

DETECTION OF ORGANIC SULFUR BY ^{15}N AND ^{19}F NMR VIA FORMATION OF IMINOSULFURANES

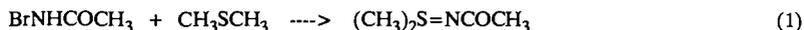
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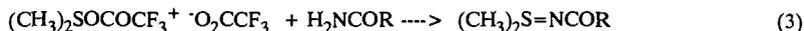
INTRODUCTION

Determination of the forms of organic sulfur in coal remains a topic of wide interest in coal science. Recent efforts to characterize organic sulfur include analysis by XANES (1-3), pyrolytic methods (4-7), mass spectrometric analysis of coal extracts (8), and preparation of ^{13}C -labelled sulfonium salts from organic sulfides (9). Direct observation of the ^{33}S nucleus by NMR is unsatisfactory, due to low natural abundance, poor receptivity, and unfavorable quadrupolar relaxation properties. ^{13}C NMR is of limited utility for the indirect analysis of sulfur, since ^{13}C chemical shifts for carbons with sulfur substituents are similar to those of carbons with carbon substituents. The aim of the present study is to develop NMR methods for characterization of organic sulfur functional groups which do not suffer from the ambiguities of pyrolytic and hydrolytic methods. Thus, we have examined the potential for spectroscopic discrimination of categories of organic substituents at sulfur by conversion of organic sulfides to iminosulfuranes, $\text{R}_2\text{S}=\text{NR}$, for analysis by ^{15}N NMR spectroscopy (10). In this paper, we present results of measurement of ^{15}N chemical shifts for various alkyl and aryl substituents at sulfur. We discuss a second approach under study, the attachment of ^{19}F labels to groups attached to sulfur, with *chemical* selectivity providing the basis for structural discrimination.

Iminosulfuranes have been prepared from the reaction of N-haloamides with dialkyl sulfides (eq 1) (11). The reaction is selective for dialkyl sulfides: diaryl sulfides and aryl alkyl sulfides are unreactive.

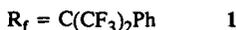


Iminosulfuranes have been prepared by the reaction of sulfoxides with trifluoroacetic anhydride or oxalyl chloride (eqs 2-3) (12). The intermediate sulfonium salt formed in eq. 2 can be trapped at low temperature (-60°C) with an appropriate amide to form the iminosulfurane (eq 3). At temperatures above -30°C , the intermediate undergoes the Pummerer rearrangement (eq 4).

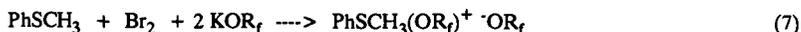




Finally, diaryl sulfides can be converted to diaryldialkoxysulfuranes ($\text{R}_f = \text{C}(\text{CF}_3)_2\text{Ph}$) by reaction with bromine or chlorine and a suitable alkoxide in dry aprotic solvents (ether, tetrahydrofuran, CCl_4). The diaryldialkoxo sulfuranes, e.g., **1**, can be isolated or easily prepared *in situ* for reaction with a wide variety of amides and amines to form iminosulfuranes (eq 6) (13). The acidic alcohol R_fOH is conveniently removed by basic aqueous extraction. The main requirements for application of this reaction in a coal product environment are (1) the absence of water, which hydrolyzes sulfuranes to sulfoxides, and (2) phenolic OH groups and other active hydrogen-containing groups must be alkylated to prevent oxidation.



In this paper, we examine the possibility of discriminating between diaryl sulfides and alkyl sulfides by converting diaryl sulfides to iminosulfuranes, while arylalkyl sulfides are selectively converted to the Pummerer rearrangement product under the same reaction conditions. Sulfonium salts formed from arylalkyl sulfides (eq 7) do not form iminosulfuranes when the R_fO^- anion is present (eq 8), but rather undergo efficient Pummerer rearrangement (eq. 9). In this paper, we extend recent work which



determined ^{15}N chemical shifts for simple diaryl and dialkyl iminosulfuranes to include the dibenzothiophene structure, and we demonstrate introduction of ^{19}F and ^{15}N labels in iminosulfuranes prepared from diphenyl sulfide and dibenzothiophene. We examine reaction of a mixture of sulfides leading to selective iminosulfurane formation from a diaryl sulfide and Pummerer rearrangement from an arylalkyl sulfide. These reactions provide a strategy for *chemical* discrimination between dibenzothiophene, simple diaryl sulfides, aryl alkyl sulfides, and dialkyl sulfides.

EXPERIMENTAL

Preparation of Dibenzothiophene-N-(2,2,2-trifluoroacetyl) Iminosulfurane. The following is a representative procedure for preparation of iminosulfuranes. 2,2,2-Trifluoroacetamide (Aldrich) was dissolved in ether and decanted from an insoluble component.

The alkoxide $K^+ \cdot OC(CF_3)_2Ph$ (KOR_f) was prepared by heating R_fOH (1 eq.) and aqueous KOH (0.95 eq) at $100^\circ C$ and 10^{-2} Torr in a round bottom flask equipped with a vacuum adapter, with two interruptions to grind the white alkoxide cake to powder, following published procedures (13,14). The apparatus, reagents and solvents were rigorously dried. However, the white alkoxide powder can be quickly (less than 3-4 minutes) transferred in the open air for weighing into reaction flasks without appreciable yield losses. Similarly, solvents and reagents were quickly transferred to the oven-dried reaction flask through the air, followed by nitrogen purge of the reaction medium. Thus, dibenzothiophene (1.5 g, 8.15 mmol), and KOR_f (4.6g, 16.3 mmol) were dissolved in ca. 60 mL of dry tetrahydrofuran (Aldrich, stored over type 3A molecular sieves) in a 3-neck 100 mL round bottom flask equipped with two serum caps and a vacuum adapter. Chlorine (0.35 mL at $-78^\circ C$, 8.1 mmol), was condensed in a calibrated trap and swept into the solution in a nitrogen stream via syringe needle. (When bromine was substituted for chlorine, no iminosulfurane was formed from dibenzothiophene in reactions using ether, CCl_4 , or THF solvents.) The reaction mixture was stirred for 5 min. A THF solution of 2,2,2-trifluoroacetamide (0.92 g, 8.1 mmol) was added, and the solution was warmed to room temperature. THF was removed by rotary evaporation, and methylene chloride, 80 mL, was added. After extraction with 10% aq. KOH twice to remove acidic R_fOH , and once with water, the CH_2Cl_2 solution was dried over anhydrous $MgSO_4$ and concentrated to give crystalline product, 2.2 g (90% yield). The iminosulfurane was sparingly soluble in diethyl ether. Recrystallization from ether gave fine needles, mp $215-217^\circ C$, 1.8 g. ^{13}C NMR (75 MHz, $CDCl_3$, ppm using $CDCl_3$ center line at 77 ppm): 168.9 (quartet, $J_{CF} = 35.8$ Hz), 138.6, 135.6, 133.4, 130.4, 129.0, 122.7, 117.1 (quartet, $J_{CF} = 288$ Hz). ^{19}F NMR (282 MHz), singlet at -73.5 ppm from $CFCl_3$. 1H NMR (300 MHz, $CDCl_3$, ppm from TMS), 8.15 ppm (2H, d, $J = 7.9$ Hz), 7.92 (2H, d, $J = 7.7$ Hz), 7.71 (2H, d of t, $J = 7.6, 0.9$) 7.57 (2H, d of t, $J = 0.9, 7.9$ Hz).

Preparation of Other Iminosulfuranes. ^{15}N -Acetamide (Cambridge Isotope Laboratories) was recrystallized from $CHCl_3$ -ether for preparation of ^{15}N -acetyl iminosulfuranes. S,S-Diphenyl-N-(2,2,2-trifluoroacetyl) iminosulfurane (mp $88.5-89.5^\circ C$), dibenzothiophene- ^{15}N -acetyl iminosulfurane (mp $165-165.5^\circ C$), and S,S-diphenyl- ^{15}N -acetyl iminosulfurane (mp $94-95^\circ C$) (10) were also prepared by the method described above. Spectroscopic details will be published in detail elsewhere. Excellent crude yields of ca. 90% were achieved in all cases, with final isolated yields of pure product of typically greater than 75%. CCl_4 and diethyl ether can be substituted for THF. Unlike dibenzothiophene, diphenyl sulfide can be converted to iminosulfuranes using either bromine or chlorine. In general, iminosulfuranes can be recrystallized from ether/pentane (13).

Pummerer Rearrangement of Thioanisole. An ether solution of thioanisole was exposed to a 10% excess of Br_2 or Cl_2 at $-78^\circ C$, followed by two equivalents of KOR_f in ether. ^{13}C NMR analysis revealed clean, quantitative conversion to the Pummerer rearrangement product, $PhSCH_2OC(CF_3)_2Ph$, isolated as a clear liquid after a workup similar to that of the iminosulfuranes. ^{13}C NMR, 75 MHz, $CDCl_3$, ppm using $CDCl_3$ centerline at 77.0 ppm, 133.8, 131.9, 130.3, 129.1, 128.8, 128.3, 128.0, 127.2, 122.3 (quartet, CF_3 , $J_{CF} = 290$ Hz), 83.2 (heptet, $J_{CF} = 28.5$ Hz), 72.2. ^{19}F NMR (282 MHz), singlet at

-71.2 ppm from internal CFCl_3 . The 70 eV mass spectrum gave a strong molecular ion at m/e 366 and fragments at 227, 207, 177, 123, 109, and 77.

Reaction of mixture of Diphenylsulfide and Thioanisole. An equimolar mixture of diphenylsulfide and thioanisole were treated with Cl_2 , KOR_p and excess H_2NCOCF_3 in dry THF at -78°C . After the standard workup, the reaction mixture was examined by ^{13}C and ^{19}F NMR. This revealed complete conversion of thioanisole to the Pummerer product, $\text{PhSCH}_2\text{OR}_p$ and 60% conversion of diphenylsulfide to the iminosulfurane.

Conversion of Diphenylsulfide to S,S-Diphenyl- ^{15}N -acetylminosulfurane in the Presence of Illinois No. 6 Methylated Asphaltene. Argonne premium coal no. 301 was heated for 15 min at 435°C in tetralin (1 g coal/1.75 g tetralin) in a stainless steel tubing bomb. The products were extracted with THF. The THF solution was poured into excess hexane to precipitate asphaltene and preasphaltene. A sample of 0.8 g of the product in 30 mL THF was stirred overnight with 10 g $^{13}\text{CH}_3\text{I}$ and 1.9 g KOH in 2.5 mL water. THF was removed, and a CHCl_3 solution of the products was concentrated and thoroughly dried under vacuum at 100°C . ^{13}C NMR revealed 70% O-alkylation (50-70 ppm) and 30% C-alkylation (10-50 ppm). A mixture of 0.39 g methylated coal product, 1.8 g KOR_p , 0.49 g Ph_2S in 10 mL CCl_4 and 2 mL benzene were treated with 0.2 mL Br_2 . The reaction mixture warmed noticeably. The ^{15}N -labelled acetamide, 0.2 g, was added, the mixture was shaken for 30 min, and worked up in the standard way. Examination of a CDCl_3 solution of the products by ^{13}C and ^{15}N NMR, revealed ca. 70% conversion of Ph_2S to $\text{Ph}_2\text{S}=\text{NCOCH}_3$.

RESULTS AND DISCUSSION

Spectroscopic Discrimination of Sulfur Functional Groups. ^{15}N Chemical Shifts for N-acetylminosulfuranes. As shown in Table I, ^{15}N chemical shifts for S,S-dialkyl and S,S-diaryl N-acetylminosulfuranes span a narrow range of only ca. 10 ppm, with no separation of aryl from alkyl substituents, although changes in the nitrogen substituent lead to a chemical shift range of about 100 ppm on going from N-benzyl to N-aryl to the N-acetyl substituent. In this paper, we have added data for the dibenzothiophene structure to previously reported data (10). Overall, these data indicate that the substituent at sulfur exerts little effect on the ^{15}N chemical shift, and that no simple spectroscopic discrimination of sulfur substituents into aryl or alkyl substituents will be accomplished using ^{15}N NMR, at least for the N-acetyl substituent.

Chemical Discrimination of Sulfur Functional Groups. ^{19}F Chemical Shifts. Organic sulfides differ greatly in their reactivity to oxidizing reagents. Thus, a strategy for discrimination of sulfur functional groups using NMR spectroscopy uses chemical selectivity to attached spectroscopically distinct groups to different categories of organic sulfur. The ^{13}C and ^{19}F chemical shifts of the methyl and trifluoromethyl groups of N-acetyl and N-trifluoroacetyl iminosulfuranes are unaffected by changes in the sulfur substituents. As shown in Table I, the ^{19}F shifts of N-trifluoroacetyl groups attached to diphenyl sulfide or dibenzothiophene are nearly identical. Diaryl sulfides in a coal-derived mixture thus may be expected to yield iminosulfuranes which will appear closely

clustered at about -73.5 ppm in the ^{19}F spectrum compared to CFCl_3 , and Pummerer rearrangement products will appear around -73.5 ppm with the present choice of fluorinated alkoxide. Dibenzothiophene structures can be discriminated from diphenyl sulfide structures by selection of Br_2 or Cl_2 as an oxidant. Aryl alkyl and dialkyl sulfides are converted to Pummerer products in the sulfurane-forming reaction. Finally, dialkyl sulfides are converted to iminosulfuranes using N-bromo amides, but arylalkyl and diaryl sulfides do not react, providing a means for selective detection of dialkyl sulfides. Each of these categories of selective reaction can be used to introduce a unique ^{19}F or ^{15}N label. Introduction of two distinct ^{19}F labels for diaryl and alkyl aryl sulfides is demonstrated by the reaction of a mixture of diphenyl sulfide and thioanisole giving S,S-diphenyl-N-(2,2,2-trifluoroacetyl) iminosulfurane (^{19}F resonance at -73.5 ppm from CFCl_3) and $\text{PhSCH}_2\text{OC}(\text{CF}_3)_2\text{Ph}$ (-71.2 ppm from CFCl_3), respectively. Although the sulfurane-forming reactions may appear rather exotic for application to coal, we have shown in model compound experiments that the reactions can be successfully carried out in the presence of methylated preasphaltenes and asphaltenes, and are simple bench-top procedures.

SUMMARY

We have synthesized new iminosulfuranes from a variety of diaryl- and dialkyl sulfides and dibenzothiophene. The pattern of ^{15}N chemical shifts indicates that functional groups attached to sulfur are not simply resolved into aryl and alkyl groups. Thus, resolution of sulfur functional groups using ^{15}N NMR via iminosulfurane does not appear practicable. However, iminosulfurane formation, together with the N-haloamide reaction and the Pummerer rearrangement, provides pathways for chemical discrimination of different sulfur substituents using unique ^{15}N - or ^{19}F -labelled fragments for different categories of sulfur functional groups. In efforts currently underway, we are applying these reactions to methylated extracts and conversion products of the high-organic-sulfur containing Yugoslavian Rasa and Spanish Mequinenza lignites.

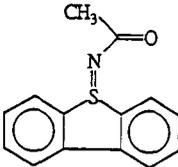
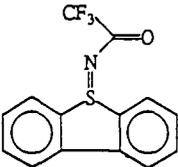
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Table I. ^{15}N and ^{19}F Chemical Shifts of Iminosulfuranes and a Pummerer Rearrangement Product

Iminosulfurane	^{15}N Chemical Shifts ^a	^{19}F Chemical Shifts ^b
$\text{Ph}_2\text{S}=\text{NC}(\text{CH}_3)_3$	-293.5	
$\text{Ph}_2\text{S}=\text{NCH}_2\text{Ph}$	-330.4	
$\text{Ph}_2\text{S}=\text{NPh}$	-284.0	
$(\text{CH}_2)_4\text{S}=\text{NCOCH}_3$	-217.8	
$\text{Ph}_2\text{S}=\text{NCOCH}_3$	-227.6	
$(\text{PhCH}_2)_2\text{S}=\text{NCOCH}_3$	-228.9	
	-219.0	
$\text{Ph}_2\text{S}=\text{NCOCF}_3$		-73.52
		-73.45
$\text{PhSCH}_2\text{OC}(\text{CF}_3)_2\text{Ph}$		-71.2

^appm from CH_3NO_2

^bppm from CFCl_3