

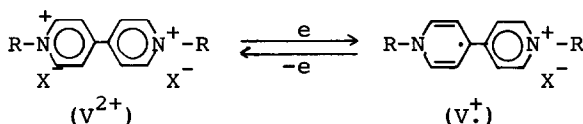
VIOLOGENS THAT PLUNDER ELECTRON FROM SOLID REDUCING AGENT.
REDUCTION OF ARYL KETONES BY ZINC POWDER IN THE PRESENCE
OF PROPYL VIOLOGEN AS AN ELECTRON TRANSFER CATALYST

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It was found that viologen (propyl viologen) acted as an Electron Transfer Catalyst (ETC) in the reduction of aryl ketones with zinc powder. α -Diketones undertook the two-electron reduction to obtain the corresponding benzoin in good yields and aromatic ketones could one-electron reduced selectively to give the corresponding pinacols.

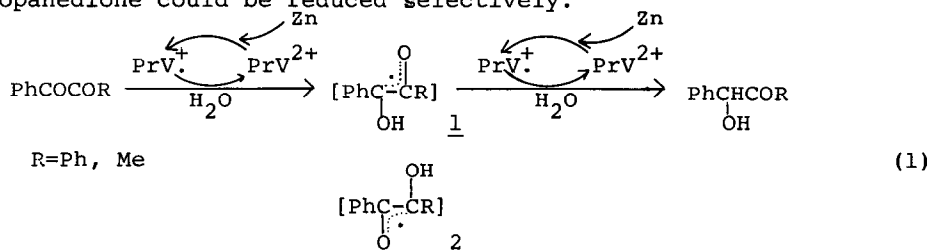
Viologen (1,1'-dialkyl-4,4'-bipyridinium, V^{2+}) is known to undergo one-electron reduction to produce the cation radical ($V^{\cdot+}$), which is easily reoxidized to V^{2+} . More recently, viologens have received much attention as an ETC in redox system,¹ especially in hydrogen production by photoreduction of water.



Further, the viologen-mediated reductions of organic compound have been reported by us.^{2,3}

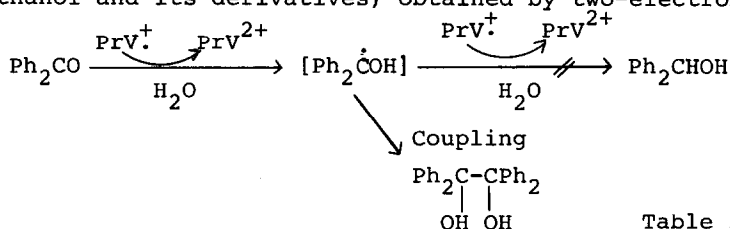
In this communication, we wish to report the reduction of aryl ketones such as α -diketones and aromatic ketones with zinc⁴ at room temperature using propyl viologen (PrV^{2+}) as a catalyst.

The reduction of α -diketones like diphenylethanedione and 1-phenyl-1,2-propanedione by zinc were carried out with or without PrV^{2+} . The reaction conditions and the results were shown in Table 1. The reduction did not occur at all in the absence of PrV^{2+} . On the other hand, the reaction proceeded smoothly in the presence of PrV^{2+} to obtain the two-electron reduced products, 2-hydroxy-1,2-diphenylethanone and 1-hydroxy-1-phenyl-2-propanone, in good yields respectively. Four-electron reduced products (diols) were not produced although zinc powder was used in excess. Further, only the carbonyl group attached to the phenyl residue in the case of 1-phenyl-1,2-propanedione could be reduced selectively.



Considering that 1 is more likely as a radical intermediate than 2 because of the stabilization by the phenyl group, scheme (1) may be reasonable to explain the regioselectivity.

Aryl ketones, which do not have α -carbonyl group, were treated in a similar condition. The results are indicated in Table 2. Although acetophenone and 4-cyanoacetophenone were not reduced even at 50°C, benzophenone and its chlorinated derivatives undertook one-electron reduction at room temperature in the presence of PrV^{2+} to yield corresponding pinacol derivatives. However, the products (diphenylmethanol and its derivatives) obtained by two-electron reduction were not obtained.



It is extremely interesting that viologen plunders electron from solid zinc and transfers electron to carbonyl compounds.

Table 1. Reduction of α -Diketones by Zinc^a

α -diketone	PrV^{2+} ^b (mmol)	product	yield(%)
PhCOCOPh	none	-	0
PhCOCOPh	0.05	PhCH(OH)COPh	92
PhCOCOCH ₃	none	-	0
PhCOCOCH ₃	0.05	PhCH(OH)COCH ₃	97

^aThe experiment was performed with 1.5 mmol of Zinc, 1.0 mmol of α -diketone, and propyl viologen in 20 mL of $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ (49:1) at room temperature for 24 h with stirring. ^b PrV^{2+} : propyl viologen.

References and Notes

- J. G. Caray, J. F. Caians, and J. E. Colchester, *J. Chem. Soc. Chem. Commun.*, **1969**, 1280; K. Kalyanasundaram, J. Kiwi, and M. Gatzel, *Helv. Chim. Acta*, **1978**, 61, 2720; A. I. Krasna, *Photochem. Photobio.*, **1979**, 29, 276; I. Okura and N. Kim-Thuan, *J. Mol. Catal.*, **1979**, 5, 331.
- K. Ageishi, T. Endo, and M. Okawara, *J. Polym. Sci. Polym. Chem. Ed.*, **1983**, 21, 175.
- Y. Saotome, T. Endo, and M. Okawara, *Macromolecules*, **1983**, 16, 881.
- It has been reported that benzophenone is reduced with Zn/NaOH in $\text{H}_2\text{O}-\text{C}_2\text{H}_5\text{OH}$ at 70°C to obtain diphenylmethanol without producing pinacol [F.Y. Wiselogle and H. Sonneborn, "Organic Syntheses," Coll. Vol I, p.90(1941)], and diphenylethanedione is also reduced with Zn in DMF- H_2O under refluxing to give 1-hydroxy-1,2-diphenylethanone (W. Kreiser, *Liebigs Ann. Chem.*, **1971**, 745, 164).

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Table 2. Reduction of Aryl Ketones^a

ketone	PrV^{2+} ^b (mmol)	pinacol(%)
PhCOCH ₃	0.05	0
PhCOCH ₃	0.05	0 ^c
p-CNC ₆ H ₄ COCH ₃	0.05	0
p-CNC ₆ H ₄ COCH ₃	0.05	0 ^c
Ph ₂ CO	none	0
Ph ₂ CO	0.05	13
Ph ₂ CO	0.20	20
Ph ₂ CO	0.20 ^d	63
p-ClC ₆ H ₄ COPh	none	0
p-ClC ₆ H ₄ COPh	0.20	57
(p-ClC ₆ H ₄) ₂ CO	none	0
(p-ClC ₆ H ₄) ₂ CO	0.20	49 ^e

^aThe experiment was performed with 1.5 mmol of zinc, 1.0 mmol of the ketone, and propyl viologen in 20 mL $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ (49:1) at room temperature for 24 h with stirring. ^b PrV^{2+} : propyl viologen. ^cat 50°C. ^dadded dropwise for 24 h. ^eNMR yield.