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SPIN TRAPPING IDENTIFICATION OF RADICAL INTERMEDIATES DURING PHOTOLYSIS OF ORGANOSELENIUM COMPOUNDS

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Summary

Radical intermediates formed during irradiation of selenides and diselenides have been trapped by using nitrosodurene. ESR spectra show that, depending upon the organoselenium compound used, the radical species results from the cleavage of either a C—Se bond or a Se—Se bond. The hyperfine coupling with ^{77}Se has been detected for RSeN(O)R′, and indicates a low spin density on the selenium.

Introduction

Photochemical reactions of selenium-containing compounds play an important part in modern organic synthesis [1,2,3] and a review of this subject has recently appeared [4]. In the present work, radical species have been generated by UV irradiation of selenides and diselenides, and trapped by reaction with nitrosodurene. The observation of hyperfine interaction with ^{77}Se constitutes the first evidence for a selenylnitroxide radical.

Experimental

The use of nitroso compounds for spin-trapping experiments was described by Terabe et al. [5]. We prepared nitrosodurene by reaction of tetramethylphenylmercury acetate with ethylnitrite. Solutions of organoselenium compounds in chloroform or benzene were irradiated in the presence of nitrosodurene using a 500 W Osram lamp. The ESR spectra were recorded on a Varian E-9 spectrometer (100 kHz field modulation, *X*-band). Experiments were performed in a flat quartz cell, the temperature of which was controlled usually at —50°C.

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Results

Nitrosodurene was found to react under UV irradiation with various organoselenium compounds to form spin adducts, the ESR parameters of which are shown in Table 1. The data clearly correspond to two types of radicals: the first type is characterized by a high *g* value and a large ^{14}N-coupling constant, while the second has *g* and $a(^{14}N)$ values similar to those reported for alkylnitroxides. One of the advantages of spin trapping with nitrosodurene is that it gives rise to a nitroxide compound for which the original radical is fixed α to the nitrogen atom, so that the identification of the adduct is much simplified. Deuteration of the methylene group in dibenzyldiselenide leads to the suppression of a triplet pattern (1/2/1), which is replaced by a partially resolved structure showing the presence of five transitions. There is no doubt that this spectrum is due to the trapping of the $PhCH_2$ (or $PhCD_2$) radical. Irradiation of diphenylsele-

TABLE 1

ESR PARAMETERS FOR NITROXIDES FORMED DURING PHOTOLYSIS OF ORGANOSELENIUM COMPOUNDS IN THE PRESENCE OF NITROSODURENE

Organoselenium compound	Nitroxide	*g*	$a(^{14}N)$ (Gauss)	$a(^{77}Se)$ (Gauss)	Additional constant (Gausss)
$PhCH_2SeSeCH_2Ph$	$PhCH_2N(O)C_{10}H_{13}$	2.006	14.1		$a^H_{CH_2} = 8.1$
$PhCD_2SeSeCD_2Ph$	$PhCD_2N(O)C_{10}H_{13}$	2.006	14.1		$a^D_{CD_2} = 1.2$
PhSeSePh	$PhSeN(O)C_{10}H_{13}$	2.0098	18.8	8.7	
$O_2NPhSeSePhNO_2$	$O_2NPhSeN(O)C_{10}H_{13}$	2.0075	16.5	7.8	
PhSePh	$PhSeN(O)C_{10}H_{13}$	2.0099	18.9		

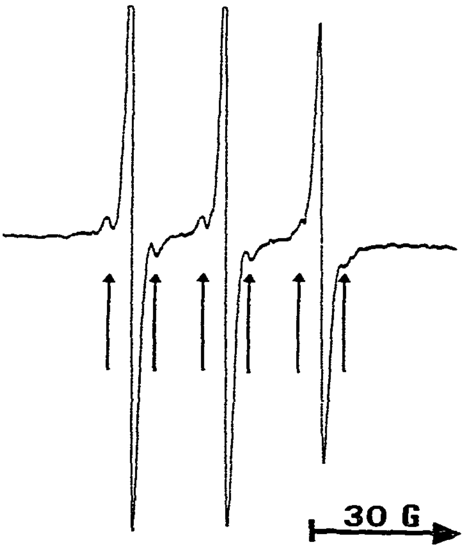


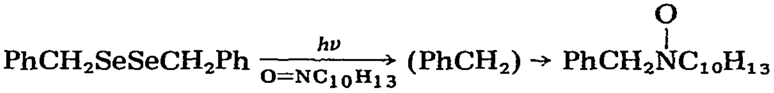
Fig. 1. ESR spectrum obtained by photolysis of diphenyldiselenide in presence of nitrosodurene. (The arrows show the signals due to ^{77}Se.)

nide leads to a nitroxide radical for which the high *g* value clearly shows that PhSe has been trapped. The corresponding spectrum is partially blurred by an additional species. At lower temperature (−60° C), it is possible to stabilize this latter radical and to identify it as $PhN(O)C_{10}H_{13}$ (*g* value and proton hyperfine structure). These results are in good accord with a Se—C bond scission. When the spectrum obtained with diphenyldiselenide is recorded at higher amplification two satellite signals are detected for each ^{14}N transition (Fig. 1). The intensities of these signals are in good accord with the natural abundance of ^{77}Se (7.5%) and with its spin number ($I = 1/2$) [6]. As the *g* and $a(^{14}N)$ values are equal to the parameters found for the spin adduct produced with PhSePh, we have identified the corresponding nitroxide as $PhSeN(O)C_{10}H_{13}$. A similar spectrum is obtained with $(o\text{-}NO_2C_6H_4Se)_2$.

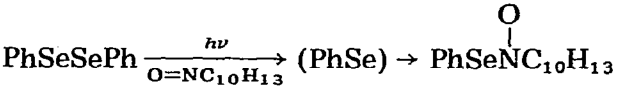
Discussion

Photolysis of diselenides

Although the photochemistry of diselenides has been intensively investigated, mechanistic conclusions have been reached only from chemical observations. Chu et al. [1] have proposed that both Se—Se and Se—C scissions occur in benzyldiselenide photolysis. Brown et al. [2] have considered that for that same compound the cleavage of the Se—Se bond is more important than that of the Se—C bond, and a similar result has been obtained for Et_2Se_2 [3]. From our results it appears that diphenyldiselenide and dibenzyldiselenide when subjected to UV irradiation in the presence of nitrosodurene, probably react by different mechanisms.



$$PhCH_2SeSeCH_2Ph \xrightarrow[O=NC_{10}H_{13}]{h\nu} (PhCH_2) \rightarrow PhCH_2\overset{O}{\overset{|}{N}}C_{10}H_{13} \qquad (1)$$



$$PhSeSePh \xrightarrow[O=NC_{10}H_{13}]{h\nu} (PhSe) \rightarrow PhSe\overset{O}{\overset{|}{N}}C_{10}H_{13} \qquad (2)$$

Equation 1 involves C—Se scission and a subsequent formation of $SeSeCH_2Ph$, which, unfortunately, we could not detect. Equation 2 implies Se—Se cleavage, but we cannot completely rule out the following origin for PhSe.

$$PhSeSePh \rightarrow Ph + PhSeSe \rightarrow PhSe + Se \qquad (3)$$

However the absence of $PhN(O)C_{10}H_{13}$ makes the sequence shown in eq. 3 very improbable.

Structure of the selenylnitroxide radical

The spectrum obtained for $PhSeN(O)C_{10}H_{13}$ (Fig. 1) is characterized by a high *g* value, which indicates some spin delocalization onto the selenium atom (spin orbit coupling constant for selenium = 1688 cm^{-1}). Two mechanisms could be involved in this delocalization, i) $^{14}Np_\pi$—$^{77}Sep_\pi$ conjugation giving rise to spin density in a ^{77}Se *s* orbital (inner shell polarization), ii) polarization of the N—Se σ orbital. As the sign of the former contribution is unknown, it is difficult to discuss the low spin density on the selenium. The coupling constant

TABLE 2

ESR PARAMETERS FOR SOME SULPHUR-CONTAINING NITROXIDES

Radical	g	^{14}N	^{33}S	Ref.
$PhSN(O)C_{10}H_{13}$	2.0065	16.0		5
$(SO)_2NO^{2-}$	2.0054	13.0	1.25	8
$PhS(O_2)N(O)Ph$		11.6		9
$BuSN(O)C(Bu)_3$	2.0071	18.5		10

for a ^{77}Se 4s electron has been evaluated as 20 120 MHz by using the $|\psi(O)|^2$ values calculated from Herman-Skillman orbitals [7] and this constant implies a ^{77}Se spin density of ~0.001 for $PhSeN(O)C_{10}H_{13}$. This value is quite similar to the sulphur spin density found for $[(SO_3)_2NO]^{2-}$, ($a(^{33}S) = 1.25$ G [8], atomic parameter for $^{33}S = 3\,400$ MHz [7]).

The electron withdrawing effect of R on the constant $a(^{14}N)$ for $RN(O)C_{10}H_{13}$ is likely to be the cause of the decrease of this coupling on going from $R = C_6H_5Se$ to $R = o\text{-}NO_2C_6H_5Se$. The electron attracting group increases the nitrogen participation in the $(NO)\pi$ orbital and thus decreases the nitrogen contribution in the $(NO)\pi^*$ orbital which containing the unpaired electron. The diminution of the $^{14}N\text{-}2p_z$ spin density involves a smaller spin polarization of the ^{77}Se s electrons and, as shown in Table 1, the resulting $a(^{77}Se)$ constant decreases. This electron withdrawing effect also seems consistent with the variations in the ^{14}N coupling constants for $PhSO_2N(O)R$ and $PhSeN(O)R$ (Table 2). This effect is probably far more important for RSO_2 than for RSe [11], and a lower $a(^{14}N)$ constant is expected for the sulfonyl compound than is found for the selenyl compound. However, it must be remembered that this discussion is based on the assumption that the nitroxide radical remains perfectly planar; a slight distortion of this structure implies the appearance of some nitrogen s-character for the orbital containing the unpaired electron and a low s-spin density of ~0.01 involves an $a(^{14}N)$ coupling constant of ~6 G.

Acknowledgment

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References

1 J.Y.C. Chu, D.G. Marsh and W.H.H. Günther, J. Amer. Chem. Soc., 97 (1975) 4905.
2 D.H. Brown, R.J. Cross and D. Millington, J. Chem. Soc. Dalton, (1977) 159.
3 R.J. Cross and D. Millington, J. Chem. Soc. Chem. Commun., (1975) 455.
4 J. Martens and K. Praefcke, J. Organometal. Chem., 198 (1980) 321.
5 S. Terabe, K. Kuruma and R. Konaka, J. Chem. Soc. Perkin II, (1973) 1252.
6 For recent E.S.R. observation of ^{77}Se see, for example, R. Franzi, M. Geoffroy and N. Leray, J. Organometal. Chem., 193 (1980) 315.
7 J.R. Morton and K.F. Preston, J. Magn. Reson., 30 (1978) 577.
8 J.J. Windle and A.K. Wiersema, J. Chem. Phys., 39 (1963) 1139.
9 Th.A.J. Wajer, H.W. Geluk, J.B.F. Engberts and T.J. De Boer, Rec. Trav. Chim. Pays-Bas, 89 (1970) 696.
10 I.H. Leaver, G.C. Ramsay and E. Suzuki, Aust. J. Chem., 22 (1969) 1891.
11 C.G. Swain and E.C. Lupton, J. Amer. Chem. Soc., 90 (1968) 4328.