

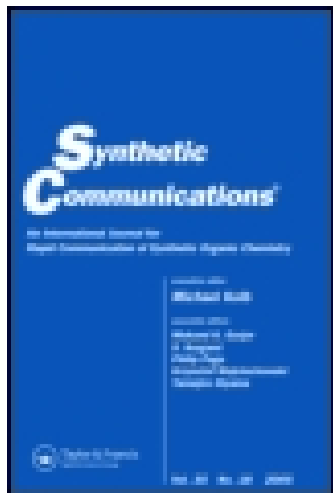
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Chemoselective and Stereoselective Debromination of Vicinal-Dibromides with Sodium Dithionite

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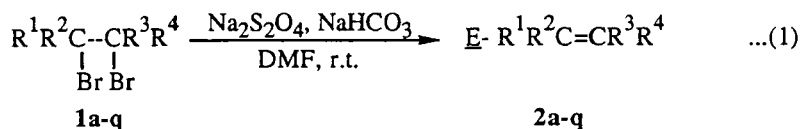
Abstract: *A simple and efficient procedure for the quantitative debromination of vic-dibromides has been reported with sodium dithionite at ambient temperature. These eliminations are chemoselective and also stereoselective.*

Debromination of vicinal-dibromides both stereospecifically and stereoselectively, resulting in the formation of olefins has been studied with diverse reducing agents.¹ Kempe *et. al.*² had reported the dehalogenation of vicinal-dihalides with sodium dithionite in refluxing DMF (155-160 °C). However recently we have reported the solvolytic dehalogenation of vicinal-dihalides with N,N-dimethylformamide (DMF) in the absence of any reagent at 155-160 °C under nitrogen atmosphere wherein DMF not only serves as a solvent but is also responsible for the dehalogenation.³ Thus we believe that the reported debromination of vicinal-dibromides with sodium dithionite in refluxing DMF² must have been brought about by DMF alone. Therefore we decided to investigate the role of sodium dithionite in debromination, if any, in different solvents at ambient temperature.

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In this communication we report a convenient procedure for the chemoselective and stereoselective debromination of vicinal-dibromides **1** to *E*-alkenes **2** with sodium dithionite in *N,N*-dimethylformamide at ambient temperature. The debrominations are usually complete in reasonable time using 1:2 molar ratio of substrate to sodium dithionite⁴ though some substrates required higher amounts of reagent (**1d**, **1o**, **1p** and **1q**). The debrominations are rapid in case of chalcone dibromides (**1f-l**), comparatively slower in 1,2-diaryl 1,2-dibromides, (**1a-d**) and very slow in case of cyclic 1,2-dibromides (**1o** and **1q**). The reactions can be generalized as in eq. 1.



No debrominations have been observed with DMF alone at ambient temperature even after 24 hr whereas quantitative debrominations were observed with DMF at reflux temperatures.³ Thus the eliminations in question are undoubtedly proceeding with the aid of sodium dithionite in DMF at ambient temperature. No debrominations have been observed with sodium dithionite in MeOH, CH₃CN or THF. Our results are listed in *Table 1*.

It is important to emphasize here that though sodium dithionite has been reported to reduce carbon-carbon double bond in chalcones, α,β -unsaturated ketones, α,β -unsaturated esters and conjugated dienoic esters in presence and absence of phase transfer catalysts under different conditions⁴, we did not observe any reduced products under our reaction conditions. It is evident from table that the reductive eliminations are chemoselective as phenyl, aryl chloro, aryl bromo, keto, acetoxy, methoxy and ester groups remained unaffected under these conditions.

Even debromination of a steroidal dibromide namely cholesteryl acetate dibromide (**1q**) can be achieved readily at ambient temperature. The eliminations are also stereoselective in nature since only **E** - **2a** was obtained from meso- and dl-**1a** and only **E** - **2m** was obtained from meso- and dl-**1m**.⁵

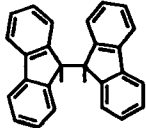
In the absence of any α -bromoalkenes, sulphones and sulphinic acids in our reactions, possibility of a E1 elimination¹ and nucleophilic attack by sodium dithionite anion⁶ has been eliminated. Involvement of an antiperiplanar E2 elimination (stereospecific) followed by isomerization has also been ruled out by comparison with a reaction of Z-stilbene and sodium dithionite.⁷ The eliminations are believed to be proceeding by single electron transfer (SET) from sodium dithionite⁸ according to scheme 1.

The free radicals from dl-**1** undergo rapid rotation to give a more stable conformation. The conformational energy difference of 4.4 Kcal/mol⁹ favors the rapid carbon-carbon bond rotation. The order of reactivity in SET reactions,¹⁰ $I > Br > Cl > F$ is consistent with our observations since only 84% of dechlorination was observed in the reaction of meso-stilbene dichloride after 24 hr using much higher molar ratio of substrate: sodium dithionite (1:10). The slower debromination in the reaction of tolan dibromide **1b** compared to **1a** further corroborates our proposal.

Experimental

Melting points were measured on a Tropical Labequip apparatus and are uncorrected. IR spectra were recorded on Perkin-Elmer model 621 and Shimadzu model 435 spectrophotometers. NMR spectra were recorded on Perkin Elmer model R-32, 90 MHz and Hitachi FT-NMR 60 MHz with TMS as internal standard. GC analyses were performed on Shimadzu chromatograph GC-9A

R ¹	Substituent R ²	R ³	R ⁴	Molar Ratio 1: Na ₂ S ₂ O ₄ ^a	Time (hr)	(%) Yield E-Olefin (2)	Found	m.p. (°C) Reported
Ph	H	H	Ph	1:2	16	94 ^c	122	122-123
Ph	-	-	Ph ^d	1:3	16	86	56-58	59
4-MeC ₆ H ₄	H	H	C ₆ H ₄ Me-4	1:2	16	88	176	179-180
4-ClC ₆ H ₄	H	H	C ₆ H ₄ Cl-4	1:7	16	80	173-176	180
Ph	H	H	COOMe	1:2	3	83	33-34	36
Ph	H	H	COPh	1:2	3	80	52-53	56
Ph	H	H	C ₆ H ₄ Me-4	1:2	3	81	74-77	79
Ph	H	H	C ₆ H ₄ Cl-4	1:2	3	83	92-94	96
Ph	H	H	C ₆ H ₄ Br-4	1:2	3	80	102	104
Ph	H	H	COCH=CHPh	1:2	3	87	108-110	110-111
Ph	H	-CO(CH ₂) ₄ -		1:2	3	83	115-116	118
4-MeOC ₆ H ₄	H	H	COPh	1:2	3	76	78-80	79
COOMe	H	H	COOMe	1:2	3	98 ^e	-	-



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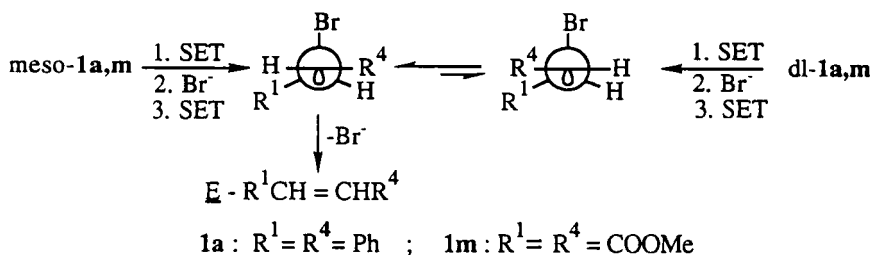


1:10 16 80 92-94 94.5

H H (CH₂)₅CH₃ 1:10 3 h - -

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All reactions done in presence of sodium bicarbonate (3 molar equivalent of sodium dithionite).
 Isolated yields of uncrystallized product unless otherwise specified (See Exp.).
 Yield 94% from meso-**1a** and 90% from dl-**1a**. GC analyses mp and spectral data confirmed the product to be *e*-stilbene from both meso-**1** and dl-**1**. Reaction time meso-**1a**-16 hr. & dl-**1a**-16 hr.
 The starting material is tolan dibromide.
 GC yield 98% from meso-**1m** and 96% from dl-**1n**.
 Analyses (GC) showed the presence of 98% cyclohexene by comparison of retention time with an authentic sample.
 Analyses (GC) showed the presence of 96% cyclooctene by comparison of retention time with an authentic sample.
 No elimination product observed even after 72 hr.



Scheme 1

equipped with a column of 5% SE-30(3m) on chromosork w and flame ionization detector using nitrogen as carrier. vic-Dibromides **1a-r** were prepared from olefins by bromine addition according to reported procedures. Dried DMF (E.Mersk) was used in all the reactions. Sodium Dithionite (SDS) was used after estimation by iodometric titration.¹¹

General Procedure for Debrominations

In a dried, round-bottomed flask, mounted over a magnetic stirrer was placed a mixture of **1** (10 mmol), sodium dithionite (see table 1 for molar ratios), sodium bicarbonate⁴ and DMF (5 mL). The system is sealed with a mercury trap. The contents of the flask was stirred at ambient temperature and the progress of the reaction is monitored by TLC (eluent: petroleum ether or petroleum ether/benzene: 1:1, V/V). After disappearance of the starting material, the contents of the flask was poured into water (~100 mL) and the mixture extracted with ether (3x10mL). The combined ethereal extract was dried over anhyd. MgSO₄ and concentrated on a Buchi rotavapour. A portion of the solid obtained on concentration was recrystallized from ethanol and identified by mp, mixed mp, IR and NMR spectra. In the case of **1m**, **1n** and **1o**, the ethereal extract was subjected only to analyses by GC.

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