Photoinduced Transacetalization using a Tris(bipyridine)ruthenium(II)–Methyl Viologen Cosensitizing System

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The title transacetalization between 2-phenoxytetrahydropyrans and octan-1-ol occurs *via* an initial one-electron exchange mechanism.

We recently reported a photoinduced transacetalization between 2-aryloxytetrahydropyrans and alcohols using an aromatic hydrocarbon–cyanoaromatic cosensitizing system, for which a novel $S_{ON}1$ mechanism was proposed.[1] Here we describe the effect of tris(bipyridine)ruthenium(II) dichloride [$Ru(bpy)_3^{2+}$] which causes photo-redox reactions by a well-defined mechanism,[2] proving the validity of this mechanism.

Almost no reaction took place when a 200 W mercury lamp was used to irradiate an equimolar mixture of 2-phenoxytetrahydropyran (**1**) and octan-1-ol in acetonitrile containing a catalytic amount of $Ru(bpy)_3^{2+}$. However, addition of methyl viologen (MV^{2+}) as cocatalyst gave the acetal (**2**) and phenol. Thus the transacetalization was achieved under nearly neutral conditions. When the 6-methyl derivative (**3**) was irradiated with octan-1-ol, a 2:8 mixture of *cis*- and *trans*-(**4**) was obtained. The isomeric ratio was not affected by the stereochemistry of the starting material (**3**). These products are stable under the reaction conditions, and the thermodynamic ratio of the stereoisomers is *ca.* 4:6.[1] Therefore the observed stereoselectivity appears to be a result of a kinetic anomeric effect in the nucleophilic reaction of octan-1-ol with the oxocarbenium intermediate. As shown in Table 1, the presence of a trace amount of water facilitated the phototransacetalization,† although 2-hydroxytetrahydropyran was

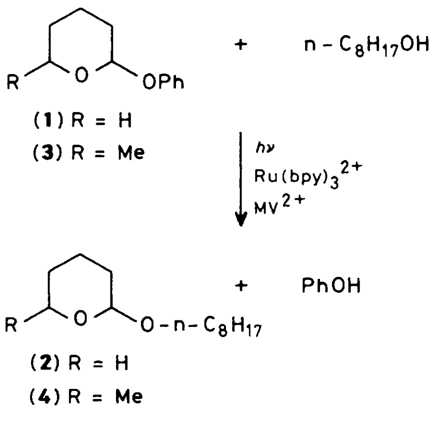

Table 1. Photosensitized transacetalization.[a]

Sub-strate	Solvent	Irradiation time/h	% Substrate conversion	% Yield[b] Acetal	% Yield[b] Phenol
(**1**)	MeCN	30	3[c]	70	97
(**1**)	MeCN[d]	30	2	88	96
(**1**)	MeCN	30	51	79	99
(**1**)	MeCN–H_2O (100:1)[e]	20	73	34[f]	99
trans-(**3**)	MeCN	30	42	92	99
cis-(**3**)	MeCN	30	32	89	95

[a] Reaction was conducted by irradiation of a mixture of the substrate, octan-1-ol, tris(2,2′-bipyridine)ruthenium(II) dichloride, and methyl viologen ($MV^{2+}\cdot 2Cl^-$) (100:100:3:3—5 molar ratio) with a 200 W high-pressure mercury arc at 20 °C. Concentrations of $Ru(bpy)_3^{2+}$ and MV^{2+} were 5×10^{-3} M and 5—8 × 10^{-3} M, respectively. [b] Based on conversion. [c] No methyl viologen was added. [d] Molecular sieves 4 Å added. [e] No reaction in 10:1 MeCN–H_2O. [f] The major byproduct was 2-hydroxytetrahydropyran.

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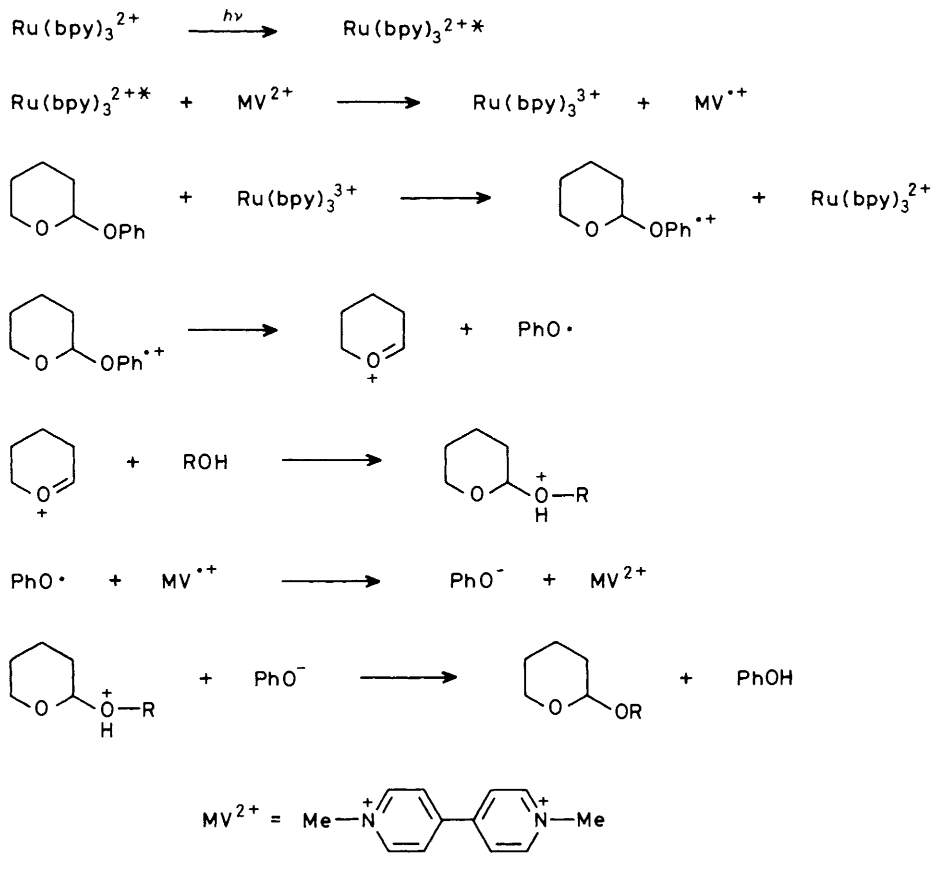
† MV^{2+} is insoluble in dry acetonitrile. 9,10-Dicyanoanthracene (soluble in anhydrous acetonitrile, $E^{\frac{1}{2}}_{red.} = -0.80$ V) also serves as cocatalyst though less effectively.



Scheme 1

obtained as the major side-product. Replacement of the $Ru(bpy)_3{}^{2+}$ catalyst by 4,4′- or 5,5′-bis-ethoxycarbonylated analogues retarded the reaction.

Thus redox properties of the substrate (**1**) [$E^{\frac{1}{2}}_{\text{ox.}}$ = 1.08 V *vs.* standard calomel electrode (S.C.E.)], excited $Ru(bpy)_3{}^{2+}$ ($E^{\frac{1}{2}}_{\text{ox.}}$ = −0.81 V),[3] $Ru(bpy)_3{}^{2+}$ ($E^{\frac{1}{2}}_{\text{ox.}}$ = 1.29 V),[4] and MV^{2+} ($E^{\frac{1}{2}}_{\text{red.}}$ = −0.46 V)[3] balance nicely for the electron-transfer reaction. Under the present and previously discovered phenanthrene (or triphenylene)–dicyanobenzene cosensitized conditions,[1] 2-aryloxytetrahydropyrans behave basically in an identical manner, indicating operation of a common $S_{\text{ON}}1$ mechanism.[4] The overall catalytic cycle is outlined in Scheme 1.

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