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Photochemical and Chemical Reduction of Nitroalkenes Using Viologens as an Electron Phase-Transfer Catalyst

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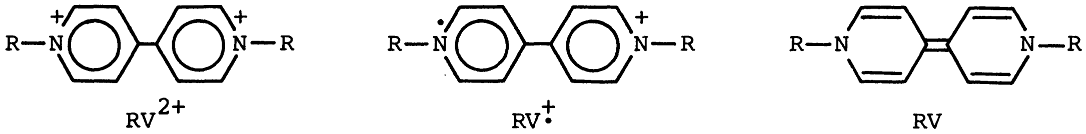
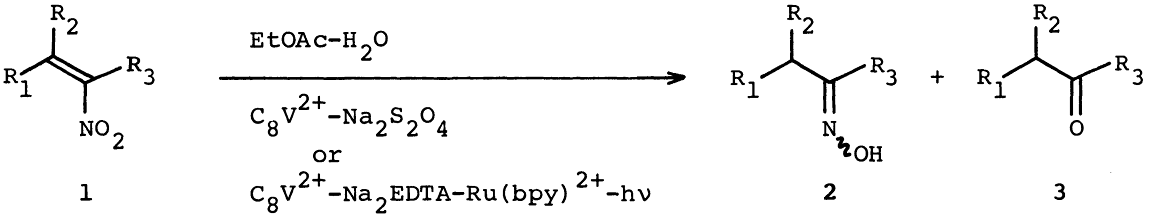
An amphiphilic electron acceptor, i.e., N,N'-dioctyl-4,4'-bipyridinium, was used as an electron carrier between water-oil two phases, in which nitroalkenes in organic phase were readily reduced to the corresponding oximes and/or carbonyl compounds.

Alkylviologens (1,1'-dialkyl-4,4'-dipyridinium salts, RV^{2+}) have been widely explored as electron acceptors and electron carriers in particular as a means of solar energy conversion and storage[1,2] since the single-electron-transfer products ($RV^{\dot{+}}$) can reduce protons to give hydrogen gas.[3] The utilization of RV^{2+} in chemical routes and in particular as a synthetic tool is a relatively unexplored field and is attracting much recent attention. The viologen-mediated reductions of organic compounds, e.g., aldehyde, ketones,[4,5] keto esters,[6] azobenzene[7] and vic-dibromides[8,9] have been reported quite recently. Among the different alkylviologens, N,N'-dioctyl-4,4'-bipyridinium dibromide (C_8V^{2+})[10] shows interesting solubilization properties, depending on its oxidation state.[11] The oxidation form, C_8V^{2+}, is soluble only in aqueous media, while the reduced form, $C_8V^{\dot{+}}$, is extracted into organic phases. Thus, electron acceptor can be used as electron carriers between two phases, leading to the reduction of substrates in organic phase. In this communication, we wish to report that nitroalkenes are readily reduced either chemically or photochemically in a two-phase system mediated by C_8V^{2+}.



To the two phase system composed of an organic ethyl acetate phase (10 mL) that includes β-nitrostyrene (**1e**, 1 mmol) and an aqueous solution (10 mL) of sodium dithionite (5 mmol), C_8V^{2+} (0.05 mmol) was added under argon. The blue color of $C_8V^{\dot{+}}$ immediately developed in the aqueous phase. Upon stirring the reaction mixture, the radical is extracted into the organic phase. After stirring for 1 h, the organic phase was condensed and chromatographed on preparative TLC (silica gel) to afford β-phenylacetaldehyde oxime (**2e**, 85%) as major product with small amount of the aldehyde (**3e**, 4%). No reduction of the nitroalkene occurs when C_8V^{2+} is excluded from the system. This implies that C_8V^{2+} mediates the reduction process. Moreover it is clear that the active reductant in the reduction is recycled in the process since the molar ratio of C_8V^{2+} to the nitroalkene is 1:20.

The photosensitized reductions of V^{2+} to $V^{\dot{+}}$ are extensively studied in particular as a means of solar energy conversion and storage.[1,2] In these systems, organometallic compounds such as ruthenium tris(bipyridine), $Ru(bpy)_3^{2+}$, or zinc porphyrins are used as sensitizers, and triethanolamine or ethylenediaminetetracarboxylic acid, EDTA, are employed as a reducing agent. Thus, in the previous systems the reducing agent solubilized in the aqueous phase could be substituted by a sensitizer and electron donor. The two phase system composed of ethyl acetate (15 mL) that includes **1e** (0.5 mmol) and aqueous phase (25 mL) that includes ruthenium tris(bipyridine) dichloride (0.025 mmol), disodium ethylenediaminetetraacetic acid (Na_2EDTA, 2.5 mmol), and C_8V^{2+} (0.05 mmol) was flushed with argon and irradiated with stirring with 500-W halogen lamp through Corning CS-052 filter (>400 nm). After a few minutes of illumination the blue color of $C_8V^{\dot{+}}$ was observed in the organic phase. After irradiation for 3 h, followed by the usual work-up, **2e** and 3e were obtained. Exclusion of either C_8V^{2+}, Na_2EDTA, $Ru(bpy)_3^{2+}$, or light from the system prevents the reduction process. These results demonstrate the photosynthetic formation of oxime via oxidation of Na_2EDTA by the nitrostyrene in a cyclic process mediated by C_8V^{2+}. In this cycle, quenching of the excited $Ru(bpy)_3^{2+}$ by C_8V^{2+} results in the photoproducts $Ru(bpy)_3^{3+}$ and $C_8V^{\dot{+}}$. The oxidized photosensitizer $Ru(bpy)_3^{3+}$ oxidizes Na_2EDTA and the sensitizer is recycled.



Using the similar procedure the other nitroalkenes (**1**) were reduced to the respective oximes (**2**) and carbonyl compounds (**3**), as summarized in Table 1. As can be seen from Table 1, the present systems can be applied to reduce various nitroalkenes bearing alkyl and aryl groups although the product ratios are somewhat sensitive to the number and type of substituents. Thus, the oximes were major products in the reduction of nitroalkenes that have 2-alkyl and 1,2-dialkyl groups. On the other hand, the carbonyl compounds came to be formed in the reduction of nitroalkenes bearing phenyl groups. Control experiments showed that the oxime is not hydrolyzed to the carbonyl compound under the reaction conditions, indicating that the latter is formed directly from the nitroalkene.

Table 1. Reduction of Nitroalkenes Using N,N'-Dioctyl-4,4'-bipyridinium Dibromide (C_8V^{2+})

1	R in 1			Method[a)]	Yield/%[b)]	
	R_1	R_2	R_3		**2**	**3**
a	H	$^nC_5H_{11}$	H	A	78.7	0
b	H	$^nC_5H_{11}$	Me	A	100	0
				B	100	0
c	H	—$(CH_2)_4$—		A	45.9	0
d	H	Ph	H	A	66.7	33.3
e	H	Ph	Me	A	91.2(85)	8.8 (4)
				B	81.1(78)	6.6 (5)
f	H	Ph	Ph	A	52.9	45.4
g	Ph	Ph	H	A	6.5	55.8
h	Ph	Ph	Ph	A	0	84.3(78)

a) Method A: chemical reduction. Method B: photochemical reduction. See text for the detailed procedure. b) Yields determined by GC analysis. The yield in parenthesis refers to isolated products.

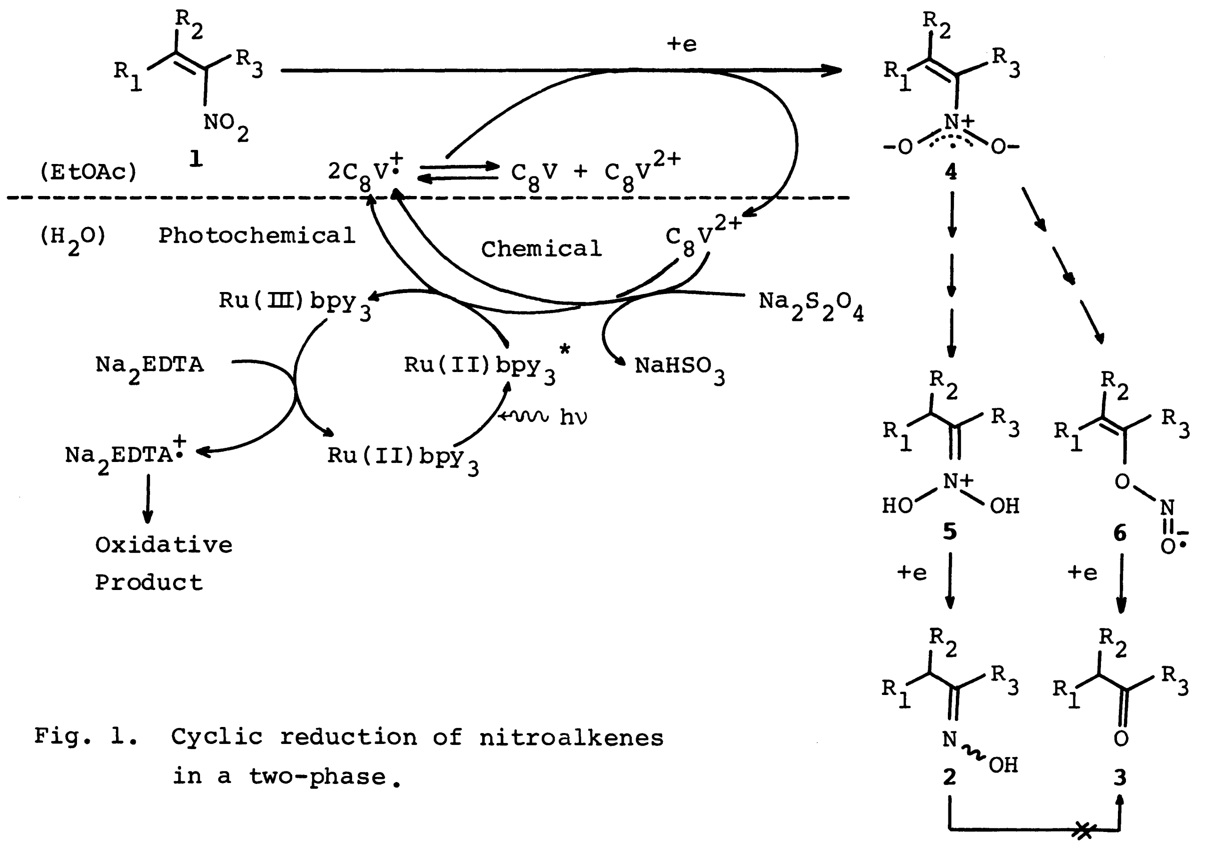


Fig. 1. Cyclic reduction of nitroalkenes in a two-phase.

The entire scheme leading to the cyclic reduction of the nitroalkenes is displayed in Fig. 1. Thus, C_8V^{2+} in the aqueous phase is reduced either by sodium dithionite in the chemical redution systems or by the excited $Ru(bpy)_3^{2+}$ in the photochemical systems to generate $C_8V^{+\cdot}$ which is extracted into the organic phase due to its hydrophilic charactor. In the organic phase $C_8V^{+\cdot}$ or its disproportionation product C_8V induced two-electron reduction of nitroalkenes to regenerate C_8V^{2+} which is reextracted into the aqueous phase. Consequently, the active species capable of reducing the nitroalkene is produced. Exact pathway from **1** to **2** and/or 3 is not known at present. The scheme in Fig. 1 is quite analogous to that given for the photochemical reduction of nitroalkenes.$^{12)}$ Thus, the nitroalkenes initially accept an electron from C_8V and/or $C_8V^{+\cdot}$ to generate anion radical (**4**), which either undergoes proton and/or hydrogen abstraction, followed by subsequent one-electron-transfer to form oxime, or rearranges to vinyl nitrite anion radical (**6**) followed by subsequent one-electron-transfer and release of nitrogen oxide to afford ketone, depending on the structure of nitroalkene. The latter process is especially favorable when phenyl group is introduced on the alkene moiety. This is partially because the enol form is much more stable due to resonance stabilization by phenyl group.

References

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