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Photostimulated Reduction of Nitriles by SmI_2

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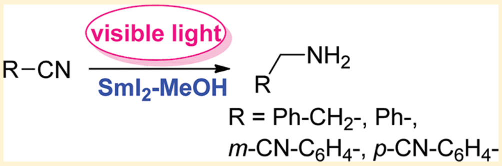
S Supporting Information

ABSTRACT: Despite their high electron-withdrawing strength, nitriles are not good electron acceptors and therefore are hard to reduce. In this work, using photostimulation in the visible region, we examined the reactivity of aliphatic and aromatic, mono- and dicyano compounds in reaction with SmI_2. A proton donor that complexes efficiently with SmI_2 must be used. Maximum yield was obtained at ca.0.2 M MeOH. Aromatic nitriles were more reactive than aliphatic nitriles, which exhibited negligible yields. Phenylacetonitrile presents an intermediate reactivity. The mechanism of the reaction involves coordination of the SmI_2 to the lone pair of the nitrile nitrogen followed by an inner sphere electron transfer. Surprisingly, *m*-dicyanobenzene was less reactive than the monocyano derivative benzonitrile. This was traced to the lower ability of the dicyano compound to coordinate to the SmI_2 due to, as was shown by quantum mechanical calculations, its lone pair having an energy significantly lower than that of benzonitrile. It is noteworthy that at the SmI_2 initial concentration used (0.04M), light penetrates only the 0.4 mm outer layer of the reaction mixture. Therefore the photostimulation effect observed was due to irradiation of only 4% of the total reaction volume, implying that under optimal conditions the effect should be 25 times larger.

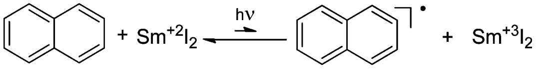


INTRODUCTION

Samarium iodide is one of the most commonly used single electron transfer reagents.[1] Its reduction potential in THF was measured to be 1.33 eV.[2] The classical way to increase its reduction potential is by using HMPA as an additive.[3] A less exploited method, although very efficient, is photostimulation using visible light.[4] A detailed mechanism by which excitation enhances the electron transfer was described by Flowers et al.[4c] We have found that light stimulation is so effective that reactions carried out under laboratory fluorescent light were much enhanced compared to those carried out in the dark. Traditionally, photostimulated electron transfer reactions from SmI_2 were limited to dissociative electron transfer reactions,[4] namely, the electron transfer was the rate-determining step and the radical anion, if at all formed, had a very short lifetime before undergoing mesolytic cleavage as shown in eq 1.

$$R{-}X \xrightarrow[h\nu]{SmI_2} R\bullet + X^{\ominus} \qquad (1)$$

In one of our previous papers we broadened the scope of photostimulated electron transfer reactions from dissociative electron transfer reactions to the reduction of double and triple bonds that under normal conditions were not amenable to photostimulation.[5] This broadening was facilitated by the fact that methanol complexes efficiently to SmI_2. Thus, taking the case of naphthalene, as an example (eq 2), once the electron has been transferred to it from the SmI_2, the Sm^{3+} in the ion pair is most probably in its ground state.



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The fact that naphthalene cannot be reduced by SmI_2 in the dark implies that the electron transfer reaction is highly endothermic, and therefore the reaction in the opposite direction, that is, back electron transfer from the naphthalene radical anion to Sm^{3+} is highly exothermic and will take place very fast. The short lifetime of the naphthalene radical anion in this example does not allow a bimolecular protonation by a proton donor from the bulk. Yet, when the proton donor (MeOH) is associated with the Sm^{3+} in the ion pair, protonation becomes unimolecular, enabling an efficient trapping of the radical anion before the reversal of the electron transfer process. In the present paper, we report on the photostimulated reduction of various nitriles and the approximate location of the borderline between “go no go” photostimulated reactions within the nitrile family.

RESULTS

We have studied the reduction of the aromatic and aliphatic, mono- and dicyano compounds depicted in Figure 1.

All reactions were carried out in THF under nitrogen. The first compound to be studied was benzonitrile (**BN**). Trifluoroethanol (TFE) differs in several ways from MeOH and may affect the reactions with SmI_2 in various ways.[6] However, consistent with the mechanism mentioned in the Introduction and because TFE does not complex with SmI_2, the reactions did not proceed with TFE as a proton donor under a variety of conditions and the starting material was always fully recovered. Because of the apparent short lifetime of the **BN** radical anion we retreated to MeOH. The reaction (eq 3) was performed using the following concentrations: **BN** 0.02 M, SmI_2 0.04 M, and MeOH 0.5 M.

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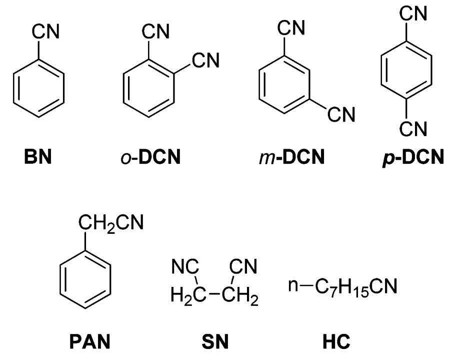
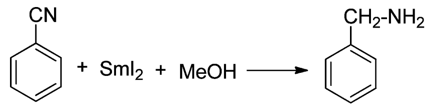


Figure 1. Substrates used in the study.



(3)

It should be noted that the concentration of SmI_2 used was sufficient for the reduction of only half of the amount of **BN**. For reasons that will be discussed later, higher concentrations of the SmI_2 were not desired. However, in order to enhance the reaction we have doubled the concentration of the substrate. A 500 W incandescent lamp was used as a light source, and the total volume of the reaction mixture was 25 mL placed in a 100 mL volumetric flask. Discoloration took place after 2.5 h, and the NMR yield was 96% (based on SmI_2). A control dark reaction was quenched at the same time, and the yield in this reaction was only 9%. These experiments show the high efficiency of the photostimulated reactions as compared to the thermal one in this case. It should be noted that no attempt was made to optimize the reaction conditions. The reaction times, for example, could have been shortened significantly by reducing the optical path by changing the geometry of the reaction vessel. Namely, the extinction coefficient ε of SmI_2 in THF is ca. 600 (depending on the concentration of the MeOH present in the reaction mixture) for absorption in the region between 550 and 650 nm. This implies that 90% of the light is absorbed (OD = 1) in a 0.4 mm layer of the reaction mixture. The rest of the reaction volume is in fact a "dark reaction". More quantitatively, it is approximately only 1 mL out of the 25 mL that undergoes the photostimulated reaction. However, in order to compare various reactions using the same stock solution and to perform the reactions simultaneously, we persisted with the above setup (see Supplementary Figure S1).

We then proceeded to examine the effect of the MeOH concentration on the reaction. The results are given in Table 1. The reaction mixtures in this case were irradiated for 30 min, quenched, and analyzed. Here the maximum yield was obtained between 0.2 and 0.5 M MeOH.

The second compound that we investigated was phenylacetonitrile (**PAN**, eq 4).

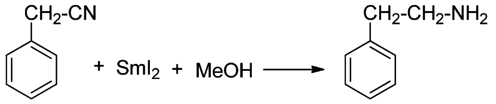


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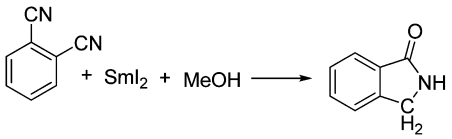
Table 1. Effect of MeOH Concentration on the Yield in the Reactions of BN

[MeOH] M	% yield
0.1	11
0.2	43
0.5	46
0.75	33
2	30
2.5	28
4	18

The following concentrations were used: **PAN** 0.02 M, SmI_2 0.04 M, and two different concentrations of MeOH, 0.2 and 0.5 M. The reactions were conducted until discoloration (ca. 8 h),[7] and the product, 2-phenylethylamine, was obtained in yields of 36% and 24%, respectively. In the control dark reaction experiment, no reaction was observed and the starting material was fully recovered. We have therefore continued our studies with 0.2 M MeOH as the standard concentration of the proton donor.

The third monocyano derivative examined was heptylcyanide (**HC**). Using the standard conditions (heptylcyanide 0.02 M, SmI_2 0.04 M, and MeOH 0.2M), discoloration was achieved after 48 h, and the yield in repetitive experiments varied between 0 and 8% based on ^1H and ^{13}C NMR. No product was observed when 0.5 M MeOH was used.

The next group to be studied was that of dicyano compounds. In the aromatic domain all three compounds react to give products (eqs 5 and 6).



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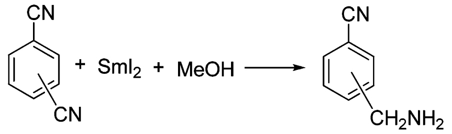


(6)

Therefore, in order to establish a reactivity order among the *ortho*, *meta*, and *para* derivatives, the reactions were conducted for 30 min only. The standard conditions were used, namely, dicyano compound 0.01 M, SmI_2 0.04 M, and MeOH 0.2 M. It should be noted that the concentration of the substrate was halved. However, the concentration ratio of SmI_2 to the cyano groups remained the same, i.e., sufficient to completely reduce one of the two cyano groups. The results are given in Table 2.

Table 2. Yields in the Photostimulated and Control Dark Reactions of the Dicyano Compounds (Quenched after 30 min)

	reaction, yield %	
substrate	photostimulated	dark
o-DCN	38	traces
m-DCN	11	0
p-DCN	68	51

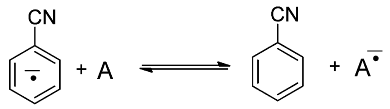
The product isolated in the case of *o*-dicyanobenzene (*o*-DCN, eq 5) was probably the result of a facile cyclization in the workup.

Finally, we have examined the reactivity of succinonitrile (**SN**) under standard conditions. In one case discoloration was achieved after 3.5 h and in the other after 5 h. No product was observed, and the starting material was fully recovered from the dark reactions quenched at the stated times.

■ DISCUSSION

The strong electron-withdrawing ability (Hammett σ = 0.628) of the cyano group[8] notwithstanding, Kagan and Namy reported that aliphatic and aromatic nitriles are unreactive toward SmI_2.[9] However, Kamochi et al. have shown that some nitriles can be reduced with SmI_2 in the presence of 85% H_3PO_4 or 50% KOH.[10a] A preliminary report of the reduction of an aliphatic nitrile using $SmI_2-H_2O-NEt_3$ has recently appeared.[10b] This is in contradistinction to the nitro group, which undergoes a rapid reduction with SmI_2[11] although its electron-withdrawing power is not much stronger (Hammett $\sigma = 0.778$)[8] than that of the cyano group. The reason for this difference lies, most probably, in the different nature of the electron-withdrawing mechanism of the two groups. Nitro acts mainly by resonance and cyano mainly by an inductive effect.[12] In a descriptive way, in the cyano group, the C−N bond is relatively very short and strong. This implies that the bonding π orbitals are very low lying in energy and by symmetry the antibonding π^* orbitals are of high energy. In contradistinction, the π^* orbitals in the nitro group exhibit a normal behavior. The unique nature of the nitrile group is manifested, for example, in the "normal" behavior of carbon acids stabilized by CN group(s), which is typical of groups that do not stabilize a negative charge at their α position by resonance but rather by an inductive effect.[13] Thus, since the reduction involves electron transfer to the LUMO of the substrate, the LUMO of the cyano group *per se* is apparently not sufficiently low to enable an easy electron transfer in our reactions. However, a combination of the cyano group with other groups may induce a change in the ability of the system to accept an electron.

Using benzonitrile as a reference, we have computed a scale of the relative electron accepting ability of the system. The calculations were performed at the B3LYP/6-31+G* level[14] on the following isodesmic reaction (eq 7; A = substrates used in this study).



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The results are given in Table 3.

Table 3. Equilibrium Energies (kcal/mol) of the Isodesmic Reaction of Equation 7

	Δ*E*, gas phase	Δ*E*, THF
p-**DCN**	−26.56	−20.51
o-**DCN**	−22.29	−18.16
m-**DCN**	−19.85	−13.13
BN	0	0
SN ***syn***	7.97	11.66
SN ***anti***	10.74	16.62
PAN	14.58	15.12
HC	25.13	19.4

As expected, for compounds with two cyano groups directly attached to the aromatic ring the equilibrium is shifted to the right, i.e., these compounds are more electrophilic than **BN**. Also, the dicyano **SN** (*syn* and *anti* conformers) are more electrophilic than the monocyano **HC**. Interestingly, the equilibrium energy of the isodesmic reaction of eq 7 increases upon going from the gas phase to THF for all the cyano derivatives except for **HC**. This apparently results from the high degree of charge localization in the latter compared to **BN**.

It should be emphasized that the electrophilicity scale provides only a rough estimate for the electron-accepted efficiency of these substrates. We have shown in the past that the Coulombic interaction between the Sm^{3+} ion and the radical anion contributes ca. 25 kcal/mol to the thermodynamics of the electron transfer reaction.[15] This electrostatic contribution is an inverse function of the distance between the two opposite charges, and in addition to the orbital overlap, it is one of the major components causing inner sphere electron transfer to be more efficient than the outer sphere electron transfer. This interaction, which is of the order of magnitude of the highest values associated with eq 7, is much dependent also on the charge distribution in the radical anion. Moreover, it depends on the polarizability of the radical anion and its ability to delocalize the charge toward the Sm^{3+} under the effect of the positive charge. A nice demonstration of the effect of the surroundings on the charge distribution can be found in **PAN**. Shown in Figure 2a is the SOMO of the radical anion in the gas phase. It shows clearly that the added electron resides mainly on the aromatic ring. However, reoptimization of the radical anion geometry with respect to energy in THF causes a major change in the geometry and in charge distribution. The cyano group, which was almost linear in the gas phase (C−C−N angle = 177.3°), is significantly bent in THF to an angle of 133.6°. In this new geometry the SOMO is highly concentrated on the cyano group. This observation is in line with the understanding that in the gas phase charges tend to be dispersed and delocalized over a large volume, whereas as the dielectric value of the medium increases, charge localization is enhanced.

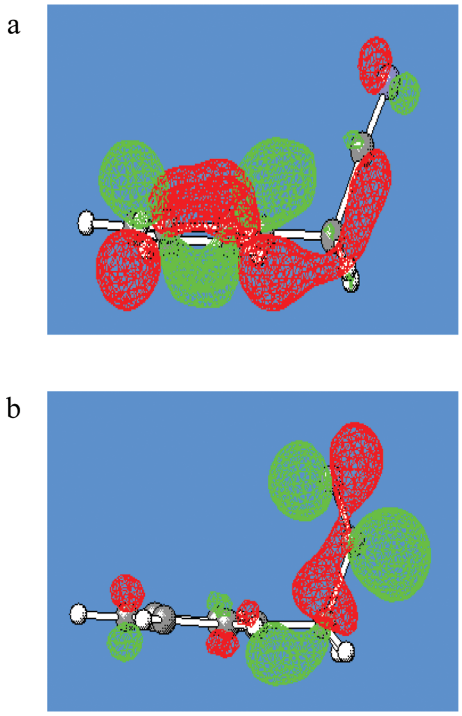


Figure 2. SOMO of **PAN** radical anion (a) in the gas phase and (b) in THF.

A similar phenomenon was also observed with **SN**. In its *syn*-clinal configuration in the gas phase, the two C−C−N angles are identical (165.5°). However, in THF charge localization takes place and one of these angles largely linearizes (174.9°) while the other angle bends to 129.9°. These changes are also evidenced from the NBO charge distribution given in Supplementary Table S1.

■ REACTION MECHANISM

One of the major experimental indications for the reaction mechanism is provided by the dependence of the reaction of **BN** on the MeOH concentration. As shown in Figure 3, the yields after a 30 min reaction, and therefore the rates, first go up with the increase in the MeOH concentration and then go down.

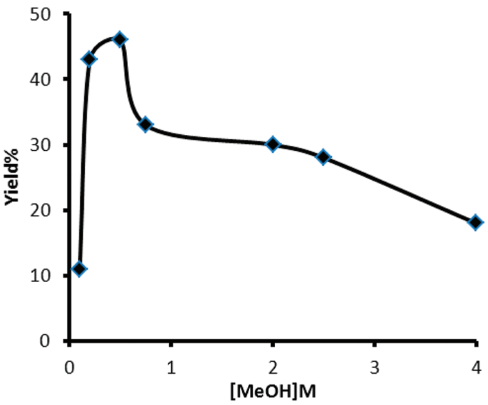


Figure 3. Yields in the photostimulated reaction of **BN** with SmI_2 as a function of MeOH concentration (see Table 1).

As was mentioned in the Introduction, protonation must occur from within the radical anion−Sm^{3+} ion pair by MeOH molecules within the solvation shell of the samarium. We have recently reported that SmI_2 coordinates to the nitrogen atom engaged in a double bond such as in imine and azo compounds.[16] The rate drop upon increasing the MeOH beyond 0.5 M suggests that the reaction is of the inner sphere electron-transfer type. We have pointed out earlier that the Coulombic interaction is a major driving force behind the electron transfer.[15] This interaction is a reciprocal function of the distance. However, the distance effect is significantly amplified by the dielectric constant of the medium between the two charges. The dielectric constant of MeOH that engulfs the samarium cation is 32.6, and that of THF that may be solvating the substrate is 7.58; that of a vacuum is 1.[17] Although dielectric constants are a bulk property and not a property of individual molecules, it is clear that this factor, which appears in the denominator of the Coulomb equation, will reduce the efficiency of the electron transfer process. This may be somewhat compensated by the increased protonation probability to capture the radical anion before it transfers its electron back to the Sm^{3+}. A possible alternative mechanism is that the electron transfer reactions are still of the inner sphere nature but only the small fraction of SmI_2 molecules that exist in equilibrium with the fully coordinated SmI_2 will be able to react. This fraction becomes smaller as the concentration of the MeOH increases. The shift between the various mechanisms is obviously continuous with overlap regions where two mechanisms operate simultaneously. The postulated coordination of the nitrile lone pair to SmI_2 finds much support in the recent finding of Flowers et al., who found that in MeCN the iodide ions are displaced from the vicinity of the Sm^{2+}, resulting in a higher conductivity of the solution and a lower stability of the reagent.[18]

A most interesting result emerges from the comparison of reactivity among the various aromatic mono- and dicyano compounds. The reactivity order within the dicyano benzene series is not unreasonable and agrees with the above calculated electrophilicity scale. Thus, the *p*-**DCN** derivative is sufficiently reactive to also display a significant reactivity in the absence of light (see Table 2). The surprising result is that the *m*-**DCN** derivative displays reactivity smaller than that of the monocyano derivative **BN**. It should be pointed out that because the reproducibility of the yields is not very great, the two reactions were conducted several times side by side and in all cases this observation was confirmed. We suggest that this observation, which contradicts the electrophilicity scale of Table 3 as well as chemical intuition, has its basis in the energy of the lone pairs on the nitrogen. Shown in Figure 4 are the molecular orbitals associated with these lone pairs along with their energies. The lone pair in **BN** is of a higher energy (10.7 kcal/mol) than the higher out of phase combination of the nitrogen lone pair orbital on *m*-**DCN**. It is highly likely that the energy of the lone pair is affecting the coordination of the SmI_2 to the substrate. The higher the energy, the better donor the lone pair is, leading to better coordination and a higher contribution of the inner sphere mechanism. This is very much in accordance with the conclusion derived from the effect of the variation MeOH concentration on the yield.

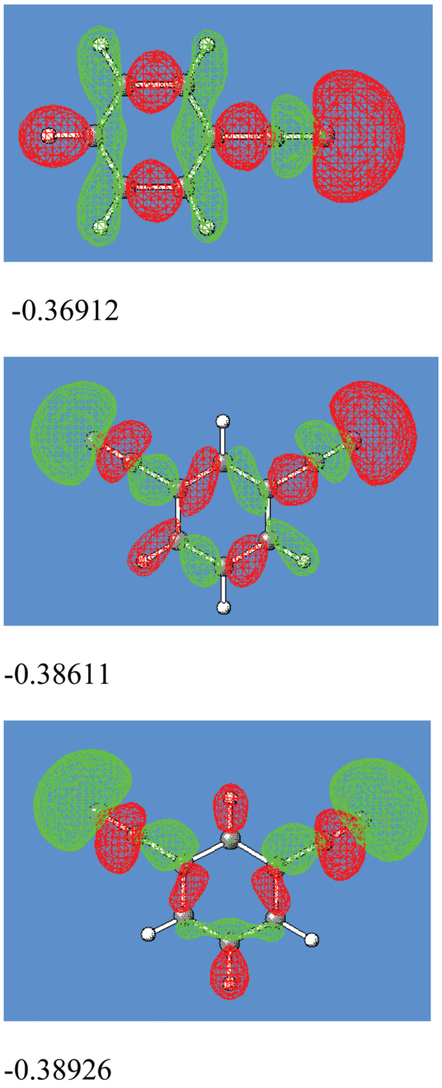


Figure 4. Nitrogen lone pairs orbitals on **BN** and *m*-**DCN** and their energies in au.

Another mechanistically interesting point is the internal selectivity of the *o*-**DCN** and *p*-**DCN**. After the completion of the first two electron−two proton reduction, a conjugated imino-cyano system is obtained. After an additional electron is accepted by this molecule, the SOMO containing the odd electron of the radical anion is nearly equally shared by the imine and the cyano functions (Figure 5).

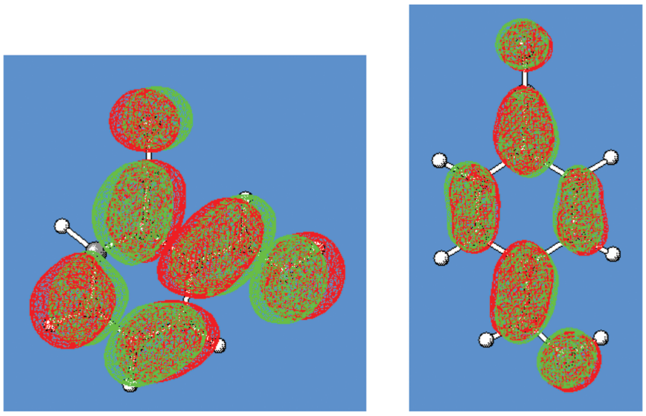
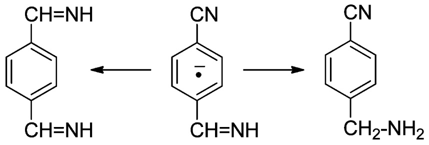


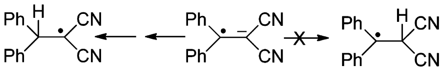
Figure 5. SOMO of the radical anions of *o*-**DCN** and *p*-**DCN**.

Thus, protonation may, in principle, take place on each of the two groups at the carbon or nitrogen atoms. This may lead to two different products (eq 8 for *p*-**DCN**).



(8)

In one of our previous reports we have shown that protonation on radical anions takes place on the site whose protonation will lead to the formation of the most stable radical product.[19] For example, in diphenyl-dicyanoethylene radical anion, the negative charge is highly localized on the malononitrile unit, yet protonation takes place preferentially on the benzylic carbon (eq 9).[20]



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We have calculated the energies of the four possible protonation products (Figure 6). The results show that protonation on the imino nitrogen is preferred over the other protonation sites. Hence, the following electron transfer will result in the formation of a benzylic anion, which will undergo protonation to yield the product which was indeed obtained.

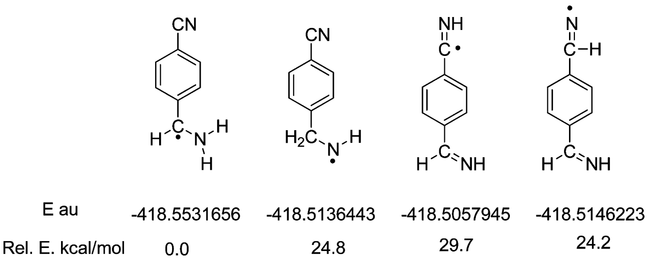

Figure 6. Radical energies.

SUMMARY AND CONCLUSIONS

The cyano group is unique in being highly electron-withdrawing yet a relatively bad electron acceptor. Its low electrophilicity makes it a difficult candidate for reduction by SmI_2 under regular conditions. We have shown that irradiation by visible light in combination with a partial solvation shell of MeOH molecules around the SmI_2 enables the reduction of cyano groups when attached directly to an aromatic ring or by a single methylene bridge. Aliphatic derivatives are not amenable to reduction under these conditions. Having a MeOH molecule or any other proton donor complexed to the SmI_2 is essential because the capture of the radical anion, which has a very short lifetime, cannot be achieved by a bimolecular protonation. This capture is enabled only by the efficient protonation from within the ion pair.

The SmI_2 transfers its electron by an inner sphere mechanism. In the first step, the SmI_2 coordinates to the lone pair of the nitrile nitrogen and then transfers the electron. This is evidenced by the dependence of the yield on the MeOH concentration. As the concentration of the MeOH increases, it complexes the SmI_2 more intensively and prevents coordination to the nitrogen lone pair. As a result, the yield goes down. The importance of this coordination step is nicely demonstrated in the comparison of the reactivity of **BN** and *m*-**DCN**. Surprisingly and counterintuitively, the latter manifests a lower reactivity with SmI_2. Apparently, the reason for this is that the lone pair on the nitrogen in the *m*-**DCN** is much lower in energy than that of **BN** and therefore *m*-**DCN** is a poorer donor, resulting in a less efficient coordination to the SmI_2 causing low yields.

An important experimental note is that, at the SmI_2 concentration used (0.04M), most of the light is absorbed in a 0.4 mm thick layer. This implies that if a different, undesired product is obtained in a dark (thermal) reaction and the desired product is obtained in a photostimulated reaction, the reaction should be conducted in a setup where the SmI_2 is added dropwise to the substrate maintaining all the time a concentration which will result in a 1−2 OD (absorbance of 90−99% of the light) and very little dark reaction.

EXPERIMENTAL SECTION

General. THF was dried over Na wire in the presence of benzophenone and distilled under an argon atmosphere. The freshly distilled THF was used for all reactions. TFE and MeOH were dried according to known procedures.[21] SmI_2 solutions of 0.1 M in THF were prepared according to a published procedure[22] and diluted as needed. The concentration of the SmI_2 solutions was spectroscopically determined (λ = 619 nm; ε = 635). Commercial benzonitrile, phenylacetonitrile, and heptylcyanide were distilled, and the solid compounds succinonitrile and *o*-, *m*-, and *p*-dicyanobenzene were recrystallized prior to use. All reaction mixtures were prepared in a glovebox under nitrogen, and the reactions were conducted in transparent glass volumetric flasks (100 mL) with airtight caps. During the irradiation, the temperature of the reaction mixture reached 40 °C. The yield of the reactions was calculated on the basis of SmI_2 consumption. The identity of the products benzylamine,[23] 2-phenylethylamine,[23] octylamine,[24] isoindolone,[25] α-amino-*m*-tolunitrile,[26] and α-amino-*p*-tolunitrile[27] were confirmed by ^1H (300 MHz) and ^{13}C (75 MHz) NMR and HRMS analyses and compared with the literature values.

Typical Reaction Procedure for the Reduction of Nitriles under Photochemical Conditions. A freshly prepared solution of SmI_2 (0.1 M) in THF was added in a glovebox to a homogeneous solution of substrate, nitrile (0.02 M) containing MeOH (0.2 M) in dry THF. The total volume of the reaction was 25 mL. The volumetric flasks were removed from the glovebox and placed next to a 500W incandescent lamp (see Supporting Information for the reactions setup). Some of the reactions were conducted until discoloration. In other cases, the reactions were stopped after a given time and the excess SmI_2 was quenched with a molecular iodine solution. The reaction mixture was diluted to 50 mL with diethyl ether in a separatory funnel, washed with 15% aqueous KOH solution (6 mL) and brine solution (20 mL), and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure at 25 °C. The crude reaction mass was analyzed by ^1H (300 MHz) and ^{13}C (75 MHz) NMR and HRMS (CI/EI).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Complete ref 12, NBO charges, experimental setup for irradiation, ^1H, ^{13}C NMR and HRMS (CI/EI) spectra, and Archive files. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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