standable from steric considerations; the greatly increased size of the 1,1,2,2-tetrachloroethane molecule should result in weaker coordination of the solvent molecule to a $[PtCl_5]^-$ group as a sixth octahedral-like ligand than in the case of methylene chloride and thus should facilitate polymerization. $[PtCl_4]_4$ will not react with $(C_6H_5)_3CCl$ in chloroform, 1,1,1-trichloroethane, *tert*-butyl chloride, or trichloroethylene. The bulkiness of these polar solvents presumably may prevent them from occupying the sixth coordination site to form a $[PtCl_5 \cdot \text{solvent}]^-$ anion which can then polymerize.

Although reaction also does not occur in nonpolar cyclohexane, which has often been used to prepare triphenylcarbenium salts,[26] a reaction does occur in benzene to yield the red product **5**. A slurry of finely powdered $[PtCl_4]_4$ in benzene is mixed with $(C_6H_5)_3CCl$ in excess of a 1:1 mole ratio at ~50° for 24 hr or more. The resultant orange-red solid is filtered under N_2 and washed several times with dry hexane. The product can then be dissolved in CH_2Cl_2 and filtered to give a red solution. More than one product may be present, because much of the solid readily dissolves in CH_2Cl_2 leaving a smaller amount of less soluble yellow powder which exhibits a different far-infrared spectrum than **5**. Crystallization from CH_2Cl_2 gave crystals of **5** suitable for X-ray diffraction studies when hexane was slowly diffused into the concentrated CH_2Cl_2 solution. These crystals are hygroscopic but can be stored indefinitely in a desiccator. Due to the difficulty in obtaining crystals, the amount of pure product **5** isolated has not exceeded a 5% yield. An X-ray diffraction study of **5** revealed it to be a triphenylcarbenium salt of the highly unusual $[Pt_4(C_6H_4)_2Cl_{14}]^{2-}$ anion (Figure 1). This tetranuclear Pt(IV) anion of idealized D_{2h} geometry consists of two $[Pt_2(C_6H_4)Cl_6]$ moieties linked to each other by two bridging chlorine atoms. Each $[Pt_2(C_6H_4)Cl_6]$ moiety is comprised of two $PtCl_2$ fragments joined by two di-μ-chloro linkages and one bridging *o*-phenylene ring. Each Pt(IV) of the $[Pt_2(C_6H_4)Cl_6]$ moiety completes its octahedral coordination sphere by dimerization through the remaining two bridging chlorine atoms to give the $[Pt_4(C_6H_4)_2Cl_{14}]^{2-}$ anion. Preparation of other examples of a benzene ring σ bonded to more than one transition metal were reported recently.[27,28] The $[Pt_4(C_6H_4)_2Cl_{14}]^{2-}$ anion provides the initial case of an X-ray determination of such a structure as well as the first Pt(IV)–phenyl compound.[29] The loss of two protons from each benzene to give an *o*-phenylene group was detected qualitatively by a bubbling of the N_2-flushed gas from the reaction flask through an $AgNO_3$ solution which precipitated the evolved HCl gas as AgCl. Clearly, a complex mechanism is involved in the formation of this product.

Detailed descriptions of the structures of these anions and the triphenylcarbenium cation as well as their chemical and physical characterization and reactions with small molecules will be reported upon completion of closely related work now in progress.

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[26] K. M. Harmon, L. Hesse, L. P. Klemann, C. W. Kocher, S. V. McKinley, and A. E. Young, *Inorg. Chem.*, 8, 1054 (1969).

[27] J. E. Dobson, R. G. Miller, and J. P. Wiggen, *J. Amer. Chem. Soc.*, **93**, 554 (1971).

[28] S. Trofimenko, *ibid.*, 93, 1808 (1971).

[29] For a review of organoplatinum(IV) compounds, see J. S. Thayer, *Organometal. Chem. Rev., Sect. A*, 5, 53 (1970).

An Unusually Large Conformational Kinetic Isotope Effect in [2.2]Metaparacyclophane

Sir:

Although zero-point vibrational energy differences are generally accepted as the origin of secondary deuterium isotope effects, a number of rationales for the necessary changes in vibrational force constants have been suggested. The relative significance of hyperconjugative, inductive, and steric factors in a given system often is unclear.[1] The steric factor, proposed by Bartell[2] and ascribed great generality by Brown, *et al.*,[3] has been isolated most strikingly in studies of conformational kinetic isotope effects.[4,5] We felt that 8-deuterio[2.2]metaparacyclophane (**1**-*d*) was an attractive subject for such a study. The free energy of activation for ring flipping in **1**-*H* had been measured as about 20 kcal/mol[6] and seemed likely to involve primarily nonbonding interaction between the 8 hydrogen and the π cloud of the para-bridged ring. The magnitude of this barrier and the rigidity and symmetry of **1** suggested that compression of the 8 carbon–hydrogen bond in the transition state probably exceeds that involved (per isotopic bond) in previously studied examples and should result in a larger isotope effect.

Oxidation of 9-bromo-2,11-dithia[3.3] metaparacyclophane[7] with metachloroperbenzoic acid gave nearly

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[1] For reviews see (a) E. R. Thorton, *Annu. Rev. Phys. Chem.*, **17**, 349 (1966); (b) E. A. Halevi, *Progr. Phys. Org. Chem.*, **1**, 109 (1963).

[2] (a) L. S. Bartell, *Tetrahedron Lett.*, 13 (1960); (b) *J. Amer. Chem. Soc.*, **83**, 3567 (1961); (c) *Iowa State J. Sci.*, **36**, 137 (1961).

[3] (a) H. C. Brown and G. J. McDonald, *J. Amer. Chem. Soc.*, 88, 2514 (1966); (b) H. C. Brown, E. Azzaro, J. G. Koelling, and G. J. McDonald, *ibid.*, 88, 2520 (1966).

[4] (a) K. Mislow, R. Graeve, A. J. Gordon, and G. H. Wahl, Jr., *ibid.*, **85**, 1199 (1963); **86**, 1733 (1964); (b) L. Melander and R. E. Carter, *Acta Chem. Scand.*, 18, 1138 (1964); (c) C. Heitner and K. T. Leffek, *Can. J. Chem.*, **44**, 2567 (1966); (d) R. E. Carter and L. Dahlgren, *Acta Chem. Scand.*, 23, 504 (1969); **24**, 633 (1970).

[5] For other examples of steric isotope effects see: (a) ref 3, (b) G. H. Cooper and J. McKenna, *Chem. Commun.*, 734 (1966); (c) M. M. Green, M. Axelrod, and K. Mislow, *J. Amer. Chem. Soc.*, 88, 861 (1966); (d) J. Almy and D. J. Cram, *ibid.*, 91, 4459 (1969); (e) G. J. Karabatsos, G. C. Sonnichsen, C. G. Papaioannou, S. E. Scheppele, and R. L. Shone, *ibid.*, **89**, 463 (1967); (f) D. N. Jones, R. Grayshan, and K. J. Wise, *J. Chem. Soc. C*, 2027 (1970).

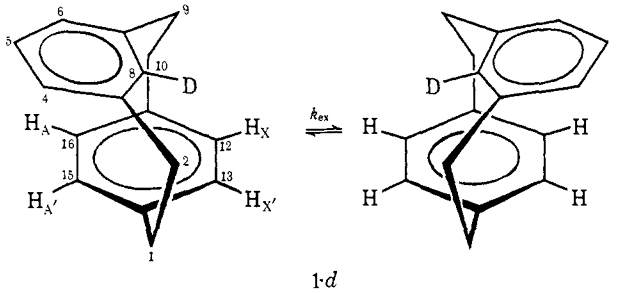
[6] (a) D. T. Hefelfinger and D. J. Cram, *J. Amer. Chem. Soc.*, **92**, 1073 (1970); **93**, 4767 (1971); (b) F. Vögtle, *Chem. Ber.*, **102**, 3077 (1969); (c) S. Akabori, S. Hayashi, M. Nawa, and K. Shiomi, *Tetrahedron Lett.*, 3727 (1969).

[7] F. Vögtle, *ibid.*, 3193 (1969).

Table I. Longitudinal Relaxation Times and Ring Flipping Rates[a]

Compd	T, °C	$(1/T_1^{X}) \times 10^2$ [b] sec⁻¹	$(1/T_1^{A}) \times 10^2$ [b] sec⁻¹	$M_0^{A}/M_{z\infty}^{A}$	$k_{ex} \times 10^2$ [f] sec⁻¹
	19.9 ± 0.3	7.61 ± 0.21	8.22 ± 0.26	1.172 ± 0.005[d]	1.41 ± 0.06
[2.2]Metaparacyclophane (**1**-*H*)	35.3 ± 0.3	7.06 ± 0.11	7.16 ± 0.14	1.949 ± 0.031[c]	6.79 ± 0.16
	47.9 ± 0.3	6.01 ± 0.26	6.19 ± 0.23	3.31 ± 0.07[d]	20.49 ± 0.88
8-Deuterio[2.2]metaparacyclophane (**1**-*d*)	35.3 ± 0.3	6.71 ± 0.14	7.01 ± 0.13	2.163 ± 0.023[c,e]	8.15 ± 0.17[e]

[a] For degassed 10% solutions (by wt) in $CDCl_3$. [b] Error given is standard deviation of the slope based on ten or more points. [c] Standard deviation of the average of seven determinations acquired over 4 different days. Each determination was based on averages of ten or more integrals of both M_0^{A} and $M_{z\infty}^{A}$. [d] Standard deviation of the average of three determinations. [e] Corrected for isotopic purity. [f] Standard deviation calculated according to normal propagation of independent errors.



1-*d*

quantitatively the corresponding bissulfone, which on pyrolysis in a flow system at 500° gave 8-bromo[2.2]-metaparacyclophane in 60–80% yield.[8] Treatment of this bromide with *n*-butyllithium in ether[9] followed by quenching with deuterium oxide gave [2.2]metaparacyclophane containing 95.7 ± 0.6% of one deuterium by mass spectral analysis; the nmr spectrum showed 94.9 ± 2.1% deuteration at the 8 position.

In a 100-MHz nmr spectrum the para-bridged ring protons of **1** give rise to a pair of narrow multiplets which are separated by 1.3 ppm and do not overlap the signals due to the other aromatic protons. Coalescence of this AA′XX′ pattern appeared to occur in **1**-*d* at a temperature 2–5° lower than that required for **1**-*H*,[10] but the distinction was subtle and drove us to a more precise method. For this purpose we chose the double irradiation technique of Forsén and Hoffman.[11] Upon sudden saturation of site X, the *z* magnetization at site A, M_z^{A}, decreases due toc hemical exchange according to eq 1, where M_0^{A} is the initial magnetization,

$$dM_z^{A}/dt = M_0^{A}/T_1^{A} - M_z^{A}(k_{ex} + 1/T_1^{A}) \qquad (1)$$

T_1^{A} the longitudinal relaxation time of site A, and k_{ex} the rate constant for chemical exchange; in the limit of infinite time M_z^{A} is given by $M_0^{A}/(T_1^{A}k_{ex} + 1)$.[11] Rather than extract both T_1^{A} and k_{ex} from the decay curve, we found it convenient to measure T_1^{A} and $M_0^{A}/M_{z\infty}^{A}$ independently, k_{ex} being given by eq 2.

$$k_{ex} = (1/T_1^{A})(M_0^{A}/M_{z\infty}^{A} - 1) \qquad (2)$$

For T_1 measurements we employed a program written for a Varian 620i dedicated computer and Varian XL-100 nmr spectrometer.[12,13] The technique involves application of a 180° pulse to invert the *z* magnetization at all sites followed after a varied interval by an analyzing 90° pulse. Fourier transformation of the free induction decay gives a spectrum which reflects the instantaneous values of M_z at each site. In general, for a system involving chemical exchange, recovery from the inverted to the equilibrium value of the *z* magnetization at a given site would not be expected to follow simple first-order kinetics. However, in both **1**-*H* and **1**-*d* the close similarity of the T_1's of sites A and X (Table I) makes recovery at each site effectively independent of chemical exchange, as evidenced by good first-order kinetic behavior over two half-lives.

The calculated values for the chemical exchange constants are presented in Table I. In accord with our expectations, the isotope effect is inverse and its magnitude, $k_D/k_H = 1.20 \pm 0.04$ ($\Delta\Delta F^{\ddagger} = 112$ cal/mol), is twice as large per deuterium as any other conformational kinetic isotope effect of which we are aware. Rate constants determined at three temperatures give a good Arrhenius plot for **1**-*H*, from which are calculated $\Delta H^{\ddagger} = 17.0 \pm 0.5$ kcal/mol and $\Delta S^{\ddagger} = -8.8 \pm 2.4$ eu; nevertheless the uncertainties[14] in these values make an effort to dissect the isotope effect into enthalpic and entropic components unwarranted by our method.

As has been emphasized, steric isotope effects have their origin in zero-point energy differences.[1a,4d] Accordingly, the above effect demands a net increase of 300 cm⁻¹ in the vibrational frequencies of the isotopic bond on going to the transition state.[15] The effect is steric in that nonbonding repulsions in the structurally tight transition state apparently are responsible for this increase in vibrational frequencies. Using the method and potential function of Bartell[2b] one can calculate that in the transition state the 8 hydrogen would have to come within 2.7 Å of the carbons in the para-bridged ring to produce the observed effect; that this is reasonable is seen from molecular models, which show that in the absence of any distortion the approach distance would be a mere 2 Å. The relative contributions of various factors to the nonbonding repulsion in this system are unknown, but consideration of the closeness and symmetry of the interaction suggests that

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(8) Satisfactory spectroscopic and analytical data have been obtained for all new compounds.

(9) The organolithium derivative and other derivatives with substituents at the 8 position in [2.2]metaparacyclophane are being characterized and will be the subject of a future publication.

(10) T_c for 1-*H* in perchlorobutadiene was about 157° ($\Delta\nu$ = 131 Hz, 100-MHz spectrometer). All temperatures in our work have been calibrated with either methanol or ethylene glycol according to the equations of A. L. Van Geet, *Anal. Chem.*, **40**, 2227 (1968).

(11) S. Forsén and R. A. Hoffman, *Acta Chem. Scand.*, **17**, 1787 (1963); *J. Chem. Phys.*, **39**, 2892 (1963); **40**, 1189 (1964).

(12) We wish to thank Drs. R. Freeman and H. W. D. Hill of Varian for a copy of their program.

(13) R. Freeman and H. W. D. Hill, *J. Chem. Phys.*, **51**, 3140 (1969); **53**, 4103 (1970).

(14) Calculated by the method of R. C. Petersen, J. H. Markgraf, and S. D. Ross, *J. Amer. Chem. Soc.*, **83**, 3819 (1961).

(15) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey, and S. Suzuki, *ibid.*, **80**, 2326 (1958).

strong, albeit destabilizing, orbital mixing involving the isotopic bond and the π cloud may be important.

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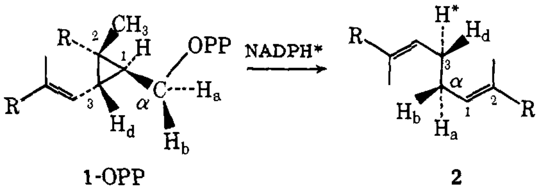
Model Studies of Terpene Biosynthesis. Stereoselective Ionization of *N*-Methyl-4-[(αS,1R,3R)-chrysanthemyloxy]pyridinium-d_1 Iodide[1]

Sir:

The stereospecific head-to-head condensation of two molecules of farnesyl pyrophosphate during the biosynthesis of squalene (**2**) is known to proceed through a

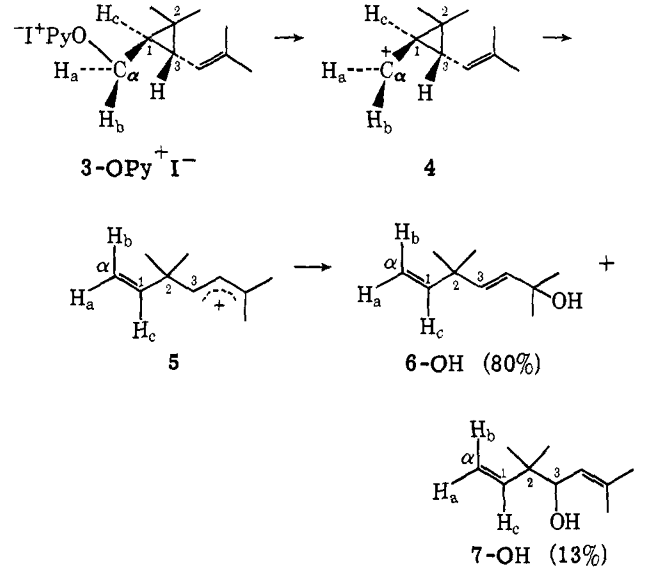


1-OPP **2**

C_{30} cyclopropylcarbinyl intermediate, presqualene pyrophosphate (**1-OPP**, R = homogeranyl).[2,3] We have proposed a mechanism in which the stereochemistry of all but the last step leading from **1-OPP** to **2** can be attributed to the solvolytic properties of cyclopropylcarbinyl cations with minimal special orientation by an enzyme.[2a] Recently, Trost and coworkers demonstrated that the skeletal rearrangements required for biosynthesis of squalene from presqualene pyrophosphate were possible under normal solvolysis conditions in a C_{10} model system.[4] If the configuration of C_α is to be inverted during a solvolytic rearrangement in a manner analogous to that found for squalene, C_α must assume a specific orientation with respect to the cyclopropane ring during heterolysis of the C_α–O bond. Based on work with alkyl-substituted cyclopropylcarbinyl derivatives,[5] we suggested that a conformation in which the leaving group was trans to the C_1–C_3 cyclopropane bond would facilitate ionization by utilizing the vinyl substituent at C_3 for delocalization of charge. Subsequent inversion of C_α is consistent with stereochemical studies of cyclopropylcarbinyl rearrangements.[6] However, in a recent paper Kispert and coworkers[7] reported, on the basis of semiempirical calculations (INDO approximation), that interaction between positively charged C_α and the vinyl substituent at C_3 through the cyclopropane ring is expected to be very small or nonexistent.

N-Methyl-4-[chrysanthemyloxy]pyridinium iodide (**3-OPy$^+$I$^-$**) should provide a suitable C_{10} model system with which to determine the preferred stereochemistry at C_α during ionization of presqualene pyrophosphate.[8] Hydrolysis of **3-OPy$^+$I$^-$** is known to give a mixture of alcohols with two major components, yomogi alcohol (**6-OH**), 80%, and artemisia alcohol (**7-OH**), 13%, in which only the C_1–C_3 cyclopropane bond has been ruptured (Scheme I).[9] Although two cationic intermediates are thought to precede formation of alcohols **6-OH** and **7-OH**,[10] the stereochemistry of C_α during ionization of **3-OPy$^+$I$^-$** should determine the relative positions of H_a, H_b, and H_c in the allylic alcohols. Rotation about the C_α–C_1 bond cannot occur during the solvolytic lifetime of **4**,[5,11] and the rearrangement **4** → **5** does not alter the relative positions of protons at C_α and C_1. Therefore, the preferred orientation for C–O bond heterolysis can be deduced by replacing H_a with deuterium and examining the proton distribution at C_α in hydrolysis products **6-OH** and **7-OH**.

Scheme I. Hydrolysis of *N*-Methyl-4-[chrysanthemyloxy]pyridinium Iodide



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[1] We wish to acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Research Corporation, and the University of Utah Research Fund for support of this work.

[2] (a) H. C. Rilling, C. D. Poulter, W. W. Epstein, and B. Larsen, *J. Amer. Chem. Soc.*, **93**, 1783 (1971); (b) L. J. Altman, R. C. Kowerski, and H. C. Rilling, *ibid.*, **93**, 1782 (1971); (c) R. M. Coates and W. H. Robinson, *ibid.*, **93**, 1785 (1971); (d) W. W. Epstein and H. C. Rilling, *J. Biol. Chem.*, **245**, 4597 (1970); (e) J. Edmond G. Popják, S.-M. Wong, and V. P. Williams, *ibid.*, **246**, 6254 (1971); (f) R. V. M. Campbell, L. Crombie, and G. Pattenden, *Chem. Commun.*, 218 (1971).

[3] A structurally analogous C_{40} pyrophosphate is an intermediate in phytoene biosynthesis: L. J. Altman, L. Ash, R. C. Kowerski, W. W. Epstein, B. R. Larsen, H. C. Rilling, F. Muscio, and D. E. Gregonis, *J. Amer. Chem. Soc.*, **94**, 3257 (1972).

[4] B. M. Trost, P. Conway, and J. Stanton, *Chem. Commun.*, 1639 (1971).

[5] (a) C. D. Poulter, E. C. Friedrich, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 4274 (1970); (b) C. D. Poulter and S. Winstein, *ibid.*, **92**, 4282 (1970).

[6] (a) K. B. Wiberg and G. Szeimies, *ibid.*, **92**, 571 (1970); (b) J. E. Baldwin and W. D. Fogelsong, *ibid.*, **90**, 4303 (1968); (c) Z. Majerski and P. von R. Schleyer, *ibid.*, **93**, 665 (1971); (d) G. A. Olah, C. L. Jeuell, D. P. Kelly, and R. D. Porter, *ibid.*, **94**, 146 (1972).

[7] L. D. Kispert, C. Engelman, C. Dyas, and C. U. Pittman, Jr., *ibid.*, **93**, 6948 (1971).

[8] Replacing the homogeranyl substituents by methyl groups should not alter the reactivity of the cyclopropylcarbinyl core of **1-OPP**.

[9] C. D. Poulter, S. G. Moesinger, and W. W. Epstein, *Tetrahedron Lett.*, 67 (1972).

[10] C. D. Poulter and S. G. Moesinger, Abstracts, 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 1971, ORGN 43.

[11] (a) D. S. Kabakoff and E. Namanworth, *J. Amer. Chem. Soc.*, **92**, 3234 (1970); (b) B. R. Ree and J. C. Martin, *ibid.*, **92**, 1660 (1970); (c) V. Buss, R. Gleiter, and P. von R. Schleyer, *ibid.*, **93**, 3927 (1971).