bengal (2.0×10^{-3} M) was irradiated under a current of oxygen for 30 min at 20 °C in the standard manner.[12] After removal of the solvent under reduced pressure, the GLC analysis (columns A and C) of the product mixture showed that the major product was **7a** (48%) by comparing its retention time of GLC with that of the authentic sample prepared independently. **7a** was isolated by preparative GLC (column F, column temperature 200 °C), and its spectral data agreed with those of the authentic sample described below.

A 400-mg (1.69 mmol) sample of **5a** and 600 mg (3.48 mmol) of 85% *m*-chloroperbenzoic acid (MCPBA) were dissolved in 50 mL of $CHCl_3$, and the resultant solution was stirred at 20 °C for 2 days. The solution was washed sequentially with sodium sulfite solution, aqueous $NaHCO_3$, and water, dried (Na_2SO_4), and evaporated in vacuo to afford 425 mg of two isomers (4:1) of propellane lactone in 98% yield. The two isomers were separated by preparative GLC (columns E and F, column temperature 200 °C), and the major isomer was **7a**: mp 103–104 °C; IR (KBr) 1775, 1740, 1210, 1080, 950 cm^{-1}; MS *m/e* 252 (M^+), 208, 166, 148 (base); ^1H NMR (CCl_4) δ 1.12–2.00 (m, 16 H), 2.16 (s, 3 H), 5.84 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 20.01 (t), 20.34 (t), 20.79 (t and q), 22.94 (t), 27.48 (t), 29.37 (t), 30.08 (t), 36.39 (t), 43.79 (s), 72.77 (d), 83.82 (s), 169.90 (s), 172.20 (s). Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.64; H, 7.99. Found: C, 66.66; H, 8.30.

Thermal Isomerization of 10–12 to 13–15. After compounds **10–12** were heated in degassed sealed capillaries at 200, 220, and 240 °C for 5, 15, and 40 min, respectively, their IR spectra showed the carbonyl absorption at 1730 cm^{-1} in each case.

Registry No. 1, 71734-13-9; 2, 71734-14-0; 3, 71734-15-1; **5a**, 71987-75-2; **5b**, 71987-76-3; **5c**, 7176-87-6; **6a**, 71987-77-4; **6b**, 71987-78-5; **6c**, 71987-79-6; **7a**, 71987-80-9; **9**, 71987-81-0; **10**, 71987-82-1; **11**, 71987-83-2; **12**, 71987-84-3; **13**, 71987-85-4; **14**, 71987-86-5; **15**, 71987-87-6.

(12) Denny, R. W.; Nickon, A. *Org. React.* **1973**, *20*, 133.

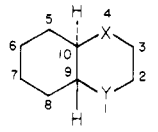
Carbon-13 Nuclear Magnetic Resonance Spectra of *trans*-1-Thiadecalin, *trans*-1,4-Dithiadecalin, *trans*-1,4-Oxathiadecalin, and the Corresponding Sulfoxides and Sulfones

Robert P. Rooney and Slayton A. Evans, Jr.*

The William Rand Kenan, Jr. Laboratories of Chemistry, The University of North Carolina, Chapel Hill, North Carolina 27514

Received June 5, 1979

During the course of our research dealing with the quantitative conformational aspects of heterosubstituted *trans*-decalins,[1] it became apparent that an examination of the ^{13}C NMR shifts of these molecules might provide useful information about interactions of sulfinyl and sulfonyl groups with neighboring carbons. Although a number of reports are available describing the influence of sulfinyl and sulfonyl groups on the shifts of proximal carbons,[2] much of the information is difficult to correlate in a useful way because of uncertainties in conformational distribution in acyclic systems and the lack of a large number of systematic studies on conformationally homogeneous compounds. The compounds described below are of the *trans*-decalin structure which ensures conformational rigidity as well as stereochemical similarity.



X = O, S, CH_2
Y = S, SO(ax), SO(eq), SO_2

Results and Discussion

Syntheses. The preparations of *trans*-1,4-oxathiadecalin (**1**), the isomeric sulfoxides (**2α**, **2β**), and the sulfone (**3**), as well as *trans*-1-thiadecalin (**4**) and *trans*-1,4-dithiadecalin (**7**), have been previously described.[1,3,6]

Oxidation of thiadecalin **4** with 1 equiv of *m*-chloroperoxybenzoic acid (mCPBA) gave sulfoxides **5α** and **5β** in 55% yield. Thiadecalin 1,1-dioxide **6** was obtained by exhaustive oxidation of **4** with hydrogen peroxide in acetic acid.[5] The diastereoisomeric dithiadecalin sulfoxides, **8α** and **8β**, were prepared from oxidation of **7** with a 0.5 equiv of hydrogen peroxide in acetic acid[7] while sulfone **9** was obtained from potassium permanganate oxidation of **8**.[8]

Stereochemical Assignments. The trans stereochemistry about the C9,C10 ring junction for oxathiadecalin **1**, thiadecalin **4**, and dithiadecalin **7** has been determined from the methods of syntheses.[1,3b,6] Establishment of the axial and equatorial configuration of the isomeric sulfoxides was based primarily on the expected differences in ^{13}C shifts of Cβ and Cγ carbons. For example, the isomer of the pair with the larger upfield Cγ shifts and smaller downfield Cβ shifts was assigned the β (axial) configuration.

^{13}C NMR Spectral Data. The ^{13}C NMR shift assignments were based on anticipated shifts due to the inductive/field effects[9] of oxygen and sulfur atoms in the ring and particularly the effects of sulfinyl and sulfonyl moieties in conjunction with the multiplicity of the carbon signals during coherent proton off-resonance decoupling experiments.[10] The data are discussed in terms of β and γ effects as oxygen substitution on sulfur is altered. Thus, the β carbons are *adjacent* to the sulfur atom and β to the substituent on the sulfur atom (e.g., lone pair electrons or oxygen atom).

^{13}C NMR Spectra of Sulfides. The ^{13}C NMR chemical shifts of thiadecalin **4** have been previously assigned,[11] while only the assignments of C2, C3, C9, and C10 of oxathiadecalin **1** have been made.[1] The chemical shift of C2 in **1**[12] previously assigned as δ 32.74 is now reassigned as

(1) D. M. Frieze, P. F. Hughes, R. L. Merrill, and S. A. Evans, Jr., *J. Org. Chem.*, **42**, 2206 (1977).

(2) (a) G. Barbarella, P. Dembeck, A. Garbesi, and A. Fava, *Org. Magn. Reson.*, **8**, 108 (1976); (b) S. S. McCrachren and S. A. Evans, Jr., *J. Org. Chem.*, **44**, 3551 (1979); (c) G. A. Olah, D. J. Donovan, H. C. Lin, H. Mayr, P. Andreozzi, and G. Klopman, *ibid.*, **43**, 2268 (1978).

(3) (a) V. I. Dronov, V. P. Krivonogov, and V. S. Nikitina, *Khim. Geterotsikl. Soedin.*, **6**, 335 (1970); *Chem. Abstr.* **73**, 66363j (1970); (b) P. K. Claus, F. W. Vierhapper, and R. L. Willer, *J. Org. Chem.*, **42**, 4016 (1977).

(4) C. R. Johnson and D. M. McCants, *J. Am. Chem. Soc.*, **87**, 1109 (1965).

(5) For a summary describing the oxidation/reduction reactions of organosulfur compounds, see E. Block, "Reactions of Organosulfur Compounds", Academic Press, New York, 1978, Chapter 1, p 16.

(6) C. C. J. Culvenor, W. Davies, D. G. Hawthorne, P. L. MacDonald, and A. V. Robertson, *Aust. J. Chem.*, **20**, 2207 (1967).

(7) W. E. Parham and M. D. Bhavsar, *J. Org. Chem.*, **28**, 2686 (1963).

(8) (a) F. D. Chatterway and E. G. Kellet, *J. Chem. Soc.*, 1352 (1930); (b) H. B. Henbest and S. A. Khan, *Chem. Commun.*, 1036 (1968); (c) S. A. Khan, J. B. Lambert, O. Hernadez, and F. A. Carey, *J. Am. Chem. Soc.*, **97**, 1468 (1975).

(9) J. A. Hirsch and E. Havinga, *J. Org. Chem.*, **41**, 455 (1976).

(10) R. R. Ernst, *J. Chem. Phys.*, **45**, 3845 (1966).

(11) F. W. Vierhapper and R. L. Willer, *J. Org. Chem.*, **42**, 4024 (1977).

(12) In ref 1, the proper nomenclature system applicable to 1,4-oxathiadecalin requires the methylene carbon adjacent to sulfur to be referred to as C3; however, in this report the same methylene carbon adjacent to sulfur is C2. This change in nomenclature allows for a clearer presentation of the ^{13}C NMR data, particularly with reference to compounds **4**, **5**, and **6**.

0022-3263/80/1945-0180$01.00/0

Table I. ^{13}C NMR Chemical Shift Data (Parts per Million) for Substituted Thiadecalins[a]

X	Y	compd	C2	C3	C4	C5	C6	C7	C8	C9	C10	ref
O	S	1	28.89	68.78		32.74	24.97	25.90	30.75	43.96	82.57	1,[a] this work
	SO	2β	45.99	57.30		32.38	24.21	25.33	25.96	57.14	70.12	1,[a] this work
	SO	2α	51.84	63.13		32.17	24.14	24.81	25.66	66.66	77.34	1,[a] this work
	SO_2	3	52.62	65.03		31.78	23.82	24.04	18.91	65.75	78.95	1,[a] this work
CH_2	S	4	30.00	28.21	34.37	34.52	26.32	26.73	32.54	46.94	44.21	11, this work
	SO	5β	46.45	15.71	32.89	33.84	25.53	26.06	27.74	59.57	31.27	this work
	SO	5α	51.47	21.75	32.89	33.14	25.39	25.45	27.01	67.11	38.74	this work
	SO_2	6	51.59	23.15	32.06	32.78	24.78	25.17	20.29	65.06	39.83	this work
	SCH_3^+,PF_6^-	10α	41.32	23.35	31.84	33.82	25.48	25.81	28.52	58.83	40.30	20
	SCH_3^+,PF_6^-	10β	36.41	16.10	30.80	33.94	25.43	26.75	28.69	52.50	34.42	20
	$S{=}NC_6H_5Cl$	11α	48.55	22.94	32.37	33.34	25.54	25.28	27.62	66.55	40.03	21
	$S{=}NC_6H_5Cl$	11β	43.67	16.49	32.66	34.07	25.86	25.24	28.11	59.46	31.75	21
S	S	7	31.26	31.26		32.71	26.46	26.46	32.71	47.13	47.13	this work
	SO	8β	47.14	17.85		31.90	25.60	25.71	28.28	59.47	33.91	this work
	SO	8α	52.56	25.40		31.39	24.81	25.09	26.77	67.95	43.10	this work
	SO_2	9	53.48	26.45		30.98	24.41	25.10	20.23	67.84	44.07	this work

[a] Only the partial ^{13}C NMR spectra of 1, 2α, 2β, and 3 were previously reported in ref 1.

δ 28.89. This value seems more reasonable when comparison is made with the monocyclic analogue, 1,4-oxathiane, where C2 is δ 27.0[13] We have found it informative to compare the chemical shifts of 1, 4, and 7 with those of *trans*-decalin.[14] For instance, replacement of the C1 methylene group by sulfur (*trans*-decalin → **4**) leads to a downfield shift of the α carbons, C2 and C9, by 2.83 and 2.73 ppm, respectively. Substitution of two sulfur atoms at C1 and C4 (*trans*-decalin → **7**) affords a slightly larger downfield shift of C2, C3 and C9, C10 ($\Delta\delta$ = 4.09 and 2.91 ppm, respectively). These comparisons clearly indicate that the α effect of divalent sulfur is slightly deshielding. The α effect of oxygen is substantial, causing downfield shifts of 40.57 and 38.36 ppm for C3 and C10, respectively, in the conversion of **1** → **4**. The α effects of oxygen and sulfur in these systems are entirely consistent with the expected electronegativity influence.[15]

β-SO Effects. Oxidation of a sulfide to a sulfoxide leads to deshielding of the carbons β to the sulfinyl oxygen atom. This "β-SO effect equals $\delta_{C\beta}$(sulfoxide) − $\delta_{C\beta}$(sulfide) and probably arises from an inductive effect from the partial positive charge on the sulfinyl sulfur[15,16] coupled with the inherent β effect of the oxygen substituent on sulfur.[2a]

In the axial sulfoxides, **2β**, **5β**, and **8β**, the average deshielding effects at C2 and C9 are 16.5 and 12.7 ppm, respectively; however, in the equatorial diastereoisomers, the average β-SO values are larger and virtually identical: 21.9 for C2 and 21.2 ppm for C9. The difference of ca. 7 ppm between the average β-SO effects in the axial and equatorial sulfoxides (14.6 ppm for axial and 21.6 ppm for equatorial) is nearly three times as large as the difference between the β shifts for C_β of the axial and equatorial hydroxy in *cis*- and *trans*-4-*tert*-butylcyclohexanol.[17] Buchanan and Durst,[18] having made a similar observation in their study of thiane 1-oxide, attributed the difference to a stronger electric field effect from the axial sulfinyl oxygen atom. Carey et al.[19] have used X-ray crystallographic data of diastereoisomeric 1,3-dithiane 1-oxides as a basis for evaluation of various proposals including (a) differential overlap of the sulfur 3p orbital with C_β–C_γ σ^* orbitals, (b) electronegativity differences caused by changes in Cβ–S(O)–Cβ valence angles and sulfinyl oxygen bond lengths, (c) the electric field effect, and (d) conformational interactions. All of these proposals appear to have merit, depending on the system, with no particular one having extensive applicability. From our analysis it is clear that one cannot relate the difference in β-SO effects for axial and equatorial sulfoxides to a unique property of the sulfinyl oxygen bond entirely. This seems particularly evident since the β shift in axial *S*-methylthiadecalin sulfonium salt is ca. 5.5 ppm upfield from that of the equatorial isomer.[20]

β-SO_2 Effects. The influence of the greater electropositive character of the sulfonyl sulfur relative to that of the sulfinyl sulfur, as well as the additional β oxygen effect, is evident from a comparison of the average magnitudes

(13) W. A. Szarek, D. M. Vyas, A.-M. Sepulchre, S. D. Gero, and G. Lukacs, *Can. J. Chem.*, **52**, 2041 (1974).
(14) The appropriate ^{13}C shifts for *trans*-decalin are C1, C4, C5, C8 = 34.74; C2, C3, C6, C7 = 27.17; C9, C10 = 44.22 ppm: see D. K. Dalling, D. M. Grant, and E. G. Paul, *J. Am. Chem. Soc.*, **95**, 3718 (1973).
(15) J. B. Lambert, D. A. Netzel, Hsieng-ning Sun, and K. K. Lilianstrom, *J. Am. Chem. Soc.*, **98**, 3778 (1976).
(16) Unpublished results with J. C. Dyer, The University of North Carolina.
(17) J. D. Roberts, F. J. Weigert, J. I. Kroschwitz, and H. J. Reich, *J. Am. Chem. Soc.*, **92**, 1338 (1970).
(18) G. W. Buchanan and T. Durst, *Tetrahedron Lett.*, 1683 (1975).
(19) F. A. Carey, O. D. Dailey, and W. C. Hutton, *J. Org. Chem.*, **43**, 96 (1978).
(20) R. L. Willer and E. L. Eliel, *Org. Magn. Reson.*, **9**, 285 (1977).

Table II. β-SO, β-SO_2, γ-SO, and γ-SO_2 ^{13}C NMR Substituent Effects[a]

	β-SO		β-SO_2		γ-SO			γ-SO_2		
compd	C2	C9	C2	C9	C3	C8	C10	C3	C8	C10
2β	17.10	13.18			−11.58	−4.79	−12.45			
2α	22.95	22.62			−5.68	−5.09	−5.29			
3			23.73	21.79				−3.75	−11.84	−3.63
5β	16.45	12.63			−12.50	−4.80	−12.94			
5α	21.47	20.17			−6.46	−5.53	−5.47			
6			21.59	18.12				−5.06	−12.25	−4.38
8β	15.88	12.34			−13.41	−4.43	−13.22			
8α	21.30	20.82			−5.86	−5.94	−4.03			
9			22.22	20.71				−4.81	−12.48	−3.06

[a] β-SO, β-SO_2, γ-SO, and γ-SO_2 effects are defined as $\Delta\delta = \delta_{\text{oxide(s)}} - \delta_{\text{sulfide}}$.

of the shifts at C2 and C6. Average β-SO_2 effects for carbons C2 and C9, 22.5 and 20.2, respectively, are roughly 3 ppm greater than the average β-SO values (e.g., 19.2 and 17.0 ppm, respectively).

γ-SO Effects. In the axial sulfoxides, γ-SO effects reflect net shielding and average −12 ppm at C3 and C10. Interestingly, C8 is also γ gauche to the sulfinyl oxygen atom, but γSO averages only −5 ppm, which is less than half of that observed for C3 and C10. In the equatorial sulfoxides, 2α, 5α, and 8α, γ-SO ranges from −4 to −6 ppm at C3 and C10. In all three equatorial sulfoxides, C8 exhibits γ-SO values nearly identical with those of the same carbon in the axial sulfoxide isomers. This is, of course, understandable since C8 in each compound is gauche to the sulfinyl oxygen atom.

It is obvious from examination of these data that it is not a sufficient condition for a carbon to be gauche to oxygen in order to experience a large upfield shift. We suggest that there is an additional factor which is crucial in the determination of the magnitude of γ-SO: the orientation of the γ carbon with respect to the sulfur lone pair electrons. Specifically, when the lone pair is anti to a carbon atom, for example, C3 in the axial sulfoxides, γ-SO averages −12 ppm. Conversely, when the lone pair electrons are gauche to a carbon (C3 in the equatorial sulfoxides and C8 in both the axial and equatorial diastereoisomers), γ-SO is only −5 ppm. A similar pattern is evident in the ^{13}C NMR spectra of the methylsulfonium salts of *trans*-thiadecalin examined by Willer and Eliel.[20] Here, C3, C8, and C10 in the equatorial methylsulfonium salt experience 4 ppm upfield shifts relative to those in **4**. By contrast, C3 and C10 in the axial compound, which are anti to the lone pair, experience upfield shifts of 10–12 ppm, while C8 is shifted only 4 ppm upfield.[20] Further evidence lending support to the importance of the lone pair electrons on sulfur comes from the ^{13}C NMR spectra of *N*-(4-chlorophenyl)-*trans*-1-thiadecalin-1-imides.[21] Claus et al.[21] have shown that C3 and C10 in the equatorial isomer are shielded by 4–5 ppm and C8 by nearly 5 ppm when comparison is made with the same carbons in **4**. On the other hand, C3 and C10 are shielded by 11–12 ppm while C8 is shielded by only ca. 4.5 ppm in the axial isomer.

Based on the results reported here, it would seem reasonable to apportion the contributions to the shielding of γ carbons in sulfoxides as follows: γ-SO (gauche) = −5 ppm; γ-SO (anti) = −5 ppm; γ lone pair electrons (anti) = −7 ppm; γ lone pair electrons (gauche) = 0 ppm. Although the mechanisms of shielding by the gauche sulfinyl oxygen cannot be described quantitatively at the present time, it does seem likely that the γ gauche array of carbon and second row heteroatoms (in general) causing shielding is operable here too. A shielding contribution to the γ gauche array by the lone-pair electrons may well have an origin in the overlap of the nonbonding 3p orbital of sulfur with the Cβ–Cγ σ* orbital.[19,22] On the other hand, the γ-SO (anti) effect may be related to the conjugative transfer of charge as proposed by Eliel et al.[23]

γ-SO_2 Effects. The γ-SO_2 effects at C3 and C10 are generally 1–2 ppm smaller than the γ-SO effects in the equatorial sulfoxides. Presumably, these γ-SO_2 effects are due to the gauche relationship between the axial sulfonyl oxygen and the γ carbons. At C8, γ-SO_2 is considerably larger, in some instances as much as three times as large as γ-SO_2 at C3 and C10. Since C8 is gauche to both sulfonyl oxygen atoms, one might have predicted this increased shielding. The necessity of a doubly gauche array for extensive shielding has, in fact, already been suggested by Fava et al.[2] and recently demonstrated by Fawcett et al.,[24] who arrived at a value of 9.39 ± 1.64 ppm as the shift difference resulting from a carbon gauche to both oxygens (sulfone) and a carbon gauche to only one (sulfoxide).

Experimental Section

Melting points were obtained in a Mel-Temp melting point apparatus with an open capillary tube and are uncorrected.

Microanalyses were performed by Integral Microanalytical Laboratories, Inc., Raleigh, N.C.

^{13}C NMR FT spectra were recorded on a Varian Model XL-100-12 NMR spectrometer controlled by a 620/f computer. All FT spectra were obtained at ambient temperature (ca. 30 °C) and Fourier transforms were based upon 8K data points with off-resonance and noise decoupling. The ^{13}C NMR chemical shifts of samples as 5–15 (v/v %) deuteriochloroform ($CDCl_3$) solutions are presented in parts per million (δ) downfield from internal tetramethylsilane (Me_4Si), and these values are considered accurate to ±0.03 ppm, unless otherwise indicated.

α,β-*trans*-1-Thiadecalin 1-Oxides (5α,5β) from *m*-Chloroperbenzoic Acid Oxidation of 4. *trans*-1-Thiadecalin (264 mg, 1.69 mmol) was dissolved in 20 mL of methylene chloride and cooled to 0–5 °C (ice bath). A solution of *m*-chloroperoxybenzoic acid (330 mg, 1.65 mmol) in methylene chloride (20 mL) was added dropwise to the methylene chloride solution of sulfide **1**. After 6 h, the resulting solution was allowed to warm to ambient temperature. The solution was washed with an aqueous 5% solution of sodium bicarbonate (3 × 25 mL), dried ($MgSO_4$), and concentrated to dryness (rotary evaporator) to afford an opaque oil which later solidified (218 mg, 76.7%). Purification by column chromatography using neutral alumina and methylene chloride–ethyl acetate (1:1) as the eluent afforded 33 mg of a colorless solid as fraction 1 (mp 82.5–86.0 °C), later identified as 5β, and 69 mg of a crystalline material as fraction 2, later identified as 5α (mp 72.0–74.0 °C). Anal. Calcd for $C_9H_{16}SO$: C, 62.73; H,

(21) P. K. Claus, W. Rieder, and F. W. Vierhapper, *Monatsh. Chem.*, **109**, 631 (1978).

(22) J. Klein and H. Stollar, *Tetrahedron*, **30**, 2541 (1974).

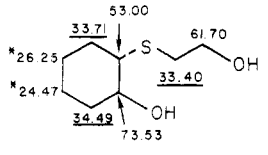
(23) E. L. Eliel, W. F. Bailey, L. D. Kopp, R. L. Willer, D. M. Grant, R. Bertrand, K. A. Christensen, D. K. Dalling, M. W. Duch, E. Wenkert, F. M. Schell, and D. W. Cockran, *J. Am. Chem. Soc.*, **97**, 322 (1975).

(24) A. H. Fawcett, K. J. Ivin, and C. D. Stewart, *Org. Magn. Reson.*, 11, 3 (1978).

9.38; S, 18.60. Found (fraction 1): C, 62.51, H. 9.09; S. 18.32. Found (fraction 2): C, 62.59; H. 9.49; S, 18.41.

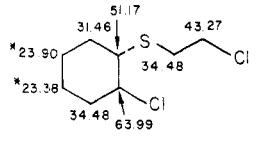
***trans*-1-Thiadecalin 1,1-dioxide (6).** *trans*-1-Thiadecalin (234 mg, 1.50 mmol) was dissolved in a solution of 7 mL of acetic acid and 4 mL of 30% hydrogen peroxide. The resulting solution was refluxed for 0.75 h, cooled to ambient temperature, neutralized with sodium bicarbonate, and finally extracted with methylene chloride (3 × 75 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated to dryness (rotary evaporator) to afford 198 mg (70.2%) of a colorless crystalline solid. Purification using column chromatography (neutral alumina with hexanes, then hexanes–methylene chloride (1:1), and finally methylene chloride as eluents) gave 114 mg (41.0%) of thiadecalin sulfone **6**: mp 114.0–115.8 °C. Anal. Calcd for $C_9H_{16}SO_2$: C, 57.40; H, 8.58; S, 17.03. Found: C, 57.46; H, 8.79; S, 17.33.

***trans*-2-Hydroxycyclohexyl 2-Hydroxyethyl Sulfide.** Sodium (1.15 g, 0.050 mol) and 2-mercaptoethanol (39.0 g, 0.50 mol) were dissolved in absolute ethanol (150 mL) under a nitrogen atmosphere. Cyclohexene oxide (49.0 g, 0.50 mol) was added to the above solution dropwise (1.5 h), stirred at ambient temperature for 0.5 h, then refluxed overnight (approximately 20 h). The solution was allowed to cool to ambient temperature and diluted with 400 mL of water. The resulting mixture was extracted with ethyl ether (3 × 150 mL) and the ethereal solution was dried ($MgSO_4$) and filtered. The ether solvent was removed (rotary evaporator) to afford an oily residue which was distilled (bp 158–167 °C at 2.0–2.8 torr) to give 17.8 g of a white solid: mp 43–48 °C (lit.[25] mp 46 °C).



* and ___ are interchangeable

***trans*-2-Chlorocyclohexyl 2-Chloroethyl Sulfide.** A solution of *trans*-2-hydroxycyclohexyl 2-hydroxyethyl sulfide (8.8 g, 50 mmol) in 50 mL of ethyl ether was added to a solution containing thionyl chloride (9.0 mL, 14.6 g, 130 mmol) in 50 mL of dry ether over a period of 1 h. The solution was stirred at ambient temperature for 48 h. Removal of the ether solvent and excess thionyl chloride (rotary evaporator) followed by distillation at reduced pressure (2.6 torr) afforded a clear yellow liquid (8.8 g, 83%): bp 143 °C [lit.[26] mp 84–86 °C (0.2 torr)].



* are interchangeable

***trans*-1,4-Dithiadecalin (7).** 2-Chlorocyclohexyl 2-chloroethyl sulfide (3.3 g, 150 mmol) in 15 mL of ethanol was added to an ethanol–water (1:1) solution of sodium sulfide nonahydrate (7.2 g, 0.30 mol). The resulting solution was stirred for 2 h at 60 °C and poured over ice. The colorless solid which precipitated was collected by filtration and purified by sublimation (70 °C, 1.2 torr) and column chromatography (using alumina as solid support and cyclohexane and cyclohexane–methylene chloride (1:1) as eluents) to afford 720 mg (27%) of a crystalline solid: mp 72–75.5 °C [lit.[6] mp 77–78 °C].

***α,β-trans*-1,4-Dithiadecalin 1-Oxides (8α,8β).** Hydrogen peroxide (30%, 0.6 mL, 5 mmol) in 15 mL of acetic acid was added slowly to a solution containing *trans*-1, 4-dithiadecalin (1.74 g, 10.0 mmol) in acetic acid (25 mL). The solution was stirred overnight (20 h), diluted with water (50 mL) to precipitate unreacted starting material, filtered, and finally neutralized with saturated sodium bicarbonate (solution). The resulting mixture was extracted with methylene chloride (3 × 50 mL) and dried ($MgSO_4$), and the solvent was removed (rotary evaporator) to give a colorless solid. Purification by column chromatography (alumina, cyclohexane, cyclohexane–methylene chloride (1:1), methylene chloride, and methylene chloride–ethyl acetate (3:1) solvents) gave 100 mg of a crystalline material as fraction 1, later identified as 8β (mp 113.0–114.0 °C); 58 mg of crystalline material as fraction 2 (mp 88–100 °C); 124 mg of colorless solid as fraction 3, later identified as 8α (mp 120.2–121.5 °C). Anal. Calcd for $C_8H_{14}SO$: C, 50.49; H, 7.41; S, 33.69. Found (fraction 1): C, 50.62; H, 7.40; S, 33.40. Found (fraction 3): C, 50.64; H, 7.61; S, 33.45.

***trans*-1,4-Dithiadecalin 1,1-Dioxide (9).** A mixture of the two dithiadecalin sulfoxides 8α and 8β (95 mg, 0.50 mmol) was suspended in a solution containing magnesium sulfate (150 mg) in 20 mL of water. An aqueous solution of potassium permanganate (53 mg, 0.33 mmol) was added slowly to the suspension and the resulting mixture was stirred for 2 h. The reaction mixture was treated with excess sodium bisulfite to dissolve the manganese dioxide. The clear aqueous solution was extracted with methylene chloride (3 × 25 mL). The methylene chloride solution was dried ($MgSO_4$) and concentrated to dryness (rotary evaporator) to give 81 mg (79%) of a crystalline solid. This material was purified by column chromatography (alumina, cyclohexane, cyclohexane–methylene chloride (1:1), methylene chloride, and methylene chloride–ethyl acetate (5:1) solvents) to give 49 mg (48%) of analytically pure material: mp 138–142 °C. Anal. Calcd for $C_8H_{14}S_2O_2$: C, 46.57; H, 6.84; S, 31.08. Found: C, 46.49; H, 6.81; S, 30.91.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Graduate Fellowship Program sponsored by the National Science Foundation (Grant No. SP-178-21239) for a fellowship to R.P.R. We thank Dr. David L. Harris for recording numerous ^{13}C NMR spectra related to this research. Purchase of the NMR instrument was made possible by NSF Instrument Grants GU-2059, 2059-Amendment I, and GP-37602 and by NIH Grant 5S05RR07072.

Registry No. 1, 62015-71-8; 2α, 62057-86-7; 2β, 62015-75-2; 3, 62015-76-3; 4, 54340-73-7; 5α, 67530-09-0; 5β, 67530-10-3; 6, 71989-44-1; 7, 16291-03-5; 8α, 71989-45-2; 8β, 72028-92-3; 9, 71989-46-3; *trans*-2-hydroxycyclohexyl 2-hydroxyethyl sulfide, 71989-47-4; 2-mercaptoethanol, 60-24-2; cyclohexene oxide, 286-20-4; *trans*-2-chlorocyclohexyl 2-chloroethyl sulfide, 71989-48-5.

(25) L. N. Owen and P. N. Smith, *J. Chem. Soc.*, 2973 (1951).
(26) R. C. Fuson, C. C. Price, R. A. Bauman, O. H. Bullitt, W. R. Hatchard, and E. W. Maynert, *J. Org. Chem.*, 11, 469 (1946).

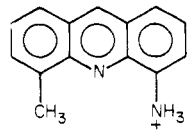
A Spectrophotometric Probe for Studying Solvent-Sorting Effects

F. M. Menger* and T. D. Singh

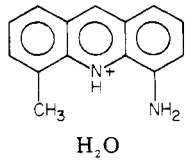
Department of Chemistry, Emory University, Atlanta, Georgia 30322

Received July 19, 1979

Over three decades ago Craig discovered an exception to the rule that aminoacridines in dilute acid protonate at the ring nitrogen.[1] Protonation of 4-amino-5-methylacridine in acidic *ethanol* occurs on the primary amino group (although in *water* the ring nitrogen remains the more basic atom):



C_2H_5OH



H_2O

(1) Craig, D. P. *J. Chem. Soc.* **1946**, 534. Note that this article uses a numbering system which has now been replaced.

0022-3263/80/1945-0183$01.00/0