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Radical Transport Reaction. Concurrent Transfer of Electron and Proton

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Concurrent transport of electron and proton on the same molecule; formal hydrogen-transfer reaction, is successfully realized in aprotic media by using 1-butyl-4,4′-bipyridinium cation radical (BuPPH$^{+\cdot}$), which is prepared from 1-butyl-4-(4-pyridyl)pyridinium ion. Hydrogen reduction with BuPPH$^{+\cdot}$ was discriminated from electron reduction with octylviologen cation radical by the chemoselective reduction preferring enedione to *vic*-dibromide in aprotic media.

Alkylviologens (1,1′-dialkyl-4,4′-bipyridinium, RV^{2+}) are well-known to undergo one-electron reduction to give the resonance-stabilized cation radicals (RV$^{+\cdot}$), which in turn easily release an electron to regenerate RV^{2+}. On the merits of their reversible redox reactions with large negative potentials, they have been widely used as effective electron carriers in a variety of studies in photochemistry,[1)] solar energy conversion and storage,[2)] and organic synthesis,[3,4)] In all cases, however, alkylviologen served as an electron-transfer agent, and the overall reactions were most frequently completed with protons which were supplied from a large excess of surrounding protic media.

Our interests had been focused on the functions of alkylviologens as a catalytic electron mediator across a liquid membrane and a cation transporter coupled therewith, which led us to explore the potentialities of viologen analogues to transport concurrently both an electron and a cationic species, formally equivalent to a radical species. In the first place, we examined the hydrogen-transfer reduction as the simplest example of this scheme. On the basis of the structure of alkylviologens, one of the two *N*-alkyl groups was replaced with a protic hydrogen, which was expected to be transferred along with an electron (Scheme 1). In this article, we report that 1-butyl-4,4′-bipyridinium cation radical (BuPPH$^{+\cdot}$) functions efficiently as a formal hydrogen-transfer agent in aprotic media, and the scheme is exemplified by the selective reduction preferring enedione to *vic*-dibromide.

Results and Discussion

1-Butyl-4-(4-pyridyl)pyridinium ion (BuPP$^+$) showed the lowest redox potential, −0.48 V vs. NHE, in a pH$<$3 region,[5)] where it is in the form of 1-butyl-4,4′-bipyridinium (BuPPH^{2+}). The formation of BuPPH$^{+\cdot}$ X$^-$, where X denotes halogen, was effected by the reduction of BuPP$^+$Br$^-$ [6)] with zinc under acid conditions (Scheme 1), and was characterized by a strong sharp band at 400 nm and a weak broad one at 610 nm, resembling those of alkylviologen cation radicals (e.g. that of octylviologen, C$_8$V$^{+\cdot}$). The blue coloration lasted long enough stably under unaerobic conditions.

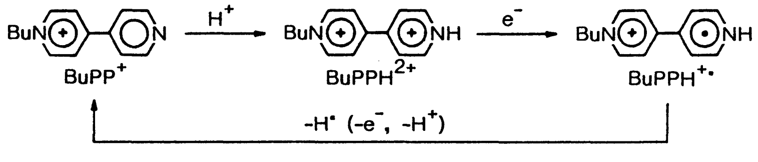
When prepared in the two-phase system of aqueous buffer and dichloromethane, BuPPH$^{+\cdot}$ X$^-$ was partitioned only in the aqueous phase, but it could be incorporated into the dichloromethane phase by anion-exchanging the halide for highly lipophilic tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate (TFPB$^-$)[7)] (Eq. 1). BuPPH$^{+\cdot}$ was also prepared under anhydrous conditions by using anhydrous TsOH in DMF (Eq. 2). For comparison, other radical analogues having no protic hydrogens within each molecule were prepared according to Eqs. 3—5. In every case, an excess of zinc was filtered off before use.

In order to prove the efficacy of BuPPH$^{+\cdot}$ as a hydrogen-transfer agent, two types of model substrates were selected to be reduced. One is (*E*)-1,4-diphenyl-2-

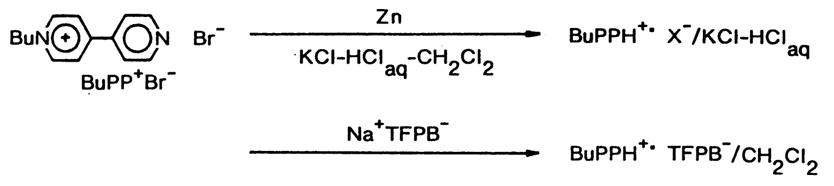
Table 1. Reduction of Enedione **1** and *vic*-Dibromide **3**

Entry	Reductant	Additive	Yield/%[a)]	
			2 in (A)	**4** in (B)
1	BuPPH$^{+\cdot}$TFPB^{-} [b)] /CH$_2$Cl$_2$		97[c)]	38
2	BuPPH$^{+\cdot}$TsO$^-$/DMF		99	97
3	BuPP$^\cdot$/DMF		7[d)]	84[c)]
4	C$_8$V$^{+\cdot}$X$^-$ [e)]/CH$_2$Cl$_2$		Trace[d)]	Quant.
5	C$_8$V$^{+\cdot}$Br$^-$/DMF		Trace[d)]	Quant.
6	C$_8$V$^{+\cdot}$Br$^-$/DMF	TsOH	27	64
7	C$_8$V$^{+\cdot}$Br$^-$/DMF	PyH$^+$TsO$^-$	34	70

a) Isolated yield. b) See the text. c) Molar ratio of substrate/reductant=1 : 3.3. d) **1** was recovered only in a small amount. e) X denotes halogen.



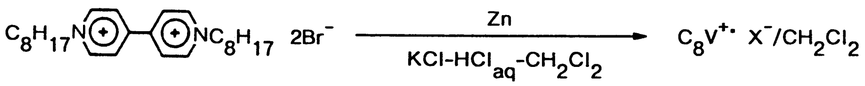
Scheme 1.



(1)

$$\mathrm{BuPP^{+}Br^{-}} \xrightarrow[\mathrm{DMF}]{\mathrm{TsOH,\ Zn}} \mathrm{BuPPH^{+\bullet}\ TsO^{-}/DMF} \qquad (2)$$

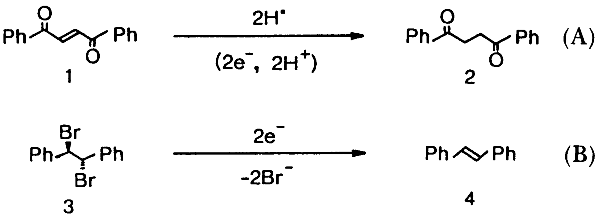
$$\mathrm{BuPP^{+}Br^{-}} \xrightarrow[\mathrm{DMF}]{\mathrm{Zn}} \mathrm{BuPP^{\bullet}\ /DMF} \qquad (3)$$



(4)

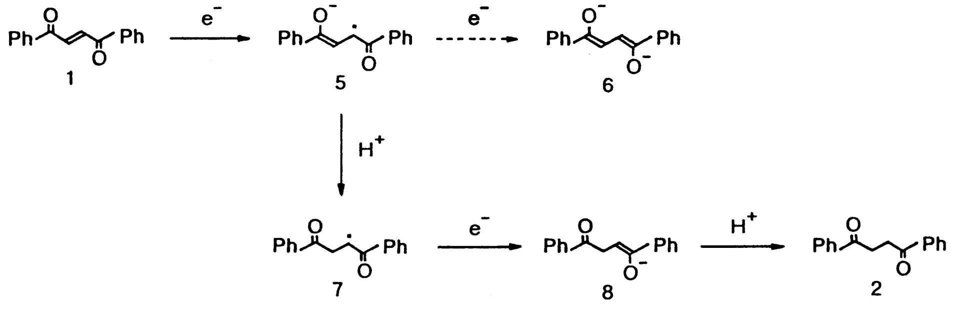
$$\mathrm{C_8V^{2+}2Br^{-}} \xrightarrow[\mathrm{DMF}]{\mathrm{Zn}} \mathrm{C_8V^{+\bullet}\ Br^{-}/DMF} \qquad (5)$$

butene-1,4-dione (**1**), whose reduction to 1,4-diketone **2** requires proton source for its completion (System (A)), and the other is *meso*-1,2-dibromo-1,2-diphenylethane (**3**), which can be debrominated to olefin **4** by accepting electrons alone (System (B)). The reducing efficiencies of BuPPH‡ are summarized in Table 1, in comparisons with those of BuPP• and $C_8V^{\ddagger}$ in the two reaction systems (A) and (B).

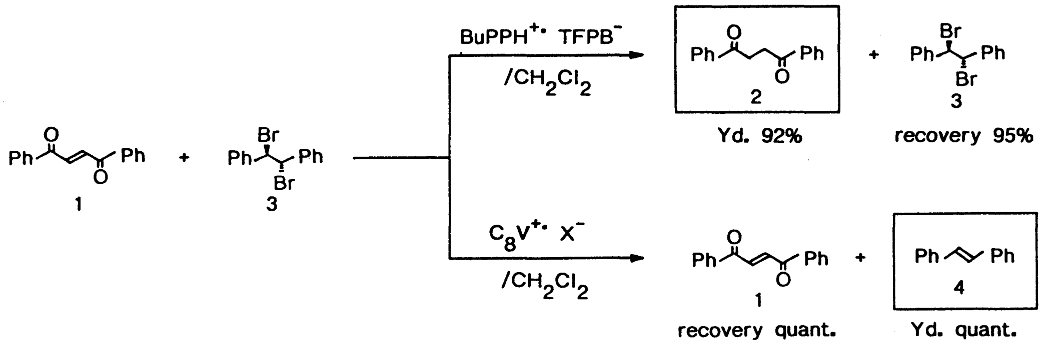


As shown in Table 1, BuPPH‡ worked dually as a hydrogen-reducing agent in the system (A),[8] as well as an electron-reducing agent in the system (B) both in dichloromethane and DMF (Entries 1 and 2), though seemed more favorable to the former system (A). By contrast, $C_8V^{\ddagger}$ served only as an electron-reducing agent in such aprotic media to afford the debrominated product in the system (B), and when applied to the system (A), afforded only a trace amount of the hydrogenated product (Entries 4 and 5). In the same reaction systems, BuPP• which had no protic hydrogens in the molecule showed similar chemoselectivities to those of $C_8V^{\ddagger}$ (Entry 3 vs. Entry 5). The highly efficient reduction of the system (A) in the presence of protic hydrogens may be explained as follows: Enedione **1** initially accepts an electron to give the anion radical **5**, which is difficult to accept an additional electron to the dianion **6**. However, if the anion radical **5** is protonated in situ to the radical **7**, then it is easily reduced further to yield the expected product **2** (Scheme 2). Therefore, when the separate proton source such as TsOH or pyridinium tosylate (PyH^{+} TsO^{-}) was added, the reduction of the system (A) proceeded even with $C_8V^{\ddagger}$, though did to much less extent than the reaction with BuPPH. (Entries 6 and 7 vs. Entry 2). These results indicate that the protic hydrogen which is carried concurrently with an electron on the same molecule promoted the hydrogenation of the system (A) more efficiently than that carried separately from the electron, thus, the concurrent transport of an electron and a proton; formal hydrogen transfer, was successfully attained by BuPPH‡.

These observations forced us to examine the effica-



Scheme 2.



Scheme 3.

Table 2. Reduction of α,β-Unsaturated Ketones with BuPPH$^{+\cdot}$ in DMF

Substrate	Product	Temp	Time/h	Yield/%
p-Benzoquinone	Hydroquinone	r.t.	20	60
Diphenyl diketone	Benzoin	r.t.	10	83
Chalcone	1,3-Diphenyl-1-propanone	r.t.	4	11

cies of hydrogen and electron transfer in terms of chemoselectivities in the reduction of enedione **1** and *vic*-dibromide **3**. When the equimolar mixture of **1** and **3** was treated with BuPPH$^{+\cdot}$ or C$_8$V$^{+\cdot}$ in dichloromethane, the reduction of **1** or **3** proceeded selectively without affecting the other substrate which could be recovered in each case (Scheme 3). In these reactions it is noted that BuPPH$^{+\cdot}$ favors exclusively the hydrogen reduction and the chemoselective reduction between **1** and **3** can be achieved simply by the selection of the present two types of bipyridinium salts. BuPPH$^{+\cdot}$ could hydrogenate some analogous substrates, as shown in Table 2, though in the last line rather poor yield resulted.

This reagent would be also useful as hydrogen-transporting agent through a hydrophobic liquid membrane, combined with the photosensitized formation of 4,4′-bipyridinium cation radicals.[3b,4a)]

Experimental

Materials. BuPP$^+$Br$^-$ was prepared from the reaction of 4,4′-bipyridine with butyl bromide in acetonitrile according to the literature.[6,9)] When BuPP$^+$Br$^-$ was stirred with powdered zinc in DMF under an argon atmosphere, the blue coloration was rapidly developed due to the formation of BuPP$^\cdot$; VIS 736.2 (relative absorbance 0.05), 665 (sh, 0.16), 607.6 (0.31), 400.8 (1.00), 390 (0.67), and 375 nm (0.43). The absorption maxima of its protonated form, BuPPH$^{+\cdot}$, developed in the presence of an equimolar amount of TsOH were almost unchanged; VIS 736.4 (0.08), 666 (sh, 0.20), 609.6 (0.39), 400.4 (1.00), 388.6 (0.85), and 374.6 nm (0.72). These values corresponded to those of C$_8$V$^{+\cdot}$ in DMF; VIS 736.0 (relative absorbance 0.06), 660 (sh, 0.16), 608.8 (0.33), 400.8 (1.00), 390 (0.62), and 373 nm (0.37).

Procedures. Reductions of **1** or **3** with viologen analogues were carried out at room temperature, where the viologen analogue was used by 2.2 times molar amounts to the substrate, unless otherwise described, and reduced with powdered zinc to its radical form. The excess of zinc was removed before use by filtration through a disposable Teflon membrane filter (pore size of 0.5 μm) attached to the nozzle of a syringe. The product was isolated by column chromatography on silica gel, eluted with 9:1 mixture of hexane and ether.

Typical procedures of the reduction reaction were as follows:

Reduction of 1 with BuPPH$^{+\cdot}$ TFPB$^-$ in Dichloromethane: Into a two-phase mixture of dichloromethane (20 cm^3) and aqueous HCl–KCl buffer (pH 2.0, 20 cm^3) were added BuPP$^+$Br$^-$ (97 mg, 0.33 mmol) and Na$^+$TFPB$^-$ 2.5H$_2$O (308 mg, 0.33 mmol). The mixture was stirred under argon atmosphere, and was added powdered zinc (106 mg, 16.2 mmol). Blue coloration of BuPPH$^{+\cdot}$TFPB$^-$ rapidly developed in the organic phase. After stirred for 1 min at room temperature, the organic phase was filtered. The filtrate was added to **1** (24 mg, 0.10 mmol) and the reaction mixture was stirred at room temperature for 20 h. After usual work-up, 1,4-diphenyl-1,4-butanedione (**2**) (23 mg, 97% yield) was isolated.

Reduction of 1 with BuPPH$^{+\cdot}$TsO$^-$ in DMF: To a DMF solution (4 cm^3) of BuPP$^+$Br$^-$ (78 mg, 0.27 mmol) and anhydrous TsOH (46 mg, 0.27 mmol) was added powdered zinc (183 mg, 2.8 mmol) under an argon atmosphere. After stirred for 1 min at room temperature, the mixture was filtered. To the filtrate, **1** (29 mg, 0.12 mmol) in DMF (1 cm^3) was added dropwise and the reaction mixture was stirred at room temperature for 11 h. After usual work-up, 1,4-diphenyl-1,4-butanedione (**2**) (29 mg, 99% yield) was isolated.

Reduction of 1 with C$_8$V$^{+\cdot}$Br$^-$ in the Presence of TsOH: C$_8$V$^{+\cdot}$Br$^-$ in DMF was prepared from C$_8$V^{2+}2Br$^-$ (106 mg, 0.20 mmol) and zinc (126 mg, 1.9 mmol). Anhydrous TsOH (34 mg, 0.20 mmol) was added to the filtrate before the addition of **1**. After usual work-up, **2** (5.6 mg, 27% yield) was isolated.

Reduction of 3 with C$_8$V$^{+\cdot}$Br$^-$ in the Presence of TsOH: C$_8$V$^{+\cdot}$Br$^-$ in DMF was prepared in a similar manner as above. The addition of the filtrate to a mixture of anhydrous TsOH and **3** resulted in **4** (8.8 mg, 64% yield).

Reduction of a Mixture of 1 and 3 with $\text{BuPPH}^{\dot{+}}\text{TFPB}^{-}$ in Dichloromethane: $\text{BuPPH}^{\dot{+}}\text{TFPB}^{-}$ was prepared in a two-phase mixture of dichloromethane and aqueous HCl-KCl buffer (pH 2) from $\text{BuPP}^{+}\text{Br}^{-}$ (38 mg, 0.13 mmol), $\text{Na}^{+}\text{TFPB}^{-}$ $2.5\text{H}_2\text{O}$ (133 mg, 0.14 mmol) and zinc (444 mg, 6.79 mmol) in a similar manner as above. $\text{BuPPH}^{\dot{+}}\text{TFPB}^{-}$ in dichloromethane was added to a mixture of **1** (14 mg, 0.059 mmol) and **3** (20 mg, 0.059 mmol). After usual work-up, **2** (13 mg, 92% yield) and **3** (19 mg, 95% recovery) were isolated.

Reduction of a Mixture of 1 and 3 with $\text{C}_8\text{V}^{\dot{+}}\text{X}^{-}$ in Dichloromethane: $\text{C}_8\text{V}^{\dot{+}}\text{X}^{-}$ was prepared in dichloromethane from $\text{C}_8\text{V}^{2+}2\text{Br}^{-}$ (58 mg, 0.11 mmol) and zinc (350 mg, 5.35 mmol). The filtered solution of $\text{C}_8\text{V}^{\dot{+}}\text{X}^{-}$ was added to a mixture of **1** (21 mg, 0.089 mmol) and **3** (30 mg, 0.089 mmol). After usual work-up, **4** (16 mg, quantitative yield) and **1** (21 mg, quantitative recovery) were isolated.

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