Tetrahedron Letters, Vol.32, No.27, pp 3179-3182, 1991
Printed in Great Britain

0040-4039/91 \$3.00 + .00
Pergamon Press plc

REACTIONS OF TRIARYL SELENONIUM SALTS AND DIARYL SELENOXIDES WITH PHENYLLITHIUM: FIRST DETECTION OF TETRAARYL SELENURANES [10-SE-4(C4)] BY ^{77}SE, ^{1}H, AND ^{13}C NMR

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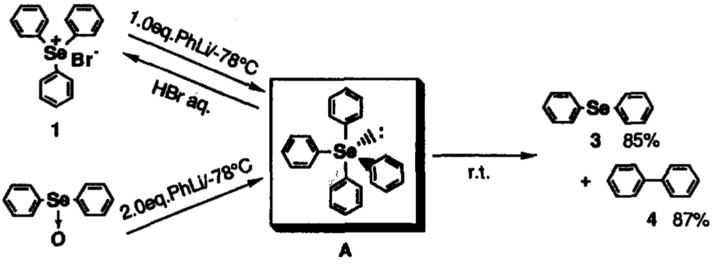
Abstract: First evidence for the formation of tetraaryl selenuranes was presented in the reaction of triphenyl selenonium salt or 2,2'-biphenylylene phenyl selenonium salt with phenyllithium by ^{77}Se, ^{1}H, ^{13}C and CH-COSY NMR studies at low temperature. These selenuranes were also formed in the reactions of the corresponding selenoxides with two equivalents of phenyllithium.

The reactions of triaryl selenonium (and sulfonium) salts with organometallic reagents have long been believed to proceed via an initial formation of σ-selenurane (or σ-sulfurane).[1] Several stable σ-selenuranes bearing electronegative ligands such as oxygen or halogen atoms have been reported.[2] No evidence for the formation of σ-selenuranes (σ-sulfuranes) bound to four carbon ligands has been presented before though Hellwinkel claimed the isolation of bis(2,2'-biphenylylene)selenurane.[3] Recently, we found that diaryl selenoxides (and sulfoxides) undergo facile ligand exchange and coupling reactions on treatment with organolithium reagents affording finally diaryl selenide and biaryl via possible formation of σ-selenuranes (σ-sulfuranes) bearing four carbon ligands.[4] We reinvestigated the reactions of triaryl selenonium salts and selenoxides with phenyllithium (PhLi). Here we report the first crucial evidence for formation of tetraaryl selenuranes [10-Se-4(C4)] in the reactions of triaryl selenonium salts and diaryl selenoxides with PhLi in tetrahydrofuran (THF) solution by low temperature ^{77}Se, ^{1}H, ^{13}C-NMR, and CH-COSY NMR experiments.[5]

When an equimolar amount of PhLi (1.02 M in cyclohexane/ether solution) was added to a suspension of selenonium salt **1** in anhydrous THF under N_2 at -78 °C, the mixture became yellowish homogeneous solution. Subsequently, the mixture was treated with 1N aqueous HBr solution to give the recovered selenonium salt **1** quantitatively. Similarly, diphenyl selenoxide (**2**) was treated with two equivalent of PhLi, then with 1N aqueous HBr solution at -78 °C afforded the same selenonium salt **1**. Further treatment of **1** and **2** with PhLi led to the ligand coupling products, diphenyl selenide (**3**) and biphenyl (**4**) in 85 and 87% yields respectively at elevating temperature as shown in Scheme 1 suggesting that a stable intermediate like σ-selenurane A should be formed at low temperature. In order to confirm the formation of this σ-selenurane as a discrete intermediate, ^{77}Se, ^{1}H, and ^{13}C NMR spectra of the reaction mixture were measured at -100 °C. Figure 1 shows the ^{77}Se NMR spectrum[6] of the 1:1 mixture of **1** and PhLi in anhydrous THF solution at -100 °C. The ^{77}Se NMR of the selenonium bromide **1** could not be obtained in THF due to its insolubility in THF (the chemical shift of **1** is



Scheme 1

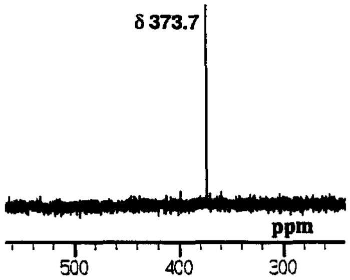


Figure 1. ^{77}Se NMR (51 MHz, THF) of A at -100 °C

observed at 483.7 ppm in $CDCl_3$ at 22 °C). Careful treatment of selenonium salt 1 in anhydrous THF solution with an equimolar amount of PhLi at -100 °C, a new ^{77}Se NMR signal appeared at 373.7 ppm and no other signals were observed at all in the range between 1600 to -200 ppm[6] at -100 °C. By elevating the temperature of the solution to 22 °C, the ^{77}Se NMR signal of A shifted significantly to the downfield as a new singlet peak at 414.2 ppm which was consistent with that of diphenyl selenide (3) at 22 °C (the chemical shift of 3 observed at 401.6 ppm in THF at -100 °C). Furthermore, on similar treatment of selenoxide 2 with PhLi in THF at -100 °C, the ^{77}Se NMR signal appeared initially at 827.0 ppm shifted also to 373.7 ppm corresponding to that of the intermediate A which was shifted again to 414.2 ppm as a sharp singlet suggesting the formation of diphenyl selenide (3). In order to confirm further the formation of selenurane A, temperature dependent ^{1}H and ^{13}C NMR experiments were carried out in anhydrous THF-d_8. The spectra are shown in Figure 2.

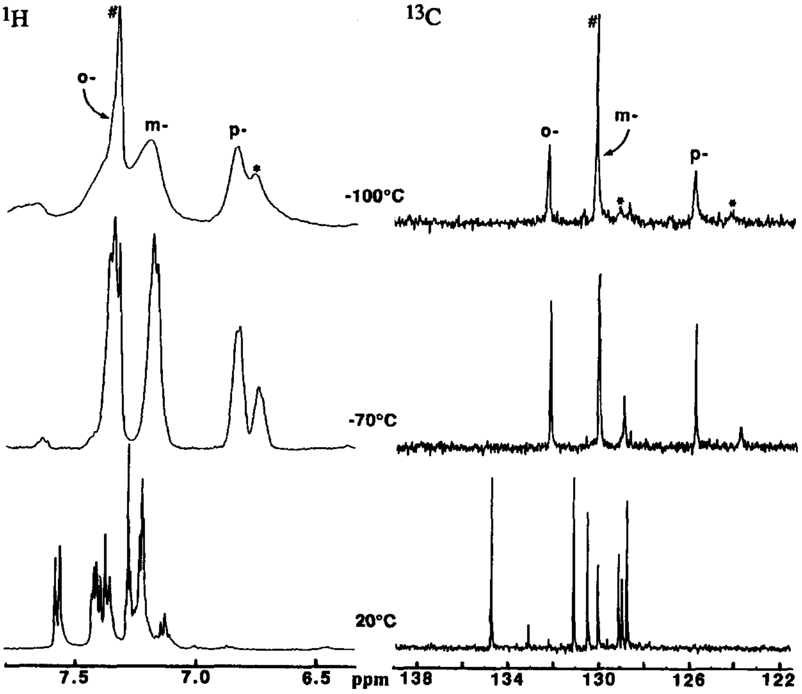


Figure 2. Temperature dependent ^{1}H and ^{13}C NMR spectra of A in THF-d_8
The spectra at 20 °C indicate the mixture of ligand coupling products 3 and 4.
(# : benzene; *: phenyl lithium)

Table 1. ^{1}H and ^{13}C NMR chemical shifts of A

nuclei	chemical shift, δ			
(-100 °C, THF-d_8)	*para*	*meta*	*ortho*	*ipso*
^{1}H$^{a)}$	6.87 (t, J=7.0Hz)	7.16 (t, J=7.0Hz)	7.33 (d, J=7.0Hz)	
^{13}C	125.8	130.0	132.2	not detect$^{b)}$

a) Coupling constants were caluculated by resolution enhanced spectra at -70 °C

b) Probably, ipso carbon has a long spin-lattice relaxation (T1). We observed the same phenomena in the case of tetraphenyl tellurane and bis(2,2'-biphenylylene)tellurane.

New sets of the ^{1}H and ^{13}C NMR chemical shifts due to the phenyl group were assigned to the corresponding ortho, meta, and para-hydrogens and carbons as summarized in Table 1. The coupling constants of each proton could be determined by taking its resolution enhanced spectrum. Furthermore, the ^{1}H and ^{13}C NMR chemical shifts of A were determined by the cross peaks observed in the two dimensional CH shift correlation (CH-COSY) NMR spectrum. Both ^{1}H and ^{13}C spectra of the reaction mixture at 22 °C were consistent with that of nearly 1:1 mixture of **3** and **4**. These NMR experiments at low temperature and the products analysis indicate that both triphenyl selenonium salt and diphenyl selenoxide react with PhLi to give an identical tetraphenyl selenurane as a discrete intermediate at low temperature which on warming to room temperature decomposes to diphenyl selenide and biphenyl. Interestingly, the four phenyl groups in the selenurane formed should have an equivalent state suggesting that the pseudorotation takes place rapidly even under low temperature as -100 °C. This result agrees well with the behavior of the known hypervalent compounds of group 16 elements, such as tetraphenyl tellurane and bis(2,2'-biphenylylene)tellurane.[7] Furthermore, we also tried to detect 2,2'-biphenylylene diphenyl selenurane (**B**) of which structure should be fixed by a five membered ring and hence be more stable than the selenurane **A**. Upon similar treatment of selenonium salt (**5**) and selenoxide (**6**) with PhLi and after work-up, phenyl o-terphenyl selenide (**7**) was obtained in 80% yield, while in the presence of HMPA (hexamethylphosphoramide) was obtained dibenzoselenophene (**8**) and biphenyl (**4**) together with **7** in 38, 40, 17% yields respectively (Scheme 2). In order to detect the σ-selenurane **B**, the ^{77}Se NMR[6] was taken under -100 °C in anhydrous THF. A sharp singlet peak due to the selenurane **B** was also observed at 397.1 ppm (Figure 4) which is nearly identical with that of **A** but different chemical shifts from either that of the starting compounds or that of the corresponding coupling products **7** (390.0 ppm) and **8** (445.9 ppm) at -100 °C.

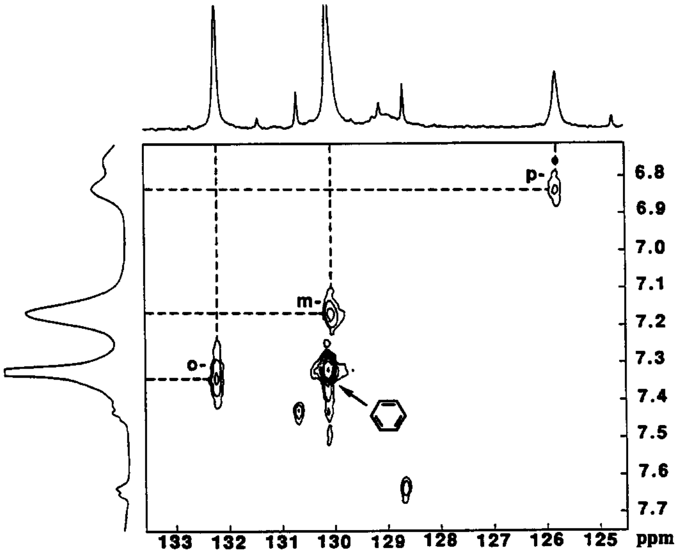
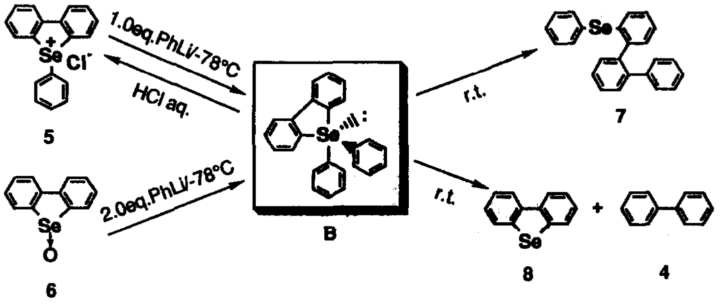


Figure 3. CH-COSY spectrum of A at -100 °C



Scheme 2

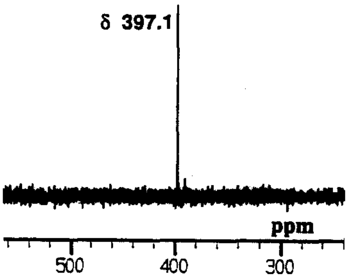


Figure 4. ^{77}Se NMR (51 MHz, THF) of **B** at -100 °C

Consequently, the present studies on the temperature dependent NMR experiments provide the first and discrete evidence for formation of tetraaryl selenuranes in the reactions of triaryl selenonium salts and diaryl selenoxides with PhLi.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research on Priority Area No. 02247101 from the Ministry of Education, Science and Culture of Japanese Government.

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4 The results have been submitted. Furukawa, N. *Heteroatom Chemistry*; Block, E. Ed.; Verlag: New York, 1990; pp. 165.

5 ^{77}Se NMR (51 MHz) spectra were obtained with JEOL EX 270. ^{1}H (400 MHz), ^{13}C (100 MHz), and CH-COSY NMR spectra were obtained with Bruker MSL 400.

6 ^{77}Se NMR chemical shifts of each selenium compounds are the relative values to that of dimethyl selenide at 22 °C.

7 No ^{13}C NMR data of tetraaryl chalcogen compounds were reported. We synthesized tetraphenyl tellurane and bis(2,2'-biphenylylene)tellurane and measured their ^{13}C NMR shifts which indicated that tellurane also undergoes rapid pseudorotation at low temperature.

(Received in Japan 25 February 1991)