Reactions of SmI_2 with Nitro Olefins

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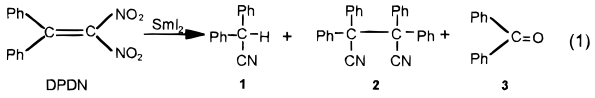
SmI_2, one of the most versatile single electron transfer reducing agents,[1] is capable of reducing nitro compounds to the corresponding hydroxylamines,[2] amines,[3,4] and azo derivatives.[3] In the absence of a proton source, the reduction results in the formation of azo- and azoxybenzene. When SmI_2 was reacted with 1,1-diphenyl-2,2-dinitroethylene (DPDN) in THF at room temperature for 2 min prior to quenching with 10% aqueous HCl, the products shown in eq 1 were obtained. Dry air quenching according to the procedure of ref 1h gave identical results.



(1)

Table 1 shows an interesting connection between the number of equivalents of SmI_2 used and the yield of the various products.

This data, plotted in Figure 1, shows that the initial consumption of the starting material is relatively low and increases significantly above 6 equiv of SmI_2. This can be taken as an indication that (a) the production of the first irreversibly formed intermediate is a relatively slow (not a diffusion-controlled) process and (b) the intermediates further down the cascade react much faster with SmI_2 than does the substrate. The monomeric product, diphenylacetonitrile (**1**), is formed in substantial amounts (>10%) only above 8 equiv of SmI_2. When 14 equiv of SmI_2 was used and the reaction was quenched after 2 h, **1** was obtained as the sole product in a quantitative yield.

It is possible that diphenylacetonitrile is obtained as a result of a reductive cleavage of the dimer, tetraphenylsuccinonitrile **2**. To test this possibility, the latter compound was independently synthesized[5] and was allowed to react with 2 equiv of SmI_2. Quenching with a 10% aqueous HCl solution after 2 min yielded 25% of diphenylacetonitrile. Thus, it is possible that tetraphenylsuccinonitrile is formed first and reacts further with SmI_2 to give diphenylacetonitrile. Nevertheless, the possibility that the excess of SmI_2 reacts with an intermediate, which otherwise would have coupled to give the dimer, can not be discarded.

The dimerization to give **2** is similar to the reaction of SmI_2 with benzophenone, which results in pinacol formation (along with benzhydrol).[3,6] It is interesting to note, however, that in spite of the noted similarity between

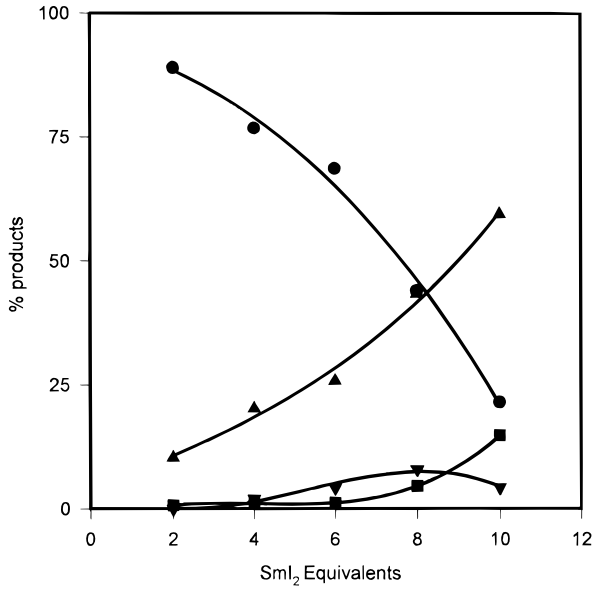
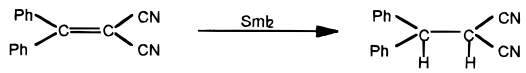


Figure 1. Product distribution in the reaction of SmI_2 with DPDN as a function of SmI_2 equivalents: ●, DPDN; ■, **1**; ▲, **2**; ▼, **3**.

Table 1. Product Distribution as a Function of the Number of SmI_2 Equivalents Used in Its Reaction with DPDN

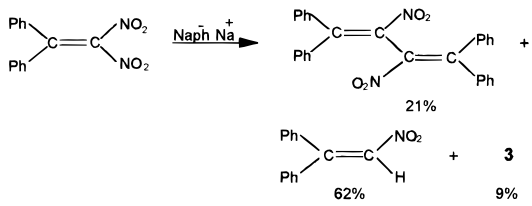
no. of SmI_2 (equiv)	DPDN	**1**	**2**	**3**
2	89	0.7	10.3	0
4	76.8	1	20.2	2
6	68.7	1.2	25.8	4.3
8	44	4.6	43.4	8
10	21.5	14.8	59.4	4.3

the C=C(CN)$_2$ and the C=O groups,[7] 1,1-diphenyl-2,2-dicyanoethylene does not yield any dimeric products. Instead, it is quantitatively reduced by 2 equiv of SmI_2 (eq 2).[8]



(2)

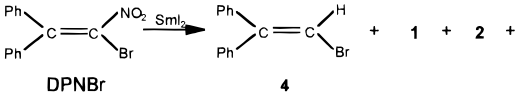
The coupling process is even more surprising when contrasted with the reaction of DPDN with sodium naphthalenide in THF. When a solution of 0.014 M DPDN in THF was allowed to react with 2.5 equivof sodium naphthalenide, an entirely different type of dimerization was obtained (eq 3).



(3)

Most likely, the trivalent Sm produced plays an important role in determining the course of the reaction.

Finally, 1,1-diphenyl-2-nitro-2-bromoethylene (DPNBr) reacts with SmI_2 in a way similar to DPDN (eq 4).



(4)

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Table 2. Product Distribution as a Function of the Number of SmI_2 Equivalents Used in Its Reaction with DPNBr

no. of SmI_2 (equiv)	DPNBr	**4**	**1**	**2**	**3**
2	57	2.3	3.7	37	0
4	26	12	6	49	7
8	8.1	10.1	40.6	36	5.2

However, this reaction differs from that of DPDN in two aspects. First, the formation of the bromo product in this reaction is not paralleled by formation of a nitro vinyl system in the reaction of DPDN. Second, the substrate consumption as a function of the number of SmI_2 equivalents used is enhanced more than twice compared with that of the DPDN reaction (Table 2). It is therefore not unreasonable to assume that, in the reaction of DPDN with SmI_2, the leaving "nitro" group undergoes at least a partial reduction (consuming this way additional equivalents of SmI_2) before it is expelled from the molecule.

Experimental Section

NMR spectra were determined on a Bruker AM 300 spectrometer. Mass spectra were determined using a VG Autospec instrument. UV spectra were recorded on a Kontron UVIKON 810 spectrophotometer, and the HPLC analyses were performed on a Waters machine equipped with an Alltech Econosil column.

Reactions of 1,1-Diphenyl-2,2-dinitroethylene (DPDN)[9] and 1,1-Diphenyl-2-nitroethylene (DPNBr)[10] with SmI_2. A commercial (Aldrich) 0.1 M THF solution of SmI_2 was used. The exact concentration of the SmI_2 was determined both by I_2 titration and by vis spectroscopy at 616 and 552 nm.

In a typical reaction, 0.026 mmol of the substrate was weighed into a 25 mL round-bottom flask that was sealed with a septum and flushed with argon. The solid was dissolved in THF, and an appropriate amount of the THF solution of SmI_2 was added in the glovebox. The total reaction volume was 5 mL. After 2 min, the reaction mixture was quenched with excess 10% HCl solution and extracted twice with dichloromethane. The organic phase was dried over Na_2SO_4, and the solvent evaporated. Analyses were carried out by HPLC and NMR in acetone-d_6. The identity of the products, diphenylacetonitrile (**1**),[5] tetraphenylsuccinonitrile[5] (**2**), and benzophenone (**3**), was established by comparison with authentic samples.

Reaction of Tetraphenylsuccinonitrile with SmI_2. The reactions were performed and analyzed employing the same procedure used for the reactions of DPDN. Quenching of the reaction mixture after 2 min gave 25% of diphenylacetonitrile (**1**). Quenching after 2 h yielded 70% of **1** (NMR yields).

Reactions of DPDN with Sodium Napthalenide. Sodium naphthalenide was prepared in the following way. To a solution of 4 g (0.031 mmol) of sublimed naphthalene in 50 mL of THF was added 0.54 g (0.023 mmol) of clean sodium chips. The reaction mixture was stirred for 1 day until the metal was completely dissolved. The concentration of the sodium naphthalenide was determined by titrating the OH^- produced by pouring a measured sample of the solution into water.

To a THF solution of DPDN (11.6 mg, 0.043 mmol) was injected a measured volume of a 0.43 M solution of sodium naphthalenide. The total volume of the reaction mixture was 3 mL. After 5 s, the reaction was quenched by excess trifluoroacetic acid and extracted twice with dichloromethane. The organic phase was dried over Na_2SO_4 and evaporated. Product distribution was determined by HPLC using 4% THF in heptane as eluent. Two of the products are known compounds: benzophenone (**3**) and 1,1-diphenyl-2-nitroethylene.[11] The dimer 1,1,4,4-tetraphenyl-2,3-dinitrobutadiene was recrystallized from a 1:1 mixture of hexane:ether: mp 260−262 °C; ^{1}H NMR δ 6.88−7.02 (m, 4H), 7.23−7.35 (m, 6H); ^{13}C NMR 138.29 s, 138.15 s, 130.52 d, 129.5 d, 130.29 d, 128.47 d, 128.56 d, 128.18 d, 152.54 s, 143.77 s; MS (EI) 448, 402, 356, 178. Satisfactory C,H,N analyses were obtained.

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