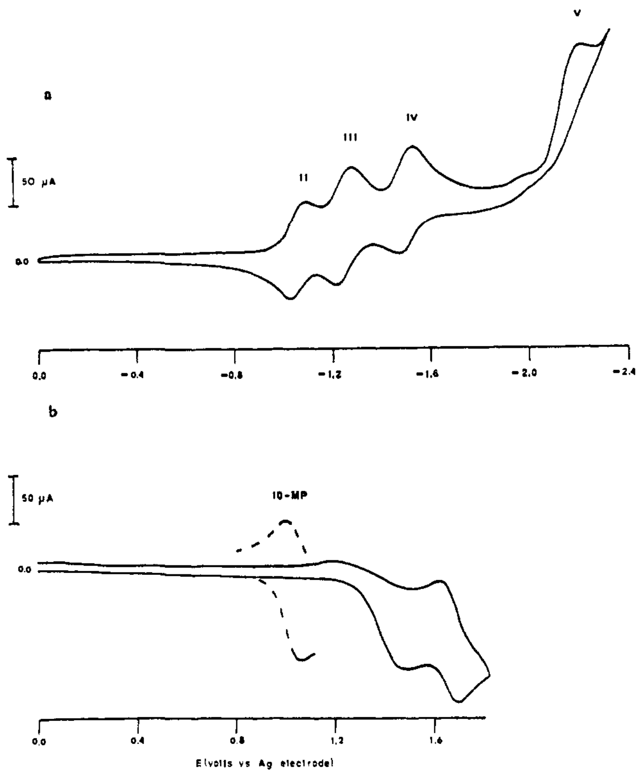

Figure 1. Cyclic voltammogram of 1 mM Ru(bipy)$_3$Cl$_2$ in acetonitrile at a Pt electrode with 0.2 M TBABF$_4$ supporting electrolyte. Scan rate = 100 mV/sec: (a) scan from 0.0 to −2.40 V; (b) scan from 0.0 to +1.80 V. The dotted portion marks the 10-methylphenothiazine oxidation wave.

longest wavelength absorption peak occurs at about 455 nm (2.7 eV) and has been assigned to a d $\rightarrow \pi^*$ transition from the singlet ground state to the singlet charge-transfer excited state.[6] Rapid intersystem crossing to the triplet state occurs and the observed emission at 608 nm (2.04 eV) is phosphorescence, greatly enhanced by spin–orbit coupling, from this state.[5,6] This state is also the emitting state in ecl. The reduction step (II) leading to the +1 species probably involves addition of an electron to the a_2 (π^*) orbital of the chelate, which shows D_3 symmetry. Similarly, the oxidation (I) to the +3 species probably involves removal of an electron from the a_1 (d) orbital. The reaction

$$\mathrm{Ru(bipy)_3}^{+} + \mathrm{Ru(bipy)_3}^{3+} \longrightarrow \mathrm{Ru(bipy)_3}^{2+*} + \mathrm{Ru(bipy)_3}^{2+} \quad (1)$$

occurs. The enthalpy of this reaction, calculated from the peak potentials of waves I and II and corrected for the entropy term,[10] is 2.6 eV and is only marginal for population of the singlet excited state, especially since in this case, unique in ecl annihilation reactions, the redox step involves two positively charged species. The reaction is quite sufficient to populate the emitting triplet state, however. Similarly, when 10-MP$\cdot^+$ is the oxidant, the reaction in eq 2 probably produces the

$$\text{10-MP}\cdot^{+} + \mathrm{Ru(bipy)_3}^{+} \longrightarrow \mathrm{Ru(bipy)_3}^{2+*} + \text{10-MP} \quad (2)$$

triplet excited state directly, although here the reaction enthalpy is marginal even for this state. This reaction demonstrates that chemiluminescence in this system can be generated by oxidation of the +1 complex,

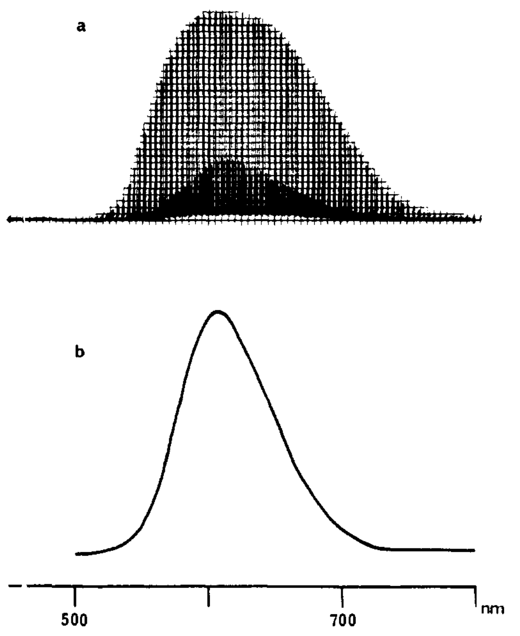

Figure 2. (a) Ecl emission spectrum of Ru(bipy)$_3$Cl$_2$ from 450 to 800 nm using a cyclic square wave at 0.2 Hz between +1.75 and −1.60 V *vs.* Ag reference electrode. (b) Fluorescence emission spectrum of Ru(bipy)$_3$Cl$_2$ in acetonitrile with excitation at 500 nm.

as well as by the reduction of the +3 species previously described.[2] More intense ecl results when the reducing species is either the 0 or −1 complex. Although the reaction enthalpy is larger when these species are the reductants, several electron transfers must occur before the ultimate emitting state is produced, so that the overall ecl process in these cases is more complicated than those described in eq 1 and 2.

Observation of ecl in systems containing metal complexes either alone or with other reactants considerably broadens the scope of possible redox reactions leading to excited state species. These combined electrochemical and spectroscopic studies should also provide information about the spectroscopic states, energy levels, and orbitals in the metal chelates.

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Received December 21, 1971

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(10) See, for example, L. R. Faulkner, H. Tachikawa, and A. J. Bard, *J. Amer. Chem. Soc.*, **94**, 691 (1972).

Nature of Photochemically Induced Transannular Hydrogen Abstractions of Taxinines

Sir:

Of the numerous taxanes[1] identified recently, those containing the 11-en-13-one chromophore are characterized by their anomalous uv absorptions[1b] due to the strained and unique cage structures (see **3**). For

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(1) (a) B. Lythgoe, K. Nakanishi, and S. Uyeo, *Proc. Chem. Soc.*, 301 (1964); (b) I. W. Harrison, R. M. Scrowston, and B. Lythgoe, *J. Chem. Soc. C*, 1933 (1966); (c) M. Dukes, D. H. Eyre, J. W. Harrison, and B. Lythgoe, *Tetrahedron Lett.*, 4765 (1965); (d) D. H. Eyre, J. W. Harrison, and B. Lythgoe, *J. Chem. Soc. C*, 452 (1967); (e) H. C. Chiang, M. C. Woods, Y. Nakadaira, and K. Nakanishi, *Chem. Commun.*, 1201 (1967); (f) M. C. Woods, H. C. Chiang, Y. Nakadaira, and K. Nakanishi, *J. Amer. Chem. Soc.*, **90**, 522 (1968); (g) D. P. Della Casa de Marcano and T. G. Halsall, *J. Chem. Soc. D*, 1382 (1970); (h) M. C. Wani, H. L. Taylor, M. E. Wall, P. Coggon, and A. T. McPhail, *J. Amer. Chem. Soc.*, **93**, 2325 (1971).

example, diacetate **2**[2] which was prepared from taxinine **1** in 56% overall yield by (i) selective hydrolysis of the 9,10-acetate,[3] (ii) 9,10-acetonide formation, (iii) hydrolysis of 2,5-acyl groups followed by 2,5-diacetylation (to give **6**), and (iv) removal of the acetonide group, exhibits the following uv maxima: (MeOH) 273 (ϵ 6300) and 342 nm (300); (dioxane) 270 (6750) and 350 nm (190). In addition, we had previously found that irradiation of a minor constituent of *Taxus cuspidata* Sieb. et Zucc. resulted in 3,11-transannular bond formation and gave rise to another naturally occurring congener.[1e] A more detailed study of the transannular reaction has been carried out in order to clarify the various factors involved in this usual photochemical reaction, which so far appears to have no precedence since the 3-H is apparently not abstracted by the carbonyl oxygen.

Irradiation of taxinine **1**, nmr ($CDCl_3$) C-12 Me at 2.28 and H-3 at 3.42 ppm (d, J = 6.5 Hz), with a 450-W high-pressure Hg lamp in dioxane for 15 min in a quartz tube gave a quantitative yield of a nonseparable 1:1 mixture of transannular products **4a–4b** (nmr ($CDCl_3$) C-12 Me at 1.25 (d, J = 7 Hz) and 1.26 (d, J = 7 Hz), H-12 at 3.45 (q, J = 7 Hz) and 3.54 ppm (q, J = 7 Hz)), which upon hydrogenation over Pd/C–AcOEt yielded the single dihydro compound **4** (R_1 = $COCH_2CH_2C_6H_5$; $R_2 = R_3$ = OAc): ir ($CHCl_3$) 1697 cm^{-1} (saturated ketone); nmr ($CDCl_3$) C-12 Me at 1.26 (d, J = 7 Hz) and H-12 at 3.48 ppm (d, J = 7 Hz).

Irradiation of diacetate **2** (ir ($CHCl_3$) 1670 cm^{-1} (enone); nmr ($CDCl_3$) C-12 Me at 2.08 and H-3 at 3.19 ppm (d, J = 6 Hz)), with a Pyrex filter[4] for 2 hr in dioxane (or *tert*-BuOH, *i*-PrOH, or C_6H_6) gave the transannular product **5** in quantitative yield: ir ($CHCl_3$) 1698 cm^{-1} (saturated ketone); nmr (pyridine) C-12 Me at 1.81 (d, J = 7.2 Hz) and H-12 at 3.73 ppm (J = 7.2 Hz). Diacetylation with Ac_2O–*p*-TsOH afforded taxinine L,[1e] a minor constituent of *T. cuspidata*.

In a formal sense the present isomerization can be explained by transfer of H-3 to C-12 and bond formation between C-3 and C-11; molecular models (see **3**) indicate that initial *transfer of H-3 to the carbonyl oxygen would be impossible* in view of the direction of the carbonyl group oxygen.

The isopropylidene derivative **6** was studied next as a model of a compound having a large separation between H-3 and the 11-ene. Irradiation[4] of **6** (uv (dioxane) 269 (ϵ 6630) and 351 nm (210); ir ($CHCl_3$) 1670 cm^{-1} (enone); nmr ($CDCl_3$) C-12 Me at 2.12 and H-3 at 3.07 ppm (d, J = 6.0 Hz)) for 5 hr in dioxane (or *tert*-BuOH or C_6H_6) gave, after tlc separation, 38% of starting material **6**, and 48% of cyclopropyl ketone **7**: uv (MeOH) 213 nm (ϵ 4870); ir ($CHCl_3$) 1723 cm^{-1} (cyclopropyl ketone); nmr ($CDCl_3$) H-3 at 2.88 ppm (d, J = 6 Hz); the CD of **7** (in MeOH), $\Delta\epsilon_{217}$ +7.5, $\Delta\epsilon_{291}$ −1.9, indicated that the cyclopropyl group had the expected β configuration.[5] In addition, there was obtained 8% of the transannular ketone **5**, which was presumably formed from **8** by liberation of the acetonide group during tlc separation.

Thus, as anticipated, the isopropylidene group had greatly hindered the occurrence of transannular bond formation by pulling apart the H-3 and 11-ene. This leads to preferential occurrence of the skeletal rearrangement initiated by cleavage of the 1–15 bond; the facile transformation is presumably due to the strained ring system as it has been shown[6] that steroidal 4-substituted 4-en-3-ones with a moiety similar to that present in **6** (12-substituted 11-en-13-one) are unreactive and do not undergo the well-known conversion to cyclopropyl ketones.

Tetraacetate **9** prepared by acetylation of **2** and subsequent hydrogenation over Pd/C in acetone provided a suitable model to investigate the influence of the double bond allylic to H-3. Stereomodels of **9** and **2** show that the spatial relations between H-3 and 11-ene are very similar in the two compounds, and hence a difference in reactivity can safely be attributed to the 4 substituent. Irradiation[4] of **9** (uv (dioxane) 267 (7000) and 350 nm (ϵ 140); ir ($CDCl_3$) 1670 cm^{-1} (enone); nmr ($CDCl_3$) C-12 Me at 2.25 and H-3 at *ca.* 2.7 ppm (m)) in *tert*-BuOH (*but not in C_6H_6*) for 10 hr gave, after tlc separation, 65% of the isomeric cyclopropyl ketone **10** (uv (MeOH) 210 nm (ϵ 4900); CD (MeOH) $\Delta\epsilon_{215}$ +4.8, $\Delta\epsilon_{290}$ −2.4; ir ($CHCl_3$) 1725 cm^{-1} (cyclopropyl ketone); nmr ($CDCl_3$) H-3 at 2.54 ppm (dd, J = 5, 11 Hz)), and 32% of the solvent adduct **11**[7]: ir (KBr) 1715 cm^{-1} (ketone); nmr (C_6D_6) C-12 Me at 1.05 (d, J = 7 Hz), *tert*-Bu at 1.47, H-12 at 1.92 (q, J = 7 Hz), H-3 at 1.82 ppm (br s). It is to be noted that unlike **1**, **2**, and **6**, the photoirradiation of **9** did not proceed in benzene.

The quantum yield at 365 nm for the conversion of **6** (disappearance) to **7–8** in dioxane and that for **9** to **10–11** in *tert*-BuOH were both 0.002, and were not affected by the presence of piperylene or cyclohexa-1,3-diene.[8] However, as both reactions were effectively sensitized by acetophenone at 312 nm they can safely be regarded as proceeding *via* the triplet state.

As described above, the rearrangement of **9** and **10–11** occurs in *tert*-BuOH but not in benzene. This difference can be attributed to the nature of the lowest triplet state, namely, in the polar solvent *tert*-BuOH, the π,π^* singlet and n,π^* singlet states are stabilized and destabilized, respectively, and this could lead to a T_1 (π,π^*) state. In contrast, the lowest reactive state in the nonpolar benzene would be T_1 (n,π^*). Hence the fact that the reaction of **9** proceeded only in *tert*-BuOH indicates that the reactive species is T_1 (π,π^*) (see also ref 6). On the other hand, as the conversion of **6** to **7** can take place in benzene as well, it can be assumed that in this case the energy difference between the n,π^* and π,π^* triplet states is so small that the skeletal rearrangement occurs even if the T_2 state were π,π^* in benzene.

Finally, the transannular hydrogen abstraction of **2**[9] leading to **5** was also found to be a triplet reaction as it

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[2] The structures of all compounds described have been corroborated by extensive spectroscopic measurements. Every single proton in all nmr spectra has been characterized, except for assignments of individual *tert*-methyl groups in certain cases. Only the minimum pertinent data are given.

[3] J. N. Baxter, B. Lythgoe, B. Scales, S. Trippett, and B. K. Blount, *Proc. Chem. Soc.*, 9 (1958).

[4] All irradiations were carried out under similar conditions except for solvents and irradiation period.

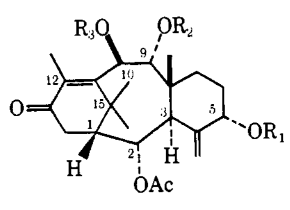
[5] K. Kuriyama, H. Tada, Y. K. Sawa, S. Ito, and I. Itoh, *Tetrahedron Lett.*, 2539 (1968).

[6] D. Bellus and K. Schaffner, *Helv. Chim. Acta*, **52**, 1010 (1969).

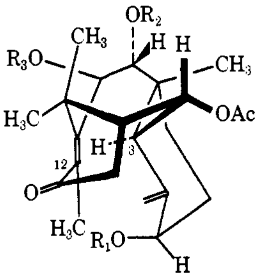
[7] A β configuration is assigned to the *tert*-BuO group because of severe steric hindrance on the α face.

[8] It is possible that no quenching was detected because of the low quantum yield.

[9] The T_1 energy as estimated from the phosphorescence spectrum was 69.2 kcal/mol (in EtOH at 77°K). We are grateful to Professor



trans
1, R_1 = COCH=CHPh; $R_2 = R_3$ = Ac
2, R_1 = Ac; $R_2 = R_3$ = H



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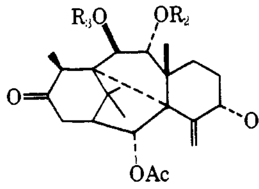
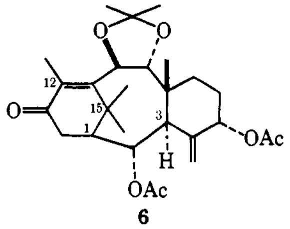
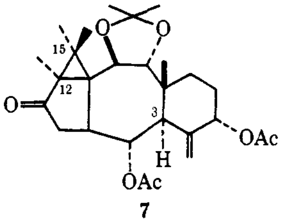


cis
4a, R_1 = COCH=CHPh; $R_2 = R_3$ = Ac
trans
b, R_1 = COCH=CHPh; $R_2 = R_3$ = Ac
5, R_1 = Ac; $R_2 = R_3$ = H



6



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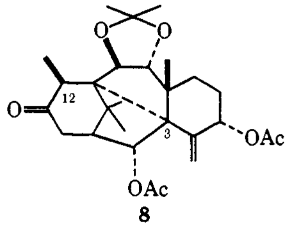

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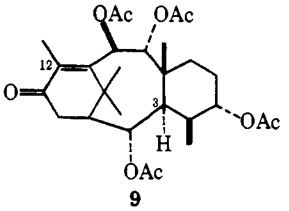

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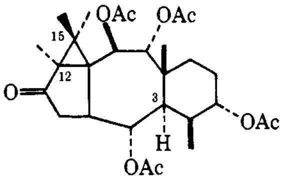

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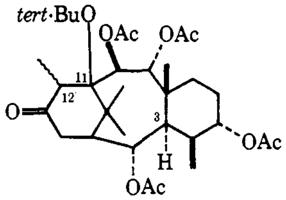

11

was both sensitized with acetophenone and quenched with piperylene and cyclohexa-1,3-diene.[10] Furthermore, the high quantum yields (disappearance) at 365 nm measured in dioxane (0.091) and *tert*-BuOH (0.078) as compared to that in nonpolar benzene (0.031), and the nonoccurrence of hydrogen transfer from the solvent *i*-PrOH, lead to the conclusion that the energy levels of T_1 and T_2 states are also close in this case and that the transformation proceeds predominantly *via* the π,π^* triplet.

In view of the extreme proximity of the H-3 to the 11-ene[1f,11] this transannular reaction can be regarded as following a concerted ${}_\sigma 2_s + {}_\pi 2_s$ route.[12,13] The possibility of an intermolecular hydrogen abstraction can be disregarded on the basis of kinetic studies[14] and the cage structure of **2** (see **3**).

Acknowledgments. We acknowledge Public Health Service Grant No. CA-11572 and the Ministry of Education, Japan, for financial support.

H. Azumi, Tohoku University, for his help in phosphorescence measurements.

(10) In the case of **1** the cinnamate group also absorbs light efficiently as the irradiation was carried out in a quartz tube. Thus, the intramolecular quenching of the enone moiety by the cinnamate group would be inefficient.

(11) *Cf.* M. Shiro, T. Sato, H. Koyama, Y. Maki, K. Nakanishi, and S. Uyeo, *Chem. Commun.*, 98 (1966).

(12) A C-11–C-12 biradical is also conceivable but less likely.

(13) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969).

(14) The photoreactions described follow a first-order kinetic equation: $\ln(e^{2.303\epsilon cd} - 1) = -2.303\Phi I_0 \epsilon dt$ in which ϵ = molar extinction coefficient of starting ketone, c = concentration of starting ketone (moles/liter), d = cell length (centimeters), I_0 = total amount of incident light (einstein liter^{-1} second^{-1}), t = reaction time, Φ = quantum yield of disappearance of starting ketone. We are grateful to Professor M. Koizumi, Tohoku University, for his help in kinetic measurements, and the personnel of Japan Spectroscopic Co., Hachioji, Tokyo, for usage of the concave radiating monochromator CRM-FA.

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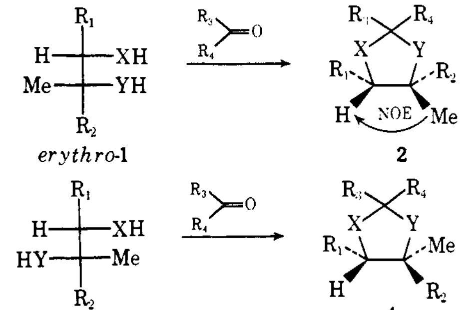
Received December 16, 1971

A General Method for Distinguishing Threo and Erythro Isomers of Certain α-Glycols and Related Compounds

Sir:

In the following we describe a method for differentiating between threo and erythro isomers. The method simply involves detection of an intramolecular nuclear Overhauser effect (NOE)[1] or W-type long-range coupling[2,3] in the nmr spectrum of an acetonide or other suitable five-membered ring derivative. Since no generalized methods seem to be known for estab-

Scheme I. Formation of Five-Membered Derivatives (X, Y:, O, NR, and S)



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(1) F. A. L. Anet and A. J. R. Bourn, *J. Amer. Chem. Soc.*, **87**, 5250 (1965); M. C. Woods, I. Miura, Y. Nakadaira, A. Terahara, M. Maruyama, and K. Nakanishi, *Tetrahedron Lett.*, 321 (1967); J. H. Noggle and R. E. Schirmer, "The Nuclear Overhauser Effect," Academic Press, New York, N. Y., 1971.

(2) S. Sternhell, *Quart. Rev., Chem. Soc.*, **23**, 236 (1969); M. Barfiels and B. Chakrabarti, *Chem. Rev.*, **69**, 757 (1969).

(3) Needless to mention, NOE is characterized by an increase in integrated intensity and a constant half-band width ($W_{1/2}$), whereas W-type coupling is characterized by an increase in peak height and a decrease in $W_{1/2}$ (no change in integrated intensity). In the present paper, we record the extent of W-type couplings in terms of height increase rather than $W_{1/2}$ decrease.