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STEREOCHEMICAL STRUCTURE DETERMINATION OF ALKENESULFONIC ACIDS AND CHLORIDES VIA NMR DIFFERENTIAL SOLVENT SHIELDING ANISOTROPY

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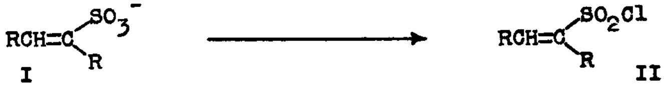
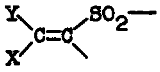
Our preceding paper[1] described a general synthesis of 2,3-dialkylethenesulfonic acid salts (I), species that do not possess vicinal olefinic protons. Their geometry, therefore, could not be unequivocally determined by usual spectroscopic methods, viz., HC=CH ir out-of-plane deformations[2a,b] and nmr coupling constants.[2c] Moreover, the insolubility of sulfonic acids and salts in solvents such as CCl_4, $CDCl_3$, and C_6D_6 precludes the application of special nmr techniques that have been useful with related olefinic systems.[3] For these and other reasons the stereochemistry of alkenesulfonic acid salts similar to I has been assumed,[4a,b] could not be ascertained,[5] or was not reported.[6]

We have now found that the geometry of I is easily determined from the nmr differential solvent shielding anisotropy exhibited by the corresponding sulfonyl chlorides (II). The quantitative conversion of a single isomer of I into a single isomer of II under neutral conditions in a nonpolar solvent at room temperature is convincing evidence that the geometry is maintained during the process.[1] The procedure described here was applied specifically to I and II in which both R's, respectively, are Me, Et, and Pr, compounds prepared from the corresponding $RCH_2SO_2CH_2R$.[7]


I II

The method is based on our observation with α,β-unsaturated sulfones of known geometry whereby we were able to correlate geometric structure with nmr anisotropic solvent shielding.[8] Namely, in changing solvents from CCl_4 to C_6D_6

the upfield displacement ($\Delta\tau$) of the resonance (τ) exhibited by protons trans to sulfonyl is greater than that exhibited by cis protons (Table I), i.e:

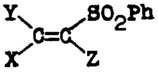


X and Y = H or alkyl

$$\Delta\tau = \tau(C_6D_6) - \tau(CCl_4) \qquad \Delta\tau_X > \Delta\tau_Y$$

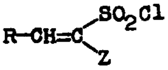
The method was then applied to the sulfonyl chlorides II to determine their stereochemistry; the results are shown in Table II.

TABLE I. ANISOTROPIC SOLVENT SHIELDING OF α,β-UNSATURATED SULFONES[a]

			Nmr						
			τ_X		τ_Y		$\Delta\tau_X$	$\Delta\tau_Y$	$\Delta\tau_X-\Delta\tau_Y$
X	Y	Z	CCl_4	C_6D_6	CCl_4	C_6D_6			
CH_3	H	H	8.10	8.82	3.18	3.32	0.72	0.14	0.58
H	CH_3	H	3.71	4.33	7.86	8.17	.62	.31	.31
CH_3	H	Me	8.18	8.79	3.13	3.10	.61	-.03	.64
H	CH_3	Me	3.93	4.48	7.87	8.05	.55	.18	.37

[a] Sample concentrations, 2-4%; recorded on a Varian A-56/60 spectrophotometer; sweep width, 500 Hz; TMS as internal standard.

TABLE II. ANISOTROPIC SOLVENT SHIELDING OF SULFONYL CHLORIDES II[a]

			Nmr						
			τ_R		$\tau_{C\underline{H}=C}$		$\Delta\tau_R$	$\Delta\tau_{C\underline{H}=C}$	$\Delta\tau_R-\Delta\tau_{C\underline{H}=C}$
R	Z		CCl_4	C_6D_6	CCl_4	C_6D_6			
CH_3	Me		8.06	9.17	3.14	3.63	1.11	0.49	0.62
CH_3CH_2	Et	CH_2	7.77	8.64	3.26	3.48	.87	.22	.65
		CH_3	8.82	9.55	"	"	.73	"	.51
$CH_3\underset{\beta}{CH_2}\underset{\alpha}{CH_2}$	Pr	α-CH_2	7.80	8.47	3.22	3.35	.67	.13	.54
		β-CH_2	8.35	9.05	"	"	.70	"	.57
		CH_3	8.98	9.42	"	"	.44	"	.31

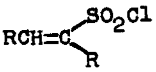
[a] Ref. a in Table I.

A comparison of the data in Tables I and II clearly indicates that the alkyl groups are <u>trans</u> to sulfonyl in the sulfonyl chlorides examined, <u>i.e.</u>, $\Delta\tau_R > \Delta\tau_{C\underline{H}=C}$ for each compound--by values of 0.58 ± 0.07 ppm.[9] These values are very close to those, 0.58 and 0.64, exhibited by the sulfones whose methyl groups are <u>trans</u> to sulfonyl, which suggests that the anisotropic influences of SO_2Ph and SO_2Cl are also quantitatively very similar. The configurations of II assigned by this method are supported by the comparable values for $\tau_{C\underline{H}=C}$ of II and the sulfones in which this proton is <u>cis</u> to sulfonyl. Likewise, the value for $\tau_{\underline{CH}_3-C=C}$ for II ($R = CH_3$) compares much more favorably with that of the sulfones in which CH_3 is <u>trans</u> to sulfonyl.

In general the small coupling constants exhibited by $(CH_a)(H_b)C=C-CH_c$ ($J_{ac} \cong$ 0-1.6 Hz; J_{bc} = 0-3 Hz) differ minutely for <u>cis</u> and <u>trans</u> isomers and cannot <u>per se</u> be used reliably to ascertain stereochemical structure.[3d,10]

The configuration of olefinic compounds possessing at least one olefinic proton has been determined by comparing the resonance exhibited by this proton with the values calculated for the <u>cis</u> and <u>trans</u> isomers from nmr shielding increments.[3b,c,d] The reliability of this method is reduced as the number and size of substituents are increased.[3c,d] As illustrated by the data in Table III, the configurations of sulfonyl chlorides II determined this way would be questionable at best. Only one observed value is within 0.17 ppm of a calculated value, which is the standard deviation reported for this method.[3b]

TABLE III. OBSERVED AND CALCULATED $\tau_{C\underline{H}=C}$ OF SULFONYL CHLORIDES II

	Nmr, $\tau_{C\underline{H}=C}$ (CCl_4)				
		Calcd for[b]		$\tau_{calcd} - \tau_{obsd}$	
R, R	Obsd[a]	<u>Cis</u> II	<u>Trans</u> II	<u>Cis</u> II	<u>Trans</u> II
Me, Me	3.14	3.42	3.59	0.28	0.45
Et, Et	3.26	3.42	3.59	.16	.33
Pr, Pr	3.22	3.42	3.59	.20	.37

[a] Ref. <u>a</u> in Table I. [b] Calculated from values tabulated in ref. 3b.

Nmr differential solvent anisotropy, therefore, enabled us to assign a *cis*-dialkyl geometry to II and thus to the alkenesulfonic acid salts, I. The results support Bordwell's proposed assignment[4a] of a *cis*-diphenyl geometry to the 2,3-diphenylethenesulfonic acid formed in reactions[4-6] related to ours.[1] The techniques decribed here should also apply to alkenesulfonic acids and chlorides devoid of olefinic protons, and to the quantitative determination of *cis* and *trans* isomers in a mixture (*cf.* Sataty[8]).

NOTES AND REFERENCES

1. C. Y. Meyers and L. L. Ho, *Tetrahedron Letters*, preceding paper.
2. (a) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, New York, 1958, Chapter 3; (b) D. J. Pasto and C. R. Johnson, "Organic Structure Determination," Prentice-Hall, Englewood Cliffs, N. J., 1969, Chapter 4; (c) *Ibid.*, Chapter 5.
3. For example: (a) T. Ladaal, *Tetrahedron Letters*, 1683 (1968); (b) U. E. Matter, C. Pascual, E. Pretsch, A. Pross, W. Simon, and S. Sternhell, *Tetrahedron*, **25**, 691 (1969); (c) *Ibid.*, **25**, 2023 (1969); (d) S. W. Tobey, *J. Org. Chem.*, **34**, 1281 (1969).
4. (a) F. G. Bordwell, J. M. Williams, and B. B. Jarvis, *J. Org. Chem.*, **33**, 2026 (1968), specifically p. 2028; (b) L. A. Carpino, L. V. McAdams, R. H. Rynbrandt, and J. W. Spiewak, *J. Amer. Chem. Soc.*, **93**, 476 (1971).
5. L. A. Paquette, *J. Amer. Chem. Soc.*, **86**, 4089 (1964), specifically footnote 5.
6. L. Ramberg and B. Bäcklund, *Arkiv Kemi, Minerol., Geol.*, **13 A**, No. 27 (1940), footnote p. 17.
7. The compounds in which R = heptyl were also prepared but in this case overlap of crucial nmr signals prevented reliable determination.
8. I. Sataty, Ph.D. Dissertation, Southern Illinois University, 1970; C. Y. Meyers and I. Sataty, National Meeting, Amer. Chem. Soc., Chicago, Sept. 1967, Abstracts, p. S 6. Differential anisotropic solvent shielding of *cis* and *trans* olefinic protons of other systems has been discussed by T. Ladaal, ref. 3a, among others.
9. These values reflect the α as well as β protons of alkyl. Significantly, the rather high value for a γ proton (0.31; last entry, Table II) indicates the long-range sensitivity of this method.
10. D. R. Davis and J. D. Roberts, *J. Amer. Chem. Soc.*, **84**, 2252 (1962).