verifying quantitative agglutination. Addition of 4 μmol of lactose, which competes with the vesicles for the lectin, resulted in complete dissolution of the lectin-vesicle precipitate, giving rise to the resuspension of single unilamellar vesicles. Electron microscopy of the deagglutinated vesicle suspension showed only small particles, verifying that extensive vesicle fusion had not occurred.

The observation that the line width of the *N*-methyl carbon resonance is insensitive to lectin-induced vesicle agglutination is strong evidence that the tumbling of phospholipid vesicles is not the major mechanism for the line narrowing observed upon sonication of phosholipid dispersions. Preliminary experiments with the ^{13}C label in the acyl chain of phospholipid give similar results. Having eliminated tumbling as a significant factor, we conclude that the line narrowing observed in NMR spectra of sonicated vesicles is most likely due to increased structural disorder in the packing of the phospholipids, relative to unsonicated dispersions. The increased disorder in the packing of the phospholipid should also be reflected in an increased lateral diffusion rate in the plane of the bilayer. Recent work has suggested that such an increase in lateral diffusion rate may occur in sonicated vesicles.[25]

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(16) Abbreviations: PC, phosphatidylcholine; ^{13}C-PC, tri[*N-methyl*-^{13}C]choline-labeled PC; ^{14}C-PC, [*N-methyl*-^{14}C]choline-labeled PC; LC, lactosyl ceramide.
(17) Egg yolk phosphatidylcholine was extracted and purified according to Litman.[18] Egg yolk phosphatidic acid was prepared by the digestion of egg yolk PC by phospholipase C according to Dawson and Hemington.[19] Tri[*N-methyl*-^{13}C]choline was synthesized by reaction of $^{13}CH_3I$ (Merck) and ethanolamine[20] and purified by ion-exchange chromatography. The ^{13}C-labeled choline was covalently attached to egg yolk phosphatidic acid as previously described.[21] [*N-methyl*-^{14}C]Choline-labeled egg PC was synthesized similarly using [*N-methyl*-^{14}C]choline from New England Nuclear, Boston, Mass. Lactosyl ceramide was purchased from Miles Laboratories, Elkhart, Ind. (*N*-palmitoyl dihydrolactocerebroside, lot no. 3). Preparation of unsonicated dispersions (multilamellar liposomes) was as follows. Solutions of LC and ^{13}C-PC or ^{14}C-PC in 2:1 choloroform–methanol were mixed in appropriate proportions in a round-bottom flask, and the solvent was removed in a rotary evaporator. After desiccation overnight against a vacuum, 4 mL of a buffer composed of 0.01 M Na_2HPO_4 and 0.2 M NaCl (pH 7.2) was added, and the lipid suspended by swirling the flask. To prepare sonicated vesicles, this dispersion was sonicated for 20 min at 4 °C under a N_2 atmosphere, followed by centrifugation at 12 000 × *g* for 20 min at 4 °C to remove titanium fragments and multilamellar liposomes.
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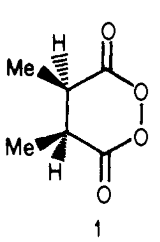
Six-Membered Cyclic Diacyl Peroxide Fragmentations. Thermal Decomposition of *meso*- and *dl*-2,3-Dimethylsuccinoyl Peroxides

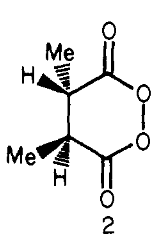
Sir:

Predictive criteria for those thermal reactions of high energy species which provide electronically excited states of product molecules are still not completely understood. The thermal decompositions of 1,2-dioxetanes which afford electronically excited n,π* states of carbonyl products are well known.[1] Efforts to study the thermal generation of electronically excited π,π* states of aromatics and simple alkenes have been hampered owing to the lack of suitable high energy precursors. Recent important work by Schuster[2] suggests that the thermal decomposition of a presumed six-membered cyclic diacyl peroxide intermediate is an efficient chemiluminescent process and provides a method for the direct chemical formation of aromatic hydrocarbon π,π* electronically excited states. This raises the question whether succinoyl peroxides on thermal decomposition would afford electronically excited states of simple alkenes. The mechanism of the decomposition of six-membered cyclic diacyl peroxides is not known and only a few examples of any six-membered cyclic diacyl peroxides exist in the literature.[3]

We report the syntheses and thermal decomposition of *meso*- and *dl*-2,3-dimethylsuccinoyl peroxides (**1** and **2**, respectively). These initial findings provide the first stereochemical study of six-membered cyclic diacyl peroxide thermal fragmentations. The data presented here are consistent with a common intermediate(s) but do not require the generation of electronically excited states of the 2-butene products.



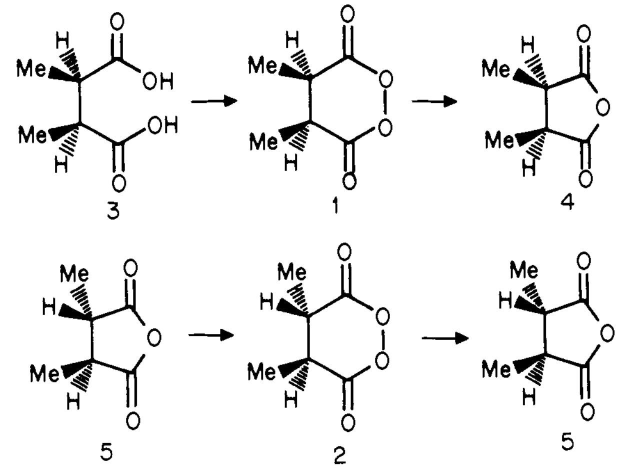
1



2

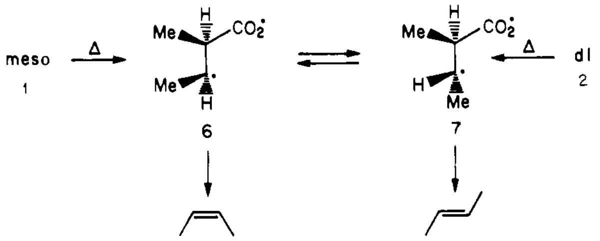
Successive treatment of 98% isomerically pure *meso*-2,3-dimethylsuccinic acid (**3**),[4,5] mp 209–210 °C, with phosphorus pentachloride and sodium peroxide,[6] afforded a white crystalline solid whose NMR and IR spectra ($\nu_{C=O}$ 1812 (m), 1783 (s) cm^{-1}) were consistent with structure **1**. The isomeric purity of **1** was determined by treatment of the peroxide with

Scheme I



triphenylphosphine[9,10] to afford the corresponding known meso cyclic anhydride **4**, 95% isomerically pure by analytical vapor phase chromatography (VPC)[11] (Scheme I). Similarly, treatment of 95% isomerically pure *dl*-2,3-dimethylsuccinic anhydride (**5**),[4,11] mp 86–88 °C, with phosphorus pentachloride and sodium peroxide afforded a white crystalline solid whose NMR and IR spectra ($\nu_{C=O}$ 1812 (m), 1781 (s) cm^{-1}) were consistent with structure **2**. The stereochemical purity of **2** was determined by treatment of the peroxide with triphenylphosphine[9,10] to afford the corresponding known *dl* cyclic anhydride **5**, 98% isomerically pure by analytical VPC[11] (Scheme I). Both cyclic peroxides could be conveniently dissolved in CH_2Cl_2 or THF and smoothly evolved CO_2 when warmed to 95 °C.[12] Relative amounts of *cis*- and *trans*-2-butene products from the thermal decomposition of *meso*- and *dl*-2,3-dimethylsuccinoyl peroxides in solution (0.005 M, degassed,[13] sealed tubes) and in the vapor phase[14] are reported in Table I.[15]

The remarkable similarity in the stereochemistry of the *cis*- and *trans*-2-butene products suggests a *common intermediate* or set of intermediates. One reasonable possibility is the carboxy radicals (**6** and **7**) which might undergo rapid equilibration before decarboxylation to olefin.



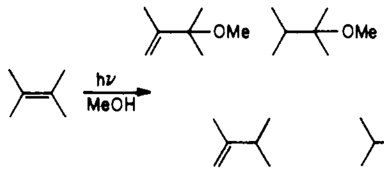
Thermochemical estimates[16] suggest that there is sufficient energy released in these fragmentations to populate the triplet state of 2-butene ($E_T \sim 78$ kcal mol^{-1}).[17] The kinetics of the cis/trans photosensitized isomerization of 2-butene in the gas phase reveals a branching ratio for triplet 2-butene of 1.02.[18] The lack of correspondence for the trans/cis ratios between the benzene sensitized triplet 2-butene (50:50) and the peroxide decomposition data presented here (68:32) demands that the triplet, if formed at all, cannot be the *only* intermediate in this reaction.

Recent work by Kropp and his group[19] has shown that direct irradiation of simple tetra- and trisubstituted olefins in methanol provide both saturated and unsaturated ethers and hydrocarbon isomers. The formation of ether products from direct irradiation in hydroxylic media has been interpreted by them in terms of nucleophilic trapping of low lying π,R(3s) Rydberg excited states.

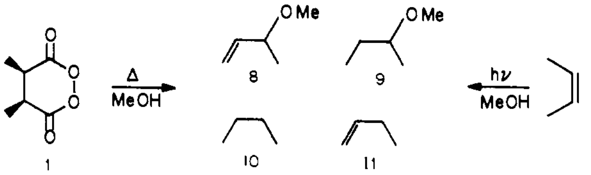
Table I. Stereochemistry of 2-Butenes from Decomposition of **1** and **2**[a]

Compd	Temp, °C	Conditions		
meso-**1**	47	THF	69	31
	92	THF	68	32
	92	CH_2Cl_2	68	32
	276	Gas	67	33
	357	Gas	63	37
dl-**2**	47	THF	69	31
	92	THF	70	30
	92	CH_2Cl_2	67	33
	276	Gas	61	39
	357	Gas	62	38

[a] Ratios of *cis*- and *trans*-2-butenes were determined by VPC analysis using 20 ft × 1/8 in. 10% dibutyl tetrachlorophthalate, flame ionization detector. Typical absolute yields were 40–60% using 2-methylbutane as an internal standard. A few percent butane and 1-butene were also observed.



Accordingly, we have carried out the thermal decomposition of the six-membered cyclic peroxide **1** in *methanol* at 95 °C and find *cis*- and *trans*-2-butenes as the major products (trans:cis, 68:32 ratio) similar to the other solution results (Table I). *In addition* four other products (~9% total), consisting of the saturated and unsaturated ethers **8** and **9** and the isomerized hydrocarbons **10–11**, are observed.[20,21] Experiments in our laboratories show that direct irradiation[23] of 2-butenes in methanol afford these same products (**8–11**).



Although we cannot rule out the possibility of a Rydberg state of 2-butene being generated in these fragmentations, the observation of a small component of saturated and unsaturated methyl ethers may simply correspond to a competing peroxide decomposition pathway in methanol which affords the radical cation of 2-butene. The origin of these methyl ethers will require further investigation.

In summary, the similar stereochemistry of the 2-butene products in the *dl*- and meso peroxide decompositions suggests a common intermediate(s). Although the results could be interpreted as involving, *in part*, the intermediacy of electronically excited states, there are sufficiently reasonable alternative explanations, which do not involve excited-state pathways, that, at this point, it is still premature to identify succinoyl peroxide decompositions as routes for the thermal generation of the excited states of simple alkenes.

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(5) The pure meso diacid was obtained by recrystallization from a mixture of *dl* and meso diacid in 10 N HCl. Treatment of the meso diacid, mp 209-210 °C, with diazomethane afforded the corresponding meso diester, dimethyl 2,3-dimethylsuccinate, 98% isomerically pure by analytical VPC.[8]

(6) The meso and *dl* diacid chlorides (bp 40-50 °C at 0.1 mm), both >97% isomerically pure,[7] were taken up in CH_2Cl_2 and added to sodium peroxide in water buffered with NaH_2PO_4 and Na_2HPO_4.[3b]

(7) The isomeric purities of the diacid chlorides were determined by quenching in methanol and analyzing the corresponding *meso-* and *dl*-dimethyl esters by analytical VPC.[8]

(8) *meso-* and *dl*-dimethyl 2,3-dimethylsuccinate were separated by VPC on UCON 550X stationary phase at 130 °C, relative retention times 1 and 1.14, respectively.

(9) R. Hiatt in "Organic Peroxides", Vol. II, D. Swern, Ed., Wiley-Interscience, New York, N.Y., 1971, Chapter VIII.

(10) Controls show that the *dl* and meso peroxides **1** and **2** react with triphenylphosphine in CH_2Cl_2 at similar rates.

(11) *meso-* and *dl*-2,3-dimethylsuccinic anhydrides were separated by VPC on PMPE(6-R) stationary phase at 180 °C, relative retention times 1.14 and 1.0, respectively.

(12) However, these peroxides are extremely shock sensitive in the solid state and will explode upon rapid heating.

(13) Added O_2 had no effect on the product stereochemistry.

(14) Chamber pyrolysis, 5 s.

(15) The cis:trans ratios of 2-butenes were constant with time (10-40% conversion). Control experiments show that neither *cis*-4-octene nor *cis*-stilbene isomerize (<1% detectable) in the presence of decomposing peroxides **1** or **2**. A first-order rate constant for the appearance of 2-butenes from **1** was measured for 1 half-life ($k \sim 7.6 \times 10^{-4}\ s^{-1}$ in THF at 46.9 °C). We cannot rigorously rule out any competition from induced decomposition.

(16) S. W. Benson, "Thermochemical Kinetics", 2nd ed, Wiley, New York, N.Y., 1976. We estimate the $\Delta H_r \sim 59$ kcal mol^{-1} and $E_a \sim 25$–30 kcal mol^{-2} for the peroxide decompositions **1** or **2** → 2-butenes.

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(20) 3.4% 3-methoxy-1-butene (**8**), 3.8% 2-methoxybutane (**9**), 0.1% butane (**10**), 1.4% 1-butene (**11**).

(21) The identities of the ether and hydrocarbon products **9-11** from both the peroxide decompositions in methanol and the direct irradiation of 2-butenes in methanol were confirmed by gas chromatographic–mass spectroscopic analysis[22] and compared with authentic samples.

(22) ¼ in. × 6 ft 3% UCON 550X glass column interfaced to a Finnegan 9500 mass spectrometer. We thank Mr. Ray Haack for his assistance in carrying out these experiments.

(23) Using a Hanovia 450-W medium-pressure mercury arc and a water-cooled quartz immersion well.

(24) Alfred P. Sloan Research Fellow, 1977-1979.

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Framework Electron Count in Metalloheteroboranes. Platinathiadecaboranes

Sir:

Recent reports indicate that certain metalloheteroboranes formed from the more electron-rich transition elements have "exceptional" structures. For instance, 3-(Et_2NCS_2)-3,1,2-$AuC_2B_9H_{11}$[1] and 8,8-$(Me_3P)_2$-7,8,10-$CPtCB_8H_{10}$[2] have been found by x-ray crystallography to have open (nido) structures rather than the more symmetric closo structures anticipated on the basis of framework electron count.[3-5]

Our recent investigation of metallothiaboranes has led to the preparation of platinathiaboranes which could be characterized as closo $L_2Pt\ (SB_8H_8)$ molecules with "exceptional" nido structures on the basis of x-ray crystallography alone. However, additional evidence shows that they have nido framework electron counts and are correctly characterized as $(PMe_2Ph)_2Pt(SB_8H_{10})$ (I), $(PEt_3)_2Pt(SB_8H_{10})$ (II), $(PPh_3)_2Pt(SB_8H_{10})$ (III), and $(PPh_3)_2Pt(SB_8H_9{\cdot}OEt)$ (IV). I-IV appear to be very similar to the $L_2M(SB_9H_9)$ [M = Pd, Pt] complexes reported previously.[6]

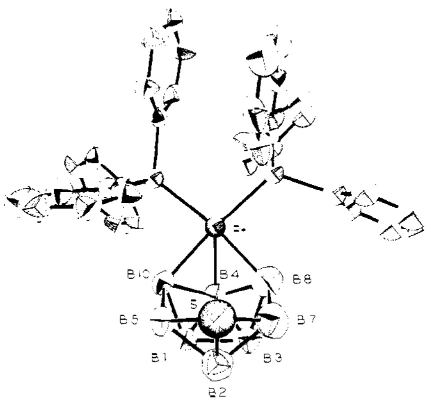

Figure 1. Molecular structure of 9,9-$(PPh_3)_2$-6,9-$SPtB_8H_{10}$. Hydrogen atoms not shown. The numbering convention for the platinathiaborane cluster is shown with the shaded atoms 6 and 9 being S and Pt, respectively.

The reaction of L_4Pt (L = PMe_2Ph, PEt_3, PPh_3) with 1-SB_9H_9 in dry refluxing ethanol or methanol under nitrogen gives white to pale yellow crystals of I-III, respectively, in 75% yield. When $(PPh_3)_2Pt(C_2H_4)$ is used instead of L_4Pt, IV results. The products are air stable in crystalline form but were generally recrystallized from methylene chloride/alcohol in an inert atmosphere. The dimethylphenylphosphine and triethylphosphine derivatives (I and II) have been characterized by mass spectroscopy, IR, ^1H and ^{11}B NMR, and elemental analysis. However, we have been unable to obtain a mass spectral molecular weight of III and IV.

Single crystal x-ray studies of III and IV using conventional Patterson and Fourier difference techniques show that the framework structure is nido for both (Figure 1). Crystal data for III, 9,9-$(PPh_3)_2$-6,9-$SPtB_8H_{10}$: mol wt 848.3; monoclinic; space group $P2_1/n$; $a = 11.522\ (5)$, $b = 20.005\ (5)$, $c = 16.398\ (4)$ Å; $\beta = 95.74\ (3)°$; $V = 3760\ (2)$ Å^3; $d_{obsd} = 1.49\ (1)$, $d_{calcd} = 1.498$ g cm^3; $Z = 4$; μ (Mo Kα) = 40.88 cm^{-1}; $R_1 = 0.043$ and $R_2 = 0.049$ for 5430 collected reflections (3211 with $I \geq 3\sigma(I)$). Crystal data for IV, 8-EtO-9,9-$(PPh_3)_2$-6,9-$SPtB_8H_9$: mol wt 892.4; monoclinic; space group $P2_1/n$; $a = 13.336\ (4)$, $b = 21.034\ (5)$, $c = 14.545\ (3)$ Å; $\beta = 103.04\ (2)°$; $V = 3974\ (2)$ Å^3; $d_{obsd} = 1.48\ (1)$, $d_{calcd} = 1.491$ g cm^3; $Z = 4$, μ (Mo Kα) = 38.75 cm^{-1}; $R_1 = 0.54$ and $R_2 = 0.059$ at this stage for 5968 collected reflections (2962 with $I \geq 3\sigma(I)$). The skeletal structure shows that Pt achieves effective square-planar coordination in which three boron atoms of the thiaborane ligand (B-4, B-8, and B-10) act as a bidentate moiety: Pt-B distances for III (Å): 9-4 = 1.184 (16), 9-8 = 2.242 (15), 9-10 = 2.222 (17). A similar η^3 bonding was observed in $(Me_2PhP)_2PtB_3H_7$.[7] However, because of the disorder associated with the $B_3H_7^-$ ligand in the latter structure, the present one gives the clearest definition of η^3 bonding between Pt and a borane cluster.

The cluster structure is clearly open with nonbonding interactions between the Pt and boron atoms 5 and 7 (3.48 and 3.49 Å) and the sulfur (3.89 Å). In view of recent contentions that a nido structure is not confined to "electron-rich" systems, but appears to be related simply to the presence of a formal d^8 or d^9 metal,[1,8] we sought to establish firmly the framework electron count in III. The critical ambiguity revolves around the number of hydrogen atoms associated with the cluster which cannot be determined unambiguously by x-ray crystallography in this case because of the dominant scattering by