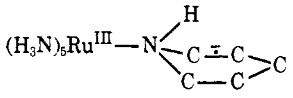
nism may be proposed to account for these observations.

$$\mathrm{Ru(NH_3)_5py^{2+}\ (^1A_1)} + h\nu \longrightarrow \mathrm{Ru(NH_3)_5py^{2+}\ (^*CT)}$$

$$\mathrm{^*CT} \longrightarrow \mathrm{^1A_1}$$

$$\mathrm{^*CT} \longrightarrow \underset{\mathrm{I}}{\mathrm{Ru^{III}(NH_3)_5(py^-)}} \qquad (1)$$

$\mathrm{I + H^+} \rightleftharpoons$



(2)

II

$$\mathrm{I} \longrightarrow \mathrm{^1A_1} \qquad (3)$$

$$\mathrm{II + H_2O} \longrightarrow \mathrm{Ru(NH_3)_5OH_2^{2+} + Hpy^+} \qquad (4)$$

At present it is not clear whether the pH-independent path for pyridine aquation occurs from I in competition with back-electron transfer (3) or whether the net ligand aquation reactions are to be associated with the population of other (*e.g.*, ligand field) excited states. Our observations do require that $\mathrm{p}K_a \geq 4$ for II; it also appears that the acid-independent term of k_{obsd} is to be associated with pyridine aquation as indicated in (4).

It is to be observed that an intermediate analogous to I has been observed in the pulse radiolysis of $\mathrm{(H_3N)_5CoO_2CC_6H_4NO_2^{2+}}$.[12] The lifetime of the electron adduct of nitrobenzoate coordinated to cobalt(III) varies from 10^{-2} to 2.5×10^{-6} sec for the ortho and meta isomers, respectively.[12] The similarly long lifetimes for aromatic radical anions coordinated to either cobalt(III) or ruthenium(III) suggest a significant activation barrier[13,14] to the intramolecular electron-transfer reactions which generate the stable divalent metal complex. At least for the systems we have studied it seems reasonable to attribute this barrier to structural changes in the ligand such as the change in hybridization of the pyridine nitrogen which we have indicated in I. In the case of $\mathrm{Ru(NH_3)_5py^{2+}}$ the proposed intermediate I also provides a convenient means of accounting for the pH dependence of the transient lifetime.

Although the transient species which we have observed must be regarded as primary photochemical products, they apparently decay largely in a way which regenerates the original substrate. In the case of the triplet sensitizers, $\mathrm{Ru(bipy)_3^{2+}}$ and $\mathrm{Ru(phen)_3^{2+}}$, any significant photoreaction, particularly a long-lived bleaching reaction, could affect estimates of the number of triplet states populated in sensitization reactions.[15] To estimate product yields we have used a solution of naphthalene in ethanol as a filter for the flash lamps to ensure irradiation of only the low-energy CTTL bands. Using pyridine aquation from $\mathrm{Ru(NH_3)_5py^{2+}}$ as an approximate actinometric reference, we estimate that the yields of transient from CTTL irradiation of $\mathrm{M(bipy)_3^{2+}}$ and $\mathrm{M(phen)_3^{2+}}$ are approximately 10^{-3}. Thus even in 1 *M* [H$^+$], a correction would only be significant in the $\mathrm{Ru(bipy)_3^{2+}}$ sensitized product yields obtained if absorbed light intensities were greater than about 10 einsteins l.$^{-1}$ sec^{-1}.

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[12] (a) M. Z. Hoffman and M. Simic, *J. Amer. Chem. Soc.*, **94**, 1757 (1972); (b) M. Z. Hoffman, private communication.

[13] In their analogous studies on cobalt complexes, Hoffman, *et al.*,[12] have postulated that relatively long-lived (compared to the case of $\mathrm{Co(NH_3)_5O_2CC_6H_5^{2+}}$ where no transient is observed) transients result due to localization of the electron at $\mathrm{NO_2}$. However, it does not seem that electron localization far from the metal center is a sufficient condition as the intrinsic barriers to reduction of cobalt(III) complexes seem generally very small.[14] It seems more likely to us that long-lived transients can only be observed, regardless of the central metal, when electron capture by the ligand results in some structural change within the ligand.

[14] D. P. Rillema, J. F. Endicott, and R. C. Patel, *J. Amer. Chem. Soc.*, **94**, 394 (1972); (b) D. P. Rillema and J. F. Endicott, *Inorg. Chem.*, in press; (c) *J. Amer. Chem. Soc.*, submitted for publication; (d) J. F. Endicott, R. R. Schroeder, and D. R. Ferrier, *J. Phys. Chem.*, submitted for publication.

[15] It should also be noted that net production of $\mathrm{Ru(bipy)_3^{3+}}$ can be a complication when $\mathrm{Ru(bipy)_3^{2+}}$ is used as a sensitizer. This may come about through electron transfer from $\mathrm{Ru^{III}(bipy)_2(H^+}$-$\mathrm{bipy^-)}$ as noted above or through the oxidation of $\mathrm{Ru(bipy)_3^{2+}}$ by radical fragments.

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The Stereoselective and Stereospecific Thermal Isomerizations of *trans*-1,2-Di(prop-1′-enyl)cyclopropanes

Sir:

Pioneering studies by Vogel[1,2] and by Doering and Roth[3,4] on the thermal isomerizations of *cis*-divinylcyclopropanes have been extended spectacularly, leading to new concepts and examples of fluxional isomerism and degenerate rearrangements. The discovery that *trans*-1,2-divinylcyclopropane may be converted at 190° to cyclohepta-1,4-diene[5] has not been pursued with a similar vigor. Whether the rearrangement involves a diradical-mediated Cope process, or an epimerization followed by a conventional Cope isomerization,[5] has been an unaddressed question.

Natural products derived from the essential oil of *Dictyopteris*, an odiferous seaweed, and from the female gametes of the brown alga *Ectocarpus siliculosus* have revived interest in *trans*-1,2-dialkenylcyclopropanes.[6-14] In the course of this work Pettus and Moore[14] provided the first data pertinent to the mechanism of the Cope rearrangement of *trans*-dialkenylcyclopropanes, by demonstrating that dictyopterenes A and B rearrange thermally to the cyclohepta-1,4-dienes **1** and **2** with some degree of stereoselectivity;[15]

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[1] E. Vogel, *Angew. Chem.*, 72, 4 (1960).

[2] E. Vogel, K.-H. Ott, and K. Gajek, *Justus Liebigs Ann. Chem.*, **644**, 172 (1961).

[3] W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).

[4] W. von E. Doering and W. R. Roth, *Angew. Chem., Int. Ed. Engl.*, 2, 115 (1963).

[5] E. Vogel and R. Erb, *ibid.*, 1, 53 (1962).

[6] R. E. Moore, J. A. Pettus, Jr., and M. S. Doty, *Tetrahedron Lett.*, 4787 (1968).

[7] A. W. Brugstahler and C. M. Groginsky, *Trans. Kans. Acad. Sci.*, 72, 486 (1969).

[8] G. Ohloff and W. Pickenhagen, *Helv. Chim. Acta*, **52**, 880 (1969).

[9] K. C. Das and B. Weinstein, *Tetrahedron Lett.*, 3459 (1969).

[10] J. A. Pettus, Jr., and R. E. Moore, *Chem. Commun.*, 1093 (1970).

[11] D. G. Müller, L. Jaenicke, M. Donike, and T. Akintori, *Science*, **171**, 817 (1971).

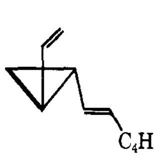
[12] L. Jaenicke, T. Akintori, and D. G. Müller, *Angew. Chem., Int. Ed. Engl.*, **10**, 492 (1971).

[13] B. Weinstein, A. Ali, and D. Sarantakis, *Chem. Commun.*, 940 (1971).

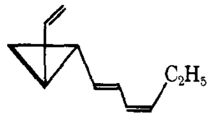
[14] J. A. Pettus, Jr., and R. E. Moore, *J. Amer. Chem. Soc.*, **93**, 3087 (1971).

[15] For the distinction between the adjectives "stereoselective" and "stereospecific" see E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, p 436; K. Mislow, "Introduction to Stereochemistry," W. A. Benjamin, New York, N.Y., 1965, pp 128, 137.

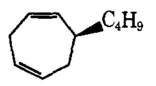
the optically active cyclopropanes give optically active cyclohepta-1,4-dienes.



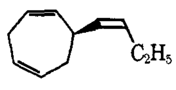
A



B

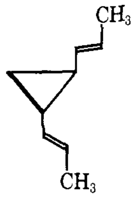


1



2

To gain information regarding the stereochemical disposition at both migration termini we have prepared and isomerized the three isomeric *trans*-1,2-di(prop-1′-enyl)cyclopropanes **3**, **4**, and **5**.



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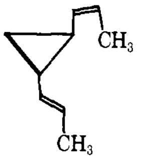
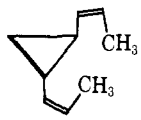


4

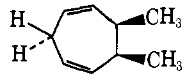


5

The ttt isomer **3** was prepared from hexa-*trans*-2,-*trans*-4-dienal, through $LiAlH_4$ reduction, Simmons-Smith cyclopropanation,[16] oxidation of the cyclopropylcarbinol with activated MnO_2, and coupling of the resultant aldehyde with ethylidenetriphenylphosphorane.[8,17] The hydrocarbon product, purified by glpc on a squalene column, had a strong infrared band at 958 cm^{-1} and the expected mass and nmr spectral characteristics.

The other isomers were obtained from *trans*-cyclopropanedicarboxylate[18] which through $LiAlH_4$ reduction, Ce^{IV} oxidation,[19] and a Wittig condensation led to a mixture of **4** (995 and 712 cm^{-1}) and **5** (713 cm^{-1}).

Isomer **3** is completely converted to *cis*-6,7-dimethylcyclohepta-1,4-diene (**6**) within 4.3 hr at 178°. The nmr spectrum of the C_9H_{14} product showed an AB pattern (δ_A 3.07, δ_B 2.55, J_{AB} = 19 Hz) for the nonequivalent protons at C-3.



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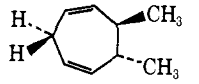

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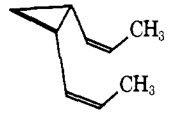

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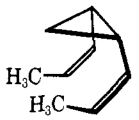
The ttc isomer gave complete conversion to *trans*-6,7-dimethylcyclohepta-1,4-diene (**7**) within 4.2 hr at 179°; the nmr spectrum of the product showed magnetically equivalent C-3 protons at δ 2.79.

Under the same conditions, isomer **5** was partially converted to an equilibrium proportion of *cis,cis,cis*-di(prop-1′-enyl)cyclopropane (**8**); only a few per cent of the monocyclic product was detected. The structural assignment for the newly produced C_9H_{14} material followed from its mass and nmr spectra; the latter showed an A_2BC pattern of cyclopropyl hydrogen absorptions and two equivalent cis double bonds (J_{vic} = 10 Hz).

That the ccc isomer **8** does not rearrange readily at 179° to form dimethylcyclohepta-1,4-diene must be associated with severe methyl–methyl repulsions in conformation **9**; similar stability with respect to Cope rearrangement has been observed in 3,3-dimethyl-*cis*-1,2-dialkenylcyclopropanes.[20,21]



9

The highly stereoselective and stereospecific reactions shown by the isomeric 1,2-di(prop-1′-enyl)cyclopropanes are consistent with a mechanistic sequence involving first epimerization, then, for the tct and tcc isomers, a normal Cope rearrangement through a boat-like geometry at the transition state. An alternative hypothesis, direct formation of cycloheptadienes through diradical intermediates, fails to account as plausibly for the observed differences among the three *trans*-dipropenylcyclopropanes: if it were the mechanism, all three substrates would be expected to give Cope products at comparable rates. The epimerization process itself might involve diradical intermediates, or conceivably a thermally allowed[22] Smith inversion.[23] Further work on the epimerization mechanism is in progress.

Acknowledgment. This work was supported by grants from the National Science Foundation and Hoffmann-LaRoche, Inc.

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[16] E. LeGoff, *J. Org. Chem.*, **29**, 2048 (1964).

[17] M. Schlosser and K. F. Christmann, *Justus Liebigs Ann. Chem.*, **708**, 1 (1967).

[18] G. B. Payne, *J. Org. Chem.*, **32**, 3351 (1967).

[19] L. B. Young and W. S. Trahanovsky, *ibid.*, **32**, 2349 (1967).

[20] T. Sasaki, S. Eguchi, M. Ohno, and T. Umemura, *Tetrahedron Lett.*, 3895 (1970).

[21] T. Sasaki, S. Eguchi, and M. Ohno, *J. Org. Chem.*, **37**, 466 (1972).

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[23] F. T. Smith, *J. Chem. Phys.*, **29**, 235 (1958).

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Formation of 2-Indanone and Benzocyclobutene from the Pyrolysis of Phenyl Propargyl Ether[1]

Sir:

We have found that the low-pressure (10^{-3}–10^{-5} Torr) gas-phase pyrolysis[2] of phenyl propargyl ether[4-6] gives rise to fair yields of 2-indanone and benzocyclo-

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[1] (a) Based on work by P. W. M. in partial fulfillment of the requirements for the Ph.D. degree at Iowa State University. (b) We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work by Grant No. 3219-A.

[2] The pyrolysis apparatus has been previously described.[3]

[3] W. S. Trahanovsky, C. C. Ong, J. G. Pataky, F. L. Weitl, P. W. Mullen, J. C. Clardy, and R. S. Hansen, *J. Org. Chem.* **36**, 3575 (1971).

[4] These ethers were prepared from the appropriate phenol, propargyl chloride or bromide, and potassium carbonate using the method previously described.[5,6]

[5] C. D. Hurd and F. L. Cohen, *J. Amer. Chem. Soc.*, **53**, 1068 (1931).

[6] Y. Okajima, *Yakugaku Zasshi*, **80**, 318 (1960); *Chem. Abstr.*, **54**, 18487*h* (1960).