134. *Stereochemistry of the Diels–Alder Reaction with Ethylenic Sulphoxides. Part VII.*[1] *Proton Magnetic Resonance Spectra of Bicyclic Sulphides, Sulphoxides, and Sulphones.*

By H. Hogeveen, G. Maccagnani, F. Montanari, and F. Taddei.

Proton magnetic resonance spectra of thio-, sulphinyl-, and sulphonyl-norbornene- and -norbornane-carboxylic acids have been measured in $NaOD-D_2O$ solution; chemical shifts and coupling constants have been determined. The anisotropic effect of the double bond on protons 1—4, and of the phenyl ring on proton 4 has been evaluated.

Proton magnetic resonance spectroscopy has been applied successfully to configurational problems in bicyclic systems;[2-4] for instance, we[5] used it when assigning the configuration at the sulphur atom in norbornene and norbornane sulphoxides. Details are now reported for carboxy-sulphides, -sulphoxides, and -sulphones in these series. The compounds, all of known configuration, were prepared by Diels–Alder reaction, between cyclopentadiene and β-phenylsulphonyl- and β-phenylsulphinyl-acrylic acids, as previously described.[5-7] Spectra have been recorded for 0·5N-solutions of sodium deuteroxide in deuterium oxide.

RESULTS

The spectra of norbornene derivatives are usually easier to analyse than those of norbornane derivatives, because in the proton magnetic resonance spectra of the latter the signals of the 5- and 6-protons overlap with others at higher field. The chemical shifts are collected in Tables 1 and 2.

The multiplet of the phenyl group, present for all the derivatives, lies at lowest magnetic field (−335 to −370 c./sec.); its fine structure and position vary with the configuration of the substituent (*endo* or *exo*) and with the type of group (S, SO, or SO_2) bonded to phenyl. For example, for the *cis-endo*-compounds (I)—(IV), a shift of 22 c./sec. to lower field is observed on passing from sulphide (I) to sulphoxides (III) and (IV), and one of 31 c./sec. on passing from the same sulphide (I) to the sulphone (II).

The spectra of the unsaturated derivatives show two asymmetrical multiplets at −260 to −300 c./sec., which disappear on hydrogenation, and these are assigned to the ethylenic 5- and 6-protons. The multiplets can be considered as an AB group, with additional fine structure arising from spin–spin interactions with H-1 and H-4. The separation between the two ethylenic protons varies with the nature and configuration of the 2- and 3-substituents.

The sharp peak at about −190 c./sec. belongs to protium oxide, present as an impurity in the deuterium oxide as well as formed in salt-formation by the carboxyl group.

For the unsaturated derivatives the resonance line in the region −90 to −120 c./sec., belonging to H-1, could not be resolved, because of coupling with other protons (*e.g.*, H-2, H-6, and H-7). However, the coupling constants $J(1,2)$ and $J(1,6)$ could be derived from multiplets of the 2- and 6-protons. This assignment is in agreement with the nearly constant chemical shift due to the presence of a carboxyl ion at position 2 in all the compounds. Small variations in position of this line depend whether this group is in the *endo*- or *exo*-position, and interaction of the latter with the 3-substituent. For the saturated compounds the line due to the 1-proton is shifted upfield by about 35 c./sec. (Table 2).

The peaks corresponding to the methylenic 7-protons form a multiplet of AB type and are observed at highest magnetic field. Because of direct and long-range coupling with other protons the multiplet components are not sharp (half-width ∼10 c./sec.). The distance

[1] Part VI, Hogeveen and Montanari, *J.*, 1963, 4864.
[2] Fraser, *Canad. J. Chem.*, 1962, **40**, 78.
[3] Wiberg, Lowrey, and Nist, *J. Amer. Chem. Soc.*, 1962, **84**, 1594.
[4] Anet, *Tetrahedron Letters*, 1962, 1219.
[5] Ghersetti, Hogeveen, Maccagnani, Montanari, and Taddei, *J.*, 1963, 3718.
[6] Montanari *et al.*, *Gazzetta*, (*a*) 1959, **89**, 1564; (*b*) 1960, **90**, 709; 1962, **92**, 1168, 1182; *Boll. sci. Fac. Chim. ind. Bologna*, 1960, **18**, 52.
[7] Hogeveen, Montanari, and Taddei, *J.*, 1964, in the press.

TABLE 1.

Proton chemical shifts * in norbornene derivatives.

	γ(1)	γ(2-en)	γ(2-ex)	γ(3-en)	γ(3-ex)	γ(4)	γ(5) †	γ(6) †	γ(7α)	γ(7β)	γ(Ph)
I	−106·8		−121·8		−161·9	−80·0	−275·3	−296·8	0	0	−368·4
	(6·80)		(6·53)		(5·82)	(7·27)	(3·81)	(3·43)	(8·69)	(8·69)	(2·16)
II	−104·6		−110·2		−149·3	−84·0	−275·8	−295·0	0	0	−337·8
	(6·84)		(6·74)		(6·04)	(7·20)	(3·80)	(3·46)	(8·69)	(8·69)	(2·70)
III	−112·3		−108·7		−154·3	−112·3	−285·8	−294·5	−19·2	−19·2	−360·0
	(6·70)		(6·76)		(5·96)	(6·70)	(3·62)	(3·47)	(8·35)	(8·35)	(2·31)
IV	−118·7		−112·6		−127·8	−44·4	−273·0	−283·6	0	0	−359·6
	(6·59)		(6·69)		(6·43)	(7·90)	(3·85)	(3·66)	(8·69)	(8·69)	(2·32)
V	−111·6		−79·1	−111·6		−106·3	−271·1	−285·4	−17·2	−32·4	−358·7
	(6·71)		(7·29)	(6·71)		(6·81)	(3·88)	(3·63)	(8·39)	(8·12)	(2·33)
VI	−105·3		−105·3	−100·0		−105·3	−275·2	−279·4	−9·1	−26·2	−359·3
	(6·82)		(6·82)	(6·92)		(6·82)	(3·81)	(3·74)	(8·53)	(8·23)	(2·32)
VII	−108·8		−108·8	−123·5		−108·8	−276·1	−276·1	−10·6	−34·4	−365·5
	(6·76)		(6·76)	(6·50)		(6·76)	(3·80)	(3·80)	(8·50)	(8·08)	(2·21)
VIII	−108·5		−121·5	−78·2		−78·2	−274·0	−274·0	−9·5	−24·2	−336·1
	(6·77)		(6·54)	(7·30)		(7·30)	(3·83)	(3·83)	(8·52)	(8·26)	(2·73)
IX	−92·7	−64·9			−156·8	−99·7	−269·2	−289·2	−18·2	−18·2	−339·6
	(7·05)	(7·54)			(5·91)	(6·92)	(3·92)	(3·56)	(8·37)	(8·37)	(2·67)
X	−103·6	−70·4			−168·0	−103·6	−274·2	−292·8	−15·7	−15·7	−367·1
	(6·85)	(7·44)			(5·71)	(6·85)	(3·83)	(3·50)	(8·41)	(8·41)	(2·18)
XI	−96·7	−76·3		−124·4		−96·7	−258·0	−284·2	−5·7	−65·1	−367·7
	(6·98)	(7·34)		(6·49)		(6·98)	(4·12)	(3·65)	(8·59)	(7·54)	(2·17)
XII	−106·8					−84·2	−279·1	−298·6	0	0	−364·2
	(6·80)					(7·20)	(3·74)	(3·40)	(8·69)	(8·69)	(2·23)
XIII	−104·9	−70·4				−100·2	−279·7	−297·1	−16·2	−16·2	−365·2
	(6·83)	(7·44)				(6·91)	(3·73)	(3·42)	(8·40)	(8·40)	(2·22)
XIV	−109·8			−109·8		−105·9	−276·6	−276·6	−10·6	(35·0)	−364·0
	(6·74)			(6·74)		(6·81)	(3·79)	(3·79)	(8·50)	(8·07)	(2·24)

* Values in parentheses are in τ units. For (Me)₃C–OH, $\tau = 8.69$ (Green, McCleverty, Pratt, and Wilkinson, *J.*, 1961, 4854). Similarly in Table 2. † The position of H-5 and H-6 may be reversed.

(I)   (II)   (III)   (IV)   (V)   (VI)

(VII)   (VIII)   (IX)   (X)   (XI)

(XII)   (XIII)   (XIV)
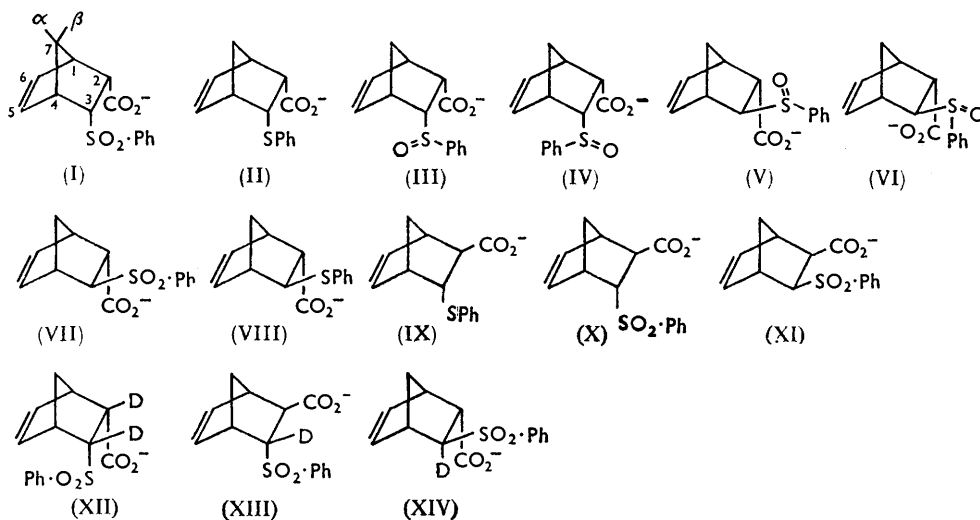
between the peaks of the 7α- and 7β-proton depends on the substituents in positions 2 and 3: it is smallest when the substituents are in the *endo-* and largest when they are in the *exo-* position.

The chemical shifts of protons 2, 3, and 4 are strongly affected by the type and position of the substituents. Therefore they can be used to study the configuration of the bicyclic compounds. In the spectrum of the *cis-endo*-sulphone (I) (Fig. 1) the multiplets of protons 2 and 3, at −121·8 and −161·9 c./sec., respectively, are of AB type, with additional splitting due to protons 1 and 4. This assignment was confirmed by exchange of proton 3 with deuterium.
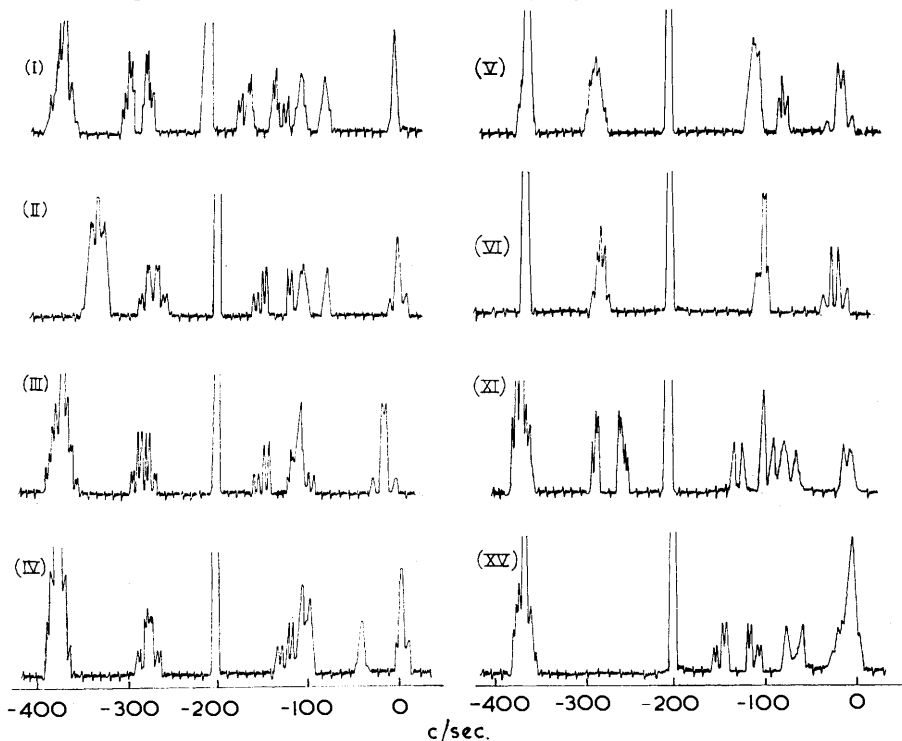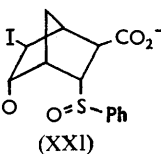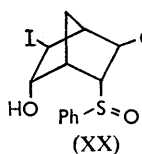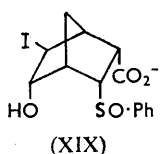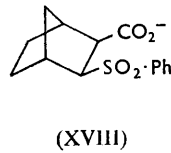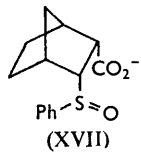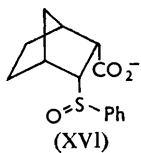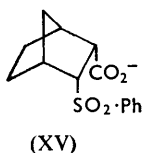
FIG. 1. FIG. 2.

Proton magnetic resonance spectra of compounds designated.

TABLE 2.

Proton chemical shifts in norbornane derivatives.

	$\gamma(1)$	$\gamma(2\text{-}en)$	$\gamma(2\text{-}ex)$	$\gamma(3\text{-}en)$	$\gamma(3\text{-}ex)$	$\gamma(4)$	$\gamma(5)$	$\gamma(6)$	$\gamma(7\alpha)$	$\gamma(7\beta)$	$\gamma(\text{Ph})$	$\gamma(\text{OH})$
XV	−73·8		−103·9		−144·6	−51·5	∼0	∼0	0	0	−364·2	
	(7·38)		(6·85)		(6·13)	(7·78)	(∼8·7)	(∼8·7)	(8·69)	(8·69)	(2·23)	
XVI	−78·8		−91·0		−134·4	−84·7	0	0	∼−4·5	−24·2	−362·8	
	(7·29)		(7·08)		(6·31)	(7·19)	(8·69)	(8·69)	(∼8·6)	(8·26)	(2·26)	
XVII	−79·8		−103·7		−103·7	∼−20	−10·1	0	−5·0	−27·1	−356·5	
	(7·28)		(6·85)		(6·85)	(∼8·3)	(8·51)	(8·69)	(8·60)	(8·21)	(2·37)	
XVIII	−61·8	−85·4		−131·1		−61·8	−2·7	8·2	0	−56·9	−365·8	
	(7·60)	(7·18)		(6·37)		(7·60)	(8·64)	(8·83)	(8·69)	(7·68)	(2·21)	
XIX	−115·2		−115·2		−170·6	−94·6	−3·0	−15·7	−39·8	−29·3	−357·6	−175·2
	(6·65)		(6·65)		(5·67)	(7·01)	(8·64)	(8·41)	(7·99)	(8·17)	(2·35)	(5·58)
XX	−84·5	−85·9			−146·9	−61·0	−35·0	−146·9	−25·3	−57·9	−359·0	−146·9
	(7·19)	(7·17)			(6·09)	(7·61)	(8·07)	(6·09)	(8·24)	(7·66)	(2·33)	(6·09)
XXI	−87·7	−69·3			−150·2	−184·5	−33·4	−150·2	−33·4	−50·8	−361·2	−150·2
	(7·14)	(7·46)			(6·03)	(5·42)	(8·10)	(6·03)	(8·10)	(7·79)	(2·29)	(6·03)

(XV) (XVI) (XVII) (XVIII)

(XIX) (XX) (XXI)

The multiplet at $-161\cdot9$ c./sec. disappears, while that at $-121\cdot8$ c./sec. changes to a slightly broader line. The deuteration at position 3 is accompanied by the slower inversion *endo* $\longrightarrow$ *exo* of the phenylsulphonyl group ($k_{H-D}/k_{inv.} = 15$),[7] and thus the peaks corresponding to protons 2 and 3 in the *trans-exo*-sulphone (VII) can be identified. The peak at $-121\cdot8$ c./sec. disappears also with the 2,3-dideuterated derivative [7] (XII). The positions of the other peaks remain almost unchanged. The line of proton 4 in sulphone (I), at $-80\cdot0$ c./sec., is rather broad on account of coupling with protons 3, 5, and 7.

With the *cis-endo*-sulphide (II) the peaks of protons 2 and 3 are shifted to higher field ($-110\cdot2$ and $-149\cdot3$ c./sec., respectively), compared with the corresponding compound (I), while that for proton 4 lies at $-84\cdot0$ c./sec. The distance between the peaks of protons 2 and 3 changes from ~40 c./sec. for compounds (I) and (II) to $45\cdot6$ and $15\cdot2$ c./sec. for compounds (III) and (IV), respectively. For the sulphoxide (III) the 4-proton signal lies at $-112\cdot3$ c./sec., together with that of proton 1, while for the sulphoxide (IV) it is shifted to much higher magnetic field ($-41\cdot4$ c./sec.). This difference is caused by the ring current of the phenyl group in compound (IV). In fact, the most probable conformation of sulphoxide [*anti*, (IV)] is one where the 4-proton lies above the phenyl ring, as previously [5] discussed. In the saturated sulphoxide [*anti*, (XVII)] the same situation occurs. The exact position of the peak cannot be determined, for it is masked by those of protons 5—7. Intensity measurements confirm, however, the presence of the 4-proton line in the multiplet, and its chemical shift was estimated to be about -20 c./sec. The peak due to the 4-proton in the *syn*-isomer (XVI) lies at $-84\cdot7$ c./sec. Therefore, the saturated sulphoxides [*syn*, (XVI); *anti*, (XVII)] show the same relative spectral behaviour as the unsaturated sulphoxides (III) and (IV).

DISCUSSION

Karplus [8] has correlated the magnitude of coupling constants between protons on adjacent carbon atoms with the dihedral angles between the carbon–hydrogen bonds. For all the *cis-endo*-compounds described here the values of the coupling constants $J(1,2)$, $J(3,4)$, $J(4,5)$, and $J(1,6)$ lie between $2\cdot3$ and $3\cdot4$ c./sec. For the *trans*-compounds, $J(4,5)$ and $J(1,6)$ still lie in the interval $2\cdot1$—$3\cdot6$ c./sec., but $J(1,2-en)$ and $J(3-en,4)$ are lower than 1 c./sec. (Table 3). J values between $2\cdot1$ and $3\cdot6$ c./sec. correspond [8] to dihedral angles of 50—60°, and those lower than 1 c./sec. to dihedral angles of $\sim90°$. This is in qualitative agreement with the dihedral angles obtained from molecular models on the basis of the *endo,exo*-configurations previously assigned.[1,5,6]

TABLE 3.

Proton coupling constants in norbornene derivatives.

	$J(1,2)$	$J(1,6)$	$J(2,3)$	$J(3,4)$	$J(4,5)$	$J(5,6)$	$J(7\alpha,7\beta)$
I	2·3	2·9	10·1	2·8	2·9	5·1	
II	2·7	2·3	9·6	3·4	2·3	4·5	~9
III	3·4	2·8	7·8	3·4	2·8	5·6	9·4
IV	2·5	2·6	6·6	2·5	2·6	6·5	
V	2·5	2·9	3·7		2·6	6·3	8·9
VI	2·1	2·1			2·1	4·6	8·9
VII			4·9	<1			9·2
VIII	2·6		3·4	<1			8·3
IX		3·2	2·8	2·8	3·6	4·3	
X	<1	3·1	5·0	2·6	3·1	5·6	
XI	<1	3·7	9·4	<1	3·1	5·7	8·7

For a series of 2-*endo*-substituted hexachlorobicyclo[2,2,1]hept-5-enes Williamson [9] found a linear correlation between $J(2-ex,3-ex)$, $J(2-ex,3-en)$, and $J(3-ex,3-en)$ and the electronegativity of the substituent (as defined by Cavanaugh and Dailey [10]). In our series a linear relation exists between $J(2-ex,3-en)$ of *trans*-derivatives (VI)—(VIII) and the

[8] Karplus, *J. Chem. Phys.*, 1959, **30**, 11.
[9] Williamson, *J. Amer. Chem. Soc.*, 1963, **85**, 516.
[10] Cavanaugh and Dailey, *J. Chem. Phys.*, 1961, **34**, 1099.

electronegativities of EtS, Et·SO, and Et·SO$_2$ groups (2·64, 2·67, and 2·81, respectively [11]), employed instead of those of PhS, Ph·SO, and Ph·SO$_2$ which are not available. An analogous correlation with $J(2\text{-}ex,3\text{-}ex)$ does not occur with the *cis*-derivatives (I)—(IV), probably owing to direct interactions through space between CO$_2^-$ at position 2 and *cis*-substituents at position 3, which were previously [1] invoked to explain the acidity measurements.

We may suppose that the variation in chemical shift of protons 1—4 due to hydrogenation is mainly caused by anisotropy of the double bond. These variations are shown in Table 4 and agree with values (0·54—0·61) derived from Fraser's results.[2]

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TABLE 4.

Variation of chemical shifts due to hydrogenation of the C:C bond.

Δ (p.p.m.) = $[\gamma(\text{CH·CH}) - \gamma(\text{C:C})]/56\cdot4$ (c./sec.).

</div>

		H-1	H-2*ex*	H-2*en*	H-3*ex*	H-3*en*	H-4
(I) →	(XV)	+0·58	+0·31		+0·65		+0·50
(III) →	(XVI)	+0·59	+0·32		+0·36		+0·49
(IV) →	(XVII)	+0·69	+0·16		+0·42		+0·43
(XI) →	(XVIII)	+0·62		−0·17		−0·12	+0·62

Hydrogenation of the double bond in the norbornene system shifts the lines due to protons 2 and 3 in *endo-* or *exo*-position to lower and higher magnetic field, respectively.[2] Table 4 shows also that lines due to protons 1 and 4 are shifted to higher field by saturation of the double bond. However, while Δ(p.p.m.) of protons 2 and 3 varies appreciably with the nature of the substituent, the variations for the bridgehead protons 1 and 4 are much smaller (0·58—0·69 for H-1 and 0·43—0·62 for H-4). The contribution made by the magnetic anisotropy of a C:C double bond to the chemical shift is given by the formula: [12,13]

$$\delta = \frac{10^{24}}{3NR^3}(1 - 3\cos^2\gamma)\Delta\chi$$

where $\Delta\chi$ is the difference between the components of magnetic susceptibility perpendicular to the plane and parallel to the axis of the double bond, γ is the angle subtended at the normal to this plane by the line, of length R (in Å), joining the proton to the centre of the double bond. The nearly constant shift Δ (p.p.m.) for protons 1 and 2 can be used to derive $\Delta\chi$: by assuming $R = 2\cdot8$ Å and $\gamma = 85°$ on the basis of molecular models, a value of about $23\cdot10^{-6}$ cm.^{3} mole^{-1} is obtained for $\Delta\chi$. Now the formula can be applied to compute δ for the *endo-* and *exo*-protons 2 and 3. This has been done by using the values $R_{en} = 2\cdot7$ Å, $R_{ex} = 3\cdot5$ Å, $\gamma_{en} \approx 80°$, $\gamma_{ex} \approx 45°$; the following results were obtained:

$$\text{H}_{en} \approx -0\cdot32 \text{ (exp. } -0\cdot12 \text{ to } -0\cdot17)$$

$$\text{H}_{ex} \approx 0\cdot27 \text{ (exp. } 0\cdot16 \text{ to } 0\cdot65)$$

Keeping in mind that (i) other contributions to the chemical shift exist beside magnetic anisotropy, (ii) the γ-values employed are rather subjective (that implies a large uncertainty of δ for $\gamma \approx 45°$), we conclude that the agreement is reasonable.

All our compounds contain a phenyl group bonded to the bicyclic system through S, SO, or SO$_2$. It has been found [14] that in 1,2-diphenylcyclopentane the phenyl ring gives a narrow peak or a broad multiplet, depending on the degree of free rotation. In our bicyclic systems both types of absorption signal occur, but it is probable that, besides

[11] Biscarini, Taddei, and Zauli, *Boll. sci. Fac. Chim. ind. Bologna*, 1963, **21**, 169.
[12] Pople, Schneider, and Bernstein, " High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, 1959, pp. 119 *et seq.*
[13] Pritchard and Lauterbur, *J. Amer. Chem. Soc.*, 1961, **83**, 2105.
[14] Curtin, Gruess, Hendrickson, and Knipmeyer, *J. Amer. Chem. Soc.*, 1961, **83**, 4838; 1962, **84**, 863.

steric factors, the nature of the bonding group (S, SO, or SO_2) and the interactions between Ph, C:C, and CO_2^- will affect the form of the resonance signal. Therefore, it is not possible to draw conclusions about the rotational freedom of the phenyl ring.

It is evident that a diamagnetic effect by the π-electron cloud of the phenyl ring operates on the protons which lie above the plane of the ring. The large shift (−44·4 c./sec.) to higher field of the 4-proton line of the *cis-anti*-sulphoxide (IV) was previously [5] related to this effect, while for the sulphoxides [*cis-syn*, (III); and *trans*, (V) and (VI)] the 4-proton peaks are at −112·3, −106·3, and −105·3 c./sec., respectively.

Thus, as previously postulated,[5] the *anti*-isomer (IV) easily reaches a conformation in which proton 4 lies above the plane of the phenyl ring. An analogous conformation is much less probable for the *syn*-isomer (III) and the *trans*-isomers (V) and (VI). For the *cis*-sulphone (I) and *cis*-sulphide (II) the 4-proton peak falls at −80·0 and −84·0 c./sec., respectively; these values reflect a situation in which the phenyl group, in respect of proton 4, occupies a preferred position intermediate between the two extreme possibilities in the corresponding sulphoxides (III) and (IV).[5] In addition, it may be supposed that at least in some of the *cis-* and *trans*-sulphoxides and -sulphones deshielding of proton 4 by the sulphinyl and sulphonyl group takes place. The contribution of the ring-current to the shift of the 4-proton line of the *anti*-sulphoxide (IV) can be calculated by using Pople's free-electron model, as modified by Waugh and Fessenden: [15]

$$\delta = \frac{nc^2}{24\pi mc^2a} B_0(\rho, z)$$

In their formula the chemical shift δ is proportional to $B_0(\rho,z)$, which has been tabulated [15] as a function of the cylindrical co-ordinates ρ and z. For the smallest distance of proton 4 from the centre of the ring, two limiting conformations are considered: (i) maximum paramagnetic contribution of the phenyl ring (proton in the plane of the ring); (ii) maximum diamagnetic contribution of the ring (phenyl group rotated 90° from the former conformation). By assuming ρ and z to be 3·0 and 0 in case (i), and 1·0 and 1·7 in case (ii), δ is found to be −0·4 p.p.m. for case (i) and +1·6 p.p.m. for case (ii). This means that, even with completely free rotation of the phenyl group around the Ar–S bond, the diamagnetic is larger than the paramagnetic contribution. If we take as reference compounds the *trans*-sulphoxides (V) and (VI), where the ring effect on proton 4 may be assumed to be negligible, the experimental value of δ is +1·10 p.p.m., in reasonable agreement with the computed values.

Further, the magnetic anisotropy of carboxyl,[16] sulphinyl,[13] and sulphonyl groups can affect the protons of the bicyclic system. This is shown by the chemical shifts of proton 7 (Tables 1 and 2), one of which (probably 7β-H) is generally shifted to low field more than the other. The largest effect on 7β-H is caused by *exo*-Ph·SO_2 in compounds (VII) and (XIV), but it increases also when both Ph·SO_2 and CO_2^- are *exo* [compounds (XI) and (XVIII)]. When only the carboxyl group is *exo* [compounds (IX), (X), and (XIII)] both 7-protons are equally affected.

The chemical shifts of the 7-protons may give information about the *syn,anti*-configurations at the sulphur atom in the *trans*-sulphoxides (V) and (VI). For the sulphoxide of m. p. 193—194° 7-protons peaks are found at −17·2 and −32·4 c./sec. (average −24·8 c./sec.), and for the sulphoxide of m. p. 204—205° at −9·1 and −26·2 c./sec. (average −17·7 c./sec.). Models show that the sulphinyl-oxygen atom in the *syn*-isomer lies closer to the methylene bridge than in the *anti*-isomer. On this basis, a *syn*-configuration [(V)] can be assigned to the former isomer and an *anti*-configuration to the latter, in agreement with those derived from acidity constants.[1]

[15] Waugh and Fessenden, *J. Amer. Chem. Soc.*, 1957, **79**, 846; Waugh, *ibid.*, 1958, **80**, 6697.
[16] Jackman, " Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Oxford, 1959.

EXPERIMENTAL

Syntheses of the bicyclic compounds have been reported elsewhere.[5,6b,7]

Proton Magnetic Resonance Spectra.—The spectra were recorded with a Varian DP-60 spectrometer, operating at 56·4 Mc./sec. Calibration was by the side-band technique, with 1% t-butyl alcohol as internal standard. Chemical shifts (± 1 c./sec.) and coupling constants ($\pm 0·3$ c./sec.) are the average of five measurements.

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