matography afforded pure acyl azide in excellent yields (benzoyl azide 85%, cinnamoyl azide 83%, *p*-chlorobenzoyl azide 90%, *p*-nitrobenzoyl azide 92%, crotonyl azide 80%).

5. Typical experimental procedure: To the solution of **2** prepared as above, was added epoxide (4 mmol) in chloroform (10 mL) and the solution was stirred for 2 hrs at rt. Dilution of the reaction mixture with chloroform (10 mL), usual workup, GC analysis to check the isomeric ratio, and column chromatography on silica gel afforded the major isomer.
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Reduction of N-Arylmaleimides with Sodium Dithionite: Observation of Dimeric Products

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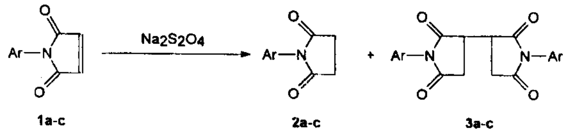
Sodium dithionite ($Na_2S_2O_4$) is a readily available and versatile reducing agent.[1] However, due to the lack of solubility of the reagent in organic solvent, its use has been somewhat limited. Polar solvents such as H_2O/dioxane and H_2O/DMF mixture or phase-transfer catalysts (PTC) have been used to overcome this problem.[2-5] Though there is good possibility of the involvement of one-electron transfer steps in the reduction reactions with sodium dithionite, no unequivocal evidences for the mechanism such as dimerized products from radical intermediates have been observed. We have been interested in the utilization of sodium dithionite for reduction of various organic substrates by electron transfer steps and used viologen (N,N'-dialkyl-4,4'-bipyridinium salt) as an electron-transfer catalyst for the dithionite reduction of α-halogeno ketones,[6a] α-nitrosulfones,[6b] *gem*-bromonitro compounds,[6c] α-nitro ketones,[6c] nitroarenes,[6d] *tertiary* nitroalkanes,[6e] azobenzenes,[6f] and azoxybenzenes[6f] in CH_2Cl_2/H_2O two-phase system or CH_3CN/H_2O medium.

Several investigators have reported sodium dithionite reductions of vinyl compounds conjugated with carbonyl group.[3-5,7] It was showen that α,β-unsaturated aldehydes, ketones, and esters are exclusively reduced to the corresponding saturated aldehydes, ketones, and esters in H_2O/benzene reaction medium using PTC.[3,5] Camps *et al.* also obtained similar results that reduction of 2,4-alkanedienoic acids and esters gives the corresponding 3-alkenoic acids and esters.[4] On the other hand, Kerber and Starnick reported the formation of symmetric sulfone, $(H_2NCOCH_2CH_2)_2SO_2$, from the reaction of acrylamide with sodium dithionite in water,[7] and Fornasier *et al.* showed that an α,β-unsaturated ketone, *R*-(−)-carvone, is reduced to the corresponding cyclohexanol derivatives in water in the presence of β-cyclodextrin.[5]

The difference in the reaction products depending on the nature of vinyl compounds conjugated with carbonyl group and the difference in the reactivity of sodium dithionite depending on the reaction medium[5,6e,6f] make it worthwhile to investigate the reaction of other $\alpha.\beta$-unsaturated carbonyl compounds with dithionite in different solvents. Here, we report the results on the reaction of N-arylmaleimides **1** with dithionite in CH_3CN/H_2O medium: we obtained the mixture of N-arylsuccinimides **2** and dimeric products **3** (Scheme 1), which could be taken as an evidence for the involvement of one-electron transfer step in the reduction.

N-Arylmaleimides except the commercially available N-phenylmaleimide were prepared starting from maleic anhydride and the aniline derivatives *via* the corresponding maleanilic acid.[8] N-Arylmaleimide (1 mmol) was reacted with sodium dithionite (0.8 g, 4.5 mmol) in 20 mL CH_3CN-12 mL H_2O containing K_2CO_3 (0.69 g, 5 mmol) at 35 °C



a: Ar = phenyl
b: Ar = 4-methoxyphenyl
c: Ar = 4-chlorophenyl

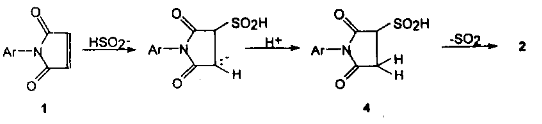
Scheme 1.

Table 1. Yields and Product Ratios in the Reduction of N-Arylmaleimides with Sodium Dithionite

Entry	N-Arylmaleimide	Yield (%)	Product Ratio (**2**:**3**)
1	phenylmaleimide, **1a**	66	3.1:1
2	N-(4-methoxyphenyl)maleimide, **1b**	50	3.0:1
3	N-(4-chlorophenyl)maleimide, **1c**	62	1.4:1

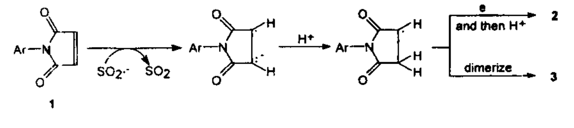
under a nitrogen atmosphere for 2 h. The acetonitrile solvent in the reaction mixture was removed by evaporation, and the remainder was extracted with ethyl acetate (15 mL ×5). The combined organic layers were dried with anhydrous Na_2SO_4 and concentrated to give a solid residue, a mixture of N-arylsuccinimide and the dimeric product (Table 1). The two products were separated by recrystallization from methanol: the dimeric product was filtered and the filtrate was purified by silica gel column chromatography (eluent: ethyl acetate) to afford the analytically pure corresponding succinimide. In case of N-phenylmaleimide (**1a**), N-phenylsuccinimide (**2a**) and the dimeric product (**3a**) were obtained with 50% and 16% yields, respectively. The products were characterized by mass and NMR spectroscopic methods.[9] Two carbonyl carbon peaks (δ 178.6 and 176.1), and four aromatic carbon peaks (δ 133.6, 130.2, 129.8, and 128.1), and two aliphatic carbon peaks (δ 41.1 and 33.2) of molecular formula $C_{20}H_{16}O_4N_2$ (determined from high resolution mass data) confirm the structure of **3a**. The reduction of N-(4-methoxyphenyl)-maleimide **1b** and N-(4-chlorophenyl)maleimide **1c** also gave the mixture of the corresponding N-arylsuccinimides and the dimeric products (Table 1, entries 2 and 3). Addition of dioctyl viologen (N, N'-dioctyl-4,4'-bipyridinium salt) to the reaction mixture as an electron-transfer catalyst didn't make any significant difference in the yields and the product ratios.

It was generally proposed that the major reaction pathway of dithionite reduction of organic substrates is *via* the formation of sulfinate intermediate and then prototropic shift with concomitant loss of SO_2 to yield the reduced product.[2,4] (eq 1): the sulfoxylate anion, HSO_2^-, is formed through rapid fragmentation of $S_2O_4^{2-}$ by the reaction with water, *i.e.*, $S_2O_4^{2}$ +H_2O → HSO_2^- +HSO_3^-. However, the dimeric products **3** are hardly expected from this pathway in CH_3CN/H_2O medium used in this work.



(1)

Another possible process is *via* one-electron transfer step as shown in eq 2.



(2)

The presence of the radical anion $SO_2^{\cdot-}$ in solutions of decomposing $S_2O_4^{2}$ was observed by esr[11] and the mechanism accords with the formation of the dimeric products **3**. Also, this seems to be the reason why the use of electron transfer catalyst, dioctyl viologen, does not make significant effects on the reaction. To the best of our knowledge, this is the first demonstration that the reduction of olefinic compounds by sodium dithionite can be proceeded by one-electron transfer step in the absence of electron-transfer catalysts. However, at this moment, we cannot rule out the possibility that the sulfinate intermediate process (eq. 1) competes with the one-electron transfer step to produce the succinimide **2**. The detailed mechanism for reduction of maleimides with dithionite, and elucidation of the factors affecting the one-electron transfer step, as well as other applicability of sodium dithionite as reducing agent in organic reactions are under investigation.

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9. **2a**: mp 155 °C (lit.[10] 156 °C); MS, 93 (27%), 119 (46%), 120 (28%), and 175 (100%). **3a**: mp 261.5 °C; MS, 119 (27%), 174 (27%), 175 (91%), 348 (100%), and 349 (21%); HR MS, 348.1136 (calcd for $C_{20}H_{16}O_4N_2$ 348.1110); ^1H NMR (CD_3CN), δ 7.54-7.42 (3H, m), 7.26-7.22 (2H, m), 3.67-3.61 (1H, m), 3.04 (1H, dd, *J*=18, 8.8 Hz), and 2.91 (1H, dd, *J*=18, 5.6 Hz); ^{13}C NMR (CD_3CN), δ 178.6, 176.1, 133.6, 130.2, 129.8, 128.1, 41.1, and 33.2.
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