied as DEMA quenchers: perfluorocyclohexane (PFCH) and *n*-propyl bromide. Not surprisingly the alkyl bromide quenches the DEMA fluorescence at the diffusion-controlled rate. It can be assumed that the mode of quenching in this case is electron (or charge) transfer from the photoexcited amine to the *n*-propyl bromide on the basis of the electronegativity of the bromine atom. Complications arising from the ground state association between DEMA and *n*-propyl bromide are probably unimportant because of the weakness of the interaction and the concentrations of the species used in the quenching experiments (see ref. 22). The possible role of the bromine atom in the quencher molecule acting as a heavy atom perturber in inducing intersystem crossing in the amine is interesting to consider. The location of the triplet state(s) in the aliphatic amines is unknown, although the lowest triplet state in ammonia is thought to lie about 4×10^3 cm^{-1} below that of the (n,3s) singlet state [23]. Based on low temperature emission studies, however, Muto *et al.* [3] assigned phosphorescence from 1,4-diazabicyclo-[2.2.2]-octane at about 2×10^3 cm^{-1} lower than the fluorescence spectrum.

The moderately high efficiency of DEMA fluorescence quenching by PFCH is surprising in view of the initial presumption we might have that this quencher would have acted as an "inert" solvent toward the photoexcited amine. This observation is consistent, however, with the recent report by Alford *et al.* [24] that TEA fluorescence is quenched at the diffusion-controlled rate by perfluoromethylcyclohexane in cyclohexane solution. The considerably lower quenching efficiency of PFCH reported here (about 0.1 of the diffusion-controlled rate) might be a consequence of the slightly higher ionization potential of the amine used, a difference in the intrinsic efficiency of the particular fluorocarbon used, or the somewhat lower amine concentration employed in this study. It seems likely, nevertheless, in view of this discussion, that the quenching mode involves electron (or charge) transfer between the photoexcited amine and the fluorocarbon.

Finally, we turn to two quenchers not listed in Table 1, namely piperidine (a secondary amine) and molecular oxygen. Piperidine was studied because of the interesting observation that, while the ditertiary amine N,N'-dimethylpiperazine (NNDMP) is strongly emissive in *n*-hexane solution ($\phi_f = 0.4$) and has a considerably red-shifted emission spectrum ($\lambda_{max} = 315$ nm), the related diamine N-methylpiperazine (NMPZ) is very weakly emissive ($\phi_f = 0.003$) [25]. To probe further the nature of this phenomenon, the intermolecular fluorescence quenching of N-methylpiperidine (NMP) by piperidine was studied in *n*-hexane solution. The results obtained from the linear dynamic Stern–Volmer plot over a piperidine concentration range from about 1×10^{-3} to about 8×10^{-3} provide a k_Q value of 2.1×10^{10} M^{-1} s^{-1}. Thus, this quenching takes place at (or nearly at) the diffusion-limited rate.

The mechanism of this quenching is not clear. It can be presumed that the S_1–S_0 level of piperidine is higher than that of NMP on the basis of what is known about the spectroscopy of other secondary amines *vis-à-vis*

tertiary amines [26]. Also, it is known that the secondary (and primary) amines are significantly less emissive than the tertiary amines (by perhaps five orders of magnitude) [27]. Thus, even if energy transfer to piperidine were to be affected by NMP, sensitized fluorescence by piperidine would not be observed. Another interesting hypothesis regarding the quenching process is that the N-hydrogen atom on piperidine is hydrogen bonded to the excited NMP molecule (NMP*) or that it is abstracted by NMP*. The intramolecular quenching observed in NMPZ implies that a reorganization (perhaps to a boat-like conformation) takes place in the excited state which facilitates the NMP* - - - H—N interaction. (See ref. 1 for a discussion of some properties of NNDMP and NMP in the vapor phase.)

The oxygen quenching of saturated amine fluorescence is an anticipated phenomenon and we report here the preliminary results of such an investigation [28]. In these experiments the TEA fluorescence lifetime and quantum intensities were measured in nitrogen-purged n-hexane solution and in air-equilibrated and oxygen-saturated solutions. The oxygen concentration dependence of both the amine fluorescence lifetime and the relative quantum intensity indicate that the quenching process is complex. For example, the lifetimes (ns) and relative intensities of the nitrogen-purged, air-equilibrated and oxygen-saturated TEA solutions (1.5×10^{-4} M in n-hexane at 20 °C) are 30.0 and 1.00, 6.2 and 0.13, and about 0.6 and 0.010 respectively. Using these three data it can be seen that both the dynamic and the static Stern—Volmer plots curve sharply upward. Using a value of the concentration of dissolved oxygen in n-hexane of 3.09×10^{-3} M, the data imply a k_Q value (i.e. $\Delta(1/\tau_f)/\Delta[O_2]$) of 4.1×10^{10} M^{-1} s^{-1}, which is consistent with a diffusion-controlled process involving oxygen [29, 30]. The sharp upward curvature in the Stern—Volmer plots may be a consequence of static quenching, which is anticipated at higher oxygen concentrations, arising from the well-known oxygen—amine "contact" donor—acceptor complex [31]. Indeed, while the optical densities of the nitrogen-purged and the air-equilibrated TEA solutions (measured at a wavelength of 230 nm) were identical within experimental error, the optical density increased by a factor of about 2 in the oxygen-saturated solution, and this is indicative of the oxygen—amine ground state association. The complications which are thus placed on the oxygen quenching of amines await further investigation for the ultimate clarification of this interaction.

3. Conclusions

The fluorescence of saturated tertiary amines, while very intense in saturated hydrocarbon solutions (and in the vapor phase), is susceptible to quenching by a wide variety of molecules. The only other common solvent media in which the amines retain their emissivity are saturated ethers, although the fluorescence efficiency is diminished and the spectrum is considerably red shifted. It appears that fluorescence quenching of the amines

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can be effected by several different mechanisms, perhaps simultaneously under certain circumstances. These modes include energy transfer, electron (or charge) transfer and hydrogen bonding. Fluorescence quenching via exciplex formation is also an accompanying process for certain molecules such as benzene. In this study, however, no evidence of exciplex emission was obtained. A general empirical conclusion reached by this investigation is that the amines are less strongly quenched by those molecules which (1) are non-polar, (2) do not possess low-lying S_1 states (less than about 45×10^3 cm^{-1}) and (3) are incapable of undergoing hydrogen bonding with the amine.

4. Experimental section

The fluorescence lifetime measurements were carried out using a time-correlated single-photon apparatus previously described [32]. Decay curves usually spanned 2 - 3 decades of the amine fluorescence intensity and were analyzed by a convolute-and-compare method in which the criterion of acceptability is the minimization of the residuals between the convoluted and observed decay functions.

n-Hexane (distilled in glass) was dried over CaH_2 prior to use. DEMA (Pfaltz and Bauer Inc.) was distilled (boiling point 66 °C) over $LiAlH_4$ and stored under anhydrous conditions. Ethyl acetate (Baker) was washed with 5% aqueous Na_2CO_3 solution followed by saturated $CaCl_2$ solution, It was dried over anhydrous K_2CO_3 and was finally distilled over P_2O_5. Acetic acid (glacial) was refluxed with 5% $KMnO_4$ and was then distilled from P_2O_5. Acetonitrile was predried over CaH_2 and was distilled from P_2O_5 such that the middle third of the distillate was retained. DMSO (Aldrich) was predried using CaH_2 and was subsequently distilled under reduced pressure. DMF (Matheson, Coleman and Bell spectroquality) was stirred with KOH and distilled from CaO. PFCH (Peninsular Research Inc.) was used without further purification. 1-Dimethylamine-2-propyne (Aldrich) was distilled under reduced pressure before use.

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