Journal of Organometallic Chemistry, 107 (1976) 15—22

CHEMISTRY OF ORGANOSILICON COMPOUNDS

LXXXV *. AN ELECTRON SPIN RESONANCE STUDY ON PHOTO-INDUCED RADICALS OF (*p*-NITROBENZYL)TRIMETHYLSILANE AND RELATED NITROBENZENE DERIVATIVES

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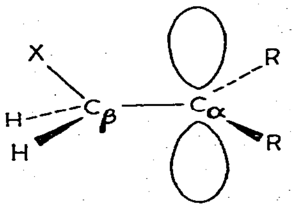
(Received August 15th, 1975)

Summary

Seven *p*-substituted phenyl alkoxynitroxides [p-Y-$C_6H_4N(O^\bullet)OCH(CH_3)$-$OC_2H_5$; Y = H, CH_3, C_2H_5, $SiMe_3$, CH_2SiMe_3, $CH_2CH_2SiMe_3$, and CH_2OCH_3] were generated from the corresponding nitrobenzenes by photolysis in diethyl ether and hyperfine coupling constants have been assigned. The *p*-(trimethylsilyl)methyl derivative gave the largest nitrogen and the smallest benzylic proton coupling constants which indicates the importance of σ—π conjugation between the (C—Si) σ-bonding orbital and the π-molecular orbital of the nitroxide radical. Results of similar anion radicals were compared and discussed.

Introduction

The conformational preference of β-substituted ethyl radicals of the type X—C—C$^\bullet$ as determined from the hyperfine coupling constants (hfcc) in their ESR spectra are subjects which have been discussed extensively in recent years. A number of studies on the Group IVB metal-substituted ethyl and other related radicals [1] have indicated that the conformation favored at low temperature is I in which X eclipses the half-filled *p*-orbital (X = SiR_3, GeR_3, and SnR_3).



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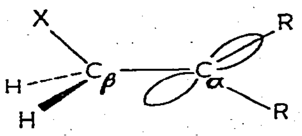

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* Presented in part at the 30th Annual Meeting of the Chemical Society of Japan, Higashi-Osaka, April 1974: Abstract, III, 1688; for part LXXXIV see ref. 2.

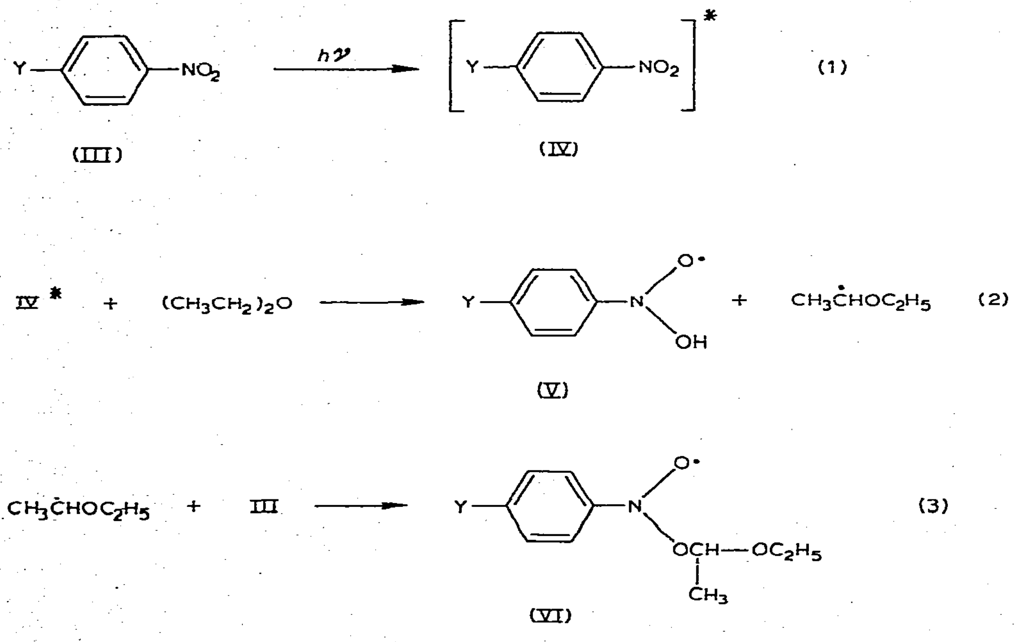
Kawamura and Kochi [1d] have discussed the origin of such conformational preference in terms of both σ—π and homo(p—d) conjugations. Although their estimation of the relative importance in both interactions has since been criticised [3], their interpretation seems to be reasonable [4] and the relative importance of both interactions should be variable. In this connection, it can be noted that σ(C—M)—π conjugation (M = Si, Ge, and Sn) involves the intramolecular electron transfer from the occupied C—M σ-bonding orbital to the singly-occupied molecular orbital (SOMO), while in homo(p—d) conjugation, the electron transfer is from the SOMO to the σ^*(C—M) or the vacant d(M) orbital [5,6].

We now report the ESR spectra of substituted phenyl alkoxynitroxides including the p-(trimethylsilyl)methyl derivative in an attempt to shed light on this problem.

Results

Generally, substituted nitrobenzenes can generate the corresponding nitroxides in ethereal solvents under irradiation with ultraviolet light as shown in Scheme 1 [7].

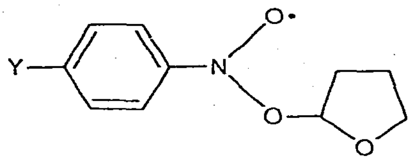
SCHEME 1



(VIa) Y = H; (VIb) Y = $SiMe_3$; (VIc) Y = CH_3; (VId) Y = CH_2CH_3; (VIe) Y = CH_2SiMe_3;
(VIf) Y = $CH_2CH_2SiMe_3$; (VIg) Y = CH_2OCH_3.

The observed ESR signal was first assigned to V [7], but was later established to be VI [8]. Following this method the ESR spectra of unsubstituted and six p-substituted phenyl alkoxynitroxides, produced by the photolysis of the corresponding nitrobenzenes in diethyl ether, were taken at temperatures in the range —60 to ≈25°C. Figures 1—3 represent ESR spectra of VIb, VIe, VIg as typical examples.

The spectrum of the radical VIb shows a 1 : 1 : 1 triplet due to ^{14}N (a_N = 14.6 G) which splits further into two sets of 1 : 2 : 1 triplets due to *ortho* (a_2 = 3.04 G) and *meta* (a_3 = 1.03 G) protons of the phenyl ring. These split further into a small doublet due to an alkoxy proton. The spectra of the radicals containing a *p*-(substituted-methyl) group were complicated by a further splitting due to the benzylic protons, but could be analyzed rather easily with the aid of the known assignments of unsubstituted nitroxide VIIa. Thus, hfcc values of VIa and VIb are almost the same as those of VIIa [7] and VIIb [8d], respectively, except for the hfcc due to alkoxy H, although a_N of VIb was smaller than that of VIIb [8d] *.



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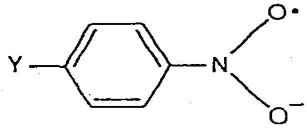

(VIII)*

The hfcc values and assignments of VI at —50°C are tabulated in Table 1. Although the ESR signals were observed at relatively high temperatures, they became contaminated by signals from secondary paramagnetic species at the elevated temperature. In all cases the values of hfcc showed no detectable variations with temperature changes.

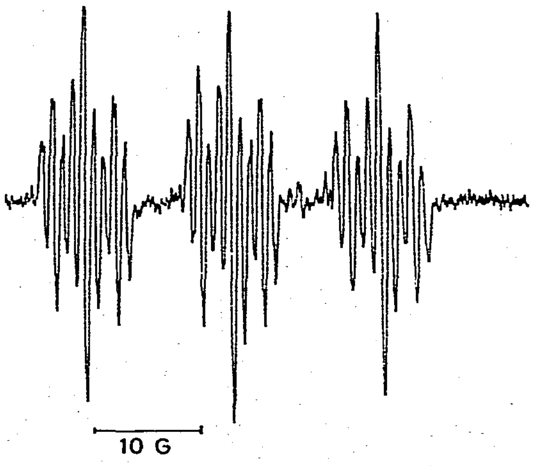

Fig. 1. ESR spectrum of the photo-induced radical of (p-nitrophenyl)trimethylsilane in diethyl ether at —50°C.

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* Throughout VI, VII, and VIII, the same suffix stands for the same substituent.

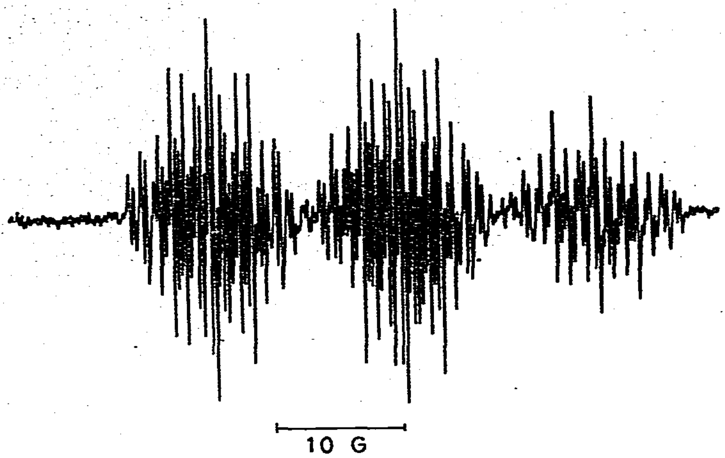


Fig. 2. ESR spectrum of the photo-induced radical of (*p*-nitrobenzyl)trimethylsilane in diethyl ether at —50°C.

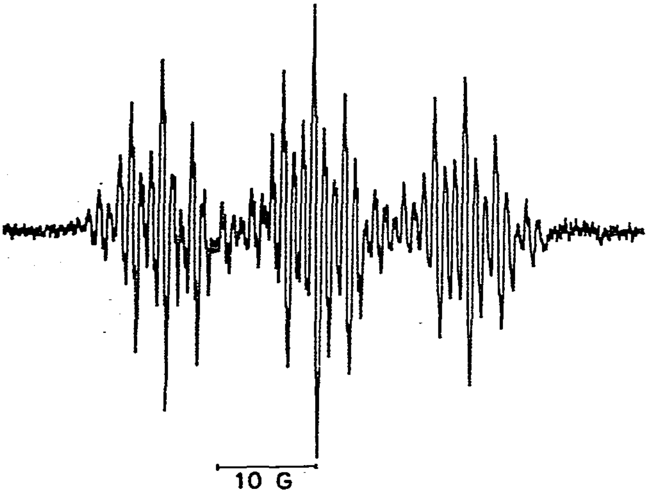


Fig. 3. ESR spectrum of the photo-induced radical of (*p*-methoxymethyl)nitrobenzene in diethyl ether at —50°C.

TABLE 1

HFCC VALUES (G) FOR *p*-SUBSTITUTED PHENYL ALKOXY NITROXIDES (VI) AT —50°C

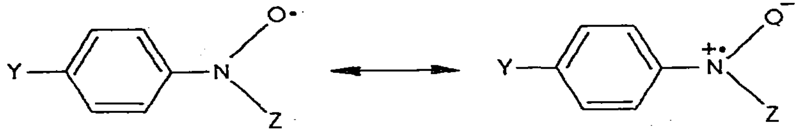
Compound	Y	a_N	a_2	a_3	a_β [a]	$a_{H'}$ [b]	Other [a]
VIa	H	15.0	3.10	1.04		0.20	3.10 [c]
VIb	Me_3Si	14.6	3.04	1.03		0.23	
VIc	H_3C	15.3	3.05	1.05	3.40	0.29	
VId	CH_3CH_2	15.3	3.04	1.03	2.46	0.29	
VIe	Me_3SiCH_2	15.6	3.00	1.00	2.10	0.28	
VIf	$Me_3SiCH_2CH_2$	15.3	3.03	1.05	2.50	0.14	
VIg	CH_3OCH_2	15.0	3.05	1.08	3.05	0.29	

[a] Benzylic hydrogen. [b] Alkoxy hydrogen. [c] *Para* hydrogen in the phenyl ring.

Discussions

Coupling constants for nitrogen atoms (a_N)

At first our attention is focused on the values of the nitrogen coupling constants. Substituent effects on a_N of phenyl nitroxides have been well discussed by Janzen [8b,9], who reported that the values of a_N for *para-* and *meta-*substituted VII and VIII decrease with electron-withdrawing substituents and increase with electron-donating substituents as shown by the linear correlation of a_N values with Hammett's σ constants. The success of such correlations is attributed to a normal substituent effect on the relative contribution of the two main resonance forms for the nitroxide function. This substituent effect indirectly influences the spin density on the nitrogen atom and hence on the values of a_N.



The a_N values of VI can be interpreted in conformity with this idea. The smallest a_N found in the *p*-trimethylsilyl derivative VIb may be ascribed to the electron-withdrawing nature of the trimethylsilyl group due to $(p\text{—}d)\pi$ conjugation [8d] which has been well discussed in studies on a number of silyl-substituted aromatic anion radicals [10] and on other types of radicals [11].

The introduction of *p*-methyl, *p*-ethyl, and *p*-(trimethylsilyl)ethyl groups to the benzene ring increases the values of a_N by approximately 0.3 G from the unsubstituted compound according to their electron-donating nature. The electron-donating effect of methyl may be reduced by the substitution of a methyl hydrogen with a methoxy group. Thus, the value of a_N of VIg was found to be reduced to the same value as of VIa.

It should be noted that the largest a_N value was found for the *p*-(trimethylsilyl)methyl derivative VIe. Therefore, the (trimethylsilyl)methyl group is the most electron-donating substituent among those examined. Since the strongly electron-donating nature of (trimethylsilyl)methyl groups can be explained only in terms of $(\sigma\text{—}\pi)$ conjugation [12], these facts indicate that the enhanced $\sigma\text{—}\pi$-conjugation between the C—Si σ-bonding orbital and the SOMO of phenyl alkoxynitroxide is more important than homo$(p\text{—}d)\pi$ conjugation.

Coupling constants for aromatic (a_n) and benzylic protons (a_β)

The values of hfcc for aromatic protons, a_2 and a_3, of VI are around 3.05 and 1.05 G, respectively. The constancy of a_2 and a_3 for *p*-substituted phenyl alkoxynitroxides indicates that the spin densities at the 2 and 3 positions are insensitive to the character of the substituent. These data suggest at the same time that the spin density at the 4 position ($\rho_{C(4)}$) is also essentially constant. The point of interest for conformational information is the angular dependence of the benzylic proton coupling constants (a_β). The values of a_β can be expressed in eq. 4 where B_0 and B are constants and θ is the angle between the C(4)—C—H plane and the axis of the p_z orbital on the trigonal carbon atom as shown in IX [13].

$$a_\beta = \rho_{C(4)}(B_0 + B\cos^2\theta) \tag{4}$$

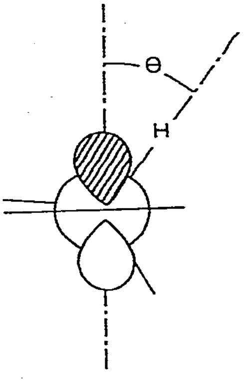
Since the substituted methyl groups in the nitroxides are not rigidly oriented, a_β is actually a time-averaged quantity as stated in eq. 5. Evaluation of the average quantity in eq. 5 was done quantum mechanically by Stone and Maki [14] under the assumption of a simple two fold sinusoidal barrier height (V_0). In

$$a_\beta = \rho_{C(4)}(B_0 + B\langle\cos^2\theta\rangle) \qquad (5)$$

order to simplify the comparison of β-proton coupling constants within a series of related radicals, McKinney and Geske [15] defined R as an extent of the conformational preference (eq. 6). This expression is applicable when $\rho_{C(4)}$ is

$$R = a_\beta / a_{\beta\text{-}CH_3} = 2\langle\cos^2\theta\rangle \qquad (6)$$

constant and when B_0 is nearly zero in eq. 4. Both assumptions are reasonable for the isotropic system discussed here. Following the treatment of Stone and Maki, we can expect that the R is smaller than unity, and decreases with increasing V_0 for the preferred conformation of I, and that R is larger than unity, and increases with increasing V_0 for II. The R values observed for VI are tabulated in Table 2 together with the corresponding values for VIII in acetonitrile.



(IX)

TABLE 2

R VALUES OF NITROXIDE RADICALS [a]

Y (≡GCH$_2$)	*R* (VI)	*R* (VIII) [b]
H$_3$C	1.00	1.00 [c]
CH$_3$CH$_2$	0.72	0.74 [c]
Me$_3$SiCH$_2$CH$_2$	0.74	0.73 [d]
Me$_3$SiCH$_2$	0.62	0.69 [e]
CH$_3$OCH$_2$	0.90	0.62 [f]

[a] Defined by eq. 6. [b] Obtained by electrolysis in acetonitrile. [c] Ref. 23. [d] This work: $a_N = 10.9$, $a_2 = 3.38$, $a_3 = 1.10$, and $a_\beta = 2.92$ G. [e] Ref. 17. [f] This work: $a_N = 10.1$, $a_2 = 3.36$, $a_3 = 1.11$, and $a_\beta = 2.47$ G. The value of $a_\beta = 2.57$ G in DMSO was also reported by Danen et al. [24].

The fact that all of the values of a_β for methylene protons were smaller than those for methyl protons of VIc indicates that the G—CH$_2$ (=Y) bond eclipses the p_π orbital in the preferred conformation. One of the important factors which favor the conformation I over the conformation II is the steric repulsion between a G group and *ortho* hydrogen atoms, because I is preferred in VId and VIg while the bisected conformations are preferred in propyl [1a] and β-alkoxyethyl [1a,16] radicals. The values of a_β increase in the order of (trimethylsilyl)methyl $<$ ethyl $\approx$ (trimethylsilyl)ethyl $<$ methoxymethyl $<$ methyl. This order is roughly in accord with the decreasing order of the magnitude of a_N in the series. Thus, in the G—CH$_2$—C(sp^2) system the trimethylsilyl group stabilizes the preferred conformation I as a consequence of the enhanced σ(C—G)—π conjugation more than methyl or (trimethylsilyl)methyl groups.

Recently Kawamura, Kono, Akao, and Yonezawa [17] observed the ESR spectrum of the anion radical derived from (p-nitrobenzyl)trimethylsilane which similarly showed a small hfcc for benzylic hydrogens. Table 2 also lists R values of anion radicals of nitrobenzenes VIII and there is a good parallelism between R values of VI and VIII except for p-methoxymethyl derivatives. The reason why the R value of VIII is so small is not clear at this moment.

Recent ab initio molecular orbital calculations [18] have indicated that the barriers to rotation about the C$_\alpha$—C$_\beta$ bond in several ethyl radicals with β substituents, (I, II: R = H), which are taken as approximately the values of E(I) — E(II), are considerably smaller than those in the corresponding cations. However, we can conclude that σ—π conjugation in radicals can determine the preferred conformation of substituted ethyl radicals, although the magnitude of the rotation barrier is significantly smaller than that observed in the corresponding cations.

Experimental

Materials. Nitrobenzene, o-nitrotoluene, and p-nitroethylbenzene were commercially available. (p-Nitrophenyl)trimethylsilane [19], (p-nitrobenzyl)trimethylsilane [20], (p-nitrophenylethyl)trimethylsilane [20], and p-nitrobenzyl methyl ether [21] were prepared by the known procedures. All the samples were purified by fractional distillation before use.

ESR measurements. Photolysis. Solutions of the substituted nitrobenzenes in diethyl ether were degassed by freeze-thaw cycles. Photolysis of a solution contained in a Pyrex tube (ϕ = 3 mm) was carried out in the cavity of a Varian E-12 ESR spectrometer. Radiation was effected by an Ushio super-high pressure 500 W mercury lamp.

Electrolysis. The nitrobenzene anion radicals were generated electrochemically in acetonitrile using tetraethylammonium perchlorate as a supporting electrolyte. The spectrometer was operated at X-band frequencies and the magnet field sweep was calibrated in the way using Fremy's salt (a_N = 13.07 G) [22].

Acknowledgement

The authors are grateful to Professor J.K. Kochi for discussion and to Dr. T. Kawamura for making his results available prior to publication. They also thank Toshiba Silicone Co., Ltd., for a gift of chlorosilanes. Samples VIb, VId, and VIf were prepared by Mr. T. Murao.

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