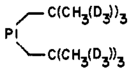
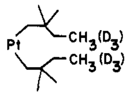
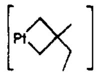
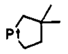
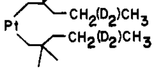
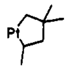
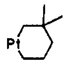
Table I. Conversion of Dialkylbis(triethylphosphine)platinum(II) Complexes to Bis(triethylphosphine)-Platinacycloalkanes[a]

PtR_2	Platinacycloalkane, *% Yield*	E_a[b]	log A	$\Delta H^{\ddagger}$[b]	$\Delta S^{\ddagger}$[b]	k_H/k_D[c]
 1	 2, *100*[d]	49±4[d]	20±2[d]	48±4[d]	30±9[d]	3.0[d]
 3	 4, *0.5*[e]  5, *99.5*[e]	42±2	20±1	41±2	30±5	3.2±0.1
 6	 7, *23*  8, *68*  9, *9*	43±2	20±2	42±2	30±9	2.8±0.2[f]

[a] Product yields, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ for cyclometallations of 1, 3, and 6 are reported for reactions at 157, 126, and 146 °C, respectively. Yields are based on $^{31}P\{^1H\}$NMR spectroscopy and refer to the undeuterated compounds. Compounds 2 and 5 were isolated in 71% and 78% yields, respectively.[11] [b] E_a and $\Delta H^{\ddagger}$ are expressed in kcal mol^{-1}, $\Delta S^{\ddagger}$ in eu. [c] Isotope effects are those observed for the deuterium substitution indicated in PtR_2. [d] From ref 9. [e] Estimated from the yield of the deuterated species: see the text. [f] See ref 13.

in Table I is loss of alkane by reductive elimination from an intermediate which already contains a metallacylic ring (**12** → **13**, Scheme I).[14] The *relative* yields of metallacycles of different sizes but comparable structures formed during decomposition of a common starting material should therefore reflect in major part differences in the energies of the metallacyclic rings present in the transition states. The compounds in Table I afforded two comparable pairs: **4** and **5** and **7** and **9**. (Both require formation of metallacylic rings by oxidative addition of methyl C–H bonds to platinum.) Decomposition of undeuterated **3** (126 °C) yields **5** as the only observed product, but decomposition of **3**-d_6 yields **5**-d_3 and **4**-d_2 in relative yields of 50:1. We estimate the relative rates of formation of undeuterated **5** and **4** by dividing the relative yield of **4**-d_2 by the observed kinetic isotope effect (3.2, Table I): this division yields $k_{3\to5}/k_{3\to4} = 160$. After accounting for the numbers of equivalent C–H bonds, the corresponding statistically corrected ratio of rate constants is $k_{3\to5}/k_{3\to4} = 320$, and correponds to $\Delta G^{\ddagger}_{3\to4} - \Delta G^{\ddagger}_{3\to5} \simeq 4.6$ kcal mol^{-1}. Similiar comparison of statistically corrected rate constants based on the yields of products from **6** indicates that $\Delta G^{\ddagger}_{6\to7} - \Delta G^{\ddagger}_{6\to9} = -0.24$ kcal mol^{-1} and $\Delta G^{\ddagger}_{6\to7} - \Delta G^{\ddagger}_{6\to8} = 1.8$ kcal mol^{-1}.

These values of $\Delta\Delta G^{\ddagger}$ obviously do not correspond exactly to the differences in strain energies between four- and five-, and four- and six-membered platinacyclic rings. Contributions to $\Delta\Delta H^{\ddagger}$ could arise from differences in steric or electronic interactions in transition states, having nothing to do with ring strain, or differences in the extent of bond breaking or bond forming in these transition states; differences in $\Delta\Delta S^{\ddagger}$ are significant in many reactions which form rings from linear precursors.[15] Although we have no way of estimating these effects, we believe that the differences in structure characterizing the two pairs of metallacycles **4** and **5** and **7** and **9** are sufficiently small that most of the possible contributions to $\Delta\Delta G^{\ddagger}$ unrelated to metallacyclic ring strain should be small.

Although this work does not provide accurate numerical estimates of ring strain in this series of platinacyclic rings, it strongly suggests that the strain in a platinacyclobutane is much smaller than that in cyclobutane itself. This suggestion is significant in rationalizing why metallacyclobutanes seem to be more important as intermediates in organometallic reactions than cyclobutanes are in organic reactions and explaining why isomerization of five-membered to four-membered metallacycles[4] appears to be more facile than the corresponding reactions in all-carbon systems.[16]

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(14) The assignment of the rate-limiting step to reductive elimination (**11** → **12**) rather than oxidative addition (**10** → **11**) is based on the large value of log *A*. For comparison, log *A* = 14 for an analogous reaction involving dissociation of a phosphine [$(Et_3P)_2PtEt_2 \to Et_3P + Et_3PPtEt_2$: McCarthy, T. J.; Nuzzo, R. N.; Whitesides, G. M. *J. Am. Chem. Soc.*, in press].

(15) DeTar, D. F.; Luthra, N. P. *J. Am. Chem. Soc.* **1980**, *102*, 4505-12 and references cited therein.

(16) Redmore, D.; Gutsche, C. D. *Adv. Alicyclic Chem.* **1971**, *3*, 1-138.

Conformational Control of Reactivity and Regioselectivity in Singlet Oxygen Ene Reactions: Relationship to the Rotational Barriers of Acyclic Alkylethylenes

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A puzzling aspect of the singlet oxygen ene reaction,[1] shown below, is the "cis effect" in acyclic trisubstituted alkenes: allylic hydrogens on the disubstituted side of the alkene linkage are abstracted more readily than those on the monosubstituted side.[2-5] We wish to point out that the "cis effect" for singlet oxygen ene reactions of acyclic alkenes, as well as subtle regiochemical and

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* To whom correspondence should be addressed at the University of Pittsburgh.

† On leave from Rhode Island College, 1979-1980.

§ On leave from Osaka University, 1980.

(1) Reviews: (a) Frimer, A. A. *Chem. Rev.* **1979**, *79*, 359. (b) Gollnick, K.; Kuhn, H. J. In "Singlet Oxygen", Wasserman, H. H.; Murray, R. W., Eds.; Academic Press: New York, 1979; Chapter 8.

(2) Schulte-Elte, K. H.; Muller, B. L.; Rautenstrauch, V. *Helv. Chim. Acta* **1978**, *61*, 2777. Schulte-Elte, K. H.; Muller, B. L.; Pamingle, H. *Ibid.* **1979**, *62*, 816. Schulte-Elte, K. H.; Muller, B. L.; Ohloff, G. *Nouv. J. Chem.* **1978**, *2*, 427.

(3) Orfanopoulos, M.; Grdina, M. B.; Stephenson, L. M. *J. Am. Chem. Soc.* **1979**, *101*, 275.

(4) Schulte-Elte, K. H.; Rautenstrauch, V. *J. Am. Chem. Soc.* **1980**, *102*, 1738.

(5) Nickon, A.; Chuang, V. T.; Daniels, P. J. L.; Denny, R. W.; DiGiorgio, J. B.; Tsunetsugu, J.; Vilhuber, H. G.; Werstiuk, E. *J. Am. Chem. Soc.* **1972**, *94*, 5517.

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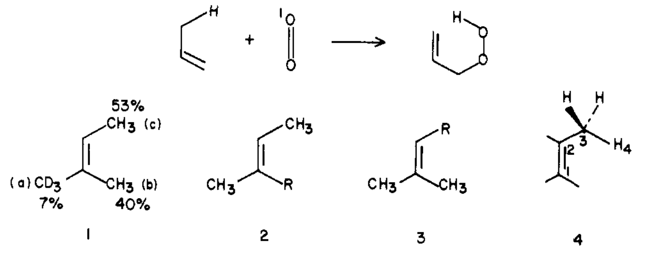
Scheme I



reactivity effects, can result from the remarkably large changes in alkyl group conformational barriers caused by substituents, an explanation closely related to that recently offered for the cis effect in cycloalkenes by Schulte-Elte and Rautenstrauch.[4]

Scheme I gives a specific example of the cis effect; the numbers are percentages of hydrogen abstraction at various positions.[3] More generally, the hydrogens on the methyl groups on the disubstituted sides of **2** and **3** are more reactive in the singlet oxygen ene reaction than the methyls on the monosubstituted side, whether R is alkyl, alkoxy, cyclopropyl, or aryl. This stereoselectivity and the low regioselectivity of these reactions even when R is a potent radical or cation stabilizer are convincing evidence against diradical[6] or zwitterionic[7] intermediates which have been proposed for these reactions.

Schulte-Elte and Rautenstrauch proposed that hydrogen abstraction occurs on the side of the cycloalkene double bond which has two allylic CH bonds more or less perpendicular to the alkene plane.[4] Stephenson postulated that secondary orbital interactions between the oxygen LUMO and the allylic hydrogen contribution to the HOMO stabilize the transition state. When two of these interactions occur on the cis side of a trisubstituted alkene,[8a] the transition state is said to accrue additional stabilization. Bartlett and Frimer identify this attractive interaction as hydrogen bonding.[8b]

We suggest instead that these effects can be rationalized by the simple postulate that in the concerted ene reaction transition state,[8c,d] the bond to the allylic hydrogen which is being abstracted must be nearly perpendicular to the alkene plane, as proposed by Gollnick and others.[1] For propene and other methylated ethylenes, the eclipsed conformation, **4** (dihedral <1234 = 0°), is an energy minimum and the staggered (<1234 = 180°) is an energy maximum. The perpendicular conformation[10] (<1234 = 90°) is intermediate in energy. We postulate that the differences in reactivities of acyclic alkenes are related to the differences in energy required to achieve the perpendicular conformation. Since the activation energies for alkylethylene–singlet oxygen ene reactions in the gas phase are very low (0–5 kcal/mol),[1,9] apparently trivial differences in rotational barriers are of the correct order of magnitude to explain reactivity differences.

The left column of Figure 1 shows the experimental rotational barriers for methyl groups in propene and the butenes.[11] While a trans methyl has little influence on the rotational barrier of a methyl group, a geminal methyl raises the barrier and a cis methyl reduces the barrier to less than one-half the barrier in propene.[11,12]

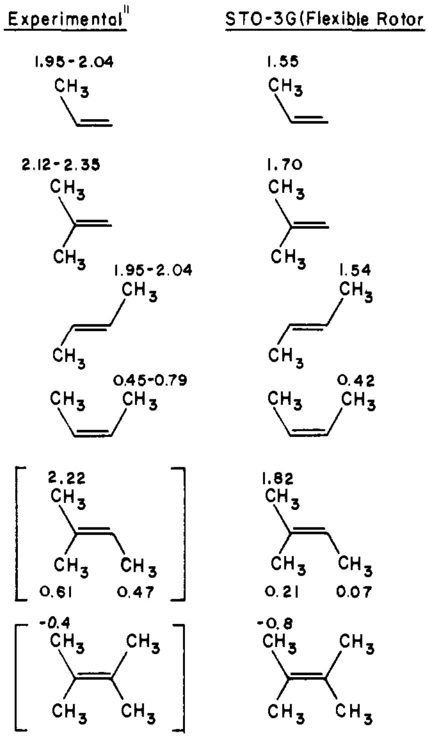


Figure 1. Experimental and calculated rotational barriers. Calculated barriers for the top four molecules are from Radom and Pople.[13] The values in brackets are estimated by assuming that STO-3G rotational barriers are 0.4 kcal/mol too low. The 2,3-dimethyl-2-butene value is for conversion of the all eclipsed to the monoperpendicular conformation.

Table I. Relative Energies (STO-3G) of Various Conformations of 2-Methyl-2-butene, 2,3-Dimethyl-2-butene, and Methoxypropenes[a]

alkene	energy, kcal/mol eclipsed	perpendicular	staggered
2-methyl-2-butene			
(a)	≡0[c]	0.92	1.82
(b)	≡0	0.26	0.21
(c)	≡0	0.08	0.07
2,3-dimethyl-2-butene			
all methyls rotated	1.11	≡0[d]	
one methyl group (other three eclipsed)	1.11	0.85	0.35
trans-1-methoxypropene with anti (syn) methoxy	≡0[e]	0.82 (0.79)	1.64 (1.58)
cis-1-methoxypropene with anti methoxy	≡0[f]	0.56	1.13
2-methoxypropene with anti (syn) methoxy	≡0[g]	1.56 (1.81)	2.94 (3.32)

[a] All bond lengths and angles were standard except for CCC angles, which were optimized for each conformation. For the *anti*-methoxypropenes, a transoid C=COC conformation was assumed with a COC angle fixed at 117° and a staggered ether methyl. CC=C and OC=C angles were optimized. [b] For the syn species, a cisoid C=COC conformation was assumed with ∠COC = 117° and a staggered ether methyl. The heavy atom angles were fixed at the values optimized for the anti species. [c] $E = -192.82525$ au. Optimization of all in-plane angles and heavy atom bond lengths lowered this value by 1.4 kcal/mol, to -192.82754 au. [d] $E = -231.40326$ au. [e] $E = -228.07568$ au. [f] $E = -228.07584$ au. [g] $E = -228.07365$ au.

Ab initio STO-3G calculations by Pople and co-workers using the flexible rotor approximation reproduce these trends quite

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(6) Harding, L. B.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1977**, *99*, 4520; **1980**, *102*, 439; *Tetrahedron Lett.* **1978**, 747.

(7) Jefford, C. W. *Tetrahedron Lett.* **1979**, 985. Although we discount the generality of zwitterionic intermediates, such species are formed with very electron-rich alkenes and singlet oxygen in polar solvents.

(8) (a) Stephenson, L. M. *Tetrahedron Lett.* **1980**, 1005. (b) Bartlett, P. D.; Frimer, A. A. *Heterocycles* **1978**, 11, 419. (c) The bridging interaction of one terminus of $^1O_2$ with the alkene π bond was suggested by K. Yamaguchi (*Jpn. Chem. Rev.* **1973**, *1*, 292) and S. Inagaki and K. Fukui (*J. Am. Chem. Soc.* **1975**, *97*, 7480). (d) Frimer, A. A.; Bartlett, P. D.; Boschung, A. F.; Jewett, J. G. *J. Am. Chem. Soc.* **1977**, *99*, 7977.

(9) Ashford, R. D.; Ogryzlo, E. A. *J. Am. Chem. Soc.* **1975**, *97*, 3604.

(10) If only a 3-fold component to the barrier is assumed, the energy of the perpendicular conformation should be 0.71 times the difference between the energy of the eclipsed and staggered.

(11) A compilation of experimental studies of rotational barriers in these molecules can be found in Table VI of Hehre and Pople [Hehre, W. J.; Pople, J. A. J. *Am. Chem. Soc.*, **1975**, *97*, 6941]. In addition to these values, Durig et al. [Durig, J. R.; Hudson, J. D.; Natter, W. J. *J. Chem. Phys.*, **1979**, *70*, 5747] report barriers of 0.79 and 2.04 kcal/mol for *cis*- and *trans*-2-butene, respectively.

(12) Epiotis, N. D.; Yates, R. L.; Bernardi, F. *J. Am. Chem. Soc.*, **1975**, 97, 5961.

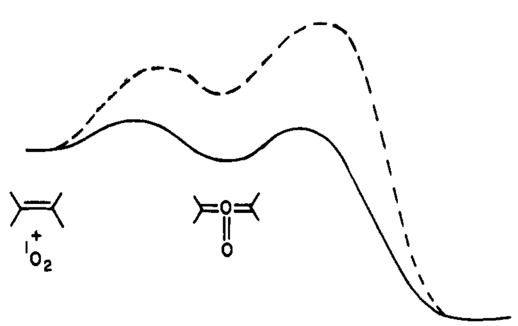

Figure 2. Proposed energy profiles for (heavy line) tetrasubstituted-alkene and (dashed line) unhindered-alkene ene reactions.

satisfactorily for propene and the butenes, although all the calculated barriers are 0.4–0.5 kcal/mol too low.[13] We have carried out calculations on 2-methyl-2-butene and 2,3-dimethyl-2-butene to complete the series of polymethylethylenes. The relative energies of various conformations are given in Table I. The optimized angles compare very well with those calculated by Lifson and Ermer by molecular mechanics.[15] In brackets in Figure 1, we give the corrected values of rotational barriers for these two molecules.

For the three methyl groups of 2-methyl-2-butene, the rotational barriers increase as the experimentally observed rates of hydrogen abstraction decrease! Thus, the greater reactivity of alkyl groups on the disubstituted side of this molecule may arise from the relative ease of rotating one CH bond on one of these methyls to the perpendicular conformation in the transition state. Since all groups lower the rotational barrier of a cis methyl, this explanation of the cis effect is quite general.

For example, the cis methoxy effect can also be explained by consideration of rotational barriers. Table I gives the methyl rotational barriers for methoxypropenes. The trans, cis, and geminal methoxy groups change the vinylic methyl rotation barrier by $\sim$0.1, −0.4, and 1.3–1.8 kcal/mol, respectively. Assuming that lower rotational barriers lead to higher reactivity, a methoxy group activates a cis methyl, greatly deactivates a gem methyl, and has little effect on a trans methyl. This accounts very well for the stereochemical and regiochemical preference observed in singlet oxygen ene reactions of these molecules.[3] Similarly, cyclopropyls and phenyls, indeed any group, are expected to reduce the rotational barriers of cis methyls and increase reactivity toward singlet oxygen. For example, the barriers in *cis*-2-fluoropropene, *trans*-2-fluoropropene, and 1-fluoropropene are 1.06, 2.20, 2.45 kcal/mol.[14]

Subtleties in reactivity can all be accounted for in a similar way. The activation energy for the ene reaction of *cis*-2-butene (6.5 kcal/mol) with singlet oxygen is 0.8 kcal/mol lower than that for *trans*-2-butene (7.3 kcal/mol.).[9] This cis compound has a 1.2–1.5 kcal/mol lower rotational barrier than the trans, and to rotate a methyl group from the eclipsed conformation to the perpendicualr conformation is 0.8–1.1 kcal/mol easier for *cis*-2-butene than for *trans*-2-butene.

The different isotope effects observed in various hexadeuterio-2,3-dimethyl-2-butenes[5,17] have been cited as evidence for an intermediate with a perepoxide-like geometry in singlet oxygen ene reactions.[17] We believe that these stereospecific isotope effects, and the even larger ones of this type found for triazolinedione reactions,[18] result from the special conformations of this and other tetrasubstituted alkenes in which allylic hydrogens are ideally suited for hydrogen abstraction, so that conformational effects discussed here do not contribute to the activation energies of these reactions.

Electron diffraction studies indicate that 2,3-dimethyl-2-butene has all methyl groups in the perpendicular conformation.[15] Some molecular mechanics calculations predict all-perpendicular[15] while others predict all-eclipsed[16] conformations. At the STO-3G flexible rotor level, the all-perpendicular (alternating up and down) conformation is 1.1 kcal/mol more stable than the all-eclipsed conformation. However, since the stability of the eclipsed conformation is always underestimated by 0.4 kcal/mol at this level, we believe that the difference in energy between various conformations will be only 0–0.5 kcal/mol.

Thus, the isotope effects found for deuterated tetramethylethylenes are compatible with a two-step mechanism, rate-determining formation of a complex between 2,3-dimethyl-2-butene and singlet oxygen with a perpendicular (perepoxide-like) geometry (Figure 2).[8c,17,19] The activation energy of 0.5 kcal/mol in methanol solution can be taken as an upper limit to the activation energy for formation of the perpendicular complex. The second step of the reaction has a lower activation energy, since the hydrogens are perfectly aligned for abstraction. Rotational barriers do not influence this reaction.[19,20]

With less highly substituted alkenes, the second step of the reaction is rate determining, as shown by the dashed line in Figure 2. Here, the intermediate complex should be less stable than in the tetrasubstituted alkene case, because the alkene is less electron rich; the activation energy for the second step should be increased to a large extent, since here the energy required to rotate the CH is fully manifested. In such cases, as for 2-butene, both cis and trans compounds are predicted by this model to exhibit low primary isotope effects of $\sim$1.4.

Acknowledgment. We are grateful to the National Science Foundation for financial support of this research and to L. M. Stephenson, P. D. Bartlett, C. W. Jefford, V. Rautenstruach, and K. Gollnick for valuable discussions.

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(13) Radom, L.; Pople, J. A. *J. Am.* Chem. *Soc.*, **1970**, *92*, 4786. In the "flexible rotor" model, all heavy atom angles are optimized for each conformer, while the remaining geometry is fixed at standard values.

(14) See Scarzafava, E.; Allen, L. C. *J. Am. Chem. Soc.*, **1971**, *93*, 311 and references therein.

(15) Eisma, S. W.; Altona, C.; Geise, H. J.; Mijhoff, F. C.; Renes, G. H.; *J. Mol. Struct.*, **1974**, *20*, 251.

(16) Ermer, O.; Lifson, S. *Tetrahedron*, **1974**, *30*, 2425.

(17) Grdina, B.; Orfanopoulous, M.; Stephenson, L. M. *J. Am. Chem. Soc.*, **1979**, *101*, 3111.

(18) Seymour, C. A.; Greene, F. D. *J. Am. Chem. Soc.*, **1980**, *102*, 6384.

(19) Isotopic substitution influences rotational barriers as well. For example, propene-d_3 has a barrier to rotation 0.03 kcal/mol lower than that of propene.[20] This effect, taken alone, would produce an inverse isotope effect of $\sim$0.95.

(20) Kondo, S.; Sakuri, Y.; Hirota, E.; Morino, U. *J. Mol. Spectrosc.*, **1970**, *34*, 231. Chen, S. S.; Wilhoit, R. C.; Zwolinski, B. J. *J. Chem. Phys. Ref. Data*, **1977**, *6*, 105. Hirota, E. *J. Chem. Phys.*, **1966**, *45*, 1984.

Structural Characterization of the Neutral–Ionic Phase Transition in Tetrathiafulvalene–Chloranil: Evidence for C–H···O Hydrogen Bonding

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The charge-transfer compounds composed of TTF[2] and its derivatives with the tetrahalo-*p*-benzoquinones exhibit a number of interesting, new phenomena. For example, several of these compounds were recently discovered[3] to be the first highly conducting charge-transfer compounds not to contain TCNQ[2] as the acceptor molecule. More recently, it was discovered[4] that at high

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(2) TTF = tetrathiafulvalene, chloranil = tetrachloro-*p*-benzoquinone (see Figure 1), and TCNQ = tetracyano-*p*-quinodimethane.

(3) J. B. Torrance, J. J. Mayerle, V. Y. Lee, and K. Bechgaard, *J. Am. Chem. Soc.* **101**, 4747 (1979); J. B. Torrance, J. J. Mayerle, V. Y. Lee, R. Bozio, and C. Pecile, *Solid State Commun.*, submitted for publication.

(4) J. B. Torrance, J. E. Vazquez, J. J. Mayerle, and V. Y. Lee, *Phys. Rev. Lett.*, in press.