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Conformational Analysis. 32. Conformational Energies of Methyl Sulfide, Methyl Sulfoxide, and Methyl Sulfone Groups[1]

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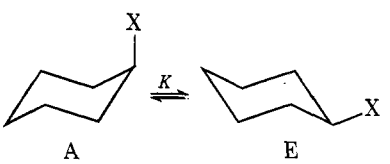
Received May 3, 1976

Conformational energy ($-\Delta G$) values for the title groups have been determined by low-temperature ^{13}C NMR signal area measurements. The values for CH_3SO_2, 2.5 kcal/mol, and CH_3SO, 1.2 kcal/mol, were determined by a "counterpoise" method, taking the ratio of the areas of the decoalesced spectra (at -95 ± 5 °C) of *cis*-4-methylcyclohexyl methyl sulfone and *cis*-4-methylcyclohexyl methyl sulfoxide and allowing for -1.7 kcal/mol as the ΔG value of the methyl group. The value for CH_3S, 1.0 kcal/mol, was determined both by an analogous method and by direct low-temperature ^{13}C NMR analysis of cyclohexyl methyl sulfide; it is in good agreement with the value in the literature.

Recently we reported[1] that the CH_3S group attached at C(5) in a 1,3-dioxane has a stronger preference for the equatorial conformation than it does when attached to a cyclohexyl ring.[2,3] In contrast, similarly placed methylsulfinyl (CH_3SO) and methylsulfonyl (CH_3SO_2) groups prefer the axial conformation. In the latter two cases, unfortunately, comparison with cyclohexyl methyl sulfoxide and sulfone was tenuous; in the case of the sulfone function, only a rather inaccurate value (2.5 kcal/mol) for phenylsulfonyl ($C_6H_5SO_2$) derived by NMR from an extremely one-sided equilibrium[4] was available; and the sulfoxide value[5] (1.9 kcal/mol) rested on the now discredited kinetic method. It is clear, however, even from the crude data, that cyclohexyl methyl sulfide, sulfoxide, and sulfone all exist with the sulfur function quite predominantly in the equatorial conformation.

The availability of ^{13}C NMR spectroscopy now makes it possible to determine, by signal area measurement at low temperature, conformational equilibria for a variety of substituents in a number of systems which were heretofore difficult to study.[6] However, measurement of signal areas[7] is difficult for conformations constituting less than 5% of the total. This difficulty can be obviated through use of a "counterpoise" method.[8] Thus, for cyclohexyl methyl sufide (**1**), it is adequate to measure the equilibrium shown in Scheme I, since the minor isomer constitutes about 6% of the total at -90 °C. But for cyclohexyl methyl sulfoxide (**2**), this value drops to 3.5% and for the sulfone **3** to much less than 1%; for the sulfoxide and sulfone functions it is desirable to measure the equilibrium shown in Scheme II, and this is preferable even for CH_3S. Here the equilibrium constants correspond to 12% of the minor isomer for **4**, 19% for **5**, and 10% for **6**, values

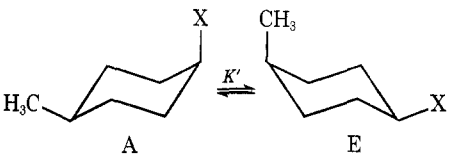
Scheme I



$\Delta G_X = -RT \ln K$

1, X = CH_3S
2, X = CH_3SO
3, X = CH_3SO_2

Scheme II



$\Delta G'_X = -RT \ln K'$

4, X = CH_3S
5, X = CH_3SO
6, X = CH_3SO_2

Table I. ^{13}C Signal Assignments in Compounds 1–15 (ppm from Me_4Si in $CDCl_3$)[a]

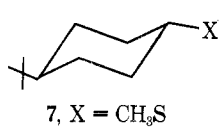
Compd	MeS	C(1)	C(2,6)[b]	C(3,5)[b]	C(4)	C(α)[c]	C(β)[d]
1	13.26	44.92	33.17	26.16	25.94		
	13.20[e]	44.94[e]	33.29[e]	26.24[e]	26.18[e]		
2	35.14	60.82	(26.07)[f]	(25.55)[f]	(25.16)[f]		
			(24.82)[f]	(25.40)[f]			
3	37.26	62.47	(25.07)[f]	(25.45)[f]	(25.07)[f]		
4	14.35	44.38	30.34	29.71	31.22	21.28	
5	36.31	61.29	24.25	30.23	30.03	20.44	
			22.44	30.75			
6	37.82	61.74	20.60	30.21	27.07	18.00	
7[e]	13.08	44.85	33.71	27.62	47.54	32.34	27.53
8	35.27	60.80	26.36	26.56	47.32	32.39	27.46
			25.28	26.36			
	35.21[e]	60.58[e]	26.27[e]	26.49[e]	47.25[e]	32.30[e]	27.43[e]
			25.07[e]	26.31[e]			
9	37.35	62.47	(26.08)[f]	(25.81)[f]	46.93	32.36	27.43
	37.38[e]	62.43[e]	(26.06)[e,f]	(25.79)[e,f]	46.92[e]	32.34[e]	27.42[e]
10[e]	14.73	44.29	31.09	21.96	48.41	32.54	27.48
10-d_4	14.72	43.97		21.75	48.35	32.55	27.48
11	37.10	61.49	27.17	23.14	47.69	32.57	27.36
			25.08	22.41			
	37.11[e]	61.33[e]	27.05[e]	23.07[e]	47.57[e]	32.49[e]	27.32[e]
11-d_4	37.08	61.08		22.88			
				22.16	47.52	32.52	27.34
12	39.68	57.76	25.12	22.14	47.06	32.58	27.44
	39.69[e]	57.79[e]	25.10[e]	22.13[e]	47.04[e]	32.56[e]	27.44[e]
12-d_4	39.68	57.46		21.94	46.93	32.58	27.45
13	13.19	44.58	33.24	35.31	32.16	22.35	
14	35.25	60.51	25.96	34.06	31.97	22.15	
			24.77	33.88			
15	37.42	62.24	25.40	33.52	31.59	21.99	

[a] In 8% solution unless otherwise indicated. [b] For the sulfoxides C(2,6) are diastereotopic and display two signals; the same is true for C(3,5). Assignment to one or other of the diastereotopic nuclei in each set has not been attempted. [c] CH_3 in methyl compounds, C_{quat} in *tert*-butyl compounds. [d] CH_3 in *tert*-butyl compounds. [e] In "concentrated" solution. [f] These assignments may have to be interchanged. However, the assignment of C(3,5) in **2** is supported by the calculations of conformational averaging of chemical shifts presented below.

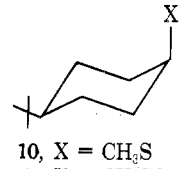
which are all easy to measure. For the equilibrium shown in Scheme II, $\Delta G' = \Delta G_X - \Delta G_{CH_3}$ whence $\Delta G_X = \Delta G' + \Delta G_{CH_3} = \Delta G' - 1.7$ kcal/mol, on the usual assumption that conformational energies are additive.

Results

The sulfides, sulfoxides, and sulfones **1–6** and the corresponding *trans*- and *cis*-4-*tert*-butyl analogues **7–12** and

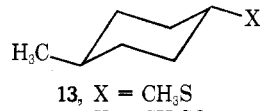


7, X = CH_3S
8, X = CH_3SO
9, X = CH_3SO_2



10, X = CH_3S
11, X = CH_3SO
12, X = CH_3SO_2

trans-4-methyl analogues **13–15** (desired for spectral comparison) were prepared by standard literature methods (see



13, X = CH_3S
14, X = CH_3SO
15, X = CH_3SO_2

Experimental Section). The ^{13}C NMR spectra of these compounds are recorded in Table I. Signal assignments were made on the basis of off-resonance decoupling, intensity measurements, and parametrization. The *C*-methyl, C(4), and C(3,5) signals can be assigned on the basis of Grant's parameters for corresponding cyclohexanes with due allowance for the upfield shift of the X substituent in the axially substituted isomers **4, 5,** and **10–12**.[9] Data for *tert*-butylcyclohexane required for reference are on record.[10] The methyl group on the X substituent as well as C(1) and C(2,) were readily assigned among the remaining signals. Only in a few cases were signals too close together for secure assignment; such situations are indicated by parentheses in Table I.

In the case of three compounds (**10, 11,** and **12**) 2,2,6,6-tetradeuterated analogues were available whose spectra supported the assignments made for the protiated species. In some cases spectra were run at two concentrations; the effect of concentration is minor (≤0.2 ppm).

With the chemical shift information of the conformationally homogeneous (anancomeric) compounds **7–15** in hand, it became easy to assign chemical shifts to individual conformational isomers of compounds **1** and **4–6** at −90 °C. (The minor conformers in **2** and **3** were not seen in the low-temperature spectra, presumably because they are present in insufficient amounts.) The pertinent information is reported in Table II which includes (in parentheses) relative area measurements of the signals in question.

On the basis of the area ratios measured, ΔG^0 values were calculated at the appropriate temperatures. A listing of these data is presented in Table III, corrected, in the case of compounds **4–6,** by 1.7 kcal/mol (the ΔG value for methyl). In Table IV the averaged values for each of the three functional groups studied are compared with values in the literature.

It is possible, also to calculate the conformational equilibrium constants K and corresponding ΔG's from averaged chemical shifts by means of the equation $K = (\delta_a - \delta)/(\delta - \delta_e)$ developed by one of us.[11] Inspection of entries **7, 8, 10,** and **11**

Table II. Low-Temperature ^{13}C NMR Spectra of Compounds 1 and 4–6 (ppm Downfield from Me_4Si)

Compd	MeS	C(1)	C(2,6)	C(3,5)	C(4)	C(Me)
1A[a]	14.70 (1)	44.28	30.41 (1)	21.39 (1)	*b*	
1E[a]	13.27 (16)	44.78	33.42 (15.8)	26.90 (16.9)	26.14	
4A[c]	14.94 (6.64)	43.79 (7.57)	30.28	29.77	33.08	23.11 (8.12)
4E[c]	13.43 (1)	45.21 (1)	27.34	31.88	26.71	17.25 (1)
5A[d,e]	36.65 (3.93)	60.42	26.26 (4.55[f])	30.91	32.60	23.04 (4.55[f])
			24.65 (4.26)	30.16		
5E[d,e]	34.76 (1)	59.95	20.91 (1)	*b*	26.58	17.13 (1)
			18.40 (1)	*b*		
5A[g,e]	36.96 (4.23)	60.59	26.26	30.85	32.57	23.03
			24.59	30.03		
5E[g,e]	35.13 (1)	60.25	20.67	*b*	26.48	17.06
			18.56	*b*		
6A[h]	39.07 (1)	*b*	24.40 (1)	*b*	32.19	22.93 (1)
6E[h]	37.08 (9.05)	61.4	19.13 (8.78)	30.15	26.21	16.99 (8.98)
6A[d]	38.95 (1)	55.84 (1)	24.48 (1)	*b*	32.2	23.01 (1)
6E[d]	36.95 (11.1)	61.27 (8.89)	19.17 (9.06)	30.20	26.39	16.98 (10.2)
13[c,i]	13.35	44.40	33.17	35.24	32.42	22.73
	[13.07]	[44.83]	[33.69]	[35.74]	[32.63]	[22.55]

[a] In 1:1 acetone-d_6/trichloroethylene at −90 °C, concentration ca. 30%. [b] Not observed. [c] In 1:1 acetone-d_6/methylene chloride at −95 °C, concentration ca. 30%. [d] In 1:1 acetone-d_6/trichloroethylene at −100 °C, concentration ca. 20%. [e] See footnote *b*, Table I, regarding the doubled signals at C(3,5) and C(2,6). [f] After correction for an overlapping peak of the minor isomer. [g] In 1:1 acetone-d_6/methylene chloride at −95 °C, concentration ca. 20%. [h] In 1:1 acetone-d_6/methylene chloride at −90 °C, concentration ca. 20%. [i] This compound is anancomeric; the data were recorded to check effect of temperature and (cf. Table I) of solvent. The data in brackets were obtained at room temperature.

Table III. Calculated $-\Delta G^0$ Values (kcal/mol) for Sulfur Functions

		Signal integrated					
Compd	Temp, °C	MeS	C(1)	C(2,6)	C(3,5)	C(4)	C(Me)
1[a]	−90	1.01	n.d.[b]	1.00	1.03	n.d.	
4[c]	−95	1.03	0.98	n.d.	n.d.	n.d.	0.96
5[a]	−100	1.19	n.d.	1.18	n.d.	n.d.	1.18
5[c]	−95	1.22	n.d.	n.d.	n.d.	n.d.	n.d.
6[c]	−90	2.50	n.d.	2.49	n.d.	n.d.	2.50
6[a]	−100	2.53	2.45	2.46	n.d.	n.d.	2.50

[a] In acetone-d_6/CHCl=CCl_2. [b] Not determined, usually because the corresponding signal in the minor isomer was not seen or not well resolved. [c] In acetone-d_6/CH_2Cl_2.

in Table I discloses that, for the sulfides and sulfoxides, only C(3,5) provides an adequate spread ($\delta_e - \delta_a$) of chemical shifts to make such a calculation reliable. The shifts δ_e and δ_a may then be taken to be the shifts of C(3,5) in **7, 8** and **10, 11,** respectively, corrected by the known global β_e effect of a *tert*-butyl substituent of 0.59 ppm.[12] Insertion of these values, and the chemical shifts δ at C(3,5) for compounds **1** and **2** gives $K = (21.37 - 26.24)/(26.24 - 27.03) = 6.16$, $\Delta G = -1.08$ kcal/mol for CH_3S, and $K = 7.14$ or 9.67, $\Delta G = -1.16$ or −1.34 kcal/mol [depending on which of the two signals for the diastereotopic carbons at C(3,5) is chosen] for CH_3SO. The former value is in excellent agreement[13] with the low-temperature value (Table IV) and the agreement of the average of the latter values, −1.25 kcal/mol, with the value in Table IV is satisfactory also.[13] The calculation for the *cis*-4-methyl-substituted compounds **4–6** is more complex, since the anticipated shifts for the axial (A) and equatorial (E) conformers in Scheme II must be computed by applying the effect of the equatorial or axial methyl substituent to the shifts calculated (vide supra) for the A and E models in Scheme I. If this is done at C(3,5), it turns out, unfortunately, that the calculated shifts for the A and E isomers in Scheme II are nearly the same. Fortunately, for the sulfones (**6, 9, 12**) one can instead use the C(1) signals for which the corrections for the distant alkyl groups[12] are small: −0.28 ppm for *tert*-butyl, −0.30 for Me_a, and −0.48 for Me_e. With these values, $K = 5.88$, $\Delta G = -1.05$ kcal/mol for **6** which gives a $-\Delta G$ value of 2.75 kcal/mol for the sulfone group, in acceptable agreement with the low-temperature value.[13]

Table IV. $-\Delta G^0$ Values (kcal/mol) for Sulfur Functions

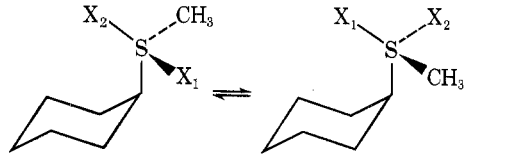
	CH_3S	CH_3SO	CH_3SO_2
This work[a]	1.00 ± 0.05	1.20 ± 0.05	2.50 ± 0.05
Lit.	1.07 ± 0.04[b]	(1.9[c])	(2.5[d])

[a] Values at −90° to −100 °C, in acetone-d_6/CHCl=CCl_2 or acetone-d_6/CH_2Cl_2. Because of the small temperature range and the apparent absence of variation in the two solvent systems, all values in Table III have been averaged. [b] Value for CD_3S at −79 °C in CS_2, ref 4. [c] Value of ref 6 for the phenylsulfinyl group; 0 °C, in 90% 2-propanol, determined by the kinetic method. [d] Value of ref 5 for the phenylsulfonyl group, room temperature in CCl_4.

Discussion

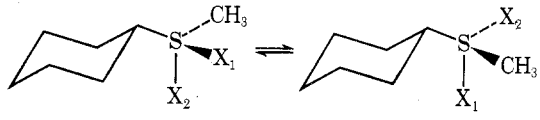
The $-\Delta G^0$ value at −90 °C for the methylthio group (Table IV) is in excellent agreement with that previously determined[4] by low-temperature ^1H NMR spectroscopy. The value previously determined by the chemical shift method in ^1H NMR, 0.7 kcal/mol,[3] is clearly too low, either because of inaccuracy of the measurement, or unsuitability of the model compounds,

Scheme III

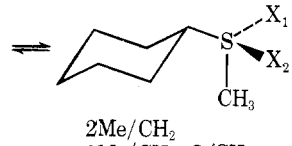


X = O or unshared pair

sulfide	Me/CH_2	Me/CH_2
sulfoxides	Me/CH_2; O/CH_2	Me/CH_2; O inside
sulfone	Me/CH_2; O/CH_2; O inside	Me/CH_2; O/CH_2; O inside



sulfide	Me/CH_2	Me/CH_2
sulfoxides	Me/CH_2; O/CH_2	Me/CH_2; 2 O/CH_2
sulfone	Me/CH_2; 3 O/CH_2	Me/CH_2; 3 O/CH_2



sulfide	$2Me/CH_2$
sulfoxides	$2Me/CH_2$; O/CH_2
sulfone	$2Me/CH_2$; 2 O/CH_2

or both. The sulfone value is much larger, as would be expected from the fact that the unshared electron pair, which confronts the ring in the sulfide,[14] is supplanted by a space-requiring oxygen atom. In both of these cases, part of the equatorial preference is undoubtedly entropic. If one assumes that the axial CH_3S and CH_3SO_2 groups will avoid the conformation in which the methyl group points into the ring, each will have two mirror-image conformations ("methyl-out") and therefore an entropy of mixing of R ln 2. For the equatorial groups one has the choice of CH_3 gauche to one or two ring methylenes in the sulfide and the combinations of one CH_3 gauche and three O gauche or two CH_3 gauche and two O gauche in the sulfone (Scheme III). From the literature it appears that both the **CH_2**–C–S–**CH_3** gauche interaction[15] and the **CH_2**–C–S–**O** gauche interaction[16] are near zero. Therefore the entropy of mixing for the equatorial CH_3S and CH_3SO_2 groups will approach R ln 3 and the entropy difference in both cases will be almost R ln 3 − R ln 2 or 0.8 eu, contributing 0.24 kcal/mol to the conformational energy at room temperature.

It follows that the additional steric interaction of the "inside" oxygen of the axial sulfone is (2.50 − 0.24) − (1.00 − 0.24) or 1.50 kcal/mol.

The axial sulfoxide will therefore exist very largely (over 90%) with the pair confronting the ring and the methyl group and oxygen atom pointing out. For an individual enantiomer of the (chiral) sulfoxide this allows only a single rotational arrangement when CH_3SO is axial as against three (vide supra) when it is equatorial. The entropic advantage for equatorial CH_3SO will therefore be R ln 3 or 2.2 eu, 1.4 eu more than for CH_3S. Thus at −95 °C, if one assumes ΔH to be the same for CH_3S and CH_3SO, ΔG should be 0.25 kcal/mol more negative for the sulfoxide. This is in excellent agreement with the experimental findings (Table IV) showing that the rather primitive assumptions (equal ΔH for MeS and MeSO, three equally populated conformations for the equatorial groups) are at least grossly correct.

Experimental Section

The ^{13}C NMR spectra were recorded on a Varian XL-100 pulsed Fourier transform nuclear magnetic resonance spectrometer. Samples were dissolved in $CDCl_3$ with tetramethylsilane (2%) as an internal standard. ^1H NMR spectra were recorded on a Varian XL-100 or Jeolco C-60 HL NMR spectrometer. The proton and carbon chemical shifts of samples as 5–20% (w/3) solutions are presented in parts per million (δ) downfield from internal tetramethylsilane (Me_4Si), and these values are accurate to ±0.01 ppm unless otherwise indicated. The low-temperature ^{13}C spectra were recorded on a Varian XL-100 using a 50:50 mixture of CH_2Cl_2–CD_3COCD_3 (or CCl_2=CHCl–CD_3COCD_3) as solvent system with Me_4Si (at the same temperature) as internal standard. Melting points were obtained in an Electrothermal melting point apparatus. Analyses were performed by Midwest Microlab, Ltd., Indianapolis, Ind., and Galbraith Laboratories, Inc., Knoxville, Tenn.

The compounds required for this study were prepared either by following standard literature procedures or as described below.

4-Methylcyclohexyl-1,1-dithiol from 4-Methylcyclohexanone, *n*-Butylamine, and Hydrogen Sulfide. The procedure used was similar to that of Magnusson.[17] Fifty-six grams (0.5 mol) of 4-methylcyclohexanone and 5 g (0.068 mol) of *n*-butylamine were dissolved in 150 ml of THF in a 1-l. three-neck flask equipped with a stirrer, gas inlet tube, thermometer, and calcium chloride tube. Fifty grams of anhydrous potassium carbonate was added, stirring commenced, and the mixture was cooled to −20 °C. Hydrogen sulfide was passed into the reaction mixture for 1 h, the temperature allowed to rise to 0 °C, and H_2S passage continued for an additional 5 h. The K_2CO_3 was filtered and washed with THF and the washings were added to the reaction mixture which was then cooled to −20 °C and acidified with 2 N hydrochloric acid. The solution was extracted with ether (3 × 150 ml) and the combined organic layer was washed with a saturated solution of sodium bicarbonate and brine and dried over anhydrous $MgSO_4$.

The dried organic layer was concentrated to ca. 250 ml, and using 23 g of $LiAlH_4$ in 150 ml of THF, the dithiol was reduced to monothiol. (The $LiAlH_4$ reaction mixture was decomposed by the addition of 45 ml of water and 250 ml of 10% sulfuric acid.) The reaction mixture was extracted with THF and dried over anhydrous $MgSO_4$ and the solvent removed on a rotary evaporator. The residue was distilled to yield 39 g (60%) of 4-methylcyclohexyl mercaptan, bp 48 °C (5 Torr) [lit.[18] bp 74–75 °C (17 Torr)].

^1H NMR ($CDCl_3$) δ 0.87 (bd, 3 H, CH_3C), 0.97–2.1 (m, 9 H, $C_{2,6,3,5,4}$ H), 2.4–2.83 and 3.03–3.37 (broad m and narrow m, 1 H, C_1 H).

4-Methylcyclohexyl Methyl Sulfide. The procedure used was similar to that of Weibull.[19] Exactly 35 g (0.27 mol) of 4-methylcyclohexyl mercaptan was placed in a 500-ml flask equipped with a magnetic stirrer and reflux condenser. To this was added 30 g of sodium hydroxide in 130 ml of water and 50 ml of ethanol. Then 34 g (0.27 mol) of dimethyl sulfate was added all at once and stirring was commenced. An exothermic reaction immediately took place and the temperature rose to 60 °C. When the solution had cooled to room temperature it was extracted with ether (3 × 100 ml). The ether extracts were combined, washed once with water and once with saturated brine, and dried over anhydrous $MgSO_4$. The ethereal solution was filtered, the solvent removed (flash evaporator), and the oily residue distilled at reduced pressure to obtain 30 g (77%) of a 45:55 mixture of *cis*- and *trans*-4-methylcyclohexyl methyl sulfide, bp 58–59 °C (10 Torr). The diastereoisomers were separated using 20% QF-1 on Chromosorb A mesh 50–80, 10-ft column at 130 °C.

^1H NMR ($CDCl_3$) cis δ 0.83 (d, J = 5.5 Hz, 3 H, CH_3C), 1.18–1.75 (m, 9 H, CH_2's and C_4 H), 1.92 (s, 3 H, CH_3S), 2.54–2.75 (m, 1 H, C_1 H_e); trans δ 0.87 (d, J = 6 Hz, 3 H, CH_3C), 0.96–2.07 (m, 9 H, CH_2's and C_4H), 2.07 (s, 3 H, CH_3S), 2.27–2.6 (m, 1 H, C_1 H_a).

***cis*-4-Methylcyclohexyl Methyl Sulfoxide.** A mixture of 1.81 g (12.5 mmol) of sulfide and 2.8 g (13 mmol) of $NaIO_4$ in 30 ml of water was stirred at 0 °C in an ice bath for 9 h. The reaction mixture was then let stand overnight (15 hr) in an icebox. The solid was filtered and washed several times with methylene chloride. The methylene chloride solution was washed once with water and dried over anhydrous $MgSO_4$. The methylene chloride was removed (flash evaporator) to obtain 1.61 g of crude sulfoxide containing 1–2% of sulfone. The impurity was removed by adsorbing the crude material dissolved in ether on an alumina column and eluting the sulfone with ether. The pure sulfoxide was then obtained by eluting with chloroform and further purification was effected by sublimation at 60 °C (0.2 Torr) to give 1.25 g (62%) of sulfoxide, mp 58–59 °C (hygroscopic).

^1H NMR ($CDCl_3$) δ 0.95 (d, J = 6 Hz, 3 H, CH_3C), 1.1–2.3 (m, 9 H, CH_2's and C_4 H), 2.45–2.75 (m, 1 H, C_1 H_e), 2.57 (s, 3 H, CH_5SO).

***trans*-4-Methylcyclohexyl Methyl Sulfoxide.** The trans sulfoxide was similarly obtained in 70% yield and recrystallized from pentane to give white plates, mp 66–67 °C.

^1H NMR ($CDCl_3$) δ 0.91 (d, J = 6 Hz, 3 H, CH_3C), 0.99–2.68 (m, 10 H, CH_2's and CH's), 2.53 (s, 3 H, CH_3SO).

***cis*-4-Methylcyclohexyl Methyl Sulfone.** A mixture of 0.72 g (5 mmol) of cis sulfide, 15 ml of 1:1 mixture of acetic acid–acetic anhydride, and 5 ml of 30% hydrogen peroxide was stirred for 3 h. Water (50 ml) was added to the reaction mixture which was then extracted with a 1:1 mixture of $CHCl_3$–CH_2Cl_2 (3 × 50 ml). The organic layer was washed with saturated solution of sodium bicarbonate and then once with water. The dried ($MgSO_4$) organic layer was concentrated (flash evaporator) to obtain crude sulfone which was purified by recrystallization from hexane to give 0.6 g (68%) of white solid, mp 71–72 °C.

^1H NMR ($CDCl_3$) δ 0.99 (d, J = 7 Hz, 3 H, CH_3C), 1.47–2.2 (m, 9 H, CH_2's and C_4 H), 2.71–2.95 (m, 1 H, C_1 H_e), 2.86 (s, 3 H, CH_3SO_2).

Anal. Calcd for $C_8H_{16}SO_2$: C, 54.51; H, 9.15. Found: C, 54.70; H, 9.03.

***trans*-4-Methylcyclohexyl Methyl Sulfone.** In a similar manner, 0.72 g (5 mmol) of trans sulfide yielded 0.62 g (71%) of sulfone after recrystallization from hexane, mp 100–101 °C.

^1H NMR ($CDCl_3$) δ 0.92 (d, J = 6.5 Hz, 3 H, CH_3C), 0.99–2.36 (m, 9 H, CH_2's and C_4H), 2.83 (s, 3 H, CH_3SO_2), 2.62–2.97 (m, 1 H, C_1 H_a).

Anal. Calcd for $C_8H_{16}SO_2$: C, 54.51; H, 9.15. Found: C, 54.24; H, 8.93.

***trans*-4-*tert*-Butylcyclohexyl Mercaptan.** This material was prepared by the procedure of Magnusson[17] as previously described,[3,20] and similarly as described above for the 4-methyl analogue. The yield of crude material was 84%, bp 98–99 °C (11.5 Torr). Gas chromatographic analysis indicated the composition to be 71.7% trans, 28.3% cis (10-ft QF-1 column at 150 °C). The material was purified either by distillation through a 48-in. double-vacuum-jacketed Podbielniak column at reduced pressure (10 Torr), using diphenylmethane as a chaser solvent (the trans isomer is the higher boiling), or (or followed by) oxidation to the disulfide by means of iodine in benzene. The disulfide was recrystallized from ethanol, mp 102–103 °C.

Anal. Calcd for $C_{20}H_{38}S_2$: C, 70.11; H, 11.18. Found: C, 70.05; H, 11.25.

The pure disulfide was reduced back to the trans mercaptan by means of lithium aluminum hydride in tetrahydrofuran[20] in 84% yield, bp 99.5–101 °C (10 Torr), $n^{20}D$ 1.4861, purity (by GLC) > 99.5%.

***trans*-4-*tert*-Butylcyclohexyl Methyl Sulfide.** This thioether was prepared from the mercaptan as described for the 4-methyl analogue above, bp 114–115 °C (12 Torr), $n^{20}D$ 1.4887 [lit.[21] bp 103–104 °C (7.5 Torr), $n^{20}D$ 1.4885].

^1H NMR ($CDCl_3$) δ 0.86 [s, 9 H, $(CH_3)_3C$], 0.95–1.47 and 1.75–1.95 (m, 9 H, CH_2's and C_4 H), 2.09 (s, 3 H, CH_3S), 2.4 (broad m, 1 H, C_1 H).

Anal. Calcd for $C_{11}H_{22}S$: C, 70.89; H, 11.90. Found: C, 71.09: H, 11.99.

***cis*-4-*tert*-Butylcyclohexyl methyl sulfide** was prepared as previously described,[21] or by methylation[17] of the cis mercaptan (see below), bp 115.5–117 °C (16 Torr), $n^{20}D$ 1.4871 [lit.[21] bp 99–100 °C (7.5 Torr), $n^{20}D$ 1.4912].

^1H NMR ($CDCl_3$) δ 0.85 [s, 9 H, $(CH_3)_3C$], 0.95–1.95 (m, 9 H, CH_2's and C_4 H), 2.03 (s, 3 H, CH_3S), 3.01 (narrow m, 1 H, C_1 H).

***cis*-4-*tert*-Butylcyclohexyl Methyl Sulfoxide.** A solution of 3.72 g (20 mmol) of *cis*-4-*tert*-butylcyclohexyl methyl sulfide in 40 ml of *p*-dioxane was cooled in an ice bath and 4.28 g (20 mmol) of $NaIO_4$ in 40 ml of distilled water was slowly added over a period of 30 min with stirring. Stirring was continued for an additional 5 h at 0 °C, after which the reaction mixture was stored overnight in the refrigerator.

The mixture was poured into 100 ml of water and the sulfoxide was extracted with methylene chloride (3 × 50 ml). The methylene chloride was washed several times with water and then dried over anhydrous $MgSO_4$. The solvent was concentrated (flash evaporator) and the crude sulfoxide was recrystallized from hexane to give 2.57 g (64%) of pure sulfoxide, mp 152.5–153.5 °C.

^1H NMR ($CDCl_3$) δ 0.88 [s, 9 H, $(CH_3)_3C$], 0.96–2.06 (m, 9 H, CH_2's and C_4 H), 2.65 (s, 3 H, CH_3SO), 2.5–2.96 (m, 1 H, C_1 H_e).

***trans*-4-*tert*-Butylcyclohexyl Methyl Sulfoxide.** The trans isomer was obtained in an analogous fashion, except that the solution was stirred in a cold-water bath overnight instead of being stored in the refrigerator. The trans sulfoxide was recrystallized from ligroin to give 0.9 g (32% based on the amount of starting material recovered from the mother liquor: ca. 1.1 g of sulfide) of pure trans sulfoxide, mp 74–75 °C.

^1H NMR ($CDCl_3$) δ 0.87 [s, 9 H, $(CH_3)_3C$], 0.9–2.7 (m, 10 H, CH_2's, CH's), 2.5 (s, 3 H, CH_3SO).

***cis*-4-*tert*-Butylcyclohexyl-*2,2,6,6-d*$_4$ Methyl Sulfide.** The procedure used was similar to that described[21] for the undeuterated compound.

A solution of 1.6 g (10 mmol) of 2,2,6,6-tetradeuterio-*trans*-4-*tert*-butylcyclohexanol[22] was converted to 2.88 g (91%) of crude tosylate as described.[23]

The crude tosylate 2.88 g (9 mmol) in 20 ml of *N*-methylpyrrolidone was allowed to react with 30 ml (20 ml of *N*-methylpyrrolidone and 10 ml of methanol) of a 0.5 M solution of potassium methyl sulfide prepared by reaction of potassium with methanethiol and the resulting mixture was heated on a steam bath for 14 h. The reaction mixture was poured into a mixture of ice and aqueous HCl and extracted three times with 25-ml portions of CH_2Cl_2. The combined methylene chloride extracts were washed three times with water and dried over $MgSO_4$. Removal of methylene chloride yielded an oil which on distillation from Kugelrohr afforded 1.55 g (80%) of *cis*-4-*tert*-butyl-2,2,6,6-tetradeuteriocyclohexyl methyl sulfide, 15% of 4-*tert*-butylcyclohexene, and ca. 5% of unknown material.

The pure cis isomer was obtained by preparative gas chromatography.

^1H NMR ($CDCl_3$) δ 0.85 [s, 9 H, $(CH_3)_3C$], 1.0–1.6 (m, 5 H, $C_{3,5,4}$ H), 2.03 (s, 3 H, CH_3S), 2.97 (broad s, 1 H, C_1 H_e).

***cis*-4-*tert*-Butylcyclohexyl-*2,2,6,6-d*$_4$ Methyl Sulfoxide.** In a similar manner as described for the undeuterated compound, 0.3 g (1.6 mmol) of *cis*-4-*tert*-butylcyclohexyl-*2,2,6,6-d*$_4$ methyl sulfide yielded 0.22 g (67%) of sulfoxide after purification of the crude material by sublimation [ca. 100 °C (0.03 Torr)], mp 149.5–151 °C.

^1H NMR ($CDCl_3$) δ 0.85 [s, 9 H, $(CH_3)_3C$], 1.0–1.86 (m, 5 H, $C_{3,5,4}$ H), 2.52 (s, 3 H, CH_3SO), 2.7 (broad s, 1 H, C_1 H_e).

***cis*-4-*tert*-Butylcyclohexyl-*2,2,6,6-d*$_4$ Methyl Sulfone.** Using 2 ml of a 1:1 mixture of HOAc/Ac_2O and 1 ml of H_2O_2 (30%), from 150 mg (0.73 mmol) of sulfoxide, 130 mg (59%) of sulfone was obtained, mp 174.5–175.5 °C.

^1H NMR ($CDCl_3$) δ 0.83 [s, 9 H, $(CH_3)_3C$], 1.03–1.7 (m, 5 H, $C_{3,5,4}$ H), 2.8 (s, 3 H, CH_3SO_2), 2.97 (broad s, 1 H, C_1 H_e).

***cis*- and *trans*-4-*tert*-butylcyclohexyl sulfones** were prepared from the sulfides in 80 and 91% yield, respectively, in the manner described for the 4-methyl analogue. The cis isomer melted at 175.5–176.5 °C (lit.[3] 176.5–177.5 °C).

^1H NMR ($CDCl_3$) δ 0.88 [s, 9 H, $(CH_3)_3C$], 1.5–1.9 and 2.25–2.6 (m, 9 H, CH_2's and C_4 H), 2.91 (s, 3 H, CH_3SO_2), 3.09 (narrow m, 1 H, C_1 H_e).

The trans isomer melted at 136.5–137.5 °C (lit.[2] 136–137 °C).

^1H NMR ($CDCl_3$) δ 0.88 [s, 9 H, $(CH_3)_3C$], 0.93–2.4 (m, 9 H, CH_2's and C_4 H), 2.78 (s, 3 H, CH_3SO_2), 2.78–3.03 (broad m, 1 H, C_1 H_a).

Anal. Calcd for $C_{11}H_{22}O_2$: C, 60.55; H, 10.09. Found: cis isomer, C, 60.23; H, 10.19; trans isomer, C, 60.54; H, 10.21.

Cyclohexyl methyl sulfoxide and sulfone were prepared as described[24] from cyclohexyl methyl sulfide (Aldrich).

Sulfoxide: ir (neat) 1040 cm^{-1} (S–O) (lit.[24] 1040 cm^{-1}).

^1H NMR ($CDCl_3$) δ 1.03–2.2 (m, 10 H, $C_{2,3,4,5}$ H), 2.47 (s, 3 H, CH_3SO), 2.27–2.7 (m, 1 H, C_1H).

Sulfone: ir (neat) 1140 and 1310 cm^{-1} (lit.[24] 1138 and 1309 cm^{-1}).

^1H NMR ($CDCl_3$) δ 0.93–2.4 (m, 10 H, $C_{2,3,4,5}$ H), 2.75 (s, 3 H, CH_3SO_2), 2.5–2.96 (m, 1 H, C_1 H).

***cis*-4-*tert*-Butylcyclohexyl Mercaptan. *cis*-4-*tert*-Butylcyclohexyl Thiocyanate.** *trans*-4-*tert*-Butylcyclohexyl *p*-toluenesulfonate[23] (31.0 g, 0.10 mol) was placed in a 500-ml three-neck round-bottom flask equipped with reflux condenser and mechanical stirrer and dissolved in the minimum amount (ca. 150 ml) of hot 95% ethanol. After addition of 29.4 g (0.30 mol) of KSCN the mixture was stirred under reflux for 12 h, cooled, and filtered, the precipitated potassium salt being thoroughly washed with ethanol which was added to the original filtrate. The ethanol solution was concentrated to one-fourth its original volume, diluted with 100 ml of water, and extracted with three 100-ml portions of ether. The combined ether extracts were washed with saturated brine, dried over $MgSO_4$, filtered, and concentrated and the product was distilled, bp 119–120 °C (2.3 Torr), yield 6.01 g (30.6%).

***cis*-4-*tert*-Butylcyclohexyl Mercaptan.** To 31.8 ml of a 1.15 M ethereal lithium aluminum hydride solution (0.0365 mol) contained in a dry 250-ml round-bottom three-neck flask equipped with a reflux condenser protected by a drying tube, mechanical stirrer, and pressure-equalized addition funnel was added 7.18 g (0.0365 mol) of *cis*-4-*tert*-butylcyclohexyl thiocyanate in 100 ml of anhydrous ether dropwise and with stirring. After addition was complete stirring was continued for 0.5 h, the solution was cooled and hydrolyzed by careful addition of 10 ml of water, and the solids were dissolved by addition of 10% sulfuric acid. The product was worked up in standard fashion and the residue distilled, bp 104 °C (15 Torr), yield 3.46 g (55.3%).

Anal. Calcd for $C_{10}H_{20}S$: C, 69.70; H, 11.70. Found: C, 70.31; H, 11.62.

***cis*-4-*tert*-Butylcyclohexyl disulfide** was prepared in the same fashion as the trans isomer in 85% yield, mp 116–117 °C after two recrystallizations from ethanol.

Anal. Calcd for $C_{20}H_{38}S_2$: C, 70.11; H, 11.18. Found: C, 70.13; H, 11.14.

Acknowledgment. This work was supported under NSF Grant CHE75-20052. We are indebted to Dr. Bruce Thill for carrying out the initial preparations of *cis*- and *trans*-4-*tert*-butylcyclohexyl mercaptan and their respective disulfides, to Mr. Rafael Shapiro for repeating the preparations and making the deuterated compounds, and to Dr. David Harris for recording the ^{13}C NMR spectra.

Registry No.—**1**, 7133-37-1; **2**, 56051-02-6; **3**, 60260-74-4; **4**, 60260-75-5; **5**, 60260-76-6; **6**, 60260-77-7; **7**, 4934-66-1; **8**, 60260-78-8; **9**, 4943-25-3; **10**, 5004-79-5; **10**-d_4, 60260-79-9; **11**, 60260-80-2; **11**-d_4, 60260-81-3; **12**, 4943-24-2; **12**-d_4, 60260-82-4; **13**, 60260-83-5; **14**, 60260-84-6; **15**, 60260-85-7; 4-methylcyclohexanone, 589-92-4; hydrogen sulfide, 7783-06-4; 4-methylcyclohexyl-1,1-dithiol, 60260-86-8; 4-methylcyclohexyl mercaptan, 60260-87-9; *trans*-4-*tert*-butylcyclohexyl mercaptan, 60260-88-0; 4-*tert*-butylcyclohexyl disulfide, 60260-89-1; 2,2,6,6-tetradeuterio-*trans*-4-*tert*-butylcyclohexanol tosylate, 51933-09-6; *cis*-4-*tert*-butycyctohexyl thiocyanate, 60260-90-4; *trans*-4-*tert*-butycyclohexyl *p*-toluenesulfonate, 7453-05-6; *cis*-4-*tert*-butylcyclohexyl mercaptan, 53273-25-9; *cis*-4-*tert*-butylcyclohexyl disulfide, 60305-05-7.

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Synthesis of the Monothiosquarate and 1,2-Dithiosquarate Ions and Their Derivatives

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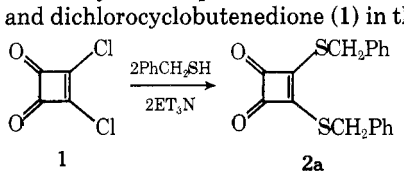
Received June 18, 1976

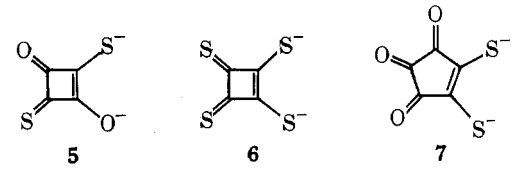
Reaction of diethyl squarate (diethoxycyclobutenedione) with 2 equiv of hydrosulfide ion gives the 1,2-dithiosquarate ion (DTS^{2-}) and reaction with 1 equiv gives the 3-ethoxycyclobutenedione-4-thiolate ion (**9**), which can be hydrolyzed to the monothiosquarate ion (MTS^{2-}). Thiosquarate ions are readily alkylated at sulfur to give alkylthio-substituted cyclobutenediones. For example, 3,4-bis(ethylthio)cyclobutenedione (**2b**) is prepared from DTS^{2-} and 3-ethoxy-4-ethylthiocyclobutenedione (**10b**) is obtained from **9**. Reaction of **10b** with 1 equiv of dimethylamine selectively replaces the ethoxy group, and reaction of **2b** with excess diethylamine gives a ring-opened product. The ir and ^1H NMR spectra of the compounds are discussed.

The monocyclic oxo carbon anions ($C_nO_n^{m-}$, n = 3–6), because of their unique electronic structures, have a number of unusual physical and chemical properties.[1,2] Several years ago we became interested in synthesizing sulfur analogues of oxo carbons and chose the four-membered ring series because of the chemistry already known for squaric acid (dihydroxycyclobutenedione) and its derivatives.[3] Addition–elimination reactions of oxygen and nitrogen nucleophiles were well known for cyclobutenediones with leaving groups on the vinyl carbons,[3–6] and some displacement reactions of sulfur nucleophiles have recently been reported.[7–14] For example, α-toluenethiol and dichlorocyclobutenedione (**1**) in the presence of base give 3,4-bis(benzylthio)cyclobutenedione (**2a**), a dithioester of squaric acid.[7,15]



1 **2a**

Since our preliminary report of the monothiosquarate ion (**3**, MTS^{2-}) and the 1,2-dithiosquarate ion (**4**, DTS^{2-}),[7] others have reported the 1,3-dithiosquarate and tetrathiosquarate ions (**5** and **6**) and the 1,2-dithiocroconate ion (**7**).[14,16] In this paper the chemistry of MTS^{2-} and DTS^{2-} and related compounds is described.



5 **6** **7**

Results and Discussion

Synthesis of Thiosquarates. The thiosquarate anions