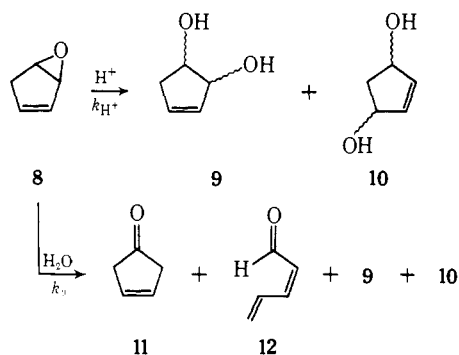
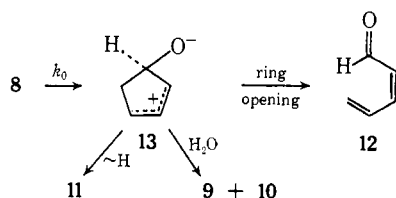


Scheme II



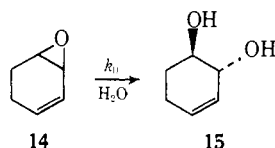
shift is required, and a mechanism whereby **11** is produced from an enol intermediate is eliminated as a major pathway. The rearrangement of **8** to **11** is therefore mechanistically analogous to the rearrangement of benzene oxide (**1**) to phenol *via* path a, Scheme I. Whether hydride migration occurs in the rate-determining step or subsequent to rate-determining formation of an intermediate zwitterion (Scheme III) has not been determined.<sup>9</sup>

Scheme III



Zwitterion **13** is potentially a common intermediate for all products obtained from the  $k_0$  process. Of particular significance is the formation of significant amounts<sup>7</sup> of *cis* and *trans* 1,4-diols, **10**, in addition to *cis* and *trans* 1,2-diols, **9**. This result is in marked contrast to that observed in the hydrolysis of 1,3-cyclohexadiene oxide (**14**), where the  $k_0$  process yielded  $\approx 98\%$  *trans*-3-cyclohexen-1,2-diol.<sup>10</sup> Different mechanisms for diol formation from **14** and from **8** by the  $k_0$  process therefore appear operative.

The presence of an hydroxide-catalyzed term in the hydrolysis of 1,3-cyclohexadiene oxide (**14**) at  $\text{pH} > 12$



and the formation of predominantly *trans* 1,2-diol **15** strongly suggests nucleophilic displacement by water in the  $k_0$  process for this epoxide. The formation of large amounts of 1,4-diols, **10**, and the absence of an hydroxide-catalyzed term in the hydrolysis of **8**<sup>11</sup> suggests a more delocalized intermediate such as **13**.<sup>12</sup>

(9) Studies of the rearrangement of naphthalene oxide show that hydride migration in the  $k_0$  process occurs subsequent to rate-determining formation of a zwitterion. See ref 3b.

(10) D. L. Whalen, *J. Amer. Chem. Soc.*, **95**, 3432 (1973).

(11) The rate of hydrolysis of **8** did not change as the concentration of KOH was varied between 0.1 and 0.5 M.

(12) The similarity of the diol mixtures obtained from the  $k_0$  process ( $\text{pH} > 7.5$ ) and the  $k_{H^+}$  process ( $\text{pH} < 5$ ) suggests a common intermediate. Protonation on the oxygen of zwitterion **13** might be expected to be fast relative to nucleophilic addition of water at the cationic center, thus leading to the same allylic cation intermediate formed by the  $k_{H^+}$  process.

The existence of a zwitterion intermediate is also suggested by the rearranged product **12**, which can potentially result from a concerted electrocyclic ring opening of **13**.

The acid-catalyzed hydrolysis of **8** at  $\text{pH} \lesssim 4.0$ , where the  $k_{H^+}$  term is much larger than the  $k_0$  term, yielded less than 2% of either **11** or **12**.<sup>13</sup> Instead, only a mixture of 1,2- and 1,4-diols, **14** and **15**, was obtained.<sup>14</sup> The observation that the hydrolysis of **8** is general acid-catalyzed by a number of buffer acids is in line with our earlier suggestion that the hydrolyses of highly reactive epoxides are likely to exhibit such catalysis.<sup>10</sup>

**Acknowledgment** is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the American Cancer Society, Maryland Section, for support of this research.

(13) The epoxide samples used in these studies were contaminated with 3% of ketone **11** and 2% of aldehyde **12**. Glpc and uv analysis of the product mixture from hydrolysis of **8** at  $\text{pH} 1-4$  indicated that the amounts of **11** and **12** present were, within experimental error, the same as were in the original epoxide sample.

(14) Nmr and glpc analyses of the diol mixture obtained from hydrolysis of **8** at  $\text{pH} 2-8$  indicated that all four possible diols (*cis* and *trans* isomers of **9** and **10**) were obtained, the ratio of 1,4-diols to 1,2-diols being *ca.* 55:45. In a private communication, Dr. Henry Z. Sable informed us that he also obtained a mixture of all four diols from hydrolysis of **8** in distilled water.

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## Mechanism of Stereoisomerization in Triarylboranes<sup>1</sup>

Sir:

In previous studies concerning the mechanism of stereoisomerization in triarylboranes<sup>2</sup> and triarylcarbenium ions,<sup>3</sup> the cumulative weight of circumstantial evidence has pointed to the two-ring flip mechanism as the mechanism of lowest energy (threshold mechanism). However, no experimental results have as yet appeared which rule out all alternatives to this mechanism. We wish to report the first direct evidence which establishes the two-ring flip as the threshold mechanism for triarylboranes and, by extension, for cognate systems.

Triarylboranes assume propeller conformations in the ground state, on the nmr time scale.<sup>2</sup> Although isomerizations of such molecules have commonly been discussed in terms of four flip mechanisms,<sup>2,3</sup> each of which involves a reversal of helicity (sense of twist), there exist alternative nonflip rearrangements (in the permutational sense) in which isomerization is *not* accompanied by a reversal of helicity.<sup>4</sup>

Previous work<sup>2,3c,d</sup> on boranes and carbenium ions, which showed that of the four flip mechanisms only the

(1) This work was supported by the National Science Foundation (GP-30257).

(2) J. F. Blount, P. Finocchiaro, D. Gust, and K. Mislow, *J. Amer. Chem. Soc.*, **95**, 7019 (1973).

(3) (a) I. I. Schuster, A. K. Colter, and R. J. Kurland, *J. Amer. Chem. Soc.*, **90**, 4679 (1968); (b) R. Breslow, L. Kaplan, and D. LaFollette, *ibid.*, **90**, 4056 (1968); (c) J. W. Rakshys, Jr., S. V. McKinley, and H. H. Freedman, *ibid.*, **93**, 6522 (1971); (d) D. Gust and K. Mislow, *ibid.*, **95**, 1535 (1973).

(4) These nonflip rearrangements may be formally thought of as rotations of zero, one, two, or all three aryl rings by  $\pi$  radians, while the nonrotating rings remain fixed.

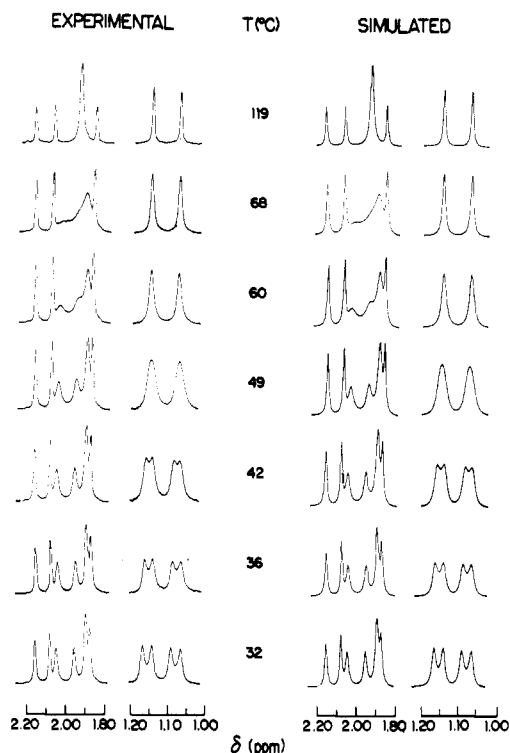
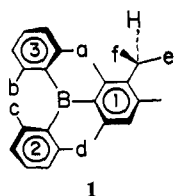


Figure 1.

two-ring flip is consistent with the experimental results, did not rule out the nonflip mechanisms, since changes of helicity were not directly monitored. On the other hand, the several studies which demonstrated a change of helicity for propeller molecules<sup>3c,5,6</sup> provided no other evidence concerning the isomerization mechanism.<sup>7</sup>

To settle this question, we have studied the temperature-dependent <sup>1</sup>H nmr spectrum of bis(2,6-xylyl)-1-(3-isopropyl-2,4,6-trimethylphenyl)borane<sup>8</sup> (**1**). The



presence of the meta isopropyl group as a diastereotopic probe permits measurement of the rate of enantiomerization of **1** (*i.e.*, the rate of reversal of helicity), whereas the presence of the xylyl methyl groups permits an independent determination of those ligand

(5) D. Hellwinkel, M. Melan, and C. R. Degel, *Tetrahedron*, **29**, 1895 (1973).

(6) (a) J. S. Hyde, R. Breslow, and C. DeBoer, *J. Amer. Chem. Soc.*, **88**, 4763 (1966); (b) L. D. Kispert, J. S. Hyde, C. de Boer, D. LaFollette, and R. Breslow, *J. Phys. Chem.*, **72**, 4276 (1968).

(7) In several carbenium ion systems, Freedman and coworkers<sup>3c</sup> observed two separate stereoisomerizations. One of these included a change of helicity, and the other was consistent with a two-ring flip mechanism. However, since the two processes were distinct, the experiment failed to rule out nonflip alternatives to the two-ring flip.

(8) The compound was prepared by reaction in ether of bis(2,6-xylyl)boron fluoride with the lithium reagent derived from 1-bromo-3-isopropyl-2,4,6-trimethylbenzene, which was obtained by bromination of isopropylmesitylene<sup>9</sup> in the presence of iron. All new compounds gave satisfactory elemental analyses, and mass spectra were consistent with the assigned structures.

(9) R. Adams and A. Ferretti, *J. Amer. Chem. Soc.*, **83**, 2559 (1961).

permutations which are independent of helicity reversal in an achiral medium.

Figure 1 displays the 100-MHz <sup>1</sup>H nmr spectra of **1** in chlorobenzene solution (methyl region, hexamethyldisiloxane as internal reference). At 32°, the three aromatic methyl resonances at  $\delta$  1.88, 2.08, and 2.16 ppm correspond to the three constitutionally distinct methyl groups on the ring bearing the isopropyl group, and the three remaining aromatic methyl resonances at  $\delta$  1.90, 1.96, and 2.05 ppm correspond to the four diastereotopic xylyl methyl groups, two of which are accidentally isochronous. The two doublets centered at  $\delta$  1.13 and 1.10 ppm ( $^3J_{\text{HH}} = 7.7$  Hz) correspond to the two diastereotopic isopropyl methyl groups. The spectrum is therefore consistent with **1** in a propeller conformation and with slow stereoisomerization on the nmr time scale at 32°.

As the temperature is raised, the xylyl methyl signals coalesce to a singlet, and the two isopropyl methyl group doublets coalesce to a single doublet (Figure 1). The results of stereoisomerization of **1** by the 16 possible rearrangements are summarized in Table I, in-

Table I

Pathway <sup>a</sup>	Resulting site exchanges <sup>b</sup>	
	Flip	Nonflip <sup>c</sup>
Zero-	(aā)(bb̄)(cc̄)(dd̄)(ef̄)(fē)	(a)(b)(c)(d)(e)(f)
[1]-	(ađ)(bĉ)(cb̄)(dā̄)(ef̄)(fē)	(ad)(bc)(da)(cb)(e)(f)
[2]-	(aā)(bb̄)(cđ)(dĉ)(ef̄)(fē)	(a)(b)(cd)(dc)(e)(f)
[3]-	(aḅ)(bā̄)(cc̄)(dđ)(ef̄)(fē)	(ab)(ba)(c)(d)(e)(f)
[1,2]-	(aḁbc̄)(ādb̄c̄)(ef̄)(fē) <sup>d</sup>	(adbc)(e)(f)
[1,3]-	(aḁbc̄)(ādb̄c̄)(ef̄)(fē) <sup>d</sup>	(acbd)(e)(f)
[2,3]-	(aḁ)(bā̄)(cđ)(dĉ)(ef̄)(fē)	(ab)(ba)(cd)(dc)(e)(f)
[1,2,3]-	(aĉ)(bđ̄)(cā̄)(db̄)(ef̄)(fē)	(ac)(bd)(ca)(db)(e)(f)

<sup>a</sup> Numerals in brackets indicate the rings which flip in flip pathways or which rotate by  $\pi$  radians in nonflip pathways. <sup>b</sup> For significance of letters, refer to structure in text. Barred letters refer to environments enantiomeric to those shown. <sup>c</sup> The enantiomeric nonflip pathways are not shown. <sup>d</sup> Since the [1,3]- and [1,2]-flips are enantiomeric, their results are considered together.

spection of which reveals that, in the absence of accidentally equivalent rates for diastereomeric processes, only one rearrangement is consistent with simultaneous averaging of all of the 2,6-xylyl methyl group environments and averaging of the environments of the diastereotopic isopropyl methyl groups. This is the two-ring flip rearrangement (the enantiomeric [1,2]- and [1,3]-flips). Line-shape analysis is consistent with this conclusion and yields rate constants which were used to calculate free energies of activation for the two-ring flip of  $\Delta G^{\ddagger}_{37} 17.8$  kcal/mol from both the coalescence of the xylyl methyl group resonances and the isopropyl methyl group resonances.<sup>10,11</sup> Our experiment thus firmly establishes the two-ring flip as the threshold mechanism for **1**.

There exists a noteworthy similarity between the present work and a study of the isomerization of *o*-isopropylphenylbis(*p,p'*-bitolyl)phosphorane (**2**) by

(10) The [2,3]-flip would be expected to have roughly the same energy of activation as the [1,2]- and [1,3]-flips. However, isomerization by this mechanism was not detectable in this experiment.

(11) The observed anisochrony of isopropyl methyl group resonances cannot be attributed to slow rotation about the isopropyl-aryl bond, since the barrier to such rotation (*e.g.*, in isopropylmesitylene) is far too low, *i.e.*, only *ca.* 13 kcal/mol.<sup>12</sup>

(12) A. Rieker and H. Kessler, *Tetrahedron Lett.*, 1227 (1969).

Whitesides and Bunting,<sup>13</sup> which arises from the circumstance that the stereochemistry of both systems may be analyzed in terms of the same abstract model: even though the stereoisomerization processes in the two systems differ vastly in mechanistic detail (*i.e.*, torsion for **1** *vs.* pseudorotation for **2**), **1** and **2** are stereochemically correspondent.<sup>14</sup>

(13) G. M. Whitesides and W. M. Bunting, *J. Amer. Chem. Soc.*, **89**, 6801 (1967).

(14) D. Gust, P. Finocchiaro, and K. Mislow, *Proc. Nat. Acad. Sci. U. S.*, **70**, 3445 (1973).

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### Environmental Effects in the Photoredox Decompositions of Acidopentaamminecobalt(III) Complexes. Contributions from Charge Transfer and Ligand Centered Excited States in $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$

Sir:

Mechanistic discussions of the chemical reactions which follow the irradiation of charge transfer to metal (CTTM) absorption bands of transition metal complexes have very often been formulated around radical pair<sup>2-5</sup> or excited state<sup>6-12</sup> models. Attempts to explore aspects of excited state models using triplet sensitizers<sup>13-17</sup> have frequently been complicated by side reactions<sup>14, 18-20</sup> of the sensitizer or by free radical reactions of likely photoredox products.<sup>17b, 21</sup> Very recently we<sup>22</sup> and Scandola<sup>23</sup> have been attempting to

(1) Partial support of this research by the National Science Foundation (Grant GP 36888X) and of a fellowship (to G. F.) from the Faculty of Sciences, the University of Chile, is gratefully acknowledged.

(2) (a) A. W. Adamson and A. H. Sporer, *J. Amer. Chem. Soc.*, **80**, 3865 (1958); (b) A. W. Adamson, *Discuss. Faraday Soc.*, **29**, 163 (1960).

(3) R. D. Lindholm and T. K. Hall, *J. Amer. Chem. Soc.*, **93**, 3525 (1971).

(4) A. Vogler and A. W. Adamson, *J. Phys. Chem.*, **74**, 67 (1970).

(5) P. D. Fleischauer, A. W. Adamson, and G. Sartori, *Progr. Inorg. Chem.*, **17**, 1 (1972).

(6) J. F. Endicott and M. Z. Hoffman, *J. Amer. Chem. Soc.*, **87**, 3348 (1965).

(7) J. F. Endicott, M. Z. Hoffman, and L. S. Beres, *J. Phys. Chem.*, **74**, 1021 (1970).

(8) G. Caspari, R. G. Hughes, J. F. Endicott, and M. Z. Hoffman, *J. Amer. Chem. Soc.*, **92**, 6801 (1970).

(9) E. R. Kantrowitz, M. Z. Hoffman, and J. F. Endicott, *J. Phys. Chem.*, **75**, 1914 (1971).

(10) E. R. Kantrowitz, M. Z. Hoffman, and K. M. Schilling, *J. Phys. Chem.*, **76**, 2493 (1972).

(11) A. F. Vaudo, E. R. Kantrowitz, M. Z. Hoffman, E. Papaconstantinou, and J. F. Endicott, *J. Amer. Chem. Soc.*, **94**, 6655 (1972).

(12) V. W. Cope, S.-N. Chen, and M. Z. Hoffman, *J. Amer. Chem. Soc.*, **95**, 3116 (1973).

(13) A. Vogler and A. W. Adamson, *J. Phys. Chem.*, **76**, 1105 (1968).

(14) H. D. Gafney and A. W. Adamson, *J. Phys. Chem.*, **76**, 1105 (1972).

(15) I. Fujuta and H. Kobayashi, *Ber. Bunsenges. Phys. Chem.*, **76**, 1105 (1972).

(16) J. N. Demas and A. W. Adamson, *J. Amer. Chem. Soc.*, **93**, 1880 (1971).

(17) (a) P. Natarajan and J. F. Endicott, *J. Amer. Chem. Soc.*, **94**, 3635 (1972); (b) *ibid.*, **95**, 2470 (1973).

(18) M. A. Scandola and F. Scandola, *J. Amer. Chem. Soc.*, **92**, 7278 (1970).

(19) H. D. Gafney and A. W. Adamson, *J. Amer. Chem. Soc.*, **94**, 8238 (1972).

(20) J. N. Demas and A. W. Adamson, *J. Amer. Chem. Soc.*, **95**, 5159 (1973).

(21) (a) P. Natarajan and J. F. Endicott, *J. Phys. Chem.*, **77**, 971 (1973); (b) *ibid.*, **77**, 1823 (1973).

(22) J. R. Barber, G. F. Ferraudi, and J. F. Endicott, work in progress.

(23) F. Scandola, C. Bartocci, and M. A. Scandola, *J. Amer. Chem. Soc.*, **95**, 7898 (1973).

probe aspects of radical pair behavior by examining the photochemistry of cobalt(III) complexes in media of varying viscosity. Scandola's work has elegantly demonstrated opposite and proportional dependencies on viscosity of the yields of  $\text{Co}^{2+}$  and  $\text{Co}(\text{NH}_3)_5\text{ONO}^{2+}$  obtained following CTTM (254 nm) excitation of  $\text{Co}(\text{NH}_3)_5\text{NO}_2^{2+}$ . This kind of photochemical behavior strongly supports the contention<sup>24</sup> that the linkage isomerization reaction is the result of radical pair recombination.

Our studies<sup>22</sup> of  $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{N}_3$ , and  $\text{NCS}$ ) complexes in a variety of solvent media appear to be leading to some unexpected insights into the nature of both radical pair species and their excited state precursors. Most importantly we find that variations of product yield with excitation wavelength ( $400 \text{ nm} \geq \lambda \geq 214 \text{ nm}$ ) and with solvent viscosity are not always in agreement with the qualitative predictions<sup>25</sup> for the simple recombination and diffusive separation reactions of radical pair species. The most striking photochemical behavior has been found for  $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$ . For this complex the quantum yield of  $\text{Co}^{2+}$  ( $\phi_{\text{Co}^{2+}}$ ) increases with increasing [glycerol] for deep ultraviolet ( $\lambda \leq 280 \text{ nm}$ ) irradiations (Figure 1). This is qualitatively opposite to the behavior reported for 254-nm irradiations of  $\text{Co}(\text{NH}_3)_5\text{NO}_2^{2+}$  and qualitatively opposite to expectation if one assumes that the only factors affecting the yield of cobalt(II) are the rates of recombination and diffusive separation of primary "radical pair" products of the type  $\{\text{Co}(\text{NH}_3)_5^{2+}, \cdot\text{R}\}$ .

It is obvious from Figure 1 that the kind of variation of  $\phi_{\text{Co}^{2+}}$  (*i.e.*, whether a decrease or an increase) with increasing [glycerol] is different for irradiation of different absorption features of  $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$ . Our studies indicate that the yields of  $\text{Co}^{2+}$  and  $\cdot\text{NCS}$  radicals are stoichiometric over the full range of excitation in aqueous solutions. Although there are many important differences of detail, deep ultraviolet irradiations of  $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ ,  $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ , and  $\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}$  have also been found to give striking increases in  $\phi_{\text{Co}^{2+}}$  with [glycerol]; furthermore we have found that photoredox yields in acetonitrile are even larger while yields in 80%  $\text{H}_3\text{PO}_4$  are the smallest we have observed.

The most striking and unique features of our observations on  $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$  pertain to irradiations in the near ultraviolet ( $350 \text{ nm} \geq \lambda > 254 \text{ nm}$ ). Over this range of excitations we find: (1)  $\phi_{\text{Co}^{2+}}$  (as well yields of  $\text{NCS}^-$  and oxidation products) to be nearly wavelength independent, (2)  $\phi_{\text{Co}^{2+}}$  decreases, qualitatively as expected, with [glycerol], and (3) in water  $\phi_{\text{Co}^{2+}}$  is strongly temperature dependent, with  $\log \phi \propto T^{-1}$  (for  $\phi$  determined at  $T = 25, 35, 50$ , and  $60^\circ$ ) and  $E_a \approx 18 \text{ kJ/mol}$ .<sup>26</sup> In 50% glycerol we found  $E_a$  to increase to about 40 kJ/mol for 350-nm irradiations and to be

(24) V. Balzani, R. Ballardini, N. Sabbatini, and L. Moggi, *Inorg. Chem.*, **7**, 1398 (1968).

(25) (a) R. M. Noyes, *Progr. React. Kinet.*, **1**, 128 (1961); (b) For a recent review see J. P. Lorand, *Progr. Inorg. Chem.*, **17**, 207 (1972); (c) Most pertinent among the predictions of the mechanical model are (i) the redox yield should increase monotonically (presumably to unity) with excitation energy and (ii) the formation of redox products ( $\text{Co}^{2+}$  and a ligand radical) requires the diffusive separation of the primary, solvent cage trapped, cobalt(II) and radical fragments. Thus one would predict redox yields to decrease as solvent viscosity is increased.

(26) Adamson<sup>2b</sup> has reported an activation energy for formation of  $\text{Co}^{2+}$  in near-ultraviolet excitations ( $\lambda \approx 370 \text{ nm}$ ) of  $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$  but that no activation energy is observed for longer wavelength ( $\lambda > 450 \text{ nm}$ ) excitations. This implies that the activation energy goes through a maximum for irradiations in this one absorption band (Figure 1).