= 211 cps) split into 1:2:1 triplets (J_{PH} = 189 cps) of 1:2:1 triplets (J_{PPF} = 81 cps).

Irrespective of the spectrum from which they were derived, the coupling constants for H_2PPF_2 agree within experimental error, and the magnitude of these *J*'s agrees well with the corresponding values for P_2H_4 and P_2F_4 (Table I). The former values, however, were determined by direct measurement and did not require analysis of second-order spectra as with P_2F_4[3] and P_2H_4.[4] The latter situation is surprising since, rigorously, H_2PPF_2 is an AA'KQXX' spin system, *i.e.*, a system requiring two AX coupling constants AX = A'X', AX' = A'X. A careful examination of the system, however, shows that it would be expected to give "deceptively simple" spectra,[5] *i.e.*, J_{FF} (*gem*) is probably large compared to the couplings between other nonequivalent nuclei[6] and $\delta_{FF'} = 0$. Thus, the observed J_{HPPF} is best explained as an average of two AX couplings.

Table I. The Coupling Constants for H_2PPF_2. A Comparison with Values for P_2F_4 and P_2H_4

	H_2PPF_2				
	^1H	^{19}F	^{31}P	P_2F_4[3]	P_2H_4[4]
J_{PF}	...	1203	1189	1198.5	...
J_{PH}	191	...	189	...	186.5
J_{PPF}	...	82	81	67.5	...
J_{PP}	...	...	211	227.4	108.2
J_{HPPF}	22	22	...	...	...
J_{PPH}	17	...	17	...	11.9

Difluorophosphine was originally prepared by the reduction of F_2PI with HI in the presence of mercury.[8] We have since found that, if PH_3 is used instead of HI, the yield of F_2PH is increased from 55 to 90% based on the amount of F_2PI taken.

$$2F_2PI + 2Hg + PH_3 \longrightarrow 2F_2PH + Hg_2I_2 + [PH] \qquad (3)$$

The synthesis represented by eq 3 is similar to those described by Harris[9] and Burg and Nixon[10] for the preparation of $(CF_3)_2PH$ and $(CF_3)PH_2$, respectively. Typically, 2.36 mmoles of F_2PI and 3.40 mmoles of PH_3 were added to a 500-cc reaction bulb containing 2 cc of triply distilled mercury. The bulb was then shaken for 15 hr before recovering the desired F_2PH (2.11 mmoles) by fractional condensation at −160°. Unreacted PH_3 (2.34 mmoles) and PF_3 (0.15 mmole) slowly pass through the −160° trap and are retained at −196°.

Acknowledgment. We gratefully thank Dr. A. Norman for the determination of certain nmr spectra with the University of Colorado nmr facilities which were in part purchased with NSF funds.

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(6) We wish to thank Dr. R. Newmark of the University of Colorado for a calculation which showed with $J_{FF'}(gem) = 200$, *i.e.*, $J_{FF'} \gg J_{HPPF}$, that the spectra of H_2PPF_2 would be "deceptively simple" and appear first order. It should also be noted that one AX coupling constant can be accommodated if a rapidly occurring process of rotation about the P–P bond coupled with inversion through the "phosphino" phosphorus atom is operative. The fact that two vicinal coupling constants are necessary to describe the spectra of P_2F_4[3] and P_2H_4[4] and the fact that calculations have shown the rate of inversion[7] through phosphorus to be slow compared to the nmr constant render this explanation suspect unless some mechanism which lowers the barrier to inversion in H_2PPF_2 is forwarded.

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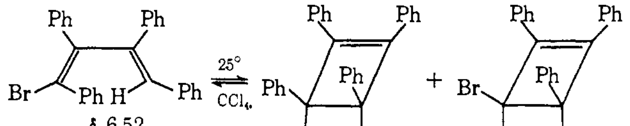
The Facile Thermal Cyclization of a Sterically Hindered Diene

Sir:

Detailed data on the activation parameters for the thermal, electrocyclic ring closure of dienes to cyclobutenes[1] are rare in comparison to that on the kinetically favored reverse process.[2] We now report preliminary details on one of a series of substituted dienes in which steric constraints lead to facile cyclization. In the present instance, diene ring closure is characterized by a $\Delta H^{\ne}$ lower than any previously reported for a cyclobutene ring opening.

The diene in question, *trans*-1-bromo-*cis*-1,2,3,4-tetraphenylbutadiene (I),[3] was prepared in 90% yield by the stereoselective 1,4 elimination of HBr from 1,4-dibromo-1,2,3,4-tetraphenyl-*trans*-2-butene[4] at 0°. In CCl_4 solution at 25°, I undergoes a thermal, electrocyclic ring closure which yields both *cis*- and *trans*-3-bromo-1,2,3,4-tetraphenylcyclobutenes (II), the presence of the latter isomer implying a violation of the Woodward–Hoffmann rules.[5] This transformation is accompanied by a decrease in the olefinic proton signal of I and the emergence and growth of two new singlets, the process continuing until equilibrium is established at the values noted.



δ 6.52
I
(26%)

δ 5.22
cis-II
(49%)

δ 4.52
trans-II
(25%)

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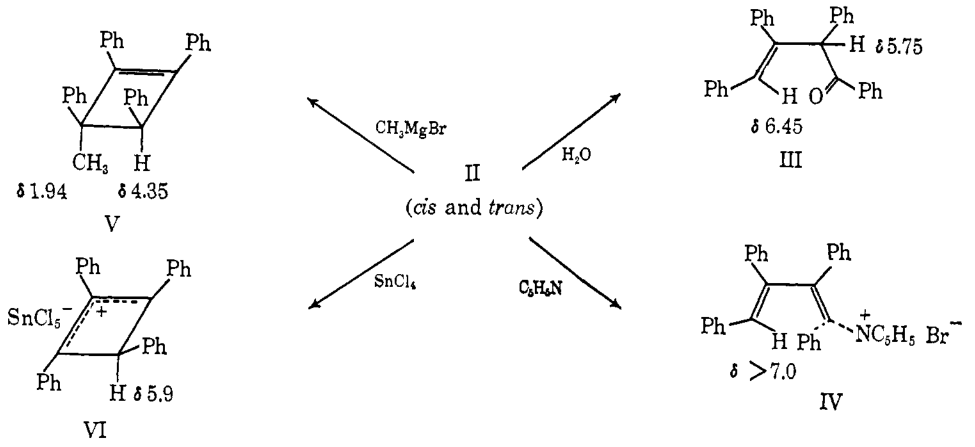
(1) The complete kinetics and thermodynamics for the cyclization of two perfluorodienes have been reported: E. W. Schlag and W. B. Peatman, *J. Am. Chem. Soc.*, **86**, 1676 (1964); J. P. Chesick, *ibid.*, **88**, 21 (1966).

(2) H. M. Frey, *Advan. Phys. Org. Chem.*, **4**, 183 (1966).

(3) All four possible stereoisomers of the 1-bromo-1,2,3,4-tetraphenylbutadienes have been prepared. Their geometries have been established by halogen–metal exchange with butyllithium followed by protonation (or deuteration) under nonisomerizing conditions (ether, 0°, 5 min). The formation of only the *trans*-1-*d*,*cis*-4-H diene from I uniquely establishes its geometry as shown.

(4) This thermally labile compound has been prepared, without specifying the position or geometry of the double bond, by A. Orechoff, *Ber.*, **47**, 89 (1914).

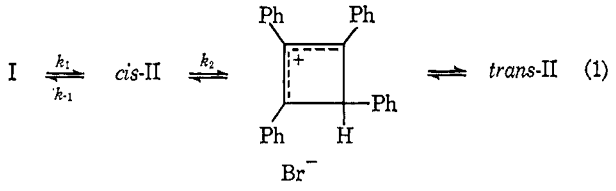
(5) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965).



Though too solvolytically unstable to separate, *cis*- and *trans*-II are readily distinguished from their valence tautomer I, not only by the nmr data,[6] but also by their reactivity toward nucleophiles. Thus II (*cis* and *trans*), but not I, reacts rapidly and stereoselectively with water and with pyridine to yield the ring-opened products III and IV, and with CH_3MgBr to give *cis*-3-methyl-1,2,3,4-tetraphenylcyclobutene (V), all in good yield.

This solvolytic activity of *cis*- and *trans*-II can be directly ascribed to their capacity to ionize to the tetraphenylcyclobutenium cation, a species stable enough to be isolated as its crystalline pentachlorostannate salt, VI.[8] Treatment of VI with bromide ion rapidly regenerates *cis*- and *trans*-II in the previously observed proportions, and these, when allowed to stand, reestablish the original mixture of I and II. These results clearly demonstrate the reversible nature of this valence isomerism and also offer a rationalization for the presence of *trans*-II, the disrotatory valence isomer of I.

Since rapid, reversible ionization of either *cis*- or *trans*-II must lead to their thermodynamic equilibration *via* their common intermediate ion IIa (eq 1), then only the conrotatory isomer, *cis*-II, need be in direct thermal equilibrium with I. This hypothesis has been experimentally verified by ascertaining the influence of solvent polarity on k_1, which is predicted to be solvent independent, as compared to k_2, a solvent-dependent step. Determination of the initial products formed from I in CCl_4 and in $CDCl_3$ (as the nonpolar and polar solvent, respectively) under otherwise identical conditions (30 min at 35°) showed that only *cis*-II is present in the former solvent whereas the latter produces the equilibrium distribution of both *cis*- and *trans*-II. Inasmuch as only k_2 is expected to increase in the more polar solvent, then these results support eq 1 and rule out the possibility of a thermal, disrotatory ring opening.



IIa

Thermodynamic data for I → II were obtained in CH_2Cl_2 solution by nmr techniques. At temperatures of 34–57°, K_{eq} (=[*cis*-II]/[I]) varied from 2.50 to 1.31, leading to $\Delta H° = -5.56 \pm 0.5$ kcal/mol and $\Delta S° = -16.3 \pm 1.5$ eu. The rate constants for the ring closure of I → II, obtained in either CD_2Cl_2 or in pyridine at five temperatures, were cleanly first order and varied from 0.86×10^{-4} sec^{-1} at 34.0° to 6.00×10^{-4} sec^{-1} at 55.0°.[9] The agreement among these data, despite the reversibility of the process in CD_2Cl_2 and its nonreversibility in pyridine, attests to both the reliability of the nmr kinetic analyses and the solvent independence of this valence tautomerism.

A least-square analysis of the Arrhenius plot yielded the activation data for the forward process (I → II): $\Delta H^{\ddagger} = 19.0 \pm 0.6$ kcal/mol, $\Delta S^{\ddagger} = -15.6 \pm 1.7$ eu, and $\Delta G^{\ddagger}_{25} = 23.6 \pm 0.5$ kcal/mol. Combining these data with the thermodyanamic results, we obtain for the reverse reaction (II → I): $\Delta H^{\ddagger} = 24.5 \pm 0.6$ kcal/mol, $\Delta S^{\ddagger} = 1.3 \pm 1.7$ eu, and $\Delta G^{\ddagger}_{25} = 24.1 \pm 0.5$ kcal/mol.

The large negative and small positive activation entropies for the forward and reverse processes, respectively, are those expected for a concerted reaction proceeding *via* a cyclic transition state.[10] The value of $\Delta H^{\ddagger}$ for ring opening (II → I) is predictably the same, within experimental error, as that for *cis*-1,2,3,4-tetraphenylcyclobutene → *cis,trans*-1,2,3,4-tetraphenylbutadiene,[7] in accord with the similar steric interactions in their respective transition states for conrotatory ring opening. Finally, we note that the remarkably low value of $\Delta H^{\ddagger}$ for the ring closure of I → II is the lowest value reported to date for such an electrocyclic process. It appears that the nonbonded interactions of the bulky diene substituents have facilitated this ring closure, and

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(6) The higher field resonance (δ 4.52) is assigned to *trans*-II by analogy with the corresponding hydrocarbons *cis*- and *trans*-tetraphenylcyclobutenes and related compounds (see footnote 10 of ref 7) and is a consequence of the shielding of the proton in the *trans* isomer by the vicinal phenyl (*cf.* D. Y. Curtin, *et al.*, *J. Am. Chem. Soc.*, **83**, 4838 (1962); **84**, 863 (1964).

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(8) Identical with the product obtained by hydride abstraction from *cis*-1,2,3,4-tetraphenylcyclobutene (unpublished results of A. E. Young) and very similar in its spectroscopic and chemical properties to 3-chloro-1,2,3,4-tetraphenylcyclobutenium pentachlorostannate (R. F. Bryan, *J. Am. Chem. Soc.*, **86**, 733 (1964)).

(9) The rate data in pyridine yield k_1 (see eq 1) directly, whereas in CD_2Cl_2 the data yield $k_1 + k_{-1}$. Under all conditions, $k_2 \gg k_1$.

(10) Except for the perfluorodienes,[1] whose thermochemistry is uniquely their own, no $\Delta S^{\ddagger}$ for diene ring closure is available for comparison. However, the $\Delta S^{\ddagger}$ for the Cope rearrangement, a comparable "no-mechanism" type reaction, has been determined to be in the range −11 to −14 eu (E. G. Foster, A. E. Cope, and F. Daniels, *J. Am. Chem. Soc.*, **69**, 1893 (1947)), in good agreement with the present results. The small positive $\Delta S^{\ddagger}$ for the ring opening of II agrees with the entropies reported for alkyl-substituted cyclobutenes (ref 2, p 18).

a detailed explanation of this phenomenon is one of the goals of this research.

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The Resistance of Radon to Oxidation in Aqueous Solution[1]

Sir:

Haseltine and Moser[2] have reported the oxidation of radon in aqueous solution. We have recently attempted to duplicate their results, and on the basis of more than 60 experiments we have become convinced that their conclusions are incorrect.

In their most convincing result, Haseltine and Moser found that when a solution 10^{-7} *M* in $^{226}RaBr_2$ and 0.1 *M* in $K_2S_2O_8$ was allowed to stand for 23 days, most of the ^{222}Rn formed could not be extracted into hexane and could not be volatilized by bubbling a gas through the solution.

We have repeated this experiment using $^{226}RaCl_2$ solutions, but otherwise duplicating the conditions of Haseltine and Moser. We found that less than 6% of the radon remained in the 23-day old persulfate solution after argon had been bubbled through it for 3 hr, or after it had been extracted with an equal volume of hexane. On the other hand, after the solution had stood for 38-39 days, 80% of the radon could not be volatilized by argon bubbling, and two-thirds of it did not extract into an equal volume of hexane. This radon could, however, be removed from solution by centrifuging in a clinical centrifuge. After the supernatant solution was withdrawn, the radon activity in the residue increased with time. This indicated that the residue contained radium, with which the radon had not yet reached equilibrium.

We have attempted to oxidize radon in the same way with the other reagents tried by Haseltine and Moser, and also with ozone and with sodium perxenate. In no case was a solution obtained from which the radon could not be removed either by bubbling in argon or by centrifuging; and whenever the radon was removed by centrifugation, it was accompanied by radium in excess of the equilibrium amount. It is noteworthy that even from some $RaCl_2$ solutions containing no other reagents, significant portions of the radon could not be volatilized, but could be removed by centrifugation.

We conclude from these studies that the phenomena observed by Haseltine and Moser do not result from oxidation of radon. They seem instead to be brought about by the precipitation of some or all of the radium by reagents or impurities in the solutions. (The sulfate that gradually builds up in persulfate solutions is one likely cause of such precipitation.) The radon that forms within the precipitate is mechanically trapped and will neither extract into hexane nor volatilize in a gas stream.

We have found no evidence for the existence of radon compounds in aqueous solution, and we hope that others will undertake to verify our conclusions.

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Received April 5, 1968

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] M. W. Haseltine and H. C. Moser, *J. Am. Chem. Soc.*, **89**, 2497 (1967).

Rapid Time Scale for Hydrogen-Atom Abstraction by Recoil Tritium Atoms. Nonequilibrium Allyl Radicals from Propylene

Sir:

We have measured the HT yield from the recoil tritium abstraction reaction with the CH_3 group of propylene, as in (1), and have compared it to the well-established correlation of hydrocarbon bond dissociation energies with such hydrogen abstraction yields.[1-6] The discrepancy between this apparent value for the allyl-H bond dissociation energy (93 kcal/mole) and the measured values by other well-established techniques (87.8 kcal/mole)[7] leads us to the conclusion that the equilibrium bond dissociation energy is not appropriate for such a comparison in this particular situation. We believe that the lower yield characteristic of a stronger bond reflects the fact that the transfer of the hydrogen atom from C_3H_5-H bonding to the T-H bonding is completed while the bond lengths (and perhaps the angles) of the C_3H_5 residue still differ substantially from those of an allyl radical in its equilibrium configuration.

$$T^* + CH_3{-}CH{=}CH_2 \longrightarrow HT + CH_2{-}CH{=}CH_2 \qquad (1)$$

The largest geometrical differences between propylene and allyl involve the C-C distances and the C-C-C bond angle. Failure to attain the equilibrium allylic configuration during H-atom transfer is thus essentially equivalent to very high vibrational excitation of the C-C stretching and C-C-C bending vibrations of the allyl radical, and represents relaxation energy not yet totally available for "loosening" of the C-H bond at the time of atom transfer. Since the C_1-C_2 and C_2-C_3 bond distances are 1.336 and 1.501 Å, respectively, in propylene,[8] and about 1.40-1.44 Å in the equilibrium allyl radical,[9] the chief geometrical deformation in terms of energy involves deviations in C-C bond distances as much as 0.1 Å.

We conclude that the time scale for the hydrogen-abstraction reaction is definitely shorter than that required for complete adjustment of geometric relationships to those of the thermally equilibrated allyl radical. By assuming that the time required for 0.1-Å adjust-

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(3) J. W. Root, W. Breckenridge, and F. S. Rowland, *J. Chem. Phys.*, **43**, 3694 (1965).

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(6) All HT yields are expressed as yields per C-H bond under equivalent conditions of exposure to energetic tritium atoms.

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(8) D. R. Lide, Jr., and D. Christensen, *J. Chem. Phys.*, **35**, 1374 (1961).

(9) C. L. Currie and D. A. Ramsay, *ibid.*, **45**, 488 (1966).