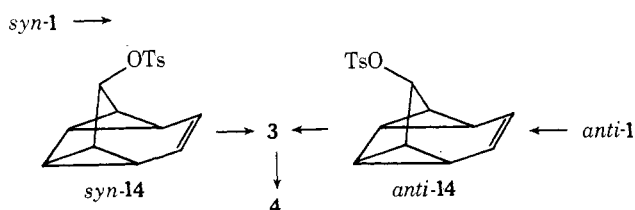


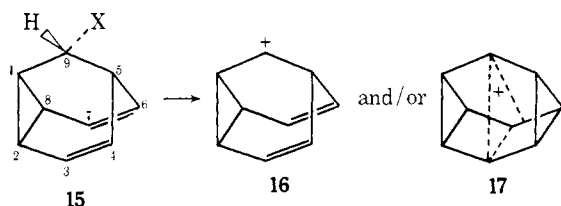
sis of **1-9-d** in methanol afforded **6-2-d**, identified by its nmr spectrum which matched closely the reported spectrum of **5-2-d**.³

We have also prepared *anti*-bicyclo[4.2.1]nona-2,4,7-trien-9-yl *p*-toluenesulfonate (*anti*-**1**).¹⁰ The product distribution obtained by solvolysis of *anti*-**1** in methanol was virtually identical with that from *syn*-**1** (Table I). Moreover, the rates of solvolysis of *syn*-**1** and *anti*-**1** in 75% aqueous methanol agreed within experimental error¹¹ (Table II).

Our results suggest that the solvolysis of *syn*-**1** is not assisted by double bond participation, as implied in **2**. Rate-determining formation of tetracyclic tosylates (**14**) by intramolecular Diels-Alder reaction would account for the similar solvolytic rates for the **1** epimers and for the small solvent effect.¹² The discussion of alternative explanations will be deferred to a full paper. The cationic intermediate of the deamination reaction, quite distinct in its behavior, may be represented by **10**, or a slightly delocalized version to explain the exclusive formation of *syn*-**11**.



We should like to contrast the bicyclo[4.2.1]nona-2,4,6-trien-9-yl cation with its isomer, the barbaralyl cation (**16**), as a typical case of vertical stabilization.¹³ The rigid barbaralyl skeleton does not permit substantial molecular distortion, and such distortion is not required to achieve optimal stabilization of positive charge at C-9. Schleyer, *et al.*,¹⁴ studying the solvolysis of barbaralyl-9-*d* tosylate (**15**, X = OTs), uncovered a degenerate rearrangement of the barbaralyl cation which distributes deuterium over the positions 3, 7, and 9. EHT calculations support a triply degenerate intermediate (**17**) as the cationic species of lowest energy.¹⁵ In less nucleophilic solvents, and on repeated formation of the barbaralyl cation, complete scrambling of D is observed in a process of slightly higher activation energy.¹⁴



Photolysis of barbaralone tosylhydrazone sodium salt in CH₃OD afforded barbaralyl methyl ether (**15**, X = OCH₃) with 80% of the deuterium at C-9 and 20% distributed over positions 3 and 7, according to ¹H and ²H nmr. When the reaction was carried out in D₂O-CH₃OD (1:1),¹⁶ the barbaralol (**15**, X = OH) contained 55% D at C-9, 34% at C-3 and C-7, and 10% at other positions. Our results, combined with those of Schleyer, *et al.*,¹⁴ strongly indicate that the amount of rearrangement depends solely on the nucleophilicity of the solvent and not on the nature of the leaving group. Solvolysis and deamination produce virtually the same barbaralyl cation.

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 - (11) Solvolyses were carried out in 75% aqueous methanol in the presence of a tenfold excess of NaHCO₃, the evolution of CO₂ being recorded. These conditions closely approach those of the preparative runs. The product distribution by glpc agreed with Table I, except for the presence of small amounts of alcohols. The accuracy of this semimicro technique is inferior to titration methods.
 - (12) A referee has pointed out that a change of solvent from acetic acid (ref 3) to 75% aqueous methanol changes the solvolytic rate of *syn*-**1** by less than a factor of 3. Winstein Y values for these solvents suggest that there should be an approximately 100-fold rate difference for rate-determining ionization.
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 - (16) The ratio of **14**, X = OCH₃ to **14**, X = OH from this experiment was 87:13. The deuterium distribution of barbaralyl methyl ether was virtually the same as that obtained in pure CH₃OD.

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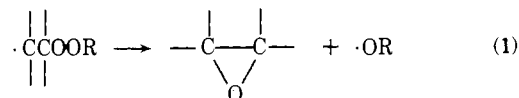
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Received June 24, 1974

Rate Constants for the Formation of Oxiranes from β -Peroxyalkyl Radicals. The *gem*-Dialkyl Effect in Homolytic Ring Closure

Sir:

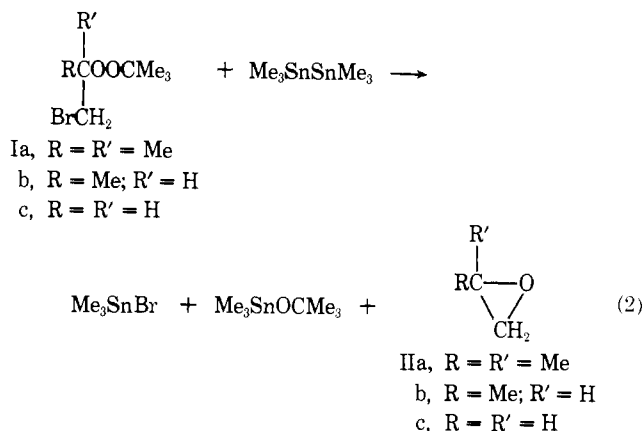
β -Peroxyalkyl radicals are involved in the decomposition of peroxides,¹ in the autoxidation of alkenes,² and in the cool flame combustion of alkanes³ and, by intramolecular homolytic substitution (SHi) at the oxygen in the 3-position, are thought to be responsible for the formation of oxiranes.



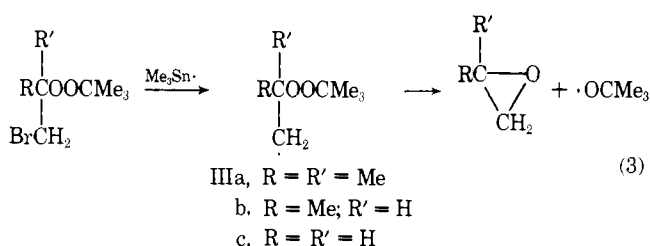
Hitherto, no method has been available for studying these cyclization reactions in isolation, and estimates of their rates, even for peroxyalkyl radicals of similar structure, have varied over a wide range.²⁻⁵

We have now prepared the β -peroxyalkyl radicals Me₃COOCMe₂CH₂·, Me₃COOCHMeCH₂·, and Me₃COOCH₂CH₂· by causing the corresponding β -bromoperoxides⁶ to react with trialkyltin radicals; the peroxyalkyl radicals have been identified by esr spectroscopy, and their rates of ring closure have been determined.

In benzene solution at 25°, the β -bromoperoxides (Ia-c) react with hexamethylditin in the presence of di-*tert*-butyl hyponitrite as initiator, to give the corresponding oxiranes (IIa-c) in excellent yield (nmr). The reaction proceeds by abstraction of bromine by the trimethyltin radical, to give the appropriate β -peroxyalkyl radical (III; eq 3),⁷ and these

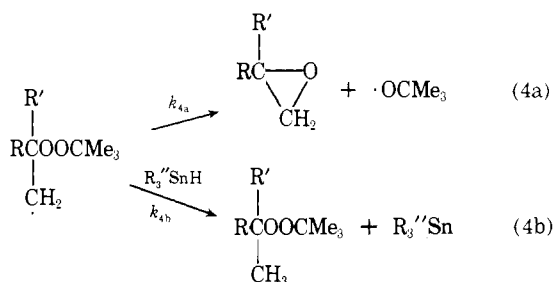


can be observed by esr spectroscopy if the reactions are carried out by photolyzing a mixture of the bromoperoxide, hexamethylditin, and di-*tert*-butyl peroxide, in toluene at -70° . The same, but more intense, spectra can be obtained if the debromination is brought about by triethylsilyl radicals generated by photolysis of a mixture of the bromoperoxide, triethylsilane, and di-*tert*-butyl peroxide in cyclopropane.⁸



The spectra which were obtained are detailed in Table I and are consistent with the structures of the radicals III; the spectra of these and related radicals are being studied in an attempt to correlate conformational effects in the radicals with the rate and stereochemistry of the ring closure.

If instead a trialkyltin hydride is used as the source of the trialkyltin radical, the ring closure (reaction 4a) competes with reduction of the radical by the tin hydride (reaction 4b), and, from an analysis of the products of the oxirane and dialkyl peroxide, the ratio of the two rate constants, k_{4a}/k_{4b} , can be determined, and if the value of k_{4b} is known, that for k_{4a} can be derived



Bromo-*tert*-butyl *tert*-butyl peroxide (Ia) was caused to react with varying amounts of tributyltin hydride, with di-*tert*-butyl hyponitrite as initiator, in benzene at 25° , and the products were analyzed by glc giving k_{4a}/k_{4b} (for Bu_3SnH) = 0.73 mol l.⁻¹. Similar reactions were carried out with triphenyltin hydride in deuteriobenzene, and the products were analyzed by nmr, giving k_{4a}/k_{4b} (for Ph_3SnH) = 0.14 mol l.⁻¹.

It has been shown that the rate constant for the abstraction of hydrogen by alkyl radicals at 25° from tributyltin hydride is close to 1×10^6 l. mol⁻¹ sec⁻¹, and for triphenyl-

Table I. Hyperfine Coupling Constants for β -Peroxyalkyl Radicals in Cyclopropane

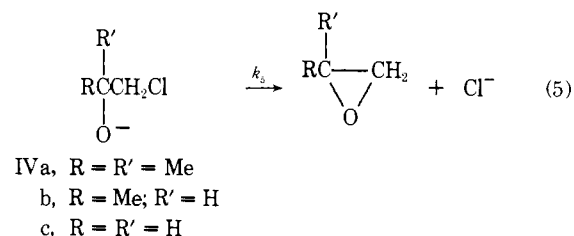
	R	R'	Temp, °C	Hyperfine coupling constants, G ^a		
				H α	H β	H γ
IIIa	Me	Me	-94	21.4 (2)		1.2 (6 ^b)
IIIb	Me	H	-100	21.8 (2)	24.0 (1)	0.5 (3)
IIIc	H	H	-95	21.4 (2)	26.6 (2 ^b)	

^a Numbers in parentheses indicate the number of interacting hydrogen atoms. ^b At low temperature the β -substituents become nonequivalent on the esr time scale presumably as a result of restriction of rotation about the C β -O bond.

tin hydride is close to 5×10^6 l. mol⁻¹ sec⁻¹, and is rather insensitive to the nature of the alkyl radical.⁹ If these values are accepted for k_{4b} , both of the above methods give a value for k_{4a} of about 7×10^5 sec⁻¹ at 25° for the radical IIIa.

2-Bromoisopropyl *tert*-butyl peroxide (Ib) was similarly caused to react with triphenyltin hydride in varying amount, and the products were analyzed by glc and nmr, giving a value for k_{4a} for the radical IIIb of about 4×10^4 sec⁻¹ at 25° . A similar reaction between 2-bromoethyl *tert*-butyl peroxide and triphenyltin hydride or tributyltin hydride gave (nmr and glc) ethyl *tert*-butyl peroxide and ethylene oxide, where it can be derived that k_{4b} for the radical IIIc is about 2×10^3 sec⁻¹ and the relative values of k_{4b} for IIIa, IIIb, and IIIc are 350:20:1.¹⁰

The introduction of one and then two methyl groups is therefore shown to increase the tendency toward ring closure.¹² This appears to be the first clear demonstration of this effect in homolytic reactions, but it is well recognized in heterolytic processes (the *gem*-dialkyl effect or the Thorpe-Ingold effect);¹⁴ the closest heterolytic analogy to our system involves the ring closure of chlorohydrins to epoxides, where the relative rate constants (k_5) for the compounds IVa, IVb, and IVc are about 250:20:1.



In small rings, this *gem*-dialkyl effect is usually ascribed to compression of the internal angle of the ring which leads to expansion of the external angle and the relief of steric strain between R and R'.

A similar technique to that described here can obviously be used for determining the rates of ring closure of γ -, δ -, and ϵ -peroxyalkyl radicals to oxetans, furans, and pyrans, respectively; this work is being continued.

Acknowledgment. We wish to thank the International Tin Research Council for the award of a Research Fellowship to B.M.

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The Linear $[(\text{Ph}_3\text{P})_2\text{N}]^+$ Cation. Crystal Structure of $[(\text{Ph}_3\text{P})_2\text{N}]^+[\text{V}(\text{CO})_6]^-$

Sir:

The remarkable ability of the bis(triphenylphosphine)-iminium cation to stabilize air-sensitive anions has led to its extensive use as a convenient counterion in metal carbonyl chemistry^{1,2} and has also facilitated the structure determinations of a large number of anionic metal carbonyls such as $[\text{M}_2(\text{CO})_{10}]^{2-}$ ($\text{M} = \text{Mo}, \text{W}$),³ $[\text{Cr}_2(\text{CO})_{10}]^-$,⁴ $[\text{M}_2\text{Ni}_3(\text{CO})_{16}]^{2-}$ ($\text{M} = \text{Mo}, \text{W}$),⁵ $[\text{HFe}(\text{CO})_4]^-$,⁶ $[\text{Fe}(\text{C}-\text{O})_4\text{CN}]^-$,⁷ $[\text{Fe}_2(\text{CO})_8]^{2-}$,⁸ $[\text{FeCo}(\text{CO})_8]^-$,⁸ $[\text{Co}(\text{CO})_4]^-$,⁹ and $[\text{HW}_2(\text{CO})_{10}]^-$.¹⁰ In all of these compounds, the $[(\text{Ph}_3\text{P})_2\text{N}]^+$ cation was found to have a bent geometry (as does the isoelectronic carbon analog $(\text{Ph}_3\text{P})_2\text{C}^{11}$) with rather constant molecular parameters: P-N-P bond angles in the range 134.6-141.8° and P-N bond lengths in the range 1.570-1.586 Å. We wish to report in this communication the existence of the hitherto unknown and unsuspected linear form of the $[(\text{Ph}_3\text{P})_2\text{N}]^+$ cation.¹²

$[(\text{Ph}_3\text{P})_2\text{N}]^+[\text{V}(\text{CO})_6]^-$ was prepared by treating commercially available $[\text{Na}(\text{diglyme})_2]^+[\text{V}(\text{CO})_6]^-$ with $[(\text{Ph}_3\text{P})_2\text{N}]^+\text{Cl}^-$.^{1a} Recrystallization *via* vapor diffusion¹³ in methylene chloride-diethyl ether afforded pale yellow, light-sensitive crystals of the compound. Crystal data: space group $R\bar{3}$ (rhombohedral); $a = 9.761$ (6) Å, $\alpha = 91.93$ (3)°, $V = 928.3$ Å³, $Z = 1$, $\rho(\text{obsd}) = 1.32$ g cm⁻³, $\rho(\text{calcd}) = 1.35$ g cm⁻³. Data were collected on an automated Nonius CAD-3 diffractometer with Mo $K\alpha$ radiation up to a 2θ maximum of 45°. The structure was solved by heavy atom methods and refined to a final R factor of 7.5% for 595 independent nonzero reflections.¹⁴

The $[\text{V}(\text{CO})_6]^-$ anion (Figure 1) is situated on a site of symmetry $\bar{3}(S_6)$ and is octahedral within experimental error. The six carbonyl groups are symmetry related to each other in such a way that there is one independent V-C distance (1.931 (9) Å), one independent C-O distance (1.146 (11) Å), and two independent C-V-C angles (90.8 (4) and 89.2 (4)°). Unlike the neutral paramagnetic $\text{V}(\text{CO})_6$, which is believed to exhibit some Jahn-Teller distortion,¹⁵ the geometry of $[\text{V}(\text{CO})_6]^-$ has long been suspected to be

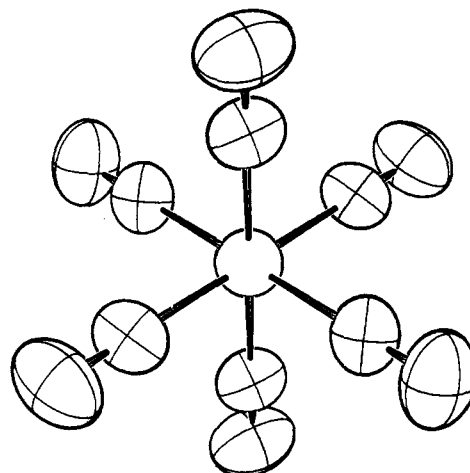


Figure 1. Geometry of $[\text{V}(\text{CO})_6]^-$, as seen down the crystallographic S_6 axis.

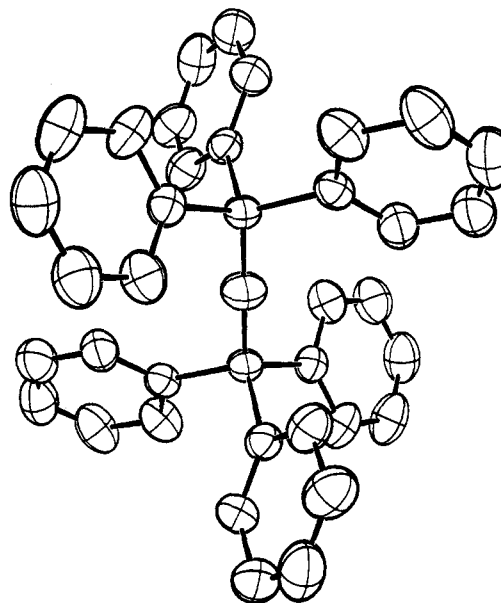
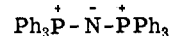


Figure 2. Geometry of the $[(\text{Ph}_3\text{P})_2\text{N}]^+$ cation in $[(\text{Ph}_3\text{P})_2\text{N}]^+[\text{V}(\text{CO})_6]^-$.

octahedral,¹⁶ but this has not been definitively proven until now. The assumption of octahedral symmetry was made in analogy to the known geometries of the isoelectronic $\text{Cr}(\text{CO})_6^{17}$ and $[\text{Mn}(\text{CO})_6]^+$.¹⁸

The $[(\text{Ph}_3\text{P})_2\text{N}]^+$ cation (Figure 2) is also situated on a site of symmetry $\bar{3}(S_6)$, with the P-N-P axis coincident with the S_6 axis. In this arrangement, the P-N-P angle is crystallographically required to be linear. Additionally, each phenyl group is symmetry related to the others, as are the two phosphorus atoms. Molecular parameters in the cation are P-N = 1.539 (2) Å, P-C = 1.788 (6) Å, N-P-C = 110.2 (2)°, and C-P-C = 108.8 (3)°.

The unanticipated linearity of the $[(\text{Ph}_3\text{P})_2\text{N}]^+$ ion in this compound¹⁹ raises some interesting questions concerning the bonding in the cation. Recent ESCA studies on $[(\text{Ph}_3\text{P})_2\text{N}]^+[\text{V}(\text{CO})_6]^-$ and other $[(\text{Ph}_3\text{P})_2\text{N}]^+$ salts²⁰ have been interpreted in favor of formalism I for the cation, implying the presence of two lone pairs on nitrogen.²¹ The bent form of the cation can be rationalized in terms of sp^2 hybridization on nitrogen, with one lone pair in an sp^2 hybrid and the other in a p orbital, the latter being free to en-



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