greater MO coefficient through dominant interaction between the low-lying LUMO of oxyallyl and high-lying HOMO of an olefin has to produce the product-determining zwitterion **5** leading to the regioisomer which was actually obtained as only a minor component, or even did not form. In addition, judging from the MO coefficients of the oxyallyl **10**, the reaction had been expected to exhibit only poor selectivity. This was not the case, however.

Thus the [3 + 4] cycloaddition involving 2-oxyallyls is occurring in a concerted manner, and both the primary and secondary frontier MO interactions are equally important in determining the regioselectivity. On the other hand, the preferred orientation of the [3 + 2] cycloaddition is the one that affords the maximal stabilization of the zwitterionic intermediate.

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Electron Nuclear Double Resonance Study of Some Nitroxide Radicals Produced in Spin Trapping

Sir:

A variety of chemicals which are capable of producing stable nitroxide radicals upon reaction with short-lived free radicals have been used as "spin traps" in the spin trapping technique.[1] Among them nitroso and nitrone compounds have been frequently used because both the spin traps and the resulting nitroxide radicals (spin adducts) are quite stable. As discussed in detail by Janzen,[1] the essential difference is that of the ESR pattern of their adducts. When one uses the nitroso compound, the adding radical is bonded directly to the nitroxide function of the spin adduct and its ESR spectrum shows hyperfine structure (hfs) from the adding group. In the nitrone case the adding radical is at the β position from the nitroxide function and shows no substantial hfs in the ESR spectrum. Phenyl-*N-tert*-butyl nitrone (PBN) is a typical nitrone spin trap and it produces stable spin adducts according to reaction 1. The spin adduct gives a characteristic ESR spectrum which consists of six lines due to one nitrogen and one β-hydrogen nucleus. Though the magnitude of the β-hydrogen hfs is the key index[2] of identifying trapped radical, the identification has not been always conclusive because the hfs of the adding group is missing. However the stability of both the spin trap and the spin adduct sometimes makes the use of a nitrone more feasible than the use of a nitroso spin trap for the investigation of reaction intermediates. In the present study the detailed obser-

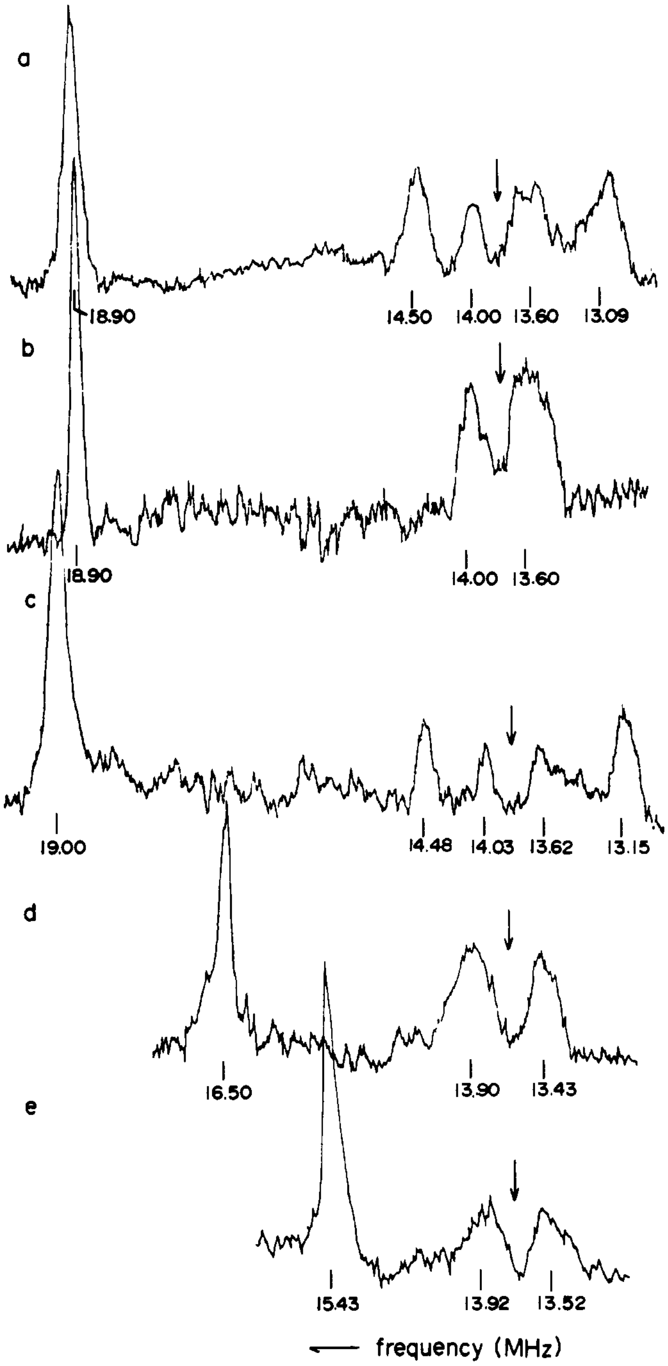
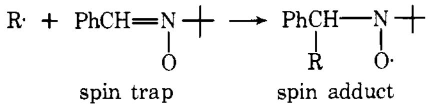


Figure 1. ENDOR spectra of spin adducts: (a) methyl adduct in toluene; (b) trideuteriomethyl adduct in toluene; (c) *n*-butyl adduct in 2-propanol; (d) phenyl adduct in toluene; (e) benzoyloxy adduct in toluene. Vertical arrow shows the free proton frequency. Note the disappearance of the signals at 14.50 and 13.09 MHz in b.


$$\mathrm{R\cdot + PhCH{=}\underset{\displaystyle O}{\underset{|}{N}}{-}C(CH_3)_3 \longrightarrow Ph\underset{\displaystyle R}{\underset{|}{C}}H{-}\underset{\displaystyle O\cdot}{\underset{|}{N}}{-}C(CH_3)_3} \qquad (1)$$

spin trap   spin adduct

Table I. Hfscs Observed in ENDOR Spectra of Spin Adducts in MHz

Adduct	β H	R[a]	Phenyl and *tert*-butyl
Methyl	10.20	1.41	0.40
Trideuteriomethyl	10.20		0.40
n-Butyl	10.36	1.33	0.41
Phenyl	5.67	0.47	0.47
Benzoyloxy	3.42	0.40	0.40

[a] R denotes adding group.

vation of the hfs of the adding group by means of electron nuclear double resonance (ENDOR) technique makes the assignment more accurate because of the characteristic ENDOR pattern for each spin adduct.

The addition of organolithium and Grignard compounds to the nitrone followed by air oxidation produces the corresponding nitroxide in high yield. This method has been sometimes used for the identification of spin adducts.[2] Most of the adducts used for the present study were synthesized by this method.

The ENDOR spectrum of methyl adduct of PBN in toluene shows three kinds of hfs from the hydrogens in it (Figure 1a). The largest hfs (10.20 MHz) is due to the β hydrogen which can be seen in the ESR spectrum. The hfs of the two groups of hydrogens which are hidden in the line width of the ESR spectrum appear in this spectrum around free proton frequency region. The trideuteriomethyl adduct shows only one hfs other than the β hydrogen which is shown in Figure 1b. The hfs of 1.41 MHz which appears in the spectrum of the methyl adduct completely disappears. This is because the frequency region of the present ENDOR spectrometer does not cover the resonance frequency of deuteron. The disappearance of the hfs in Figure 1b shows that 1.41 MHz hfs in Figure 1a can be ascribed to the methyl group of the adduct. The smallest hfs should be assigned to residual protons in phenyl and *tert*-butyl groups. The *n*-butyl adduct also produces a similar ENDOR pattern as methyl adduct (Figure 1c). The splitting of 1.33 MHz can be assigned to methylene hydrogens in the *n*-butyl group by analogy to the methyl adduct.

The phenyl adduct shows a rather different ENDOR pattern (Figure 1d). Around the free proton frequency region only one hfs is observed. The result is consistent with the fact that the hfs of the protons in the phenyl group in the methyl and *n*-butyl adducts is small. The small hfs of the phenyl protons in the phenyl adduct causes the overlap of the splitting from 19 hydrogens in phenyl and *tert*-butyl groups. The fact that the line width of the ESR spectra of alkyl spin adducts is usually wider than that of phenyl adduct is explainable by the larger hfs of the alkyl group.

Figure 1e shows the ENDOR spectrum in the thermal decomposition of benzoyl peroxide in the presence of PBN in toluene. The spectrum pattern around free proton frequency is similar to that of the phenyl adduct. However, the β hydrogen splitting is considerably smaller (3.42 MHz). This adduct has already been assigned to benzoyloxy adduct by Janzen and Blackburn.[3] The result of ENDOR does not contradict this assignment because the benzoyloxy group does not have significant hfs. The observed hfs of spin adducts determined by ENDOR are listed in Table I.

Actual radical reaction systems do not usually give a high enough concentration of spin adduct for the observation of a ENDOR spectrum. Presently the ENDOR technique is applicable only to limited examples of spin trapping systems because of the relatively low concentrations of spin adducts. Improvements in the experimental conditions of ENDOR are now in progress.

Throughout the observation of ENDOR spectra the optimum signal appeared at relatively higher temperatures ($-30\sim-50$ °C) for protons which have smaller hfs and at lower temperatures ($-60\sim-90$ °C) for β hydrogens. The external magnetic field was fixed at the central peak of the ESR spectrum during the sweep of the radiofrequency.

Details of the ENDOR spectrometer used are described elsewhere.[4]

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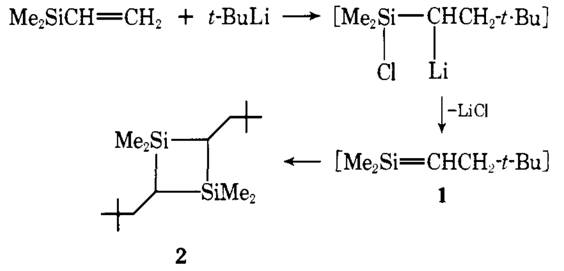
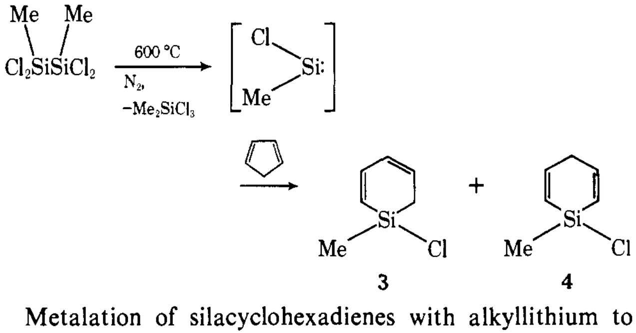
Evidence for the Generation and Trapping of a Silabenzene

Sir:

Jones and Lim[1] have recently reported that the addition of *tert*-butyllithium to vinyldimethylchlorosilane resulted in products presumably arising from silene (**1**) intermediacy. Formation of dimer **2**, coupled with the inability to trap the intermediate α-halosilyl carbanion with excess trimethylchlorosilane, strongly suggests the formation of **1** in this reaction.



We now wish to report a similar reaction which appears to proceed through the intermediacy of a long-awaited silabenzene.[2] Silacyclohexadienes are most conveniently prepared through the reaction of silylenes (the silicon analogues of carbenes) and cyclopentadiene with concomitant ring expansion.[3] Thus copyrolysis at ~600 °C (N_2 flow) of 1,1,2,2-tetrachloro-1,2-dimethyldisilane[4] and cyclopentadiene produced a mixture of 1-chloro-1-methyl-1-silacyclohexa-2,4-diene (**3**, major isomer) and the nonconjugated isomer (**4**, minor)[5] which could be separated by preparative GC.



Metalation of silacyclohexadienes with alkyllithium to produce the corresponding pentadienyl anion is a well-established process.[6] Thus we thought to generate a silabenzene