Vinyl anions normally isomerize very slowly, even at room temperature or above,[7] whereas the corresponding radicals interconvert at a measurable rate at −78° [8,9] Extrapolating to the cationic case, vinyl cations might be expected to be linear or very rapidly equilibrating, a judgment in accord with theoretical calculations[10] and with the experimental observations reported here.[11,13]

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route. Another possibility is that **3** and **4** produce the same products because they each undergo addition of HOAc followed by elimination of HI. This is rendered very unlikely by the observation that the vinyl acetate product formed from cyclopropyl vinyl iodide[1a] in AgOAc–DOAc contains *no* deuterium by nmr, ir, and mass spectral analysis (unpublished results of S. A. Sherrod and R. G. Bergman).

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(11) In our opinion, the less likely alternative is that the vinyl cation **12** is in fact a rapidly interconverting mixture of two bent ions. However, if the ions are bent, and they react with acetic acid at a diffusion-controlled rate[12] ($k \cong 10^9$ l./(mol sec)), a steady-state treatment indicates that identical product distributions can only arise from **3** and **4** if the rate constant for interconversion of "bent" stereoisomers of **12** is of the order of 10^{11} sec^{-1} or larger.

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(13) Note Added in Proof. After this communication was submitted for publication, a study of the stereochemistry of S_N1 substitution of 1,2-dianisyl-2-phenylvinyl halides was reported: Z. Rappoport, and Y. Apeloig, *ibid.*, **91**, 6734 (1969). The product stereochemistry is randomized, as is observed in our system.

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Free Radical Formation during Ozonation of a Hindered Olefin

Sir:

Although radicals are often produced from homolytic cleavages of ozone adducts[1] or insertion compounds[2] of certain saturated organic substances, no radical has heretofore been characterized or observed, to our knowledge, as a primary product of ozonation of an olefin. We wish now to report evidence for a free radical as an initial and major product of the ozonation of trimesitylvinyl alcohol (I).

Reaction of 10 mmol of I in 150 ml of 3:1 methylene chloride–methanol with 10 mmol of ozone in a nitrogen stream at −78° produced a black solution which, after being swept with nitrogen, exhibited a strong epr signal (broad singlet, 7–8 G in width, with a *g* value of 2.004 in methylene chloride–methanol, methylene chloride, or pentane). Upon reaching room temperature the reaction mixture lost its color and epr signal. The recovery of I was 58–60%. When the ozonation was carried out in pentane and the resulting solution was evaporated at −55° (0.5 mm), a purple solid was obtained, which appeared to be a mixture of the radical and I. When the solid was redissolved, an identical epr signal as before was observed. A carbon tetrachloride solution of the radical was stable for 1–2 days. The radical cannot be generated from solution of I by treatment with oxygen.

We assign structure III to the radical, based on the following evidence. When the ozonation in CH_2Cl_2–CH_3OH was repeated and hydroquinone (1 mol equiv) was added to the −78° reaction mixture, the color immediately disappeared and a 63% recovery of I was made. The ozonation was again repeated and 1.0 mol equiv of galvinoxyl, an efficient radical scavenger,[3] was added. At −35° the color and epr signals of both radicals disappeared, leaving a yellow solution. Less than a 10% recovery of I was obtained. Galvinoxyl was converted to hydrogalvinoxyl (mp 155–156°, ir)[4] and various other, probably coupling, products. Galvinoxyl was shown not to react with a solution of I in methylene chloride–methanol at −35°; at room temperature the galvinoxyl color slowly faded to yellow during a 1-day period.

These experiments show that the radical was III and was present in the −78° ozonation reaction mixture to the extent of at least 50%. At higher temperatures it readily abstracts hydrogen from its environment and reverts back to I; this occurs at −78° in the presence of hydroquinone. Addition of galvinoxyl, however, destroys III, as evidenced by the lower recovery of I. The radical III also reacts with ozone. Upon treating I with 3 mol equiv of ozone in methylene chloride–methanol at −78°, the color of the radical III disappeared; the products, however, have so far been intractable.

Further evidence for structure III for the radical is, first, that oxidation of I with sodium hypochlorite produced the same radical, as evidenced by an identical epr signal (see above). Sodium hypochlorite oxidation of 2,2-dimesitylvinyl alcohol gives a compound[5] which we have shown to have structure X [ir carbonyl band at 1720 cm^{-1}; nmr, peaks at τ 0.24 (s, aldehydic proton), 3.98 (s, olefinic proton), 3.3–3.45 (aromatic protons), 7.75–8.2 (methyl protons)], a dimer of radical IX. By analogy the radical from I should be III. Second, radical III absorbed in the same uv region (λ_{max} 280) as the original vinyl alcohol (I) but with a higher extinction coefficient, indicating a similar structure. Also, the ir spectrum of the solid mixture of the radical and I was nearly identical with that of I. Third, from the reaction mixture utilizing 1 mol equiv of ozone a 2–3% yield of a colorless compound assigned structure VIII was isolated [mp 158–159° (ethanol); *Anal.* C, H agrees with $C_{29}H_{32}O$; mol wt 396.2466 (high-resolution mass spectroscopy); ir, no hydroxyl or carbonyl absorption, ether band at 1100 cm^{-1}; nmr (all singlets), τ 3.28 (4 protons each), 3.36 (1 proton), 7.61, 7.68, 8.10 (3 protons each), 7.77, 7.97, 8.03 (6 protons each)]. The route to VIII is suggested as VI → VII → VIII (see Scheme I).

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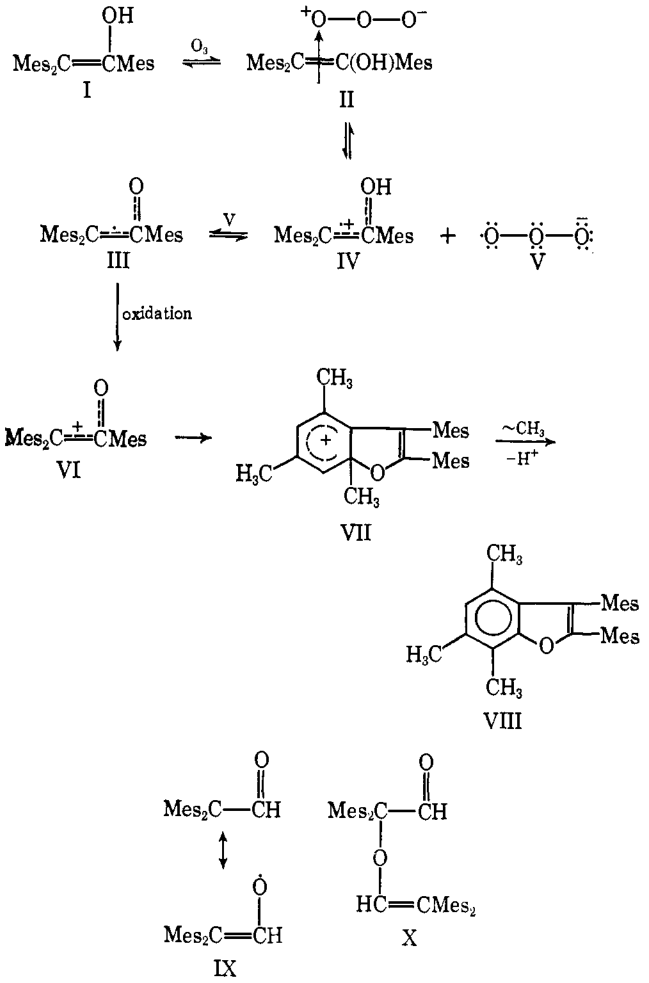
Scheme I



The unresolved singlet epr signal for III could result from a rapid electron transfer between species III and VI. Such was also found for the cation radical from oxidation of tetraanisylethylene.[6]

These results, coupled with previous theory,[7,8] suggest that ozonation of olefins proceeds *via* an initial π complex (*e.g.*, II). This usually either enters into 1,3-dipolar cycloaddition (ozonolysis) or is converted to a σ complex. The latter route increases in importance as steric hindrance to 1,3-dipolar cycloaddition increases and normally results in the formation of epoxides and other "partial cleavage" products.[8] When steric hindrance in the olefin becomes very great and radical stabilizing groups are attached to the doubly bonded carbon atoms, homolytic dissociation of the π complex (*e.g.*, to IV and V) may occur. Loss of a proton from IV (perhaps to V) gives III.

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Tetrakis(acetoxymercuri)methane

Sir:

Tetrametallomethanes in which the metal atom is silicon,[1] lead,[2] or boron[3] have been made by modified crossed Wurtz reactions, and we have recently reported that one or two boron atoms of $C[B(OMe)_2]_4$ can be replaced by tin, or two by lead.[4] We have now found that mercuric acetate replaces all four boron atoms of $C[B(OMe)_2]_4$ to yield tetrakis(acetoxymercuri)methane, $C(HgOAc)_4$, which is crystalline, water soluble, and stable.

A solution of 3.03 g of tetrakis(dimethoxyboryl)methane, $C[B(OMe)_2]_4$, in 300 ml of absolute ethanol was stirred and heated with 25 g of mercuric acetate, which nearly all dissolved as reflux approached and the product began to precipitate. After 4.5-hr refluxing the mixture was cooled to 25° and filtered to yield 10.8 g (102%) of $C(HgOAc)_4$ contaminated with mercurous acetate (less soluble) and mercuric acetate (more soluble). This was dissolved in 100 ml of boiling water and 2 ml of acetic acid, filtered to remove mercurous acetate, treated with 5 g of sodium hydroxide in 10 ml of water, and boiled to coagulate the hydroxide precipitate. The precipitate was redissolved in 100 ml of boiling water and 15 ml of acetic acid and boiled down to a volume of 35 ml. Addition of 100 ml of ethanol and cooling yielded 7.4 g of crystalline $C(HgOAc)_4$, which was further purified by repetition of the cycle. Pure $C(HgOAc)_4$, mp 265–285° dec, gives a *white* precipitate with aqueous sodium hydroxide, not gray (mercurous) or yellow (mercuric). It also gives a white precipitate (probably $C(HgCl)_4$) with stannous chloride, which is not reduced to mercury, in contrast to mercuric and mercurous salts. The nmr spectrum (in D_2O or DMSO-d_6) shows only the acetate protons. *Anal.* Calcd: C, 10.29; H, 1.15; Hg, 76.37. Found: C, 10.45; H, 1.09; Hg, 76.09.

There is no difficulty in packing four mercury atoms around a central carbon. The usual carbon–mercury distance, 2.07 Å,[5] with tetrahedral bond angles leaves 3.4 Å between mercury atoms, which is 0.1–0.3 Å greater than the van der Waals distance.[5] However, the central carbon atom is well shielded from any kind of direct attack, which may explain the rather inert character of the C–Hg bond in $C(HgOAc)_4$.

In fact, it is somewhat surprising that the fourth mercury atom is able to get into the structure at the same time the last boron is departing, as required by the concerted electrophilic displacement mechanism.[6] Although $C[B(OMe)_2]_4$ serves as a carbanion source in basic media and degrades to $CH_2[B(OMe)_2]_2$ in basic methanol,[3] this does not occur in the weakly acidic medium used for this displacement. Refluxing 0.42 g of $C[B(OMe)_2]_4$ with 0.2 ml of acetic acid in 40 ml of anhydrous methanol for 1 hr followed by evaporation of the solvent yielded 85% of unchanged $C[B(OMe)_2]_4$, purity checked by infrared spectroscopy. These are

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