and sytrene (4.5% yield). FVP of 8 at 650 °C (0.04 torr) gave 8 (93% recovery) and more volatile products, including a trace of styrene. FVP at 750 °C (0.05 torr) gave 8 (50% recovery) and more volatile products, including styrene (2.3% based on total 8 introduced).

Acknowledgment. We thank the Australian Research Grants Committee for support of this work and the National N.M.R. Centre, Canberra, for 270-MHz spectra.

Registry No. 5, 78822-89-6; 8, 78822-90-9; tetrolic acid, 590-93-2; styrene, 100-42-5.

Regiospecific Base-Catalyzed Hydrogen Exchange of Triarylsulfonium Salts

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Reactions of sulfonium salts with various nucleophilic species are of significant interests from the viewpoints of the fundamental mechanistic understanding as well as of their relevance to the adenosylmethionine-dependent biochemical methylations. In a recent mechanistic study on the reaction of triarylsulfonium salts with a number of the alkoxide nucleophiles, we have shown by the solvent isotope labeling method that the hydrocarbon products, commonly observed in such reactions, are derived via the radical intermediates rather than the corresponding anions.[1] In the course of this mechanistic study, it was necessary to determine the extent and the scope of the base-catalyzed hydrogen exchange of the triarylsulfonium salts with the protic solvent medium, and we report the results of that investigation.

Tri-*p*-tolylsulfonium bromide and triphenylsulfonium bromide were prepared in modest yields from di-*p*-tolyl sulfoxide and *p*-tolylmagnesium bromide, and diphenyl sulfoxide and phenylmagnesium bromide, respectively.[2] The base-catalyzed exchange reactions of the triarylsulfonium salts in the deuterated alcoholic solvents were carried out under argon atmosphere and the conditions given in Table I. The products were extracted with ether, and the unreacted sulfonium salts were recovered by extracting the aqueous phase with dichloromethane. The relative product ratio and the incorporation of the deuterium isotope into the products are summarized in Table I and Table II, respectively.

The multiple deuterium incorporation into the products is clearly a result of the base-catalyzed exchange occurring at the stage of the sulfonium salts, because in the control experiments none of the products, i.e., hydrocarbons, ethers and sulfides underwent the hydrogen exchange under the identical conditions given in Table I. The mass spectral data show that five hydrogens on the *p*-tolyl moiety of the sulfonium salt undergo the exchange with the protic solvent deuterium. The positions of the exchange have been determined to be ortho to the sulfonium substituent and the methyl groups by the following proton NMR analysis. While the authentic tri-*p*-tolylsulfonium bromide shows in the ^{1}H NMR spectrum the pseudo A_2B_2 pattern centered at δ 7.53 (d, 6 H, ortho H's), 7.40 (d, 6 H, meta H's), and a singlet at 2.314 (9 H, methyl), the partially deuterated tri-*p*-tolylsulfonium bromide recovered from run 1 shows the following ^{1}H NMR spectral data: δ 7.53 (d, 1.7 H corresponding to 72% D incorporation at ortho positions), 7.40 (a large singlet with satellite doublet, 6 H, meta H's), and three poorly resolved singlets at 2.314, 2.302, 2.292, representing the methyl-d_0, d_1, and d_2, respectively (total 2.3 H corresponding to an overall 74% D incorporation at the methyl positions). Similar ^{1}H NMR analyses on the di-*p*-tolyl sulfide [pseudo A_2B_2 at 7.23 (ortho H's), 7.09 (meta H's), and singlet at 2.31 (methyl)] obtained from runs 1 and 2 have also corroborated the above determination on the exchange positions. It is of interest to note that the degree of the exchange is quite similar for the ortho (72%) and the methyl (74%) positions in the tri-*p*-tolylsulfonium bromide under the conditions studied.

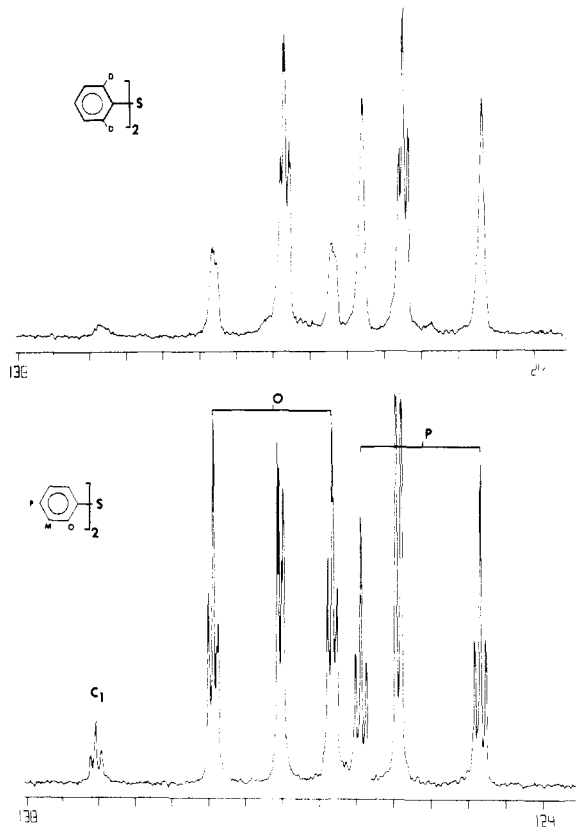

Figure 1. Completely coupled C-13 spectra of authentic (bottom) and partially deuterated (top) diphenyl sulfide.

For the triphenylsulfonium bromide system, the mass spectral data (Table II) show that only two hydrogens of the each phenyl moiety are exchangeable, but the position of the exchange could not be readily determined based on the ^{1}H NMR analysis because of the nonresolution of the ortho, meta, and para hydrogens either in triphenylsulfonium bromide or in diphenyl sulfide. However, ^{13}C NMR analysis made on the diphenyl sulfide product in run 3 has allowed an unambiguous determination of the exchange positions. The wide-band proton noise-decoupled ^{13}C NMR of authentic diphenyl sulfide shows well-resolved signals at δ 135.797 (C-1), 130.994 (ortho), 129.182 (meta), and 127.000 (para). The assignments of the peaks have been made based on the splitting patterns in the completely coupled spectrum (Figure 1). The completely coupled ^{13}C NMR spectrum of the partially deuterated diphenyl sulfide from run 3 reveals the significantly reduced peak intensities of the ortho carbon due to the deuterium substitution, and modified splitting patterns

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Table I. Relative Product Ratio[a]

run	substrate	base/solvent	temp, °C	time, h	% yield hydrocarbon	% yield ether	% yield sulfide
1	$(p\text{-tol})_3S^+Br^-$	$(CH_3)_2CHONa/(CH_3)_2CHOD$[b]	72	23	35	45	100
2	$(p\text{-tol})_3S^+Br^-$	KOD[c]/D_2O–C_2H_5OD[d]	90	22	23	tr	100
3	$(Ph)_3S^+Br^-$	$(CH_3)_2CHONa/(CH_3)_2CHOD$[b]	65	50	2	42	100

[a] The relative product ratios were determined by GC analysis on a 5-ft, 10% FFAP column on Anakrom-SD, 60/70 mesh, and are uncorrected. [b] 2-Propanol-d_1 (98 + atom % D) from Aldrich. [c] KOD (98+ atom % D) from Aldrich. [d] D_2O (100.0 atom % D) and ethyl alcohol-d_1 (99.5+ atom % D) from Aldrich.

Table II. Deuterium Isotope Distribution[a]

product	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	d_9	d_{10}
run 1											
toluene	9.3	20.7	33.9	22.8	9.7	3.6	0	0	0	0	0
p-tolyl isopropyl ether	0	5.3	14.7	34.3	33.6	12.0	0	0	0	0	0
di-*p*-tolyl sulfide	0	0	0	7.0	10.4	16.4	22.1	19.3	15.3	7.3	2.3
run 2											
toluene	7.4	21.3	38.5	23.3	7.9	1.5	0	0	0	0	0
di-*p*-tolyl sulfide	0	0	0	1.9	4.7	13.1	28.7	25.4	15.8	7.4	2.9

	d_0	d_1	d_2	d_3	d_4
run 3					
benzene	77.0	14.0	9.0	0	0
phenyl isopropyl ether	34.8	37.2	28.0	0	0
diphenyl sulfide	17.8	21.2	24.0	22.9	14.1

[a] Determined by mass spectral analysis of the molecular ion peaks, corrected for the amounts of natural abundance of M + 1 and M + 2, and expressed in percent ratio.

of the meta and para carbons in accord with the expectation for the ortho deuteration.[3] The wide-band proton noise-decoupled ^{13}C spectrum of the partially deuterated diphenyl sulfide provides additional support for the above conclusion: three C-1 peaks separated by ca. 0.1 ppm corresponding to the d_0, d_1, and d_2 ortho substitution (secondary deuterium isotopic shifts); a singlet overlapping with an upfield shifted (ca. 0.3 ppm, primary deuterium isotopic shift) triplet ($J_{^{13}C-D}$ = 23 Hz) corresponding to the ortho carbon bearing ^1H and D; two signals again separated by ca. 0.1 ppm for the meta carbon with d_0 and d_1 at the neighboring ortho positions[4] (Figure 2). Thus, the ^{13}C NMR analysis, in conjunction with the mass spectral data, firmly establishes that the ortho positions of triphenylsulfonium bromide suffer the regiospecific hydrogen exchange with protic medium under the conditions.

The exact reasons for the observed regiospecificity of the hydrogen exchange in triarylsulfonium salts are not clear. The kinetic "coordination mechanism" commonly invoked in the regiospecific heteroatom-directed metalation[5] may be of limited merit in this case, because the positively charged sulfonium cation is not likely to be an effective ligand.[6] We suggest that the observed regiospecific deprotonation of the ortho hydrogens in the triarylsulfonium salts may be consequence of the enhanced thermodynamic acidity of the ortho hydrogens primarily due to the inductive effect of the electron-withdrawing sulfonium cation and the dipole stabilization[7] of the corresponding carbanionic species.

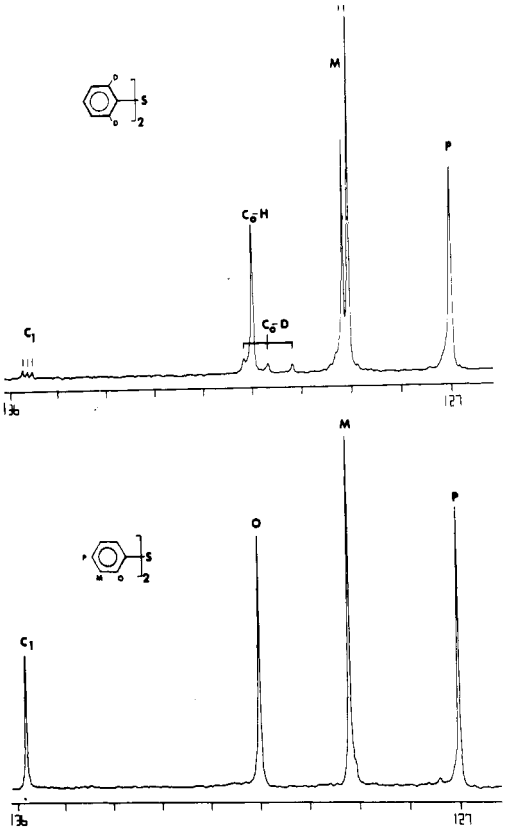

Figure 2. Wide-band proton noise-decoupled C-13 spectra of authentic (bottom) and partially deuterated (top) diphenyl sulfide.

Experimental Section

Di-*p*-tolyl sulfoxide, diphenyl sulfoxide, and diphenyl sulfide were purchased from Aldrich Chemical Co. The ^1H NMR and ^{13}C NMR spectra were measured on a Varian Associates Model

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XL-200 superconducting spectrometer, and the chemical shifts are expressed in parts per million downfield from Me_4Si. Mass spectral analyses were done on a Hewlett-Packard GC/MS Data System, Model 5982-A. GC analyses were performed with an Antek Instrument Model 300 with a flame-ionization detector.

Tri-*p*-tolylsulfonium bromide was prepared from di-*p*-tolyl sulfoxide and *p*-tolylmagnesium bromide essentially according to a literature procedure[2] and was recrystallized from $CHCl_3$/acetone: mp 289–290 °C (lit.[2] mp 285–286 °C); ^1H NMR ($CDCl_3$) δ 2.314 (s, 9 H, methyl), 7.40 (d, 6 H, meta H's), 7.53 (d, 6 H, ortho H's).

Triphenylsulfonium bromide was prepared from diphenyl sulfoxide and phenylmagnesium bromide according to a literature procedure[2] and was recrystallized from Et_2O/EtOH: mp 247–248 °C (lit.[8] mp 241–244 °C); ^1H NMR ($CDCl_3$) δ 7.6 (br); ^{13}C NMR ($CDCl_3$) δ 123.916 (C-1), 130.698 (ortho), 131.074 (meta), 134.079 (para).

Exchange Experiments. A typical run is as follows. To sodium isopropoxide prepared by dissolving Na metal (17.3 mg, 0.75 mmol) in 2-propanol-d_1 (2 mL) was added triphenylsulfonium bromide (258 mg, 0.75 mmol) in 2-propanol-d_1 (2 mL). The mixture was stirred for 50 h at 65 °C under Ar atmosphere and was poured into ice water. The products were obtained by extracting the aqueous solution with Et_2O, washing with H_2O, drying (Na_2SO_4), and evaporation. The unreacted sulfonium salt was then recovered by extracting the aqueous solution with CH_2Cl_2. After GC and GC/MS analysis, the products were separated by preparative TLC on silica gel for characterization.

Di-*p*-tolyl Sulfide. The authentic sample was prepared by reducing di-*p*-tolyl sulfoxide with phosphorus pentasulfide in CH_2Cl_2 according to a literature procedure:[9] mp 57–58 °C (lit.[9] mp 53–55 °C); ^1H NMR ($CDCl_3$) δ 2.31 (s, 6 H), 7.09 (d, 4 H, meta H's), 7.23 (d, 4 H, ortho H's); mass spectrum, *m/e* 214 (M^+), 199, 184, 181, 165, 91.

***p*-Tolyl isopropyl ether**: ^1H NMR ($CDCl_3$) δ 1.1 (d, 6 H), 2.2 (s, 3 H), 4.0 (m, 1 H), 7.2 (d, 2 H), 7.8 (d, 2 H); mass spectrum, *m/e* 150 (M^+), 108.

Phenyl isopropyl ether: ^1H NMR ($CDCl_3$) δ 1.1 (d, 6 H), 4.0 (m, 1 H), 7.4 (br, 5 H); mass spectrum, *m/e* 136 (M^+), 94.

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Reaction of Organolithium Compounds with a Triphenylcyclopropyl Derivative. The Matter of Cyclopropyl Anion Ring Opening

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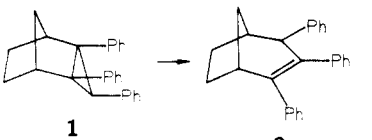
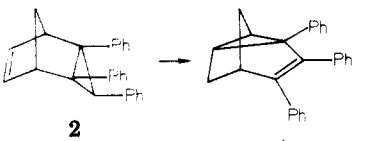
It has previously been shown that tricyclic compounds **1** and **2** react with potassium *tert*-butoxide in dimethyl sulfoxide to produce the ring opened products **3** and **4**.[1] Although these results were originally interpreted as a symmetry forbidden disrotatory opening of a cyclopropyl anion, there is now good reason to believe that this reaction proceeds by electron transfer followed by anion-radical opening of the phenyl-substituted cyclopropane.[2] Among



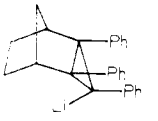
1 **3**



2 **4**

arguments presented by the Newcomb group favoring the anion radical were the facts that **1** does not undergo ring opening with KO-*t*-Bu–crown ether or lithium diisopropylamide in tetrahydrofuran.[2] Furthermore, although both *cis*- and *trans*-1,2,3-triphenylcyclopropane react with KO-*t*-Bu–Me_2SO to form a cyclopropyl anion that does not open, the long-lived triphenylcyclopropyl anion generated with *n*-BuLi does undergo ring opening.[3] Because the 1,2,3-triphenylcyclopropyl anion in Me_2SO captures a proton before it opens in a symmetry-allowed manner, it is not reasonable that a cyclopropyl anion from **1** under the same conditions would undergo a symmetry-forbidden reaction.

In addition Newcomb[2] finds that treatment of **1** with *n*-butyllithium in tetramethylethylenediamine followed by quenching with D_2O results in recovery of unrearranged **1** containing deuterium. We confirm that observation, but although Newcomb suggested that result indicated the formation of **5** the deuterium incorporation could have



5

arisen by the known metalation of one or more benzene rings by the powerful metalating agent *n*-BuLi–TMEDA.[4] Dreiding models show that the cyclopropyl proton in **1** is highly hindered by the endo protons at C-6 and C-7, making it extremely difficult for the *n*-BuLi–TMEDA complex to approach it. In our experiments the NMR spectrum of deuterated **1** shows no significant loss of H in the cyclopropyl ring. Although Newcomb has suggested that compound **5** could be initially deuterated at the ortho or para positions of the benzene ring, presumably because of benzylic anion delocalization, this is not necessarily in accord with the preferred sp^3 hybridization of cyclopropyl anions even when they are conjugated with strongly electron withdrawing substituents,[5] nor does it correlate with the reaction of cumylpotassium with D_2O, which does not result in significant ring deuteration.[6]

Apropos of this discussion we report that in contrast to compound **1**, compound **2** reacts with *n*-BuLi–TMEDA, yielding **6a**, **7a**, and **8** as shown in Scheme I.

After 6 h at room temperature in hexane, **2** and *n*-BuLi–TMEDA gave 89% of distilled product $C_{30}H_{31}D$. Preparative scale GLC revealed that 18% of the product was **8**, while the remaining 82% consisted of a mixture of **6a** and **7a**. The ultraviolet and NMR spectra of both deuterated and nondeuterated **6a** and **7a** were compared

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