

# Acidities of Hydrocarbons and Sulfur-Containing Hydrocarbons in Dimethyl Sulfoxide Solution

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**Abstract:** The relative  $pK_a$  values in  $\text{Me}_2\text{SO}$  solution of 13 hydrocarbons that form carbanions with highly dispersed negative charges on deprotonation were found to differ from literature relative ion-pair acidities in cyclohexylamine (CHA) by only  $\pm 0.7$  unit, or less, when the ion-pair  $pK_a$ 's were anchored to the  $pK_a$  of 17.9 for 9-phenylfluorene in  $\text{Me}_2\text{SO}$ . The relative  $pK_a$ 's for phenylacetylene, cyclopentadiene, and indene were found to be 2.4, 2.7, and 0.9 units higher, respectively, in  $\text{Me}_2\text{SO}$  than in CHA. Higher relative  $pK_a$ 's were also observed for  $\text{PhCH}_2\text{SO}_2\text{Ph}$ ,  $\text{PhSO}_2\text{CH}_3$ , and  $\text{PhSO}_2\text{CH}_2\text{Me}$ , by 1.9, 2.7, and 2.8 units, respectively, and for 2-phenyl-1,3-dithiane, 2-(*p*-phenylphenyl)-1,3-dithiane, 4-methyl-2,6,7-trithiabicyclo[2.2.2]octane, and 1,3-dithiane, by 0.4, 0.65, 0.8, and  $\sim 1.9$  units, respectively. The apparent higher relative acidities for these compounds in CHA is probably caused by stronger ion pairing or aggregation of the ions derived therefrom than for the hydrocarbon indicator ions with which they are being compared. These perturbations of the equilibria probably arise because of differences in the extent of charge dispersion in the acid and indicator ions. The  $pK_a$  of 1,3-dithiane itself is estimated from an average of three extrapolations to be  $39 \pm 2$  in  $\text{Me}_2\text{SO}$ . Acidities in  $\text{Me}_2\text{SO}$  for 1,3-dithianes with electron-withdrawing groups in the 2-position were observed to increase in the following order:  $2\text{-C}_6\text{H}_5 < 2\text{-}p\text{-C}_6\text{H}_5\text{phenyl} < 2\text{-CONMe}_2 < 2\text{-}E\text{-PhCH=CH} < 2\text{-CH=C-S(-CH}_2\text{)}_3 < 2\text{-CO}_2\text{Me} < 2\text{-CN}$ . The order of acidities of 3 alkylthio alkyl sulfoxides was found to be  $\text{MeSCH}_2\text{S(O)Me} < \text{EtSCH}_2\text{S(O)Et} < t\text{-BuSCH}_2\text{S(O)}t\text{-Bu}$ .

In previous papers we have reported equilibrium acidities in  $\text{Me}_2\text{SO}$  solution for a large number of hydrocarbons and sulfur-containing hydrocarbons.<sup>1</sup> In this paper we turn our attention to a number of types of sulfur compounds that are of particular interest to synthetic organic chemists. The carbanion derived from 1,3-dithiane was the first of several strongly basic ions that were shown to be useful synthetically as acyl anion equivalents since the two sulfur atoms can serve as a masked carbonyl group.<sup>2</sup> Reactions of anions derived from 2-substituted 1,3-dithianes with alkylating agents or Michael acceptors have been studied extensively.<sup>3</sup> The stereochemistry of these reactions has also received considerable attention following the discovery that 2-lithio-*cis*-4,6-dimethyl-1,3-dithiane undergoes preferential equatorial attack by electrophiles in THF.<sup>4</sup> Carbanions derived from alkylthio alkyl sulfoxides,  $\text{RSCH}_2\text{S(O)R}$ , have also been shown to be useful synthetically as acyl ion equivalents when R is Me,<sup>5</sup> Et,<sup>6</sup> or *t*-Bu.<sup>7</sup> Stereochemical evidence from protonation and alkylation experiments on 1,3-dithiane anions has been interpreted in terms of a pyramidal structure.<sup>4</sup> This interpretation has been supported by measurements of relative ion-pair acidities of 2-alkyl-substituted 1,3-dithianes where the observation of an apparent methyl acid weakening effect of unprecedented size (8  $pK_a$  units) led to the conclusion that the 1,3-dithiane anion and its 2-alkyl derivatives, when paired with the  $\text{Cs}^+$  cation, are "fully localized" and "presumably pyramidal".<sup>8</sup> However, the anion derived from 2-phenyl-1,3-dithiane, which appeared to be only a 1.5  $pK_a$  unit stronger acid than 1,3-dithiane itself in CHA, was considered to be planar. These surprising results led us to attempt measurements of these compounds in  $\text{Me}_2\text{SO}$  solution where equilibrium acidities free of ion-pairing effects can be obtained.<sup>9</sup> In this paper we make comparisons of relative  $pK_a$ 's in  $\text{Me}_2\text{SO}$  with relative ion-pair  $pK_a$ 's in CHA for these sulfur compounds and for a number of hydrocarbons.

## Results and Discussion

**Relative Acidities of Hydrocarbons in Dimethyl Sulfoxide and Cyclohexylamine (CHA) Solution.** Equilibrium acidities in low dielectric constant solvents, such as CHA, THF, or DME, are difficult (CHA) or impossible (THF or DME) to measure because of problems with ion pairing and/or aggregation. Relative ion-pair acidities ("effective  $pK_a$ 's") can be measured, however, for com-

**Table I.** Comparison of  $pK_a$  Values for Hydrocarbon Acids in  $\text{Me}_2\text{SO}$  with Ion-Pair  $pK_a$  Values in Cyclohexylamine (CHA)

acid	$pK_a^-$ ( $\text{Me}_2\text{SO}$ ) <sup>a</sup>	$pK_a^-$ ( $\text{Me}_2\text{SO}$ ) <sup>c</sup>	IP $pK_a^-$ (CHA) <sup>d</sup>	$\Delta pK_a^e$
1,3-diphenylindene	12.8		13.0	-0.2
9-phenylfluorene	17.9	(17.9)	(17.9)	(0.0)
cyclopentadiene	18.0		15.3	2.7
indene	20.1	20.1	19.0	0.9
9-benzylfluorene	21.4	21.1	20.7	0.7
9-methylfluorene	22.3		21.7	0.6
fluorene	22.6	22.3	22.1	0.5
9-isopropylfluorene	23.2		22.6	0.6
9- <i>tert</i> -butylfluorene	24.35	24.0	24.25	0.1
1,1,3-triphenylpropene	25.6		25.7	-0.1
9-phenylxanthene	27.9	27.6	27.9	0.0
phenylacetylene	28.7		22.6 <sup>f</sup>	6.1 <sup>g</sup>
( <i>p</i> -phenylphenyl)diphenylmethane	29.4	29.1	29.6	-0.2
dibenzo[ <i>a,d</i> ]cyclohepta-1,4-diene	30.1 <sup>b</sup>		30.3	-0.2
triphenylmethane	30.6	30.5	30.8	-0.2
diphenylmethane	32.2		32.5	-0.3

<sup>a</sup>Data from our laboratory (ref 1). <sup>b</sup>Present study. <sup>c</sup>Reference 12; reported as values relative to that of 9-phenylfluorene. <sup>d</sup>Reference 14;  $\text{Cs}^+$  counterion unless otherwise noted. <sup>e</sup>Value using  $\text{Li}^+$  counterion; for acids giving delocalized anions  $pK_a$  values with  $\text{Li}^+$  differ but little from those with  $\text{Cs}^+$ . <sup>f</sup> $\Delta pK_a = pK_a(\text{Me}_2\text{SO}) - pK_a(\text{CHA})$ . <sup>g</sup> $\Delta pK_a = 2.4$  in DME with  $\text{Cs}^+$  counterion (ref 15).

pounds forming highly delocalized anions, among which the kind and extent of ion pairing appears to be relatively constant.<sup>10</sup> Since

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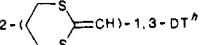
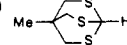
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the equilibrium constant for the acid dissociation represented by  $H-A \rightleftharpoons H^+ + A^-$  is not being measured, ion-pair  $pK_a$ 's in CHA cannot be compared *directly* with  $pK_a$ 's measured in H<sub>2</sub>O, Me<sub>2</sub>SO, or any other medium. The CHA scale was therefore anchored originally on the  $pK_a$  for 9-phenylfluorene, 9-PhFlH, in H<sub>2</sub>O/sulfolane (18.49) determined by the *H<sub>-</sub>* method in order to make comparisons with *H<sub>-</sub>*  $pK_a$ 's.<sup>10</sup> Unfortunately,  $pK_a$ 's determined by the *H<sub>-</sub>* method are now known to vary with the medium and the indicators used. For example, in EtOH/H<sub>2</sub>O 9-PhFlH has an *H<sub>-</sub>*  $pK_a$  = 18.59, and in Me<sub>2</sub>SO/H<sub>2</sub>O it is 18.38.<sup>11</sup> For that reason and because it appears desirable to relate ion-pair acidities to the Me<sub>2</sub>SO absolute scale, we have made comparisons of relative acidities in CHA and Me<sub>2</sub>SO in Table I by anchoring the CHA acidities on  $pK_a$  = 17.9, which is the value for 9-PhFlH in pure Me<sub>2</sub>SO, free of ion-pairing effects.<sup>1</sup> (Acidities in Me<sub>2</sub>SO are absolute in the sense that they are based on equilibria where acids are dissociated by the solvent acting as a base and are anchored on the solvent as a standard state.) We have also made statistical corrections for the number of acidic hydrogen atoms since the CHA acidities must be reported on a per hydrogen basis because they are relative.

Examination of Table I shows that the relative acidities of seven hydrocarbons measured in Me<sub>2</sub>SO in Shatenshtein's laboratory<sup>12</sup> agree to within  $\pm 0.3$  unit with those measured in our laboratory, when placed on the same scale. Agreement is also often surprisingly good for hydrocarbons of this type between relative acidities measured in Me<sub>2</sub>SO solution and relative ion-pair acidities measured in CHA (Table I), or DME,<sup>13</sup> or THF.<sup>14</sup> For hydrocarbons forming highly delocalized carbanions, relative acidities usually agree to within  $\pm 0.5$  unit. The relative acidities of cyclopentadiene (CpH<sub>2</sub>) and PhC $\equiv$ CH in CHA differ with those in Me<sub>2</sub>SO by 2.7 and 6.1 (Li<sup>+</sup> counterion) units, respectively, however. Note that the value for PhC $\equiv$ CH in CHA is with the Li<sup>+</sup> rather than the Cs<sup>+</sup> cation. The nature of the cation is evidently important since a large difference in relative acidities of PhC $\equiv$ CH in DME and Me<sub>2</sub>SO is also observed with Li<sup>+</sup> cation (6.7 units), but this is reduced to 2.4 units with the Cs<sup>+</sup> cation.<sup>13</sup> The apparent higher acidity of PhC $\equiv$ CH in these low dielectric constant solvents has been attributed to stronger ion pairing of the cations with the localized PhC $\equiv$ C<sup>-</sup> ion.<sup>16</sup> Unusually strong ion pairing evidently also occurs between the delocalized CpH<sup>-</sup> and Cs<sup>+</sup> ions, perhaps because they are of nearly the same size. Additional comparisons of this kind will be made in the next section for sulfur-containing acids.

**Relative Acidities of Sulfur-Containing Hydrocarbons in Me<sub>2</sub>SO and CHA Solution.** Table II summarizes data for a number of sulfur-containing hydrocarbons that have been measured in Me<sub>2</sub>SO and for some that have been measured in both Me<sub>2</sub>SO and CHA.

**Table II.** Comparison of  $pK_a$  Values for Sulfur-Containing Hydrocarbon Acids in Me<sub>2</sub>SO with Relative Ion-Pair  $pK_a$  Values in Cyclohexylamine (CHA)

acid	$pK_a$ - (Me <sub>2</sub> SO) <sup>a</sup>	IPpK <sub>a</sub> (CHA) <sup>e</sup>	$\Delta pK_a$ <sup>g</sup>
(1) 9-phenylfluorene	17.9	(17.9)	(0.0)
(2) 2-CN-1,3-DT <sup>h</sup>	19.1		
(3) 2-CO <sub>2</sub> Me-1,3-DT <sup>h</sup>	20.9		
(4) 2-PhCH=CH-1,3-DT <sup>h</sup>	26.55		
(5) 2-CONMe <sub>2</sub> -1,3-DT <sup>h</sup>	27.1		
(6)  -1,3-DT <sup>h</sup>	27.35		
(7) 2-( <i>p</i> -PhC <sub>6</sub> H <sub>4</sub> ) <sub>1,3</sub> -DT <sup>h</sup>	29.1	26.9 (28.7) <sup>f</sup>	2.2 (0.4) <sup>f</sup>
(8) 2-C <sub>6</sub> H <sub>5</sub> -1,3-DT	30.65	29.0 (30.0) <sup>f</sup>	1.6 (0.65) <sup>f</sup>
(9) 1,3-dithiane	(39) <sup>b</sup>	30.5 (37.1) <sup>f</sup>	8.5 (1.9) <sup>f</sup>
(10) (PhS) <sub>3</sub> CH	22.8 <sup>c</sup>		
(11) (PhS) <sub>2</sub> CHPh	23.0 <sup>c</sup>		
(12) PhSCHPh <sub>2</sub>	26.7 <sup>c</sup>		
(13) 	30.5 <sup>c</sup>	26.7 (29.7) <sup>f</sup>	3.8 (0.8) <sup>f</sup>
(14) (PhS) <sub>2</sub> CH <sub>2</sub>	30.8 <sup>c</sup>		
(15) PhSCH <sub>2</sub> Ph	20.8 <sup>c</sup>		
(16) ( <i>n</i> -PrS) <sub>2</sub> CH	31.3 <sup>c</sup>		
(17) PhCH <sub>2</sub> SO <sub>2</sub> Ph	23.4 <sup>d</sup>	21.5	1.9
(18) PhSO <sub>2</sub> CH <sub>3</sub>	29.0 <sup>d</sup>	26.3	2.7
(19) PhSO <sub>2</sub> CH <sub>2</sub> Me	31.0 <sup>d</sup>	28.2	2.8
(20) <i>t</i> -BuSCH <sub>2</sub> S(O)- <i>t</i> -Bu	28.0		
(21) EtSCH <sub>2</sub> S(O)Et	28.7		
(22) MeSCH <sub>2</sub> S(O)Me	29.0		

<sup>a</sup> Present results unless otherwise noted. <sup>b</sup> Extrapolated value (see text). <sup>c</sup> Reference 1g. <sup>d</sup> Reference 1h. <sup>e</sup> Reference 10. <sup>f</sup> Corrected values supplied by Professor A. Streitwieser, Jr. <sup>g</sup>  $\Delta pK_a = pK_a$  (Me<sub>2</sub>SO) - IPpK<sub>a</sub>(CHA). <sup>h</sup> DT = dithiane.

The equilibrium data in Me<sub>2</sub>SO given in Table II, together with data reported earlier,<sup>1</sup> show that  $\alpha$ -RS,  $\alpha$ -RS(O) and  $\alpha$ -RSO<sub>2</sub> groups all have powerful acidifying effects. The  $pK_a$  of methane in a solvent like Me<sub>2</sub>SO has been estimated to be  $55 \pm 3$ , based on several extrapolations.<sup>15</sup> Similar extrapolations from the  $pK_a$ 's for CH<sub>3</sub>SCH<sub>2</sub>CN (24.3) and PhSCH<sub>2</sub>CN (20.85), using a CN increment of 21 based on PhCH<sub>2</sub>CN,<sup>15b</sup> give  $pK_a$ 's for CH<sub>3</sub>SCH<sub>3</sub> and PhSCH<sub>3</sub> of about  $45 \pm 2$  and  $42 \pm 2$ , respectively. The effects of replacing a hydrogen atom in CH<sub>4</sub> by MeS, MeS(O), and MeSO<sub>2</sub> groups are thus estimated to be 10, 20, and 24  $pK_a$  units, respectively. The corresponding increases for PhS, PhS(O), and PhSO<sub>2</sub> groups are estimated to be 13, 22, and 26 units, respectively. Introduction of a PhS group into PhSCH<sub>3</sub> or PhCH<sub>3</sub> (which is estimated to have a  $pK_a$  of  $43 \pm 2$ <sup>15</sup>) causes a further 10–11 unit increase in acidity; both PhSCH<sub>2</sub>SPh and PhSCH<sub>2</sub>Ph have  $pK_a$  = 30.8 (Table II), making them slightly more acidic than PhCH<sub>2</sub>Ph ( $pK_a$  = 32.2). Further PhS substitution gives (PhS)<sub>2</sub>CH,  $pK_a$  = 22.8, and (PhS)<sub>2</sub>CHPh,  $pK_a$  = 23.0. Further Ph substitution gives Ph<sub>3</sub>CH,  $pK_a$  = 30.6, and Ph<sub>2</sub>CHSPh,  $pK_a$  = 26.7. The appreciable attenuation of the Ph vs. the PhS effects in the latter instances is caused by steric inhibition of resonance for Ph, but not for PhS. It is important to note in conjunction with the discussion of the  $pK_a$  of 1,3-dithiane, to follow, that acidifying effects of RS functions are not affected appreciably by incorporating the S atoms into rings (compare the acidities of 13 and 16).

The ion-pair  $pK_a$  of 30.5 originally reported for 1,3-dithiane in CHA (Table II)<sup>8</sup> suggested that it would be measurable in Me<sub>2</sub>SO, but no reaction occurred in Me<sub>2</sub>SO with Ph<sub>3</sub>C<sup>-</sup> ion ( $pK_{HA}$  = 30.6), indicating that 1,3-dithiane was a much weaker acid than assumed. The  $pK_a$ 's of 2-phenyl- and 2-(*p*-phenylphenyl)-1,3-dithiane (7 and 8) were measurable, however (e.g., eq 1). They were found to be 30.65 and 29.1, respectively (Table II). (The

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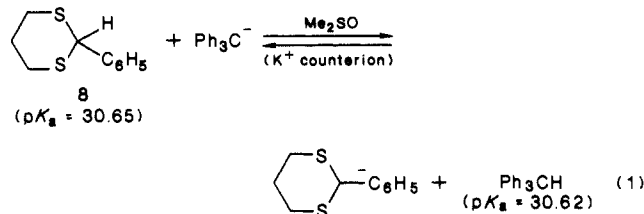
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difference in their acidities ( $\Delta pK_a = 1.55$ ) agrees reasonably well with the 2.1 difference observed in CHA.) The acidities of **7** and **8** in  $\text{Me}_2\text{SO}$ , relative to that of 9-phenylfluorene, are 2.2 and 1.6 units lower than those in CHA, however (Table II). These differences are similar to those observed for cyclopentadiene and phenylacetylene (Table I) and to those observed with sulfones **17**, **18**, and **19** (Table II). This suggests that the anions derived from the 1,3-dithianes, **7** and **8**, are also subject to stronger ion pairing in CHA than are the highly delocalized anions derived from the hydrocarbon indicators in Table I that were used to measure their acidities. This conclusion was supported by making several extrapolations to estimate the  $pK_a$  for 1,3-dithiane in  $\text{Me}_2\text{SO}$ .



Since the  $pK_a$ 's of  $(\text{PhS})_2\text{CH}_2$  (**14**) and  $(\text{PhS})_2\text{CHPh}$  (**11**) differ by 8 units, we can expect the Ph group in 2-phenyl-1,3-dithiane to exert an acidifying effect of at least 8 units. This places the  $pK_a$  of 1,3-dithiane at about 39. If we apply the CN acidifying increment of 21, used to estimate  $pK_a$ 's for  $\text{PhSCH}_3$  and  $\text{PhCH}_3$ ,<sup>15</sup> to 2-cyano-1,3-dithiane, we arrive at  $pK_a = 40$ . Finally, if the 7  $pK_a$  unit difference between the acidities of  $\text{MeSCH}_2\text{CN}$  and  $\text{CH}_3\text{CN}$  is taken as a measure of an RS acidifying effect and added to the  $pK_a$  of 31.3 for  $(n\text{-PrS})_3\text{CH}$  (**16**), the estimated  $pK_a$  of  $(\text{RS})_2\text{CH}_2$  is 38, which can be taken as a third estimate for 1,3-dithiane. We see from Table II that, when the average of these estimates of 39 is used, the apparent acidity of 1,3-dithiane, relative to 9-phenylfluorene, originally reported in CHA is 8.5 units higher than that estimated in  $\text{Me}_2\text{SO}$ , but the revised value of 37.1 is in reasonable accord, considering that it refers to ion pair aggregates rather than a monomeric species.<sup>16</sup> It follows that the relative ion-pair  $pK_a$ 's determined for 2-alkyl-1,3-dithianes in CHA are misleading and that the apparent large methyl effect is influenced by ion pairing and does not constitute evidence for a fully localized pyrimidal carbanion, as previously supposed.<sup>8,16,17</sup> Unfortunately, the presumed ion-pair  $pK_a$  of 2-methyl-1,3-dithiane in CHA (37.8) has been adopted as a standard upon which to anchor relative ion pair  $pK_a$ 's of a variety of very weak acids in THF.<sup>19</sup> As a consequence, most of the relative ion-pair  $pK_a$ 's reported in this study are several units higher than recent ion-pair  $pK_a$ 's reported in THF,<sup>14</sup> where the  $H$ - $pK_a$  of 9-phenylfluorene was used as the arbitrary anchor point.

The relative order of acidifying effects for 2-substituted 1,3-dithianes,  $\text{CN} > \text{CO}_2\text{Me} > \text{PhCH}=\text{CH} > p\text{-PhC}_6\text{H}_4 > \text{C}_6\text{H}_5$ , is similar to that observed when these functions are introduced into other substrates.<sup>1</sup> Substitution of the 1,3-dithiane-2'-ylidene-methyl moiety into the 2-position of 1,3-dithiane (entry **6**)

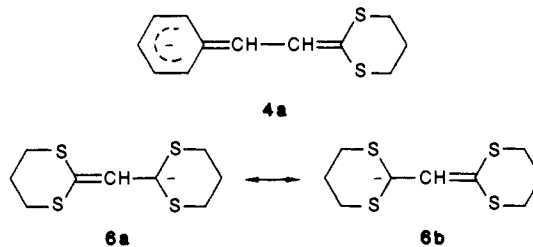
(16) After this manuscript was submitted for publication, Prof. Streitwieser kindly informed us that further investigation has revealed that the ion pair  $pK_a$  values for compounds **7**, **8**, **9**, and **13** need to be revised upward. The corrected values are shown in Table II.

(17) X-ray data show that crystalline samples of the 2-lithio derivatives of 2-methyl- and 2-phenyl-1,3-dithianes prepared by the reaction of butyllithium in THF in the presence of TMEDA differ rather markedly in structure. The methyl and phenyl groups occupy an axial position in these derivatives and the lithium atom, complexed with TMEDA and/or THF, occupies an equatorial position. The 2-Me derivative is a dimer with the Li atoms complexed only to TMEDA, whereas the 2-Ph derivative is a monomer with the Li atom complexed to one molecule each of TMEDA and THF.<sup>18</sup>

(18) Amstutz, R.; Dunitz, J. D.; Seebach, D. *Angew. Chem., Int. Ed. (Engl.)* **1981**, *20*, 465-466. Amstutz, R.; Laube, T.; Schweizer, W. B.; Seebach, D.; Dunitz, J. D. *Helv. Chim. Acta* **1984**, *67*, 224-236.

(19) (a) Fraser, R. R.; Bresse, M.; Mansour, T. S. *J. Chem. Soc., Chem. Commun.* **1983**, 620-621. (b) Fraser, R. R.; Bresse, M.; Mansour, T. S. *J. Am. Chem. Soc.* **1983**, *105*, 7790-7791. (c) Fraser, R. R.; Bresse, M.; Chuaqui-Offermanns, N.; Houk, K. N.; Rondan, N. G. *Can. J. Chem.* **1983**, *61*, 2729-2734. Fraser, R. R.; Mansour, T. S. *J. Org. Chem.* **1984**, *49*, 3442-3443.

increases the acidity by about the same amount as does the (*E*)- $\beta$ -phenylethenyl moiety (**4**). From **6** an anion with identical resonance contributors (**6a** and **6b**) is formed, but this stabilizing effect is evidently equalled by the delocalizing effect of the Ph moiety in **4** (see **4a**).



The MeS group causes a 6.5  $pK_a$  unit increase in acidity when substituted for one of the hydrogen atoms in  $\text{Me}_2\text{SO}$  to give **22**. This is similar to the 5.8 and 7 unit increases brought about for substitution of MeS for a hydrogen atom in  $\text{CH}_3\text{SO}_2\text{Ph}$  and  $\text{CH}_3\text{CN}$ , respectively. Replacement of both of the Me moieties in  $\text{MeSCH}_2\text{S(O)CH}_2\text{Me}$  (**22**), first by Et and then by *t*-Bu, to give **21** and **20**, respectively, causes additional small successive acidity increases. Acidifying effects of this kind by alkyl substitution at  $\beta$  positions to the acidic site have been observed previously and attributed to polarizability effects.<sup>13</sup> In contrast, Me substitution directly at the acidic site in sulfone **18** to give **19** causes a 2  $pK_a$  deacidifying effect. This is presumably caused by steric inhibition of solvation, perhaps coupled with an electronic effect.<sup>1h</sup>

**Summary and Conclusions.** Comparisons of acidities relative to that of 9-phenylfluorene ( $pK_a = 17.9$  in  $\text{Me}_2\text{SO}$ ) have been made for 16 hydrocarbons and 7 sulfur-containing hydrocarbons in  $\text{Me}_2\text{SO}$ , where ion pairing with the  $\text{K}^+$  counterion is absent,<sup>9</sup> with ion-pair  $pK_a$ 's in CHA. The comparisons reveal that hydrocarbons giving ions wherein the charges are highly dispersed have closely similar relative  $\text{Me}_2\text{SO}$   $pK_a$ 's and relative ion pair CHA  $pK_a$ 's. On the other hand, hydrocarbons giving ions with less dispersed charges, such as phenylacetylene on cyclopentadiene, have apparent higher acidities in low dielectric constant solvents. Saturated sulfur-containing hydrocarbons containing one  $\alpha$ -RS,  $\alpha$ -RS(O), or  $\alpha$ -RSO<sub>2</sub> function are more acidic than methane by 10-25  $pK_a$  units in a solvent like  $\text{Me}_2\text{SO}$ , but the charges in the carbanions formed are not highly dispersed. Their ion pair acidities in CHA, THF, or DME therefore appear substantially higher than those in  $\text{Me}_2\text{SO}$  when measured by using hydrocarbon indicators. For very weakly acidic compounds, such as 1,3-dithiane and its 2-alkyl derivatives, ion-pairing and aggregation effects can cause the ion-pair acidities to appear artificially high.

## Experimental Section

**Dibenz[*a, b*]cyclohepta-1,4-diene.** Dibenzosuberol (prepared by  $\text{NaBH}_4$  reduction of Aldrich suberone) was reduced by the  $\text{HCO}_2\text{H}-\text{HCO}_2\text{Na}$  method as described for the preparation of 9-(*m*-chlorophenyl)xanthene.<sup>1a</sup> Crystallization from 95% EtOH gave pale yellow crystals: mp 73-74.5 °C (lit.<sup>20</sup> mp 76-77 °C).

The other hydrocarbons listed in Table I were prepared or obtained as previously described.<sup>1</sup>

**(Alkylthio)methyl Alkyl Sulfoxides.** A commercial sample of (methylthio)methyl methyl sulfoxide was distilled twice by short-path distillation: bp 57-57.5 °C (0.15 mm) (lit.<sup>21</sup> bp 92-93 °C (2.5 mm)). Chromatography over silica gave a clear oil showing a single spot by TLC on silica.

A sample of (ethylthio)methyl ethyl sulfoxide kindly supplied by P. G. M. Wuts showed a single spot on TLC after short-path distillation: bp 61.5-62 (0.1 mm) (lit.<sup>21</sup> bp 95-97 °C (2.5 mm)).

Oxidation of bis(*tert*-butylthio)methane with 0.95 equiv of *m*-chloroperoxybenzoic acid in  $\text{CH}_2\text{Cl}_2$  gave a colorless solid. After two crystallizations from hexane the sample of (*tert*-butylthio)methyl *tert*-butyl sulfoxide melted at 74-75 °C (lit.<sup>21</sup> mp 75.0-75.9 °C).

(20) Moritani, I.; Murahashi, S.; Yoshinaga, K.; Ashitaka, H. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 1506-1511.

(21) Ogura, K.; Tsuchihashi, G. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2203-2204.

**Table III.** Equilibrium Acidity Measurements in Dimethyl Sulfoxide for 2-Substituted 1,3-Dithianes and Alkylmethyl Alkyl Sulfoxides

compd no. <sup>a</sup>	acid name	Ind <sup>a</sup>	pK <sub>a</sub> <sup>b</sup>	pK <sub>a</sub> (av)
2	2-cyano-1,3-dithiane	CNAH	19.10 ± 0.01	19.1 ± 0.02
		PFH	19.08 ± 0.01	
3	2-(methoxycarbonyl)-1,3-dithiane	MFH	20.84 ± 0.02	20.9 ± 0.06
		2NPNH	20.93 ± 0.02	
		F2	20.81 ± 0.02	
4	2-((E)-β-phenylethynyl)-1,3-dithiane	MC1PXH	26.5 ± 0.04	26.5 <sub>5</sub> ± 0.05
		TP2H	26.6 ± 0.03	
5	2-(N,N-dimethylamino)carbonyl-1,3-dithiane	PXH	27.07 ± 0.01	27.1 ± 0.08
		MC1PXH	27.02 ± 0.02	
		TP2H	27.27 ± 0.01	
6	2-[1,3-dithian-2'-ylidene]-1,3-dithiane	MC1PXH	27.42 ± 0.05	27.3 <sub>5</sub> ± 0.05
		TP2H	27.34 ± 0.01	
7	2-(p-phenylphenyl)-1,3-dithiane	DDH	29.22 ± 0.01	29.1 ± 0.1
		TXH	28.99 ± 0.02	
		PXH	29.10 <sup>c</sup>	
8	2-phenyl-1,3-dithiane	TH	30.62 ± 0.05	30.6 <sub>5</sub> ± 0.05
		DDH	30.68 <sup>c</sup>	
20	tert-butylthiomethyl tert-butyl sulfoxide	TXH	27.98 ± 0.05	28.0 ± 0.01
		PXH	28.04 <sup>c</sup>	
		MC1PXH	27.90 ± 0.05	
21	(ethylthio)methyl ethyl sulfoxide	DDH	28.76 ± 0.01	28.7 ± 0.06
		PXH	28.65 ± 0.02	
22	(methylthio)methyl methyl sulfoxide	PXH	28.95 ± 0.05	29.0 ± 0.05
		DDH	29.05 ± 0.05	

<sup>a</sup> Indicator abbreviations, names, and pK<sub>a</sub>'s have been given in earlier publications except for that of 9-benzylfluorene (F2) pK<sub>a</sub> = 21.4<sup>1</sup>.

<sup>b</sup> Average of two three-point titrations unless otherwise noted. <sup>c</sup> One three-point titration. <sup>d</sup> See Table II.

**2-Substituted 1,3-Dithianes.** The parent system was obtained commercially and purified by repeated sublimation, mp 53–54 °C. The following 2-substituted 1,3-dithianes—2-phenyl (mp 70–71 °C (lit.<sup>22</sup> mp 69–70 °C)), 2-benzyl<sup>2b</sup> (mp 34.5–35 °C), 2-(E)-phenylethyl (mp 59 °C (lit.<sup>23</sup> 57–58 °C)), and 2-(biphen-4'-yl) (mp 155–156 °C (ref 8, but no

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characterization data given))—were obtained from the corresponding aldehydes on treatment with propanedithiol by the standard procedure.<sup>24</sup> The 2-methyl and other 2-alkyl-substituted species were obtained by alkylation of 1,3-dithianyllithium and distilled just prior to use.

The methods of Seebach, Leitz, and Ehrig<sup>25</sup> were employed for the synthesis of 1,3-dithiane-2-carboxylic acid (mp 118.5–119 °C (lit. mp 114.5–116 °C)), its methyl ester (mp 28 °C (lit. mp 26–28 °C)), and N,N-dimethylamide (mp 88 °C (lit. mp 87.2–88.2 °C)). The corresponding nitrile (mp 96.5–97.5 °C (lit.<sup>26</sup> mp 91 °C)) was prepared by applying the method of Pomeroy and Craig<sup>27</sup> to 1,3-dithiane-2-carboxaldehyde.<sup>28</sup> The carboxaldehyde was also used for the synthesis of 2-(1,3-dithia-2'-ylidenemethyl)-1,3-dithiane (mp 80.5°, from 95% EtOH; anal. for C,H,S ± 0.2) by applying the trimethyl phosphite 1,3-dithian-2-ylid procedure of Corey and Markl.<sup>29</sup>

All of the 1,3-dithianes were homogeneous by TLC and displayed NMR and high resolution mass spectra in accord with the structures assigned.

**Acidity measurements in Me<sub>2</sub>SO** were carried out as previously described.<sup>1a,f</sup> The data are summarized in Table III.

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**Registry No.** **1**, 789-24-2; **2**, 33927-42-3; **3**, 56579-84-1; **4**, 69178-10-5; **5**, 51102-76-2; **6**, 103982-25-8; **7**, 54527-55-8; **8**, 5425-44-5; **9**, 505-23-7; **10**, 4832-52-4; **11**, 7695-69-4; **12**, 21122-20-3; **13**, 39137-60-5; **14**, 3561-67-9; **15**, 831-91-4; **16**, 59969-91-4; **17**, 3112-88-7; **18**, 3112-85-4; **19**, 599-70-2; **20**, 103982-26-9; **21**, 37032-07-8; **22**, 95833-70-8; di-benzo[*a,d*]cyclohepta-1,4-diene, 103982-24-7.

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