Rotational Conformers of Furan and Thiophene Thioaldehyde Anion Radicals

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The radical anions of the four isomeric furan and thiophene thioaldehydes have been obtained by photolysis, in an alkaline medium, of the corresponding thiols in the presence of di-*tert*-butyl peroxide. The same reaction also yields the four corresponding aldehyde radical anions, starting from the appropriate alcohols. The ESR spectra show that in most cases the two rotational conformers (*E* and *Z*) are present at the equilibrium. By means of appropriate methyl-substituted derivatives it has been possible to assign the structure of the two conformers. In the case of the 2-furan and 2-thiophene aldehyde anion radicals it has been also found that the conformational preference is the same as that exhibited by the corresponding molecules.

Introduction

Recently, some of us reported[1-3] that the elusive radical anion of thiobenzaldehyde can be obtained under conditions suited for ESR investigation by the photolysis of alkaline solutions (EtOK/EtOH) of benzylthiol: the yield of the radical is enhanced in the presence of di-*tert*-butyl peroxide (*t*-BuOOBu-*t*). This procedure affords a relatively high steady-state concentration of the radical anion of thiobenzaldehyde according to the equation 1:

$$\mathrm{PhCH_2SH} \xrightarrow{\mathrm{EtOK/EtOH}} \mathrm{PhCH_2S^-} \qquad (1)$$

$$t\text{-BuOOBu-}t \xrightarrow{h\nu} 2t\text{-Bu}\dot{\mathrm{O}}$$

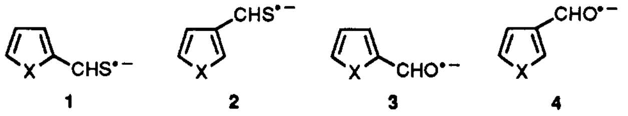
$$t\text{-Bu}\dot{\mathrm{O}} + \mathrm{PhCH_2S^-} \rightarrow t\text{-BuOH} + \mathrm{Ph\dot{C}HS^-}$$

With benzyl alcohol, the same procedure affords the radical anion of benzaldehyde.[1] This method is therefore particularly valuable for the production of thioaldehyde and aldehyde radical anions that cannot be obtained by conventional methods of reduction (chemical or electrochemical) of the parent aldehyde. This, apparently, is both a milder and a more efficient technique for the production of radicals suited for ESR investigation. In the case of the $\mathrm{Ph\dot{C}HS^-}$ anion radical the ESR spectrum displays different hyperfine splitting constants (a_H) for both the two ortho and the two meta hydrogens, as had been previously reported for the benzaldehyde radical anion.[4] This indicates that the rotation about the Ph–$\mathrm{\dot{C}HX^-}$ bond (X = S or O) is restricted. Rotational conformers of Ar–$\mathrm{\dot{C}HX^-}$ radical anions should be therefore detectable when the aryl group (Ar) lacks an axis of symmetry as, for instance, when Ar is a furan or a thiophen ring. This phenomenon has been observed previously[5,6] with a few aldehyde radical anions containing the thiophene moiety but it has not been observed for the aldehyde radical anions containing the furan group because the techniques for reducing the parent molecule do not yield such radicals.

In the present work, we had generated all the eight isomeric thioaldehyde and aldehyde radical anions of thiophene and furan. These radicals have been identified, and the nature of their rotational conformers has been investigated using ESR spectroscopy.

Results and Discussion

Well-resolved ESR spectra of radicals 1–4 were obtained at low temperature, by means of the reaction 1, starting from the appropriate thiols or alcohols. All the anion radicals of the thioaldehydes (**1a**, **1b**, **2a**, and **2b**) display a spectrum due to the superimposition of traces corresponding to a pair of closely related radicals that we identified as the *E* and *Z* rotational conformers. The corresponding-ESR parameters are collected in Table I, and a typical example of experimental and computer simulated spectra is shown in Figure 1 for the case of **1a**. In the temperature range (−70 to +25 °C) where these radicals are detectable never an exchange between the two conformers has been observed, an indication[7] that the interconversion barrier is, most likely, higher than 9–10 kcal $\mathrm{mol^{-1}}$.



1 2 3 4

a, X = O
b, X = S

Also, the radical anions of the aldehydes containing the furan moiety (**3a** and **4a**), that so far had never been reported, were easily obtained with the present method. The spectra of the aldehyde radical anions containing the thiophene ring (**3b** and **4b**) were found almost equal to those previously obtained[5] by reduction of the corresponding aldehydes. Whereas the 3-furan and 3-thiophene aldehyde radical anions (**4a** and **4b**) display only one of the two possible rotational conformers, both conformers were observed in the analogous thioaldehyde radicals **2a** and **2b**.

In all these derivatives the hyperfine splitting constants (a_H) were assigned by analogy with those of other radical

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(7) For radicals with a_H values differing by about 1–1.5 G, the rate constants that allow us to observe the exchange broadening are in the range 5×10^5–10^6 $\mathrm{s^{-1}}$, which corresponds to ΔG^* values between 9.3 and 9.7 kcal $\mathrm{mol^{-1}}$ at room temperature. See, for instance: Casarini, D.; Lunazzi, L.; Placucci, G.; Venturini, A. *J. Org. Chem.* **1991**, *56*, 414.

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Table I. Hyperfine Splitting Constants (a_H in G) and g-Factors of the Conformers of Radicals 1-4 (a, X = O; b, X = S). See Text for the Assignment of the *E* and *Z* Structures

compd (% *Z*, *E*)	H-2	H-3	H-4	H-5	CHO	CHS	g-factor	t (°C)
1a (*Z* = 60)		7.0	1.30	5.80		11.95	2.0055	−30
(*E* = 40)		6.70	1.00	5.00		12.85	2.0054	
1b (*Z* = 85)		6.75	1.50	6.25		11.68	2.0056	−5
(*E* = 15)		7.00	1.37	5.25		12.12	2.0057	
2a (*E* = 70)	7.87		1.15	0.62		14.72	2.0053_5	−55
(*Z* = 30)	7.78		1.10	0.44		14.45	2.0056	
2b (*E* = 80)	7.00		1.37	0.75		14.00	2.0060	−5
(*Z* = 20)	6.90		1.57	0.70		13.90	2.0060_5	
3a (*Z* = 80)		7.53	1.48	6.49	11.92		2.0037	−45
(*E* = 20)		7.20	1.22	5.44	13.00		2.0037_5	
3b (*Z* = 85)		7.12	1.62	7.12	10.37		2.0042_5	−40
(*E* = 15)		7.20	1.58	6.30	11.15		2.0044	
4a (*E* = 100)	9.25		1.15	0.65	14.85		2.0037	−55
4b (*E* = 100)	8.40		1.25	0.75	13.35		2.0040	+15

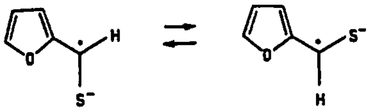
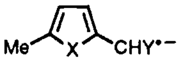


Figure 1. Experimental (top) and computer-simulated (bottom) ESR spectrum of the radical anion of furan 2-thioaldehyde (**1a**) showing the presence of a pair of rotational conformers in a 60:40 ratio. The a_H splittings and g-factors used for the simulation are reported in Table I; the line width is 0.2 G.

Table II. Hyperfine Splitting Constants (G) of 5-Methyl-Substituted Radicals 5a–5d

compd (% *Z*, *E*)	H-3	H-4	Me-5	CHO	CHS	t (°C)
5a (*Z* = 60)	7.25	1.10	6.00		11.80	−30
(*E* = 40)	7.25	1.00	5.40		12.60	
5b (*Z* = 85)	7.10	1.50	6.50		11.50	−40
(*E* = 15)	7.10	1.50	6.00		12.25	
5c (*Z* = 70)	7.87	1.37	6.50	11.60		−50
(*E* = 30)	7.60	1.00	5.37	12.90		
5d (*Z* = 85)	7.75	1.75	7.45	10.37		−40
(*E* = 15)	7.62	1.62	6.50	11.05		

anions containing the thiophene or the furan group.[6,8-12] Whereas in the case of the 3-substituted radicals the a_H values are sufficiently different as to allow one to confidently assign the splittings on the basis of such an analogy, this is not the case for the 2-furan and 2-thiophene derivatives. In the latter radicals (**1a**, **1b**, **3a**, and **3b**), in fact, the a_H splittings at positions 3 and 5 are too close to each other for an unambiguous attribution.[5] To help with the assignment, the radical anions **5a–5d**, which contain a methyl group at position 5, were examined.



5

a, X = O, Y = S
b, X = S, Y = S
c, X = O, Y = O
d, X = S, Y = O

Usually, a methyl group in an aromatic radical anion yields an a_{Me} splitting similar to the one due to the hydrogen it has replaced and, in addition, does not greatly modify the a_H values of other positions of the aromatic ring. Thus, methyl substitution is quite reliable for the assignment of a_H aromatic splittings when their relative differences are about 0.5–1.0 G or larger: this is the case for positions 3 and 5 in **1a**, **1b**, **3a**, and **3b**. As can be

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observed in Table II, the introduction of a methyl group at position 5 does not significantly affect the conformer ratio; thus, the conclusion was reached that in both conformers a larger splitting occurs at position 3 with respect to position 5 (obviously in the major conformer of **3b** the assignment was not required being $a_{H3} = a_{H5} = 7.12$ G).

From the data collected in Table I it can be also observed that the ring splittings of the radicals having the CHO moiety in position 2 (i.e., **3a** and **3b**) are larger than the corresponding splittings of the analogous thioaldehyde radicals (**1a** and **1b**, respectively). The same relationship holds for the ring splittings of the 3-furan and 3-thiophene aldehyde radicals (**4a** and **4b**) with respect to those of the corresponding derivatives (**2a** and **2b**). This observation indicates that the unpaired electron is delocalized upon the aromatic ring at a larger extent in the case of $ArCHO^{\bullet-}$ than in $ArCHS^{\bullet-}$. This feature had been already reported for other carbonyl, with respect to the corresponding thiocarbonyl anion radicals.[1,13,14] As a consequence, one would also expect a reduction of the a_{CHO} with respect to the a_{CHS} splitting, due to the lower spin density available on the HCO^-, with respect to the CHS^- moiety. Such an effect actually occurs in the case of thiophene derivatives (compare, for instance, the values of **3b** and **4b** with those of **1b** and **2b**) but not for the furan-containing radicals, where the a_{CHO} splittings of **1a** and **2a** are almost equal to the a_{CHS} splittings of **3a** and **4a**. To understand this point it has to be considered that an increasing of the a_{CHS} with respect to the a_{CHO} splitting should occur only on the assumption that the importance of the resonance forms of type A and B is the same for both X = O and X = S:

$$\underset{A}{Ar\dot{C}H{-}X^-} \leftrightarrow \underset{B}{ArCH^-{-}\dot{X}}$$

Such an assumption, however, does not seem to hold since it has been reported that in the sulfurated analogues of semidiones[15] the resonance structures having the unpaired electron on the sulfur atom (i.e., type B for X = S) are more important than those having the unpaired electron on the carbon atom (type A, X = S). Therefore, although the spin density on the CHS moiety is larger than on the CHO moiety, this does not necessarily entail an increasing of the experimental a_{CHS} splitting. For, the greater importance of form B when X is S than when X is O might drain upon the sulfur atom (and away from –CH–) the excess of spin density available to the CHS moiety. As a consequence, the a_{CHS} splitting increases, most likely, much less than expected in the thiophene and does not increase at all in the furan anion radicals investigated. This seems to be another manifestation of the lower conjugating ability of furan with respect to thiophene. This finding thus supports the suggestion of Russell et al.[15] that forms of type B are more important in thiocarbonyl than in carbonyl radical anions.

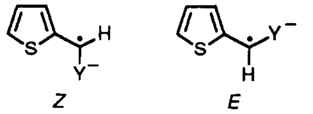
Table III. Hyperfine Splitting Constants of 3-Methyl-Substituted Radicals 6a–6d

compd (%*Z*, *E*)	Me-3	H-4	H-5	CHO	CHS	*t* (°C)
6a (*Z* = 75)	6.75	1.37	6.37		11.75	–30
(*E* = 25)	6.65	1.25	5.25		12.90	
6b (*Z* = 100	6.00	1.50	6.40		11.25	+25
6c (*Z* = 100)	7.12	1.50	6.90	11.87		–50
6d (*Z* = 100)	6.37	1.62	7.25	10.00		–35

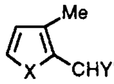
Table IV. Hyperfine Splitting Constants of Ketyl Radicals 7a–7c

compd (%*Z*, *E*)	H-3	H-4	H-5	others	*t* (°C)
7a (*Z* = 80)	7.65	1.50	6.37	10.75 (3 H)	–50
(*E* = 20)	7.50	1.25	5.75	12.25 (3 H)	
7b (*Z* = 70)	7.70	1.37	6.55	13.12 (1 H)	–60
(*E* = 30)	7.50	1.25	5.80	14.30 (1 H)	
7c (*E* = 100)	7.37	1.30	6.25		–50

For what concerns the assignment of the *E* and *Z* structures an attempt was made to solve the problem experimentally, rather than on the basis of theoretical assumptions, as it had been done in the past[5] for radical **3b**. For such a purpose the radical anions containing a methyl group in position 3 were obtained. In **6** the steric hindrance due to the methyl group should favor conformer *Z* with respect to *E*, as the repulsive interactions are expected to be much less important between a methyl and a hydrogen (*Z* conformer) than between a methyl and a sulfur (or oxygen) atom (*E* conformer). In **6b**, **6c**, and **6d** only one of the two possible conformers was detected to which, therefore, the *Z* structure could be assigned (Table III). The hfs constants of the hydrogens of the thioaldehyde or aldehyde moieties were much closer, respectively, to those of the major than to those of the minor conformers of the nonmethylated radicals **1b**, **3a**, and **3b**. It was thus possible to correlate the structure of the single *Z* conformer of **6b**, **6c**, and **6d** to that of the major conformer of **1b**, **3a**, and **3b**, hence, to assign to the latter the *Z* structure. In the case of **6a** both conformers could still be observed, but the ratio between the more stable and the less stable conformer is larger than in the nonmethylated radical **1a** (3 vs 1.5, see Tables III and I, respectively). The splittings of the major and minor conformers in **6a** match, respectively, those of the major and minor conformers of **1a**: a further support to the assignment of structures *Z* and *E*, respectively, to the more and to the less stable species.



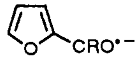
1b, Y = S
3b, Y = O



6

a, X = O, Y = S
b, X = S, Y = S
c, X = O, Y = O
d, X = S, Y = O

An independent check of this attribution was also obtained from the investigation of the ketyl radical anions **7**. Owing to the larger dimension of the alkyl group R with respect to the hydrogen atom, the proportion of the *Z* with respect to the *E* conformer should be *lower* in **7** than in **3a** (where R = H). The repulsive interactions of the R group with the hydrogen atom in position 3 of the furan



7

a, R = Me
b, R = Et
c, R = *t*-Bu

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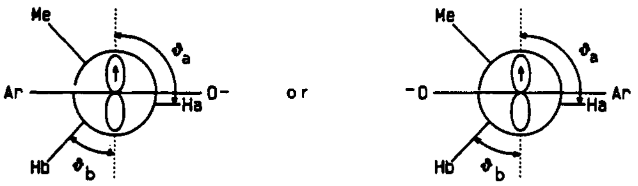
Scheme I. Newman Projections along the CH_2–$CO^{\bullet -}$ Bond for Radical Anion 7b (Ar = 2-Furan)



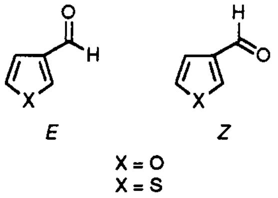
ring are in fact expected to be larger in *Z* than in *E*.[16] In the case of **7a** (R = Me), however, the modification of the conformer ratio with respect to **3a** (R = H) was too small for a reliable assignment. On the other hand, in **7c** (R = *t*-Bu) the change was so dramatic as to yield only one conformer. Most likely the one observed is conformer *E*, but we felt that the perturbations induced by the *tert*-butyl group on the a_H values are too large to allow a correlation to be made between these values (Table IV) and those of one of the two conformers of **3a** (Table I). For R = Et (**7b**), on the other hand, the ring splittings of both the major and minor conformer (Table IV) turn out to be very close, respectively, to those of the major and minor conformer of **3a**, thus allowing one to make an obvious correlation. In **7b**, the major conformer is present in lower amount (70%) than in **3a** (80%), and this confirms that in **3a** the more stable conformer has the *Z* structure: had the *E* conformer been the more stable one, we should have observed an *increasing* and not a *decreasing* of its proportion in radical **7b**.

It is also worth outlining that in *both* conformers of **7b** the CH_2 hydrogens of the ethyl group display only *one* a_H splitting, the other being too small to be observed. This clearly proves that, in addition to the Ar–CO rotation (Ar = 2-furan), also the OC–CH_2Me rotation is restricted. Furthermore, the observation of a single methylene splitting requires that one of these hydrogens (Ha) has the corresponding C–H bond nearly orthogonal to the direction of the p_z orbital of the carbonyl carbon bearing the unpaired electron (see Scheme I).

The McConnell relationship ($a_H = A + B \cos^2 \vartheta$, where $A \approx 0$)[17] indicates in fact that for $\vartheta_a \cong 90°$ the corresponding a_{Ha} is negligible. The value of a_{Hb}, corresponding to a $\vartheta_b \cong 30°$, is obviously different from zero, its value depending on the term B[17] which, in turn, depends on the spin density localized on the carbonyl carbon.

From the above reported observation it is conceivable to conclude that in the radical anions of furan and thiophene, having the CHO or CHS moiety in position 2 (**1a**, **1b**, **3a**, and **3b**), the *Z* conformer is always preferred. The ratio between the *Z* and the *E* conformation depends on the chemical structure at an extent that is difficult to rationalize. These radicals exhibit the same conformational preferences as the corresponding molecules furan 2-aldehyde and thiophene 2-aldehyde[16,18,19] (obviously such a comparison cannot be made for the thioaldehyde derivatives as the corresponding molecules do not exist). The conclusion reached here agrees with the assignment proposed by Hudson and Lewis[5] for radical **3b**, on the basis of some theoretical assumptions. The claim of these authors that the preferred conformation of radical **3b** is opposite to that of the corresponding molecule (thiophene 2-aldehyde) is due to an incorrect assignment of the conformation of the molecule itself.[5,20] At that time the studies that have reversed[5,18,19,21–23] the original incorrect assignment[20] were not yet available.

The analogy between the conformation of these radicals and that of the corresponding molecules might suggest that the same parallel behavior occurs also in the case of thiophene and furan derivatives substituted in position 3. The furan 3-aldehyde and the thiophene 3-aldehyde prefer the conformation *E*.[19,24–28]



Therefore, we are tempted to propose that also in the corresponding radical anions **4a** and **4b** the structure *E* should correspond to that of the more stable rotational conformer. Finally, since we have shown that the thioaldehyde radical anions **1a** and **1b** have the same conformational preferences as the corresponding aldehyde radical anions (**3a** and **3b**), it does not appear unreasonable to propose that in the thioaldehyde radicals **2a** and **2b** the structure *E* corresponds to that of the preferred rotational conformer.

Experimental Section

Materials. The thiols used to produce the thioaldehyde radical anions were prepared by reaction of the corresponding alcohols with thiourea[29] except the precursor of **1a**, which is commercially available. The thiols giving the thioaldehyde radical anions **2b** and **6a** have been reported.[30,31] The remaining thiols that yield, respectively, the thioaldehyde radical anions listed below were identified as follows.

Precursor of **1b**: ^1H NMR ($CDCl_3$) δ 2.0 (t, 1 H, SH), 4.0 (d, 2 H, CH_2), 6.9–7.4 (m, 3 H, Ar). Anal. Calcd for $C_5H_6S_2$: C, 46.11; H, 4.64. Found: C, 46.3; H, 4.8. Precursor of **2a**: ^1H NMR ($CDCl_3$) δ 1.8 (t, 1 H, SH), 3.6 (d, 2 H, CH_2), 6.4 (s, 1 H, Ar), 7.4 (m, 2 H, Ar). Anal. Calcd for C_5H_6OS: C, 52.60; H, 5.30. Found: C, 52.2; H, 5.0. Precursor of **5a**: ^1H NMR ($CDCl_3$) δ 2.3 (s, 3 H, CH_3), 3.4 (s br, 1 H, SH), 4.0 (s, 2 H, CH_2), 5.8 (d, 1 H, Ar), 6.15 (d, 1 H, Ar). Anal. Calcd for C_6H_6OS: C, 41.39; H, 3.47. Found: C, 41.5; H, 3.0. Precursor of **5b**: ^1H NMR ($CDCl_3$) δ 2.45 (s, 3 H, CH_3), 4.20 (s, 2 H, CH_2), 4.65 (s, br, 1 H, SH), 6.6 (d, 1 H, Ar), 6.85 (d, 1 H, Ar). Anal. Calcd for $C_6H_8S_2$: C, 50.00; H, 5.60. Found: C, 50.3; H, 5.2. Precursor of **6b**: ^1H NMR ($CDCl_3$) δ 1.9

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(t, 1 H, SH), 2.2 (s, 3 H, CH_3), 3.8 (d, 2 H, CH_2), 6.8 (d, 1 H, Ar), 7.1 (d, 1 H, Ar). Anal. Calcd for $C_6H_8S_2$: C, 50.00; H, 5.60. Found: C, 50.4; H, 5.8.

The alcohols used to obtain the thiols and to produce the corresponding aldehyde anion radicals were obtained by reduction of the analogous aldehydes with $NaBH_4$, except in the case of the commercially available precursors of **3a**, **3b**, **4a**, and **4b**. The alcohols that yield the following radical anions have been reported: **5c**,[32] **6c**,[31] **7a**,[33] **7b**,[34] and **7c**.[34] The remaining alcohols that yield, respectively, the radical anions listed below were identified as follows.

Precursor of **5d**: ^{1}H NMR ($CDCl_3$) 1.8 (s br, 1 H, OH), 2.5 (s, 3 H, CH_3), 4.8 (d, 2 H, CH_2), 6.65 (d, 1 H, Ar), 6.8 (d, 1 H, Ar). Anal. Calcd for C_6H_8OS: C, 56.24; H, 6.29. Found: C, 56.9; H, 5.8. Precursor of **6d**: ^{1}H NMR ($CDCl_3$) 1.6 (s br, 1 H, OH), 2.2 (s, 3 H, CH_3), 4.8 (d, 2 H, CH_2), 6.8 (d, 1 H, Ar), 7.15 (d, 1 H, Ar). Anal. Calcd for C_6H_8OS: C, 56.24; H, 6.29. Found: C, 56.4; H, 6.5.

Spectral Measurements. The ESR spectra were obtained by photolyzing the samples in the cavity of the spectrometer (Varian E 3) by means of a carefully focused 500-W high-pressure Hg lamp. The samples were prepared by dissolving the thiols or the alcohols in EtOK/EtOH with the addition of *t*-BuOOBu-*t*. The solutions were degassed and sealed in vacuo. The temperatures reported in the tables are those where the best signal to noise ratio was achieved; the conformer ratio, however, did not change in an appreciable manner within the temperature range examined.

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Extremely Facile Ligand-Exchange and Disproportionation Reactions of Diaryl Sulfoxides, Selenoxides, and Triarylphosphine Oxides with Organolithium and Grignard Reagents

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Diaryl sulfoxides undergo unusually rapid ligand-exchange reaction upon treatment with organolithium reagents at −95 °C. Optically pure phenyl *p*-tolyl sulfoxide (**4b**) reacted with organolithium reagents at the range from −20 to −95 °C to give facile ligand-exchange and disproportionation products, i.e., diphenyl sulfoxide (**7**), recovered **4b**, and di-*p*-tolyl sulfoxide (**8**) in a statistical ratio of 1:2:1 in quantitative yields, and the recovered **4b** was completely racemized. This facile ligand exchange was observed in the similar reactions using only diaryl selenoxides and triarylphosphine oxides. The reactions of ^{18}O-labeled phenyl *p*-tolyl sulfoxide (**4c**) with organolithium reagents gave products in a statistical ratio without ^{18}O scrambling, indicating that only the C–S bond cleavage took place under low temperature. It is suggested that the ligand exchange reactions occur by the nucleophilic attack by organolithium reagent at the sulfinyl sulfur atom, giving σ-sulfurane as an intermediate that collapses rapidly. These results suggest that the treatment of arylic sulfoxides, selenoxides, and phosphine oxides with strong bases should be effected with caution.

It has been known that alkyl aryl or haloalkyl aryl sulfoxides undergo simple substitution reaction on the sulfinyl sulfur atom upon treatment with Grignard or organolithium reagents to afford the sulfoxides in which the more electronegative ligand is usually replaced with organometallic reagents.[1] These reactions proceed with inversion of configuration at sulfur via a σ-sulfurane by analogy to the oxygen-exchange reaction of sulfoxides.[2] The procedures have been used for desulfinylation from organic compounds as well as the preparation of new Grignard or organolithium reagents,[3] and hence, these reactions have found application to various asymmetric syntheses.[4] It was found that azaheteroaryl sulfoxides react with Grignard or organolithium reagents to afford biaryls in high yields.[5] These ligand-coupling reactions have generally been observed in the reactions of sulfonium salts with organometallic reagents providing new methods of carbon–carbon bond formation. The mechanism is believed to involve a σ-sulfurane.[6] Meanwhile, a few diaryl sulfoxides have been demonstrated to give triaryl sulfonium salts on treatment with Grignard or organolithium reagents, indicating that the oxygen atom of the sulfoxides becomes a leaving group.[7] Thus, although the ligand exchange or coupling reactions of sulfoxides with organometallic reagents have been studied, whether the σ-sulfuranes [10-S-4(C_3,O_1)][8] are intermediates or transition states remain unresolved. In order to detect and investigate the nature of σ-sulfuranes, we reacted diaryl sulfoxides with organolithium or Grignard reagents under various temperatures, since it has been known that attachment of aryl ligands stabilizes the hypervalent compounds such as

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