because of the difference in position and intensity of the Cotton effects. However, *if necessary, the benzoate Cotton effects can be shifted by introducing suitable para substituents* (entry 4b in Table I, and ref 2).

A typical example of a complex molecule is the derivative of ponasterone A (a phytoecdysone)[6] (entry 6) in which the Cotton effect of the enone group is weaker than that of the dibenzoate and the Cotton effects due to the $2\beta,3\beta$-dibenzoate moiety are clearly observed. In tetrahydrotaxinine 9,10-dibenzoate (entry 8 and Figure 3),[7] the enone group shows an abnormally strong $\pi \rightarrow \pi^*$ Cotton effect at 266 mμ (and a weaker $n \rightarrow \pi^*$ Cotton effect at 350 mμ), but the dibenzoate Cotton effect is again clearly measurable. The absolute configuration of rishitin[8] is determined as depicted in **2** on the basis of this rule (entry 9). The conformations of the five-membered ring in the anomeric riboside dibenzoates are defined from the chiralities and are shown to be different (entries 10 and 11).

The present treatment is not confined to α-glycols as far as the two benzoate chromophores mutually interact to give a first Cotton effect shifted from that of noninteracting benzoates, *e.g.*, at 233 mμ instead of 225 mμ.[1] Thus in the cholestane $3\beta,6\beta$-diol derivative (1,4-dibenzoate, entry 5) the Cotton effect sign is in agreement with prediction. The glycol may also include primary alcohols; namely, the sign in the serratriol[9] and hederagenin derivatives[9] (entries 12 and 13) agree with the chirality predicted from the preferred conformation of the 1,3-dibenzoate moiety.

In the case of two chromophores (1 and 2), the rotational strength, R_{oa}, of the transition Ψ_o $(=\varphi_{1o}\varphi_{2o})$ $\rightarrow \Psi_a$ $[=(1/\sqrt{2})(\varphi_{1a}\varphi_{2o} \pm \varphi_{1o}\varphi_{2a})]$ can be for mulated as follows[10] according to the zero-order approximation of the molecular exciton theory

$$R_{oa} = (1/2)\mathrm{Im}[(\boldsymbol{\mu}_{1oa} \pm \boldsymbol{\mu}_{2oa})\cdot(\mathbf{m}_{1ao} \pm \mathbf{m}_{2ao})] \mp (1/2)\pi\tilde{\nu}_a\mathbf{R}_{12}\cdot(\boldsymbol{\mu}_{1oa}\boldsymbol{\mu}_{2oa}) \quad (1)$$

where the signs correspond to those of the wave functions, respectively. In the case of the dibenzoate, the magnetic transition moments $\mathbf{m}_{1ao}$ and $\mathbf{m}_{2ao}$ are almost zero because the 230-mμ band is the $\pi \rightarrow \pi^*$ transition. Hence the second term, the so-called dipole–dipole interaction term, makes a dominant contribution. Since the 230-mμ intramolecular charge-transfer transition has a long-axis transition moment, the electric transition moments $\boldsymbol{\mu}_{1oa}$ and $\boldsymbol{\mu}_{2oa}$ are approximately parallel to the C–O bonds of alcohols irrespective of the rotational conformation around the C–O bond. (This is of practical value as *application of the present treatment does not necessitate consideration of the benzoyloxy conformation, i.e.*, to a first approximation, *only the chiralities of the two C–O bonds need be considered.*) The second term, or the rotational strength R_{oa}, therefore, depends on the chirality of the glycol. In fact, the absolute sign obtained from a theoretical calculation is in accordance with the experimental sign.

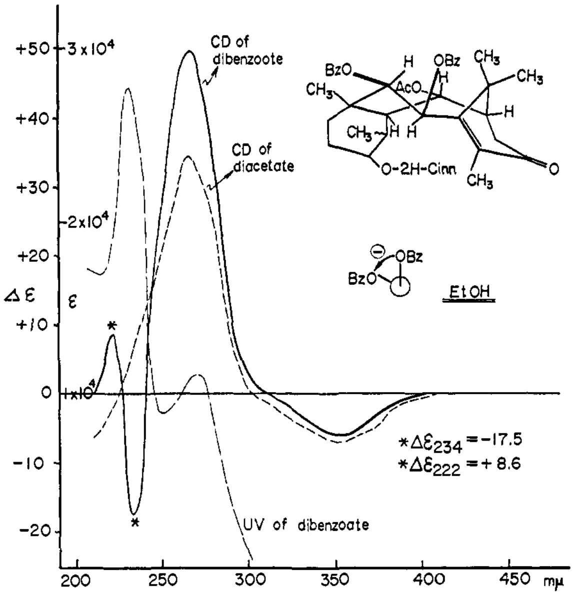

Figure 3. Tetrahydrotaxinine 9,10-dibenzoate.[7] The dibenzoate Cotton effects marked by *; —, CD of dibenzoate; - - - - - -, CD of diacetate; and — — —, uv of dibenzoate.

The second CD Cotton effect is not clear in some dibenzoates (entries 3, 7, and 10). This may be due to instrumental limitations or a strong background ellipticity arising from the extremely strong benzoate absorption at *ca.* 195 mμ ($\epsilon \approx 40{,}000$); or it may suggest that the first term in eq 1 and/or a higher order perturbation term is making an additional contribution to the Cotton effect. However, this does not detract from the usefulness of the present treatment because the first CD Cotton effects are clearly observable at the usual wavelength around 233 mμ. Extensions of the present treatment to other aromatic systems and tribenzoates will be reported shortly.[11]

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Photochemical Oxidation of Nitrogenammineruthenium(II) Compounds

Sir:

There is considerable current interest in the nitrogenammineruthenium(II) compounds as possible models for biological nitrogen reduction.[1–4] It was originally

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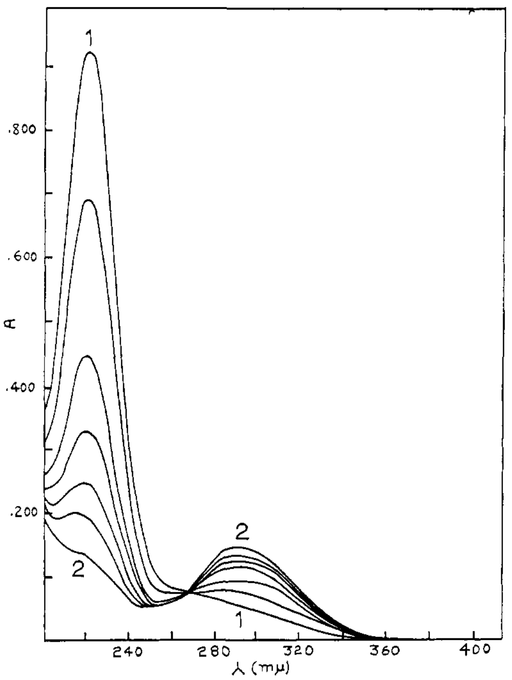

Figure 1. Change of absorption spectrum of $Ru(NH_3)_5N_2^{2+}$ during irradiation with uv light: curve 1, before irradiation; curve 2, after irradiation for 25 min; intermediate curves, approximately 4-min intervals of irradiation, beginning with curve 1. $[Ru(NH_3)_5N_2^{2+}] = 7.16 \times 10^{-4}$ *M*, in H_2O deaerated with He.

reported that the bound nitrogen in $Ru(NH_3)_5N_2^{2+}$ could be reduced by sodium borohydride,[2] but more recent work indicates this does not occur.[5]

During the course of an investigation of the chemistry of this ion in our laboratory, it was observed that the characteristic absorption peak at 221 mμ[3] of anaerobic solutions of the ion stored in quartz cells decreased significantly when kept in the light. Following this lead, we exposed a solution of $Ru(NH_3)_5N_2^{2+}$ that had been deoxygenated with He to uv light from a mercury lamp and found that the 221-mμ absorption disappeared completely and the absorption characteristic of an Ru(III) species appeared after a short period of irradiation (15 min–3 hr, depending on concentration and light intensity) (Figure 1). Since a period of 1–2 min occurred between the time the solutions were removed from the light and the recording of the spectra, a fast dark reaction is possible. This is unlikely, however, since no further change in the spectra was observed after standing in the dark for 1 hr. Solutions in which appreciable amounts of the dimer, $Ru(NH_3)_5N_2Ru(NH_3)_5^{4+}$, prepared by passing N_2 through a solution of $Ru(NH_3)_5H_2O^{2+}$ as described by Taube,[4] were present behaved similarly, with the 262-mμ absorption of the dimer disappearing. Solutions kept in the dark for this same period showed no change.

Further studies revealed that the photochemical oxidation proceeds equally well in acidic, neutral, or basic solutions. In HCl, $Ru(NH_3)_5Cl^{2+}$, identified by its absorption maximum at 330 mμ,[6] is the product, while in basic solution containing excess NH_3, $Ru(NH_3)_6^{3+}$, λ_{max} 280 mμ,[6] is formed. In neutral solutions, $Ru(NH_3)_5OH^{2+}$, absorbing at 290 mμ,[7] is formed (Figure 1). When the photolyzed solutions are treated with amalgamated Zn in dilute H_2SO_4, the Ru(III) species is reduced as indicated by the disappearance of its characteristic absorbance. By passing N_2 through the reduced solution, both $Ru(NH_3)_5N_2^{2+}$ and the dimer, $(Ru(NH_3)_5)_2N_2^{4+}$, are formed, again identified by their absorbance at 221 and 262 mμ, respectively.

The identification of the reduction product is clearly of the greatest importance. Since it is known that some Ru(II) species reduce H_2O,[8] it seemed probable that H_2 is the product. Repeated experiments under widely different conditions, however, showed only the presence of N_2 and a small amount of O_2 in the gas above the solution, as determined by mass spectrometric analysis.

As H_2 is absent, it is quite possible that the bound N_2 is reduced, since no other reducible species is present. Qualitative tests of the photolyzed solution for NH_2NH_2[9] and NH_2OH[10] were negative. In order to determine if NH_3 is produced, work is underway to synthesize and photolyze $Ru(NH_3)_5N_2^{2+}$ containing N^{15}. If the N^{15} appears in the NH_3 after photolysis then reduction of the bound N_2 will be confirmed.

The $Ru(NH_3)_5N_2Cl_2$ and $Ru(NH_3)_5N_2(BF_4)_2$ used in this work were prepared from $Ru(NH_3)_6Cl_3$ (Matthey Bishop and Co.) and NaN_3 using the procedure of Allen, *et al.*[2] The gas analysis was performed using an EAI quadrupole mass spectrometer, Model 200, and a Perkin-Elmer Hitachi RMU-GE mass spectrometer. Solutions were irradiated with a 125-W Hanovia low-pressure mercury lamp, or a 500-W Hanovia high-pressure mercury arc, depending on concentration.

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The Metal Ion Catalyzed Peroxide Oxidation of Organic Substrates. A Selective Synthesis of Imides

Sir:

The metal ion catalyzed decomposition of organic hydroperoxides and peroxyacids has been long known.[1,2] Recently there have been several reports on the oxidation of primary amines to oximes,[3] tertiary amines to amine oxides,[4–7] sulfides to sulfoxides,[8,9] and

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