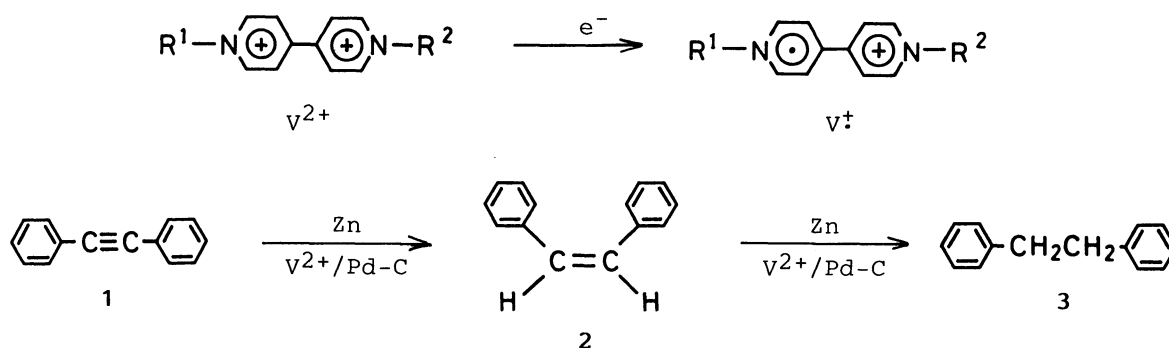


Catalytic Reduction of Diphenylacetylene by Zinc over Palladium-Carbon
Using Viologens as Electron Mediators

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Diphenylacetylene was reduced over palladium-carbon in methanol-water mixture in presence of zinc using *N,N'*-dialkyl-4,4'-bipyridinium ions (viologens) as mediators giving *cis*-stilbene as the major product and bibenzyl as the minor one. The reaction involved the direct contact of zinc with the catalyst.

Molecular designing and construction of an artificial photosynthetic system have been current target of research to convert and store the solar energy, to which *N,N'*-dialkyl-4,4'-bipyridinium ions (viologens, V^{2+}) have been proved to be distinguished electron acceptors and carriers for photo-induced charge separation.¹⁾ Recently attentions have been directed toward the use of viologens as a synthetic tool. Papers have, for example, published on the viologen-mediated reduction of aldehyde, ketones,²⁾ keto esters,³⁾ azobenzene,⁴⁾ vic-dibromides⁵⁾ and nitroalkenes⁶⁾ in homogeneous or two phase liquid systems. Viologens have also been used as an electron mediator in electrolytic reductions.⁷⁾ No studies have so far been reported on the reduction of any unsaturated hydrocarbon. In this work we examined a viologen-mediated reduction of a $C\equiv C$ triple bond in a heterogeneous system.



In 80 ml of methanol-water (9:1) mixture 0.954 mmol of diphenylacetylene (1), 0.035 mmol of *N,N'*-diethyl-4,4'-bipyridinium dibromide (EV^{2+}), 130 mg of 5%-palladium-carbon (Pd-C) and 3.83 mmol of zinc dust were stirred in the dark under nitrogen at 30 °C.⁸⁾ The reaction mixture was filtered and the precipitate was washed with warm methanol. The filtrate was partly concentrated under reduced pressure and extracted with chloroform. After removal of the solvent the residue

was found by $^1\text{H-NMR}$ to consist of *cis*-stilbene (**2**), bibenzyl (**3**) and recovered **1**.⁹ The total of molar recoveries of **1**, **2** and **3** was more than 95%.

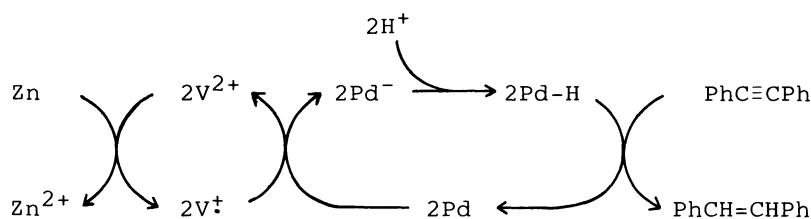
The reaction proceeded in such a way that **2** was produced predominantly until **1** was almost completely consumed, after which the second reaction to form **3** took place. This resembles the well known fact that acetylenic compounds inhibit the reductions of ethylenic compounds by hydrogen gas over palladium catalysts.¹⁰ No reaction took place when the system lacked viologen, zinc or Pd-C. Replacement of viologen by quaternary ammonium salts, such as tetrabutylammonium bromide, cetyltrimethylammonium bromide and *N*-alkylpyridinium bromide, resulted in a complete recovery of **1**. When **1** was absent in the system, little amount of zinc was consumed.

1 was reduced by using viologens with various *N*-substituents giving the results as shown in Table 1. The conversion decreased with increasing length of

Table 1. Results of the reduction of diphenylacetylene a)

Viologen	R ¹	R ²	Conversion of 1	Composition of product/%		
			%	1	2	3
none			<0.1	>99.9	<0.1	<0.1
MV ²⁺	CH ₃	CH ₃	46.5	53.5	45.9	0.6
EV ²⁺	C ₂ H ₅	C ₂ H ₅	36.5	63.5	35.6	0.9
2C ₃ V ²⁺	<i>n</i> -C ₃ H ₇	<i>n</i> -C ₃ H ₇	35.2	64.8	34.3	0.9
2C ₄ V ²⁺	<i>n</i> -C ₄ H ₉	<i>n</i> -C ₄ H ₉	34.0	66.0	33.5	0.5
2BzV ²⁺	CH ₂ C ₆ H ₅	CH ₂ C ₆ H ₅	34.7	65.3	33.2	1.5
C ₁₆ Ev ²⁺	<i>n</i> -C ₁₆ H ₃₃	C ₂ H ₅	24.5	75.5	23.8	0.7
2C ₁₆ V ²⁺	<i>n</i> -C ₁₆ H ₃₃	<i>n</i> -C ₁₆ H ₃₃	19.7	80.3	17.8	1.9

a) **1**: 0.954 mmol; viologen: 0.035 mmol; 5%-Pd-C: 130 mg; Zn: 3.83 mmol; in 80 ml of MeOH-H₂O (9:1) at 30 °C for 6 h.



Scheme 1.

alkyl substituents of the viologens. All of the viologens used herein gave **2** selectively.

Above facts suggest a mechanism involving linked redox cycles as shown in Scheme 1, in which the viologen transfers electron from zinc to palladium, and the accumulated electron reduces proton from water to generate hydrogen which without liberation adds to **1**. In order to examine which viologen in the solution or on the catalyst transfers electrons from zinc to palladium, the reduction was attempted

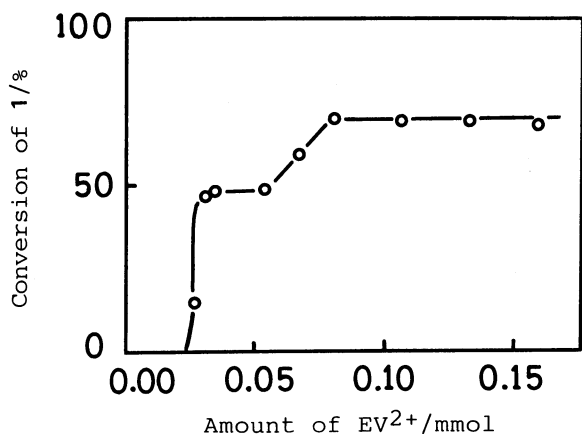


Fig. 1. Plots of the conversion of 1 against the amount of EV²⁺. 1: 0.954 mmol; Pd-C: 125 mg; Zn: 3.83 mmol; in 80 ml of MeOH-H₂O(9:1) at 30 °C for 7 h.

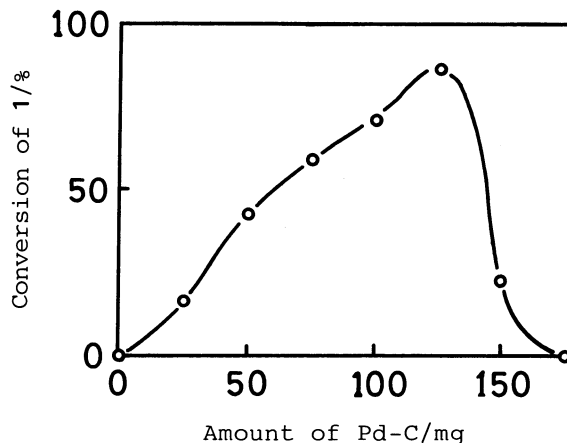


Fig. 2. Plots of the conversion of 1 against the amount of Pd-C. 1: 0.954 mmol; EV²⁺: 0.035 mmol; Zn: 3.83 mmol; in 80 ml of MeOH-H₂O(9:1) at 30 °C for 10 h.

using zinc dust placed in a closed bag of filter paper wrapped with a piece of cloth. Indeed the solution showed the characteristic blue color of the cation radical (V^{•+}) formed by the reduction of viologen, no reduction of 1 was observed, indicating that the reaction involves the direct contact of zinc with the catalyst.

Figure 1 shows the dependencies of the conversion on the concentration of EV²⁺. The reaction hardly occurred for the concentration less than 0.025 mmol, above which the reaction took place and the rate increased rapidly with increasing concentration of the viologen. The conversion reaches almost constant above the amount of EV²⁺ of 0.08 mmol, which coincides the amount for the saturation of adsorption on Pd-C determined by the absorbance of the absorption maximum of viologen at 260 nm in the methanol-water mixture.

As shown in Fig. 2 the rate increases with increasing amount of Pd-C reaching maximum at the amount of 125 mg. No reaction occurred above 175 mg. Excess Pd-C seems to adsorb EV²⁺ at the inactive site decreasing the reduction rate.

Figure 3 shows optimum methanol/water ratio of 9:1. The solvent with less water content is considered not to provide enough proton to generate hydrogen on the catalyst. On the other hand, the catalyst may reluctantly desorb the reduction product of hydrophobic nature in the solution with higher water content decreasing the reaction rate.

Nonaka et al. have hydrogenated

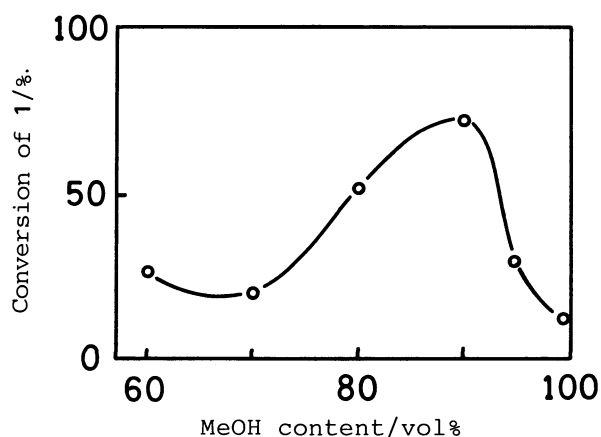


Fig. 3. Relation between the conversion of 1 and the composition of the solvent. 1: 0.954 mmol; EV²⁺: 0.035 mmol; Pd-C: 125 mg; Zn: 3.83 mmol; in 80 ml of MeOH-H₂O at 30 °C for 10 h.

diphenylacetylene with a palladium-black cathode and obtained **2**.¹¹⁾ A mechanism common to the present reaction is deduced. However the cathodic reaction affords an appreciable amount of **3** in strong acidic media, and the yield of trans-stilbene increases in strong alkaline media.

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