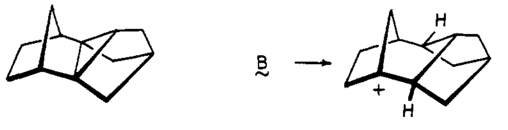
esting facets of these data is the near comparable solvolytic reactivity of secondary derivative **4-OPNB** and tertiary systems **2-OPNB** and **5-OPNB**.[8] The contrasting high propensity of **4-ODNB** for ionization and unreactivity of **6-ODNB** is notable. *This exo/endo rate ratio may well represent the largest yet determined experimentally.*[9] Product studies, conducted under $CaCO_3$-buffered conditions, reveal that **2-OPNB** (at 80 °C) leads to **1** (25%) and **2** (75%). In contrast, **4-OPNB** (95 °C) and **5-OPNB** (110 °C) solvolyze to identical mixtures of **4** (18%), **5** (70%), and hydrocarbon **8** (12%).



8 **E**

The global collection of data reported herein implicate preferential conversion of **1** to carbocation A rather than C and the existence of a significant barrier to that 1,2-hydride shift that leads from A to B. An increase in the acidity of the reaction medium facilitates this migration. Lastly, the ultimate conversion of **5** to **7**, made possible by good stereoalignment, may be driven by bridgehead strain energy considerations related to those found in manxanes and related medium-ring bicyclic compounds.[10]

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Viologens Used in "Electron Phase Transfer". Catalytic Debromination of *vic*-Dibromides under Heterophase Condition Using Viologens

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Viologens (1,1′-dialkyl-4,4′-bipyridinium, V^{2+}) are known to undergo one-electron reduction to produce the cation radicals ($V^{+}\cdot$), which is easily reoxidized to V^{2+}. Recently, viologens have received much attention as an electron-transfer catalyst (ETC) in oxidation–reduction systems,[1] especially in hydrogen production by photoreduction of proton. We, on the other hand, have been interested in the reaction using V^{2+} as ETC for the reduction of organic compounds. For instance, it was found that aromatic aldehydes and ketones,[2] α-keto esters,[3] and azobenzene[4] could be reduced smoothly in the presence of V^{2+} as ETC.

Table I. Debromination of *meso*-1,2-Dibromo-1,2-diphenylethane[a]

run	catalyst[b]	solvent	PhC=CPh, %
1a		H_2O	0
b	MV^{2+}		4
c	PrV^{2+}		2
2a		H_2O-CH_3OH (1:1)	0
b	MV^{2+}		4
c	PrV^{2+}		5
3a		CH_2Cl_2	0
b	MV^{2+}		0
c	PrV^{2+}		0
4a		H_2O-CH_2Cl_2 (1:3)	0
b	MV^{2+}		1
c	EV^{2+}		54
d	PrV^{2+}		97
e	HpV^{2+}		95
f	DdV^{2+}		95
5	Bu_4N^+		0
6	PrV^{2+}	DMF-H_2O (1:1)	35

[a] The experiment was performed with 1.4 mmol of $Na_2S_2O_4$, 1.5 mmol of K_2CO_3, 0.2 mmol of the catalyst, and 1.0 mmol of *meso*-1,2-dibromo-1,2-diphenylethane in 20 mL of the solvent at room temperature for 40 min. [b] MV^{2+} = methylviologen, PrV^{2+} = propylviologen, EV^{2+} = ethylviologen, HpV^{2+} = heptylviologen, DdV^{2+} = dodecylviologen.

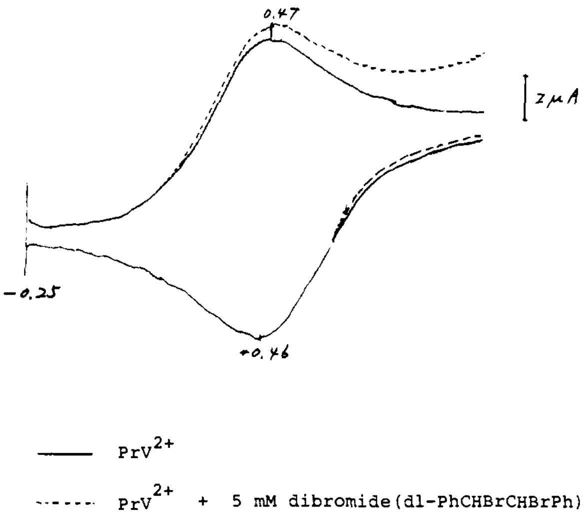

Figure 1. Cyclic voltammograms of a 1 mM PrV^{2+} solution in 0.1 M LiCl EtOH at Pt electrode, scan rate 0.1 V/s.

The technique using the phase-transfer catalyst (PTC) has been widely used in the field of the organic synthesis.[5]

We report here a study of the viologen-catalyzed debromination of *vic*-dibromides in heterophase to demonstrate "electron phase transfer" (EPT).

Many reagents[6,7] including metals, metal ions, and some nucleophilic reagents have been employed for debromination. However, sodium dithionite, which is a cheap and available reducing agent, has never been applied for debromination. Firstly, the debromination of 1,2-dibromo-1,2-diphenylethane was performed by sodium dithionite with or without various kinds of viologens, as shown in Table I. In water (runs 1a–1c) or water–methanol mixture (runs 2a–2c), debromination scarcely proceeded because of the insolubility of 1,2-dibromo-1,2-diphenylethane. However, debromination proceeded in a *N,N*-dimethylformamide (DMF)–H_2O mixture (run 6). In dichloro-

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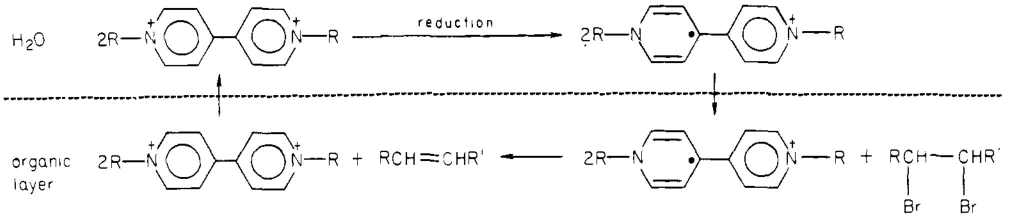
Table II. Two-Phase Dehalogenation of *vic*-Dihalide by Sodium Dithionite Using PrV^{2+} [a]

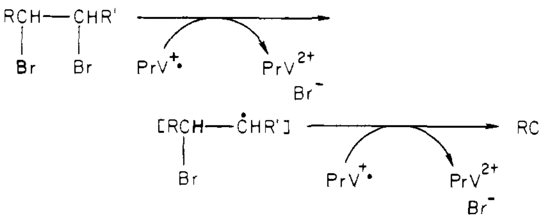
run	dihalide $[R_1CH(X)CH(X)R_2]$ config	time,[b] (min)	olefin	conv,[b] %	yield, %
1	X = Br, $R_1 = R_2$ = Ph erythro	40	*t*-PhC=CPh	100	97
2	X = Br, $R_1 = R_2$ = Ph threo	420	PhCH=CHPh[c]	100	
3	X = Br, R_1 = Ph, $R_2 = CO_2C_2H_5$ erythro	30	*t*-$PhC=CCO_2C_2H_5$	100	99
4	X = Br, R_1 = Ph, R_2 = H	150	PhC=C	100	84
5	X = Br, R_1 = Ph, $R_2 = CH_2OH$ erythro	30	*t*-$PhC=CCH_2OH$	100	94
6	X = Br, $R_1 = C_8H_{17}$, R_2 = H	720[d]	$C_8H_{17}C=$		24[e]
7	X = Br, $R_1 = CH_3$, $R_2 = CH_2OH$ erythro	330	*t*-$CH_3C=CCH_2OH$	100	97
8	X = Br, R_1, $R_2 = -(CH_2-)_6$	1440[d]	cyclooctene		47[e]
9	X = Br, R_1, $R_2 = -(CH_2-)_4$ threo	1620[d]	cyclohexene		42[e]
10	X = Cl, $R_1 = R_2$ = Ph erythro	1440[f]	*t*-PhC=CPh		34

[a] The reaction was performed with 1.4 mmol of $Na_2S_2O_4$, 1.5 mmol of K_2CO_3, 0.2 mmol of propylviologen, 1.0 mmol of dihalide in 20 mL of $H_2O-CH_2Cl_2$ (1:3) at room temperature. [b] Monitored by GLC every 10 or 30 min. [c] $E/Z = 88/12$. [d] Viologen was completely decomposed at the time indicated. [e] Product was not isolated, and the yield was determined by GLC [spontaneous dehalogenation of *vic*-dihalide did not occur at all in this condition (initial temp 80 °C; final temp 200 °C)] using 1-octanol as an internal standard. [f] Reaction was stopped at the time indicated.

Scheme I



Scheme II



methane (runs 3a–3c) dibromide was also recovered completely due to the insolubility of sodium dithionite. But *trans*-stilbene was obtained in the two-phase system using viologens (runs 4b–4f) and especially viologens having longer alkyl chains (runs 4d–4f) showed higher catalytic activity.[8] The debromination under the normal phase-transfer condition (run 5) did not proceed at the same condition as in the presence of viologens. It was demonstrated that longer alkyl chains containing viologens carried smoothly the electron to the dibromide through the heterophase, as indicated in Scheme I. Further, an electron transfer of viologen radical to the dibromide was confirmed by the examination of the effect of added dibromide on the reversibility of the cyclic voltammogram of PrV^{2+} (Figure 1).

The debromination of the various *vic*-dibromides was also tried under the same condition as run 4d in Table I. The results are summarized in Table II. Transisomers were obtained selectively from erythrodibromides, whereas trans and cis mixtures were given from *threo*-1,2-dibromo-1,2-diphenylethane (run 2). These results seems to show that the debromination may proceed by the two-step one-electron transfer not by E_2 mechanism. The dibromides that have phenyl (runs 1–5) or alkyl (run 7) groups were debrominated quantitatively. On the other hand, cyclic dibromides (runs 8 and 9) or 1,2-dibromoalkane (run 9) were not completely debrominated, and activity of viologen as the catalyst decreased gradually. Further, *vic*-dichloride (run 10) was also found to be dechlorinated. The debromination of bromodiphenylmethane was further carried out under the same condition to isolate tetraphenylethane in 50% yield. This reductive dimerization indicates that carbon radical as the intermediate is formed by the reduction of a carbon–bromine bond with $V^{+}\cdot$. The debromination described in this paper may proceed by the process in Scheme II.

Registry No. EV^{2+}, 46713-38-6; PrV^{2+}, 46903-41-7; HpV^{2+}, 47503-76-4; DdV^{2+}, 20462-61-7; *erythro*-PhCH(Br)CH(Br)Ph, 13440-24-9; *threo*-PhCH(Br)CH(Br)Ph, 70764-40-8; *erythro*-PhCH(Br)CH(Br)-$CO_2C_2H_5$, 30983-70-1; $PhCH(Br)CH_2Br$, 93-52-7; *erythro*-PhCH(Br)-$CH(Br)CH_2OH$, 83263-29-0; $C_8H_{17}CH(Br)CH_2Br$, 28467-71-2; *erythro*-$CH_3CH(Br)CH(Br)CH_2OH$, 54899-03-5; $\overline{CH_2(CH_2)_5CH(Br)CH}$-(Br), 29974-69-4; *threo*-$\overline{CH_2(CH_2)_3CH(Br)CH}$(Br), 7429-37-0; *erythro*-PhCH(Cl)CH(Cl)Ph, 15951-99-2; *trans*-PhCH=CHPh, 103-30-0; *trans*-$PhCH=CH(CO_2C_2H_5$, 4192-77-2; $PhCH=CH_2$, 100-42-5; *trans*-$PhCH=CHCH_2OH$, 872-05-9; *trans*-$CH_3CH=CHCH_2OH$, 504-61-0; cyclooctene, 931-88-4; cyclohexene, 110-83-8.

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(8) $C_3V^{+}\cdot$–$C_9V^{+}\cdot$ are soluble in water and extracted into CH_2Cl_2 from water.

Nucleophilic Additions to a Metal Carbonyl Cation: Synthesis of Metallocarboxylate and Formyl Complexes of Molybdenum

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Reactions of nucleophiles with metal carbonyl complexes have been the subject of intense scrutiny in recent years.[2] Special interest has centered on hydroxide[3] and hydride[4] additions since these produce intermediates thought to be generated in catalytic processes relating to carbon monoxide conversion.[5]

However, efforts to synthesize metallocarboxylic acids by OH^- addition to metal carbonyl complexes have resulted in few instances of isolated and fully characterized products.[6] Previous methods

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