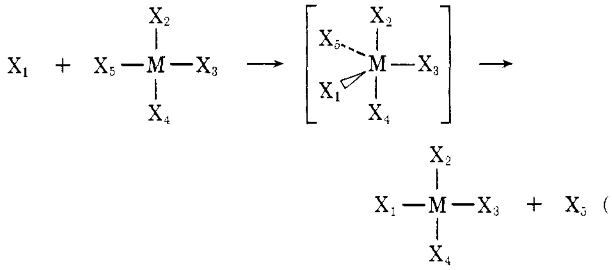
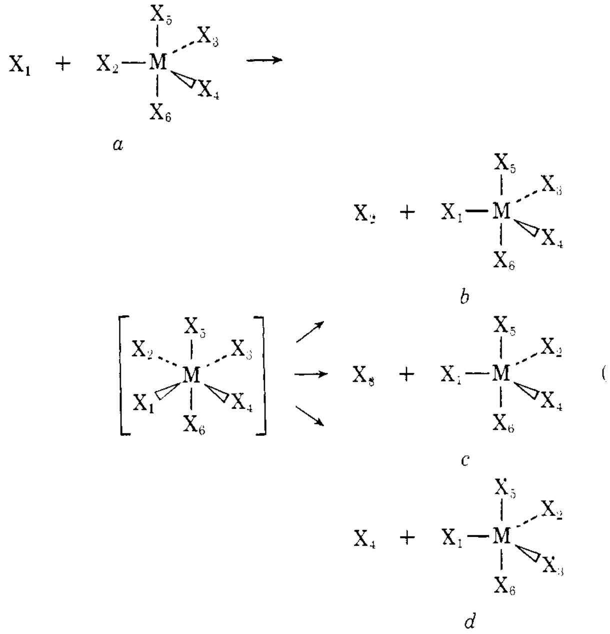
structure which is forbidden by our theorems will not be made allowed by additional instabilities.

As a practical matter, we wish to point out that in all point groups containing a three-, five-, or sevenfold axis, the nondegenerate representations are symmetric with respect to rotations about this axis. Thus, from theorems 1 and 3, no structure for which rotation about this axis converts reactants into products can be a transition state. The T_d and D_{3h} structures discussed above fall into this category. Another example would be the trigonal-bipyramid structure for the substitution (1). Although this structure cannot be the transition state, it could be a metastable intermediate (for which F would have no negative eigenvalues). There is some evidence to indicate that this is in fact the case in at least one example.[6]


(1)

The case of an evenfold axis is more complex. In reaction 2, for example, there are three distinct product sets b, c, and d which can arise from reactants a *via* the D_{4h} (or C_{4v}) structure as the transition state. The transition state is "allowed" for the reactions a → b and a → d. This is because there exists a nondegenerate representation (B_{1g}) which is antisymmetric under the operations which convert a into b or d and symmetric under the operations which leave a unchanged. On the other hand, it is "forbidden" for the reaction a → c since every nondegenerate representation is symmetric under the operation $\hat{C}_4{}^2$ which concerts a into c. Moreover, from the proof of theorem 3, it follows that if the D_{4h} structure is indeed the transition state for a → b, then there must exist a *lower energy* transition state (of different symmetry) for the reaction a → c.


(2)

From this last example it should be clear that any of the "forbidden" structures discussed above could be stationary points with a single, nondegenerate, negative eigenvalue of **F**. Theorem 3 eliminated them as transition states only for the reactants and products under consideration.

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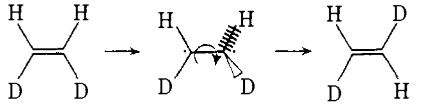
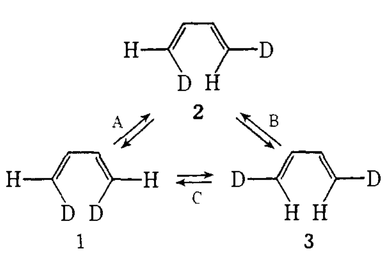
Thermal Cis–Trans Isomerization of Butadiene

Sir:

Many cis–trans isomerization reactions are now believed to proceed *via* a twisting mechanism which includes as a midpoint a species which has been termed a 1,2 diradical.[1] We wish to report that a portion of the thermal cis–trans isomerization reactions of the 1,4-dideuterio-1,3-butadienes[2] also proceeds by such a mechanism, paths A and B, below, but that a *correlated double isomerization*, path C, appears to dominate the reaction mechanism.[6]





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(6) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, N. Y., 1967, p 379.

(1) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968, p 72.

(2) The *trans,trans-* and *cis,cis*-dideuteriobutadienes were prepared in good yield from the *trans,trans-*[3] and *cis,cis*-dichlorobutadienes[4] (pure by vpc) *via* Zn–Cu couple reduction in refluxing dioxane–D_2O. The details of these procedures will be reported elsewhere. The *cis,-trans*-dideuteriobutadiene could also be prepared from the corresponding dichlorobutadiene,[4] or more conveniently by the method of Fleming.[5] The structures and deuterium contents were confirmed by nmr and mass spectral measurements. The analysis of the pyrolysis products was most conveniently accomplished by a least-squares fit to five Raman lines, at 1171, 1216, 1226, 2260, and 2280 cm^{-1}.

(3) R. Huisgen, *et al., Angew. Chem., Int. Ed. Engl.*, **75**, 585 (1966). Pure *trans,trans*-dichlorobutadiene was obtained after two recrystallizations from pentane.

(4) Prepared and purified according to the method of P. D. Bartlett and G. E. H. Wallbillich, *J. Amer. Chem. Soc.*, **91**, 409 (1969).

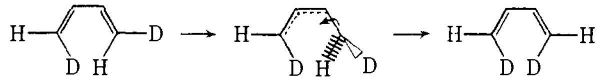
(5) I. Fleming and E. Wildsmith, *J. Chem. Soc. D*, 223 (1970).

(6) A discussion of this possibility has appeared: J. I. Brauman and W. C. Archie, Jr., *J. Amer. Chem. Soc.*, **94**, 4262 (1972).

Thus, vacuum flash pyrolysis[7] of pure *cis,cis*-**1** shows that *trans,trans*-**3** appears much more rapidly than *cis,trans*-**2** (see Figure 1). Other noteworthy features of Figure 1 are the rapid equilibration of isomers **1** and **3** to a 1:1 ratio long before isomer **2** has reached its equilibrium value of 50%, and the existence of a maximum in the curve describing formation of *trans,trans*-**3**, *at a point above its equilibrium value.* A similar set of results was obtained starting with *trans,trans*-**3**. These data require that starting with pure isomers the rates of disappearance of *cis,cis*-**1** and *trans,trans*-**3** would be much faster than the rate of disappearance of *cis,trans*-**2**. The results of these independent determinations of disappearance rates show that $k_{1\rightarrow 3} \simeq k_{3\rightarrow 1} \simeq 10(k_{2\rightarrow 1} + k_{2\rightarrow 3})$ in confirmation of this supposition. The data demand that pathway C be rapid relative to A and B.

Other data may be taken to imply the intervention of cyclobutene in the double isomerization pathway. Since the heats and entropies of formation of cyclobutene and butadiene are well known,[8a,b] and the activation parameters for the cyclobutene ring opening reaction have been accurately measured,[8b,9] the rate of ring closure of the diene to cyclobutene and hence the rate of double isomerization are calculable;[10] $\log k_{1\rightarrow 3} = 12.3 - 44.5/2.303RT$. Our measured rate constant[7] for this reaction, $k_{\text{obsd}} \simeq 12\ \text{sec}^{-1}$, may be compared to the prediction of this equation, $k_{\text{calcd}} = 50\ \text{sec}^{-1}$ at 910°K.

The isomerization of the *cis,trans*-**2** to *cis,cis*-**1** and *trans,trans*-**3** cannot involve the correlated double isomerization. By taking into account the full allylic resonance energy[1] of species **4**, a 1,2-diradical pathway can be shown to describe this reaction adequately. Thus, we estimate[10b,11] $\log k_{2\rightarrow 1}$ or $k_{2\rightarrow 3} = 12.8 - 52.5/2.303RT$. Our measured rate constant for this reaction,[7] $k'_{\text{obsd}} = 0.6\ \text{sec}^{-1}$, compares favorably with $k'_{\text{calcd}} = 1.9\ \text{sec}^{-1}$ at 910°K.



2 **4** **1**

The agreement between the calculated and observed rates for both the double isomerization and 1,2-diradical pathways is within tolerable limits.[13] In addition, at 3 Torr total pressure, the butadiene reactions have probably not yet reached the high pressure limit, a factor which would lower the rates from the calculated values.

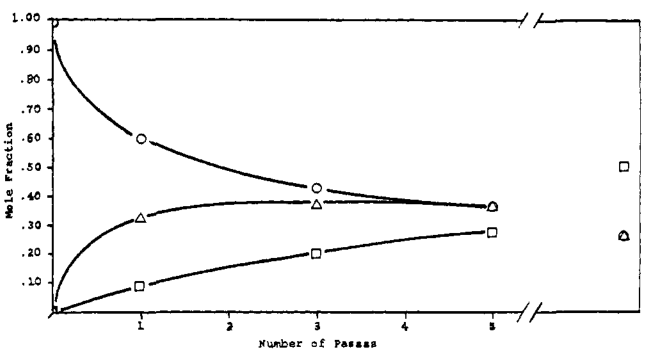


Figure 1. Pyrolysis of pure *cis,cis*-1,4-dideuterio-1,3-butadiene (○) to *trans,trans*-1,4-dideuterio-1,3-butadiene (△) and *cis,trans*-1,4-dideuterio-1,3-butadiene (□) at 910°K, at a pressure of 3 Torr; contact time per pass was ~50 msec. The points at the far right side of the graph represent the expected equilibrium values.

Previous work has led to the idea that cyclobutene pathways were involved in diene isomerization reactions. In the only direct study Doorakian and Freedman showed[14] that 2,3,4,5-tetraphenyl-2,4-hexadiene underwent double isomerizations cleanly, even after prolonged time (~100 isomerizations per molecule). However, the high degree of substitution in this system, which tends to stabilize the cyclobutene relative to the butadiene structure, makes the extension of this observation to simpler systems with substantially higher activation energies difficult. In more recent work Frey, *et al.*,[15] showed that the cis–trans isomerization of 2,3-dimethyl-1,3-pentadiene proceeds at a rate faster than that calculated for a 1,2-diradical mechanism. Unfortunately, this system lacks suitable stereochemical labeling to test for a double isomerization mechanism.

The present study shows that the fast component of diene isomerization reactions is in fact stereospecific, as required by the Woodward–Hoffmann rules[16] for a cyclobutene pathway. The system studied is, in addition, sufficiently simple that thermochemical parameters may be accurately estimated. These show quite clearly that, at all but the highest temperatures, the correlated double isomerization should predominate for butadiene, and that, in the absence of very large steric constraints in the cyclobutene or cyclobutene-like species, this mechanism should be general for dienes.

Acknowledgment. The support of the Research Corporation, E. I. du Pont de Nemours through a DuPont Young Faculty Grant (L. M. S.), the National Science Foundation (Grant No. GP-27532), and the

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(7) The pyrolysis was carried out by distillation of a sample of butadiene maintained in a reservoir at −78°, through an evacuated quartz tube maintained at 910°K, into a liquid nitrogen cooled receiver. Packing of this tube with quartz wool did not influence the results; thus, this procedure apparently eliminated the wall reactions present in static reactors. By measuring the tube pressure during pyrolysis runs, and the rate of material flow across the tube, a contact time of ~50 msec per pass is estimated and is used to determine the rate constants in this paper. Multiple pass runs were made in order to obtain data for contact times greater than 50 msec.

(8) (a) K. B. Wiberg and R. A. Fenoglio, *J. Amer. Chem. Soc.*, **90**, 3395 (1968); (b) S. W. Benson and H. E. O'Neal, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, **No. 21** (1970).

(9) R. W. Carr, Jr., and W. D. Walters, *J. Phys. Chem.*, **69**, 1073 (1965).

(10) (a) The *A* factor has been adjusted to account for the fact that the rate for isomerization will be one-half that for ring closure. (b) Based on thermochemical quantities at 298°K. Corrections to 910°K do not lead to appreciable changes in these estimated rate constants.

(11) The activation energy was obtained by superimposing the allyl resonance energy[12] of 12.5 kcal/mol on the activation energy for 1,2-dideuterioethylene cis–trans isomerization.[8b] The *A* factor was obtained by assuming an entropy of activation similar to that for styrene isomerizations.[8b]

(12) D. M. Golden, A. S. Rodgers, and S. W. Benson, *J. Amer. Chem. Soc.*, **88**, 3196 (1966).

(13) The factor of 2–4 discrepancy in the comparison of the calculated and observed rates could logically be due to an ~2-kcal/mol error in E_a calculation, a 2.3-eu error in $\Delta S^{\ddagger}$ estimate, or a factor of 2 error in the contact time per pass measurement.

(14) G. A. Doorakian and H. H. Freedman, *J. Amer. Chem. Soc.*, **90**, 5310, 6896 (1968).

(15) H. M. Frey, A. M. Lamont, and R. Walsh, *J. Chem. Soc. D*, 1583 (1970).

(16) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395 (1965).

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[17] NSF Predoctoral Trainee, 1969–1972.

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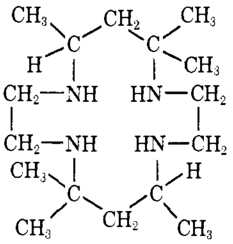
A Photochemical Synthesis of Amine Complexes Containing Cobalt(III)–Alkyl Bonds[1]

Sir:

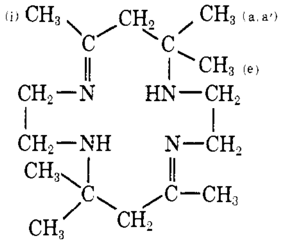
Since the discovery that coenzyme B_{12} contains a cobalt(III)–carbon bond,[2] there has been considerable interest in the preparation and properties of simpler inorganic analogs.[3] To date, inorganic complexes have been prepared containing a variety of unsaturated (generally Schiff-base) ligands in the coordination positions cis to the bound alkyl.[3] Since such complexes have become so commonplace and since previous attempts to prepare cobalt(III)–alkyl complexes containing only saturated ligand systems have failed, several authors have made theoretical or quasi-theoretical suggestions to account for the "instability" of the cobalt(III)–alkyl bond in complexes containing only saturated ligands.[3,4]

With this report we call attention to the first preparation of a cobalt(III)–alkyl complex containing only saturated ligands. We do not find these compounds to be particularly unstable, consistent with Chatt's suggestion that CH_3^- should have a large crystal field strength and that metal–alkyl decomposition depends on the rate of solvolysis;[5] but these compounds are relatively difficult to prepare.

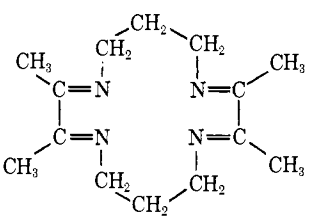
Whereas Co([14]-4,11-dieneN_4)$(OH_2)CH_3^{2+}$ and Co([14]aneN_4)$(OH_2)CH_3^{2+}$ have not been isolated from the reaction of the cobalt(I) complexes with CH_3I,[4c,6] the Co^{III}([14]tetraeneN_4)XCH_3 complexes are relatively easily prepared[4c] by this route.[7] On the other hand, all the corresponding $Co^{III}(N_4)$ complexes are oxidized at nearly diffusion-controlled rates with the dihalide radical anions, Cl_2^-, Br_2^-, and I_2^-.[8] Since it seemed likely that the $\cdot CH_3/Co^{II}(N_4)$ reactions might be relatively slow,[9] we have employed the photochemical decomposition of $Co(NH_3)_5O_2CCH_3^{2+}$ to provide a convenient source of methyl radicals[10] at sufficiently low concentrations (the photostationary state $[\cdot CH_3] \approx 10^{-8}$ *M* under our conditions) that the $\cdot CH_3/Co^{II}(N_4)$ reactions ($[Co^{III}(N_4)] \simeq 10^{-3}$ *M*) could compete effectively with radical–radical combination ($k_2 \simeq 10^{10}$ M^{-1} sec^{-1}).



[14]aneN_4



[14]-4,11-dieneN_4



[14]tetraeneN_4

$$Co(NH_3)_5O_2CCH_3^{2+} + h\nu \xrightarrow[H^+]{} Co^{2+} + 5NH_4^+ + CO_2 + \cdot CH_3$$

$$\cdot CH_3 + Co^{II}(N_4) \xrightarrow[H_2O]{} Co(N_4)(OH_2)CH_3^{2+} \quad (1)$$

$$2\cdot CH_3 \longrightarrow C_2H_6 \quad (2)$$

By monitoring changes in the charge transfer to ligand absorbancies of the cobalt(II) complexes in flash photolysis studies, we have found that $k_1 \simeq 7 \times 10^8$ M^{-1} sec^{-1} when N_4 = [14]-4,11-dieneN_4 and $k_1 \simeq 1 \times 10^8$ M^{-1} sec^{-1} when N_4 = [14]tetraeneN_4.

In the preparative experiments $[Co(NH_3)_5O_2CCH_3^{2+}] \simeq 2[Co^{II}(N_4)]$, irradiations were performed at 254 nm, using a low-pressure mercury lamp, in a nitrogen atmosphere and in acidic ($[HClO_4] \simeq 0.1$ *M*) solutions. Preparative solutions were photolyzed until the acetato complex was completely destroyed. The photolyte was then concentrated about fivefold by distillation and the [*trans*-$Co(N_4)(OH_2)CH_3](ClO_4)_2$ products were precipitated by addition of concentrated $HClO_4$.[11] The complexes were recrystallized from 0.01 *M* $HClO_4$ at about 60° (yield ~50%).

The Co^{II}([14]-4,11-dieneN_4) complexes which we employed were most likely to be predominately of the N-meso isomer of the ligand.[12] Since our preparative reactions were run in acidic solution, we would expect the product [Co([14]-4,11-dieneN_4)$(OH_2)CH_3](ClO_4)_2$ to be predominately this isomer and this assignment is confirmed by the pmr spectra (Figure 1) since only two of the geminal methyls are pairwise coupled; the axial methyl groups (CH_3(a) and CH_3(a')) experience different local fields owing to the asymmetry along the axis perpendicular to the Co–N_4 plane. We have also prepared the Co(N-*dl*-[14]-4,11-dieneN_4)$(OH_2)CH_3^{2+}$ complex in isomerically pure form by first preparing the [Co([14]-4,11-dieneN_4)(CN)$CH_3]ClO_4$ salt from Co([14]-4,11-dieneN_4)$(OH_2)CH_3^{2+}$ in methanol solu-

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[1] Partial support of this research by the Public Health Service (Grant AM 14341) is gratefully acknowledged.

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[7] Abbreviations for ligands chosen to be consistent with suggestions of V. L. Goedkin, P. H. Merrell, and D. H. Busch, *J. Amer. Chem. Soc.*, **94**, 3397 (1972).

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[11] Analytical data for recrystallized samples were as follows. (a) Calcd for [Co([14]-4,11-dieneN_4)$(OH_2)CH_3](ClO_4)_2$: C, 35.7; H, 6.48; N, 9.80; Cl, 12.4. Found: C, 35.2; H, 6.74; N, 9.77; Cl, 11.6. (b) Calcd for [Co([14]aneN_4)$(OH_2)CH_3](ClO_4)_2$: C, 35.5; H, 7.14; N, 9.75; Cl, 12.34. Found: C, 35.2; H, 7.14; N, 9.51; Cl, 11.41.

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