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The Dehalogenation of *vic*-Dihaloalkanes to Alkenes with Sodium Trithiocarbonate or Sodium Dithiocarbonate in the Presence of Phase-Transfer Catalysts

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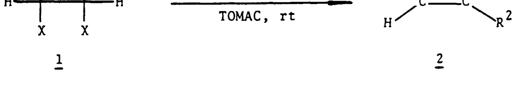
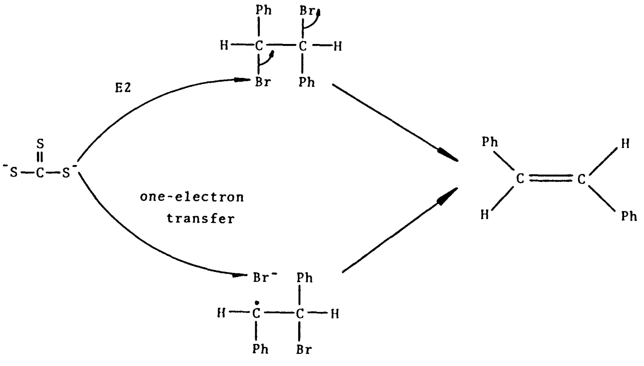
Synopsis. The reductive dehalogenation of *vic*-dihaloalkanes with aqueous sodium trithiocarbonate or sodium dithiocarbonate in the presence of a phase-transfer catalyst gave the corresponding alkenes in high yields under mild conditions.

There have been numerous reports on the methods of synthesizing various organic compounds using phase-transfer catalysts.[1] These phase-transfer systems have been effectively used to prepare many organosulfur compounds, such as sulfides[2] and dithiocarbonates.[3] Recently, we ourselves have also reported the synthesis of alkyl, aryl, alkanediyl, and cyclic trithiocarbonates in the presence of phase-transfer catalysts (PTC).[4] For the dehalogenations of *vic*-dihaloalkanes to alkenes, several procedures using a variety of reagents have been developed hitherto.[5] An interesting dehalogenation was provided by Nakayama and his co-workers.[6] They showed an effective dehalogenation of *vic*-dibromoalkanes to alkenes using aqueous sodium sulfide in the presence of a phase-transfer catalyst. The use of sodium hydrogensulfide has also been reported.[7] In the course of our investigations of the chemistry of various trithiocarbonates, we have now found that *vic*-dihaloalkanes such as 1,2-dibromo-1,2-diphenylethane (**1**) are reductively dehalogenated under mild conditions by treatment with sodium trithiocarbonate or sodium dithiocarbonate in the presence of PTC to give the corresponding alkenes in excellent yields (Scheme 1).

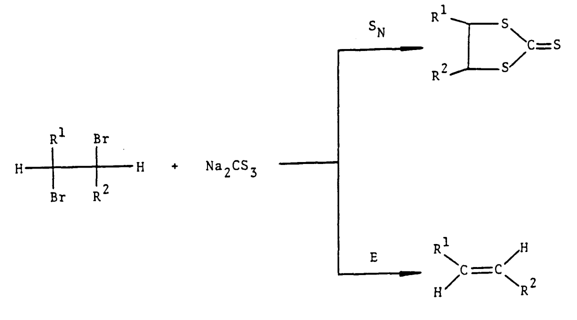
As shown in Table 1, the present reaction proceeded smoothly in the phase-transfer system when the mixture was stirred for a short period between 0 °C and room temperature. Consequently, we could obtain several alkenes from *vic*-dihaloalkanes in high yields. Trioctylmethylammonium chloride (TOMAC) was employed as a typical PTC and gave favorable results. It should be noted that the reaction of *meso*-1,2-dibromo-1,2-diphenylethane (**1a**) gave *trans*-stilbene (**2a**) exclusively (Entry 1, Table 1), whereas the *dl*-1,2-dibromo-1,2-diphenylethane (**1b**) afforded a mixture of *cis*- and *trans*-stilbene (Entry 7). No alkene was formed in the absence of PTC (Entry 4). In addition, the treatment of the *vic*-dihaloalkane (**1**) with aq. NaOH alone did not give any alkenes (Entry 6). When sodium trithiocarbonate was used as the reducing reagent, the reaction could be monitored by the decolorization of the orange color of the reaction mixture. The dehalogenation of **1a** was completely inhibited by the addition of a radical scavenger such as *N′*,*N′*-diphenyl-*N*-picrylhydrazyl to the reaction system. In the dark, we could also observe considerable retardation (Entries 1 and 2). Furthermore, the reaction of **1b** with sodium trithiocarbonate was greatly accelerated by the irradiation of a 300 W ref-lamp (Entry 8). Based on these results, the present reaction seems not to proceed through the E2-type mechanism proposed by Landini for the dehalogenation of *vic*-dihaloalkanes with sodium sulfide in the presence of PTC,[7] but through a radical mechanism involving one electron transfer which is similar to that proposed by Kormblum for the reductive elimi-



Scheme 1.



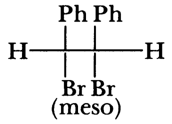
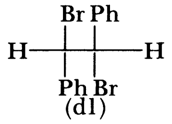
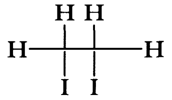
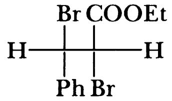
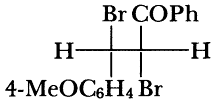
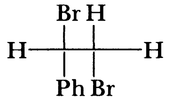
Scheme 2.



$R^1 = R^2 =$ Alkyl S_N
$R^1 = R^2 =$ Phenyl E
$R^1 =$ Phenyl, $R^2 =$ Carbonyl E
$R^1 =$ Phenyl, $R^2 =$ H E and S_N

Scheme 3.

Table 1. Reductive Dehalogenation of *vic*-Dihaloalkanes to Alkenes

Entry[a]	Substrates	Reducing Reagent	Reaction Time/min	Reaction Temp/°C	Yield/%[b]	Products	Mp/°C
1[c]	 $\mathrm{H}-\overset{\mathrm{Ph}}{\underset{\mathrm{Br}}{\vert}}-\overset{\mathrm{Ph}}{\underset{\mathrm{Br}}{\vert}}-\mathrm{H}$ (meso)	Na_2CS_3	10	rt	100	*trans*-Stilbene	118—120[9]
2[d]			10	rt	52		
3			60	0	100		
4[e]			3(h)	rt	0		
5[f]		CS_2+NaOH	60	rt	100		
6		NaOH	3(h)	rt	0		
7	 $\mathrm{H}-\overset{\mathrm{Br}}{\underset{\mathrm{Ph}}{\vert}}-\overset{\mathrm{Ph}}{\underset{\mathrm{Br}}{\vert}}-\mathrm{H}$ (dl)	Na_2CS_3	5(h)	rt	95	Stilbene[9] (cis : trans=4 : 1)[g]	
8[h]			70	rt	98		
9[f]		CS_2+NaOH	3(h)	50	95		
10[i]	 $\mathrm{H}-\overset{\mathrm{H}}{\underset{\mathrm{I}}{\vert}}-\overset{\mathrm{H}}{\underset{\mathrm{I}}{\vert}}-\mathrm{H}$	Na_2CS_3	10	rt	100	Ethene[10]	
11	 $\mathrm{H}-\overset{\mathrm{Br}}{\underset{\mathrm{Ph}}{\vert}}-\overset{\mathrm{COOEt}}{\underset{\mathrm{Br}}{\vert}}-\mathrm{H}$	Na_2CS_3	60	rt	94	Ethyl cinnamate[11]	
12[f]		CS_2+NaOH	60	rt	97		
13	 $\mathrm{H}-\overset{\mathrm{Br}}{\underset{\mathrm{4\text{-}MeOC_6H_4}}{\vert}}-\overset{\mathrm{COPh}}{\underset{\mathrm{Br}}{\vert}}-\mathrm{H}$	Na_2CS_3	60	rt	97	4-Methoxychalcone	72—74[12]
14[f]		CS_2+NaOH	60	rt	96		
15[j]	 $\mathrm{H}-\overset{\mathrm{Br}}{\underset{\mathrm{Ph}}{\vert}}-\overset{\mathrm{H}}{\underset{\mathrm{Br}}{\vert}}-\mathrm{H}$	Na_2CS_3	60	50	78	Styrene[13]	
16[f]		CS_2+NaOH	4(h)	50	73		

a) *vic*-Dihaloalkanes, 2 mmol; Na_2CS_3, 6 mmol; TOMAC, 0.08 mmol. b) Isolated yields based on substrates. c) The reaction was inhibited by the addition of a radical scavenger such as *N'*,*N'*-diphenyl-*N*-picrylhydrazyl (0.1 mmol). d) The reaction was carried out in the dark. e) The reaction was carried out in the absence of PTC. f) A mixture of CS_2 (10 mmol) and NaOH (10 mmol) in water (10 ml) was stirred for 2 h at room temperature. g) By NMR analyses. h) The reaction was carried out under irradiation by a ref-lamp. i) The ethene liberated was collected in a gas buret. j) 4-Phenyl-1,3-dithiolane-2-thione was formed in a low yield (7%).

nation of *vic*-dinitro compounds to alkenes (Scheme 2).[8]

It is noteworthy that the elimination-type reaction (E) predominates over nucleophilic substitution (S_N) for the reaction of even *vic*-dihaloalkanes bearing an electron-withdrawing group, such as phenyl and carbonyl groups with sodium trithiocarbonate (Scheme 3).

As has been mentioned above, we succeeded in a new reductive dehalogenation of *vic*-dihaloalkanes to alkenes in the phase-transfer system. We wish to emphasize that the present procedure has several advantages, namely, efficiency of conversion, simplicity of operation, and mild conditions.

Experimental

The IR spectra were obtained on a Jasco IR-G spectrometer, while the NMR spectra were measured with a Varian Gemini-200 spectrometer (200 MHz) in $CDCl_3$, using TMS as the internal standard. The elemental analyses were determined with a Yanagimoto MT-3 apparatus. The ref-lamp used was a National REF-300W. All the melting points are uncorrected.

General Procedure. To a solution of *meso*-1,2-dibromo-1,2-diphenylethane (2 mmol) in benzene (5 ml) we added a 30% aqueous Na_2CS_3 solution (6 mmol) and trioctylmethylammonium chloride (0.08 mmol), the mixture was then stirred for 10 min at room temperature. After the completion of the reaction, the organic layer was washed with water and then dried over sodium sulfate. The residue obtained by the evaporation of the solvent was passed through a short silica gel column, using dichloromethane as the eluent, to give *trans*-stilbene in a 100% yield. The structure of the products was characterized by ^{1}H NMR, IR, and elemental analyses. The physical and spectral data of the alkenes were also compared with those authentic samples.[9–13]

4-Phenyl-1,3-dithiolane-2-thione: Mp 83—85 °C; IR (KBr) 1050 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=4.10 (m, 2H, CH_2), 5.65 (m, 1H, CH), and 7.40 (m, 5H, arom). Found: C, 50.61; H, 3.96%. Calcd for $C_9H_8S_3$: C, 50.87; H, 3.77%.

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