CONCLUSIONS

An efficient synthesis has been carried out for the track pheromone of *Bombus terres*tris males.

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SYNTHESIS OF PHOTOSENSITIZER PAIRS CONTAINING $Ru(bpy)_3^{2+}$ AND AN ELECTRON ACCEPTOR (VIOLOGEN) LINKED BY A HYDROCARBON CHAIN

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Models of reaction sites (RS) for photosynthesis, whose components (a photosensitizer, electron donor, and electron acceptor) are "cross-linked" into a single molecule, are commonly used for modeling the primary photocharge separation processes in photosynthesis [1-5]. By altering the distance between the RS components, we may control the rate of electron transfer; the efficiency of the photocharge separation is significantly dependent on this rate [4, 5].

In the present work, we synthesized a fragment of an RS model containing a photosensitizer (S) molecule and primary electron acceptor (A) linked by a hydrocarbon chain of a given length. We selected the complex, $Ru(bpy)_3^{2+}$ (bpy = 2,2'-dipyridyl) and viologen (1,1'dimethyl-4,4'-dipyridyl) as S and A. These compounds are commonly used in model photocatalytic systems. The "molecular assembly" of $Ru(bpy)_3^{2+}$ -viologen was carried out according to the following scheme (see scheme on following page).

The visible spectra of solutions of (V) and (IX) (see Fig. 1a) are virtually indistinguishable from the spectrum for $(bpy)_2Ru(bpy(CH_3)_2)^{2+}$ $(bpy(CH_3)_2 = 4,4'-dimethyl-2,2'-dipyridyl)$. New absorption bands appear in the vicinity of 400 and 600 nm in the spectra of complexes (V) and (IX) upon the addition of $Na_2S_2O_4$ as a reducing agent. These bands are characteristic for the viologen group (Fig. 1a). The extinction coefficients for complexes (V) and (IX) in reduced form ($\varepsilon_{396} = 3.4 \cdot 10^4$, $\varepsilon_{450} = 1.45 \cdot 10^4$, and $\varepsilon_{602} = 1.24 \cdot 10^4$ liters/mole·cm) coincide with the extinction coefficient of $(bpy)_2Ru(bpy(CH_3)_2)^{2+}$ ($\varepsilon_{450} = 14,500$ liters/mole·cm [7]) and the methylviologen group ($\varepsilon_{395} = 3.4 \cdot 10^4$ and $\varepsilon_{602} = 1.24 \cdot 10^4$ liters/mole·cm [8]).

Aqueous solutions of complexes (V) and (IX) virtually do not luminesce (Fig. 1b), which indicates efficient quenching of the excited state of the photosensitizer bound to viologen.

EXPERIMENTAL

Chemically pure and analytically pure samples of 4,4'-dimethyl-2,2'-dipyridyl supplied by Fluka were used without additional purification. Other compounds were obtained by the methods given below. The purity of the compounds obtained were monitored by thin layer chromatography on silica gel, PMR, visible, and UV spectrophotometry.

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<u>4-Methyl-4'-(2-hydroxyethyl)-2,2'-dipyridyl (II).</u> A stoichiometric amount of 1 mole/ liter PhLi solution was added to 5 g 4,4'-dimethyl-2,2'-dipyridyl (I) in 250 ml dry THF in an argon atmosphere at 0°C. After 1 h, excess gaseous CH_2O was passed through the solution. The mixture was decomposed with water and the dipyridyl was extracted with three 100-ml ether portions. After removing the ether, the crude product was subjected to chromatography on silica gel with ethyl acetate as the eluent to give 65% (II). PMR spectrum in CDCl₃ at 90 MHz (δ , ppm): 250 s (3H, 4-CH₃), 2.97 t (2H, 1-CH₂), 4.02 t (2H, 2-CH₂), 8.36-8.65 m (6H, 2,2'-dipyridyl).

 $\frac{1-[2-(4'-Methyl-2,2'-dipyridyl-4-yl)ethyl]-4,4'-dipyridinium tosylate (III). A sample of 3 g TsCl was added at 0°C to 1 g (II) in 25 ml 1:1 pyridine-chloroform and stirred at 40-50°C for 1 h. The reaction was controlled by thin layer chromatography on silica gel. The mixture was decomposed with water and neutralized with sodium carbonate to pH 8-9. The tosylate was extracted by three 50-ml portions of chloroform. After removing the chloroform, the crude product was subjected to chromatography on silica gel using 8:1 benzene-ethyl acetate as the eluent. The yield of tosylate was 73%. Then, a mixture of 0.5 g tosylate and 0.5 g 4,4'-dipyridyl in 5 g acetonitrile was heated in a sealed ampul at 100°C for 20 h. The product was precipitated by the addition of ether and filtered to give a 68% yield. PMR spectrum in CDCl₃ at 90 MHz (<math display="inline">\delta$, ppm): 2.3 s (3H, 4'-methyl-2,2'-dipyridyl-4-yl, 4'-CH₃), 3.45 t (2H, chain, 2-CH₂), 4.88 t (chain, 1-CH₂), 7.32-8.26 m (6H, 2,2'-dipyridyl), 8.60-8.77 m (8H, 4,4'dipyridyl).

 $\frac{\text{Bis}(2,2'-\text{dipyridy}1)-\{1-[2-(4'-\text{methy}1-2,2'-\text{dipyridy}1-4-y1)\text{ethy}1]-4,4'-\text{dipyridinium}\}-}{\text{ruthenium trichloride (IV).}}$ A mixture of 0.1 g (III) and 0.1 g Ru(bpy)₂Cl₂ obtained according to Whitten et al. [6] was heated for 4-5 h at reflux in 5 ml 1:1 methanol-water. The solution was passed through a column packed with Dowex 1 × 8 anion-exchange resin



Fig. 1. a) Electronic spectrum of complex (V) in the absence (1) and presence of excess sodium dithionite (2) in borate buffer solution, 0.1 mole/liter, pH 8-9. The concentration of the complex was $2.6 \cdot 10^{-5}$ mole/liter. b) The luminescence spectra of aqueous solutions of complexes (bpy)₂Ru(bpy(CH₃)₂)²⁺ (1), (V) (2), and (IX) (3). The concentrations of the complexes were $2 \cdot 10^{-5}$ mole/liter.

(Cl⁻ form) and heated at reflux with activated charcoal for 1 h. After removal of the solvent, the complex was dissolved in methanol and precipitated by the addition of ether.

Bis(2,2'-dipyridyl)-[1-(1'-methyl-4,4'-dipyridyl-1-yl)-2-(4'-methyl-2,2'-dipyridyl-4yl)ethane]ruthenium tetrachloride (V). A mixture of 0.1 g (IV) and 0.2 ml MeI in 5 ml methanol was heated in a sealed ampul for 2-3 h at 100°C. After removal of the solvent, the complex was dissolved in water and passed through Dowex 1 × 8 resin (Cl⁻ form) and heated at reflux with activated charcoal. The solvent was removed under vacuum. The product was dissolved in methanol and the complex was precipitated by the addition of ether. PMR spectrum in D₂O at 200 MHz (δ , ppm): 2.30 s (3H, 4'-methyl-2,2'-dipyridyl-4-yl, 4'-CH₃), 3.45 t (2H, chain, 2-CH₂), 4.30 s (3H, 4,4'-dipyridyl, 1'-CH₃), 4.88 t (2H, chain, 1-CH₂), 6.95-7.05 m (2H, 4'-methyl-2,2'-dipyridyl-4-yl, H⁵,⁵'), 7.11 d (4H, 2,2'-dipyridyl, H⁵,⁵'), 7.37 d (2H, 4'-methyl-2,2'-dipyridyl-4-yl, H⁶,⁶'), 7.56 d (4H, 2,2'-dipyridyl, H⁶,⁶'), 7.75 t (4H, 2,2'-dipyridyl, H⁴,⁴'), 8.16 s (2H, 4'-methyl-2,2'-dipyridyl-4-yl, H³,³'), 8.26 d (4H, 2,2'-dipyridyl, H³,³'), 8.81 d (4H, 4,4'-dipyridyl, H³,^{3'},⁵,⁵'), 8.89 d (4H, 4,4'-dipyridyl, H²,^{2'},⁶,^{6'}).

<u>4-(5-Bromopentyl)-4'-methyl-2,2'-dipyridyl (VI)</u>. A stoichiometric amount of 1 mole/ liter ethereal PhLi was added to 1 g (I) in 50 ml THF at 0°C in an argon atmosphere. After 1 h, the solution obtained was slowly added to 6 ml 1,4-dibromobutane in 30 ml THF. The mixture was decomposed with water and the dipyridyl was extracted with three 50-ml portions of ether. The crude product was subjected to chromatography on silica gel with benzene eluent. The yield of (VI) was 60%. PMR spectrum in CDCl₃ at 90 MHz (δ , ppm): 1.77 m (6H, chain, 2,3,4-CH₂), 2.50 s (3H, 4-CH₃), 2.77 t (2H, chain, 1-CH₂), 3.42 t (2H, chain, 5-CH₂), 8.36-8.65 m (6H, 2,2'-dipyridyl).

Bis(2,2'-dipyridy1)-4-(5-bromopenty1)-4-methy1-2,2'-dipyridy1ruthenium dichloride (VII) was obtained by analogy to (IV) using ethanol as the solvent. PMR spectrum in D₂O at 90 MHz (δ , ppm): 0.9-1.60 m (6H, chain, 2,3,4-CH₂), 2.30 s (3H, 4-CH₃), 2.61 t (2H, chain, 1-CH₂), 3.37 t (2H, chain, 5-CH₂), 7.00-8.38 m (22H, 4'-methy1-2,2'-dipyridy1-4-y1, 2,2'-dipyridy1).

<u>Bis(2,2'-dipyridy1)-{1-[5-(4'-methy1-2,2'-dipyridy1-4-y1)penty1]-4,4'-dipyridinium}</u> ruthenium trichloride (VIII) was obtained by analogy to (III) using DMF as the solvent.

Bis(2,2'-dipyridyl)-[1-(1'-methyl-4,4'-dipyridyl-1-yl)-5-(4'-methyl-2,2'-dipyridyl-4yl)pentane]ruthenium tetrachloride (IX) was obtained by analogy to (V). PMR spectrum in D₂O at 200 MHz (δ , ppm): 1.28 m (2H, chain, 2-CH₂), 1.56 m (2H, chain, 3-CH₂), 1.92 m (2H, chain, 4-CH₂), 2.30 s (3H, 4'-methyl-2,2'-dipyridyl-4-yl, 4-CH₃), 2.60 t (2H, chain, 1-CH₂), 4.30 s (3H, 4,4'-dipyridyl, 1-CH₃), 4.49 t (2H, chain, 5-CH₂), 6.94 m (2H, 4'-methyl-2,2'-dipyridyl-4-yl, H⁵, 5'), 7.03-7.13 m (4H, 2,2'-dipyridyl, H⁵, 5'), 7.34 d (1H, 4'-methyl-2,2'-dipyridyl-4-yl, H⁶'), 7.39 d (1H, 4'-methyl-2,2'-dipyridyl-4-yl, H⁶), 7.56 d (4H, 2,2'-dipyridyl, H⁵, 5'), 8.11 s (2H, 4'-methyl-2,2'-dipyridyl-4-yl, H³, 3'), 8.26 d (4H, 2,2'-dipyridyl, H³, 3'), 8.78 d (4H, 4,4'-dipyridyl, H³, 3', 5, 5'), 8.84 d (4H, 4,4'-dipyridyl, H², 2', 6, 6').

CONCLUSIONS

Two $\operatorname{Ru}(\operatorname{bpy})_3^{2+}$ -viologen complexes, in which the components are linked by a hydrocarbon chain, were synthesized and characterized by PMR, visible, and UV spectrophotometry.

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SYNTHESIS OF HYDRIDOPHOSPHINES BY THE REDUCTION OF P(III)

ISOTHIOCYANATES AND CYANIDES

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In a continuation of studies on the properties of isothiocyanates [1] and cyanides [2, 3] derived from tricoordinated phosphorus acids, we investigated the reaction of these compounds with $LiAlH_4$ and found that these reactions proceed in ether at 20°C to give the corresponding P(III)-H derivatives in yields up to 70%.

$$PhPX_2 \xrightarrow{LiAlH_4} Ph-PH_2$$
(I)

X = CN, NCS

 $\begin{array}{c} Ph-P-X \xrightarrow{I.IAIH_4} Ph-P-H \\ \downarrow \\ H \\ R \\ \end{array}$ (II, III)

R = Ph, X = CN, NCS (II); R = Et, X = CN (III).

Hydridophosphines (I)-(III) were characterized by ^{31}P NMR spectroscopy; their physical indices corresponded to those given in the literature. In addition to the reported methods for the preparation of organic hydridophosphines [4], these reactions may be used for the synthesis of various P(III)-H derivatives.

EXPERIMENTAL

The ³¹P NMR spectra were taken on a KGU-4 NMR spectrometer at 10.2 MHz relative to 85% H₃PO₄. All the operations were carried out in a dry argon atmosphere.

<u>Phenylphosphine (I).</u> a. A suspension of 4.2 g phenyldicyanophosphine in 20 ml ether was added with stirring over 2 h to a suspension of 1 g LiAlH₄ in 25 ml ether. The mixture was heated at reflux for 3 h and 10 ml water and 1 ml hydrochloric acid were added. The ethereal layer was separated from the precipitate. The solvent was evaporated and the residue was distilled in vacuum to give 1.8 g (61%) (I), bp 42°C (15 mm). ³¹P NMR spectrum (δ , ppm): -122, J_{P-H} = 196 Hz [5].

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