189. *Carbanions. Part I. Sulphone-stabilised Carbanions in the Norbornene System.**

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

The rates of the base-catalysed H–D exchange in the 3-phenylsulphonylbicyclo[2,2,1]hept-5-ene-2-carboxylic acids, (*cis*) (I) and (III), (*trans*) (II), (V), and (VI), and of the base-catalysed inversion in *cis*-compounds (I), (III), and (IV), have been measured in order to study the stereochemistry and the stability of α-sulphonyl-carbanions. Exchange and inversion reactions, carried out in NaOD–D_2O and NaOH–H_2O, were followed simultaneously by proton magnetic resonance spectroscopy. For compounds (I) and (III) the ratios k_{H-D}/k_{inv} are, respectively, 15 and 4. Such low ratios may be attributed to electronic and steric effects, caused by the carboxylic anion on the sulphonyl group. Since the k_{H-D}'s of compounds (I) and (III) are equal, the difference in structure affects k_{inv}. For compounds (I) and (III) the k_{H-D}'s are 14—70 times those of compounds (V) and (VI), probably owing to electrostatic repulsion between the carboxyl anion and the catalytic species. The isotope effects on k_{H-D} and k_{inv} are small.

The results favour sp^3- rather than sp^2–p-hybridisation of the α-sulphonyl-carbanion.

Much attention has been paid to the stability and structure of α-sulphonyl-carbanions.[1-9] These ions cannot have a symmetrical structure, because the base-catalysed H–D exchange rate of optically active 1-methylheptyl phenyl sulphone exceeds[3,4,6] the rate of racemisation by factors between 10 and 2000, and the base-catalysed decarboxylation of optically active 2-methyl-2-phenylsulphonyloctanoic acid occurs with high retention of configuration.[7] Although there is no doubt about the asymmetry of the intermediate carbanions, their structure is still under discussion.

* Presented, in part, at the XIXth Internat. Congress Pure Appl. Chem., July 1963, London.

[1] Zimmerman and Thyagarajan, *J. Amer. Chem. Soc.*, (*a*) 1958, **80**, 3060; (*b*) 1960, **82**, 2505.
[2] Weinstock, Bernardi, and Pearson, *J. Amer. Chem. Soc.*, 1958, **80**, 4961.
[3] Corey and Kaiser, *J. Amer. Chem. Soc.*, 1961, **83**, 490.
[4] Cram, Scott, and Nielsen, *J. Amer. Chem. Soc.*, 1961, **83**, 3696.
[5] Breslow and Mohacsi, *J. Amer. Chem. Soc.*, 1961, **83**, 4100.
[6] Goering, Towns, and Dittmar, *J. Org. Chem.*, 1962, **27**, 736.
[7] Cram and Wingrove, *J. Amer. Chem. Soc.*, (*a*) 1962, **84**, 1496; (*b*) 1963, **85**, 1100.
[8] Cram, Partos, Pine, and Jäger, *J. Amer. Chem. Soc.*, 1962, **84**, 1742.
[9] Corey, König, and Lowry, *Tetrahedron Letters*, 1962, **12**, 515.

Two extreme cases may account for the optically active character of the ions: (i) sp^2–p-Hybridisation at the carbon atom: conjugation between the 2p-orbital of carbon and the 3d-orbitals of sulphur has to occur by way of Koch and Moffitt's " case II " conjugation [10] (2p-axis in the CSC plane) to yield an asymmetric structure; optical activity would then be lost by rotation around the C–S bond to reach the symmetrical structure (" case I " conjugation: [10] 2p-axis parallel to the O–O axis of the sulphone group); (ii) sp^3-Hybridisation at the carbon atom, whose asymmetry is very likely retained by overlap of the sp^3-orbital, occupied by the lone pair, with the 3d-orbitals of sulphur.

The latter type of asymmetry has been favoured by Cram and his co-workers [4,7,8] mainly because the first explanation would require preferential formation and stability of the asymmetric rotomer, and loss of, and attack on, the groups on the same side of the molecule. Zimmerman and Thyagarajan prefer a sp^3-hybridised α-sulphonyl-carbanion, on the basis of the dissociation constant of cyclopropyl phenyl sulphone, which is slightly larger than that of isopropyl phenyl sulphone,[1b] as well as on the basis of the stereochemistry of protonation of the 1-phenyl-2-phenylsulphonylcyclohexane conjugate base.[1a] Weinstock *et al.*[2] found that the H–D exchange rate of cyclopentyl p-tolyl sulphone is about 1·5 times larger than that of cyclohexyl p-tolyl sulphone, and concluded that the observed differences would have been much larger if the carbanions were doubly bonded to the sulphone group. A recent study [5] of d-orbital conjugation in disulphonyl-carbanions indicated that the carbanion hybridisation is probably not of sp^2–p-type when no other electron-withdrawing conjugated group (such as ethoxycarbonyl) is directly bonded to the carbon atom.

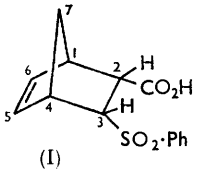
Doering [11] presented evidence that sulphonyl carbanions are sp^2–p-hybridised, on the basis of the difference in acidity of 4-methyl-2,6,7-trithiabicyclo[2,2,2]octane 2,2,6,6,7,7-hexaoxide and triethylsulphonylmethane. However, in a more recent study,[12] this difference in acidity was tentatively attributed to a field effect exerted by the sulphonyl-oxygen atoms on the carbanion. Corey *et al.*[9] have presented the following results which favour type (i) asymmetry: the decrease of the ratio k_{H-D}/k_{rac} in passing from 1,2,2-trimethylpropylphenyl to 1-methylheptyl phenyl sulphone, and the difference in the stereochemical course of the base-catalysed decarboxylation of 2-methyl-2-phenylsulphonyloctanoic acid (97% stereospecificity), and of 2,3-dihydro-2-methylthionaphthene-2-carboxylic acid 1,1-dioxide (complete racemisation). The last argument has been criticised because the structure of the cyclic sulphonyl-carbanion would not give information about the structure of an open-chain sulphonyl-carbanion,[7b] and because of the possibility of ring opening and closure [13] of the cyclic sulphone in basic conditions.

During the study of the Diels–Alder reaction of β-arylsulphinyl- and β-arylsulphonyl-acrylic acids with cyclopentadiene,[14–16] the bicyclic sulphones (I), (III) (V), and (VI) were prepared. Preliminary experiments with the *cis-endo*-acid (I) showed that base-catalysis caused inversion at the carbon atom carrying the sulphonyl group, while with the corresponding methyl ester that carrying the methoxycarbonyl group was inverted. Obviously, the relative stabilities of the intermediate carbanions determine which substituent undergoes configurational change.

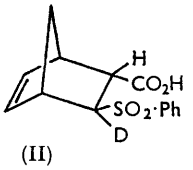
So far the sulphone-stabilised carbanions have been studied especially in relation to solvent,[4] base,[3,4] and nature of the leaving group.[4,7,9] The present paper reports a kinetic study of structural effect on the base-catalysed H–D exchange and inversion at the atom carrying the phenylsulphonyl group in the bicyclic sulphonyl-acids (I)—(VI). The influence

[10] Koch and Moffitt, *Trans. Faraday Soc.*, 1951, **47**, 7.
[11] Doering and Levy, *J. Amer. Chem. Soc.*, 1955, **77**, 509.
[12] Meyers, *Tetrahedron Letters*, 1962, 1125.
[13] Meyers, Rinaldi, and Bonoli, Abs. Papers, Meeting Amer. Chem. Soc., Divn. Org. Chem., Los Angeles, April 1—5, 1963, p. 4M.
[14] Ghersetti, Hogeveen, Maccagnani, Montanari, and Taddei, *J.*, 1963, 3718.
[15] Albera, Luciani, and Montanari, *Boll. sci. Fac. Chim. ind. Bologna*, 1960, **18**, 52.
[16] Hogeveen, Maccagnani, Montanari, and Taddei, *J.*, 1964, 682.

of *exo*- and *endo*-configuration of phenylsulphonyl and carboxy-groups (*cis*- and *trans*-series) on both reactions is presented here; the influence of *meta*- and *para*-substituents in the phenyl ring will be dealt with in a later paper.



(I)



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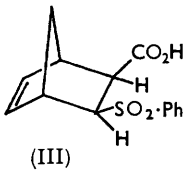

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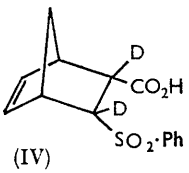

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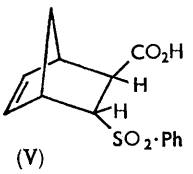

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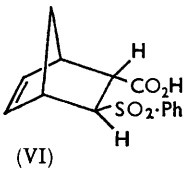


(VI)

Methods and Results

In the literature [3,4,6] the attention has been paid mainly to the optically active 1-methylheptyl phenyl sulphone, which has only one asymmetric carbon atom. The exchange and racemisation rates were generally followed by infrared analysis and by polarimetric techniques,

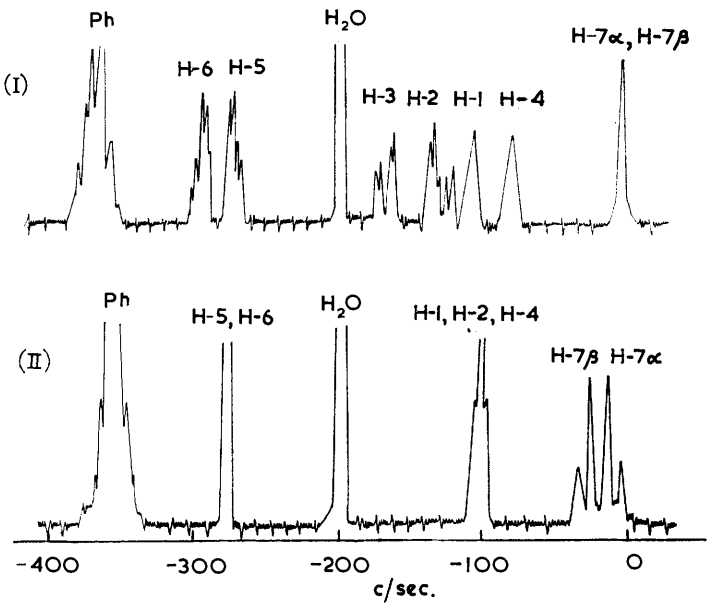


Fig. 1. Proton magnetic resonance spectra of sulphones (I) and (II) in NaOD–D_2O.

respectively. In the bicyclic sulphones four centres of asymmetry exist, and inversion at the centre carrying the phenylsulphonyl group does not lead to racemisation. Consequently both inversion and exchange rates can be followed with one analytical tool. The most convenient method was thought to be proton magnetic resonance. Since the bicyclic sulphones have very low solubility in most common organic solvents, the compounds were dissolved in aqueous alkali as sodium salts: 0·2 ml. of the solution ($C_{substrate}$ = 0·43M; C_{OD^-} = 0·40M), sealed in a proton magnetic resonance glass tube, was enough to allow both reactions to be followed simultaneously during the whole run. (In previous studies [4,6] organic solvents, and in one case [3] ethanol—water, were used.) As an illustration of the way in which this technique was used, the spectra of the acids (I) and (II) (Fig. 1) for the reaction (I) ⟶ (II) are considered. (Two

months contact of the solution with the glass walls at room temperature did not change the base concentration.)

The H–D exchange reaction may be followed in two ways: by measuring (*a*) the increase in the peak area of H_2O (present as an impurity in D_2O), or (*b*) the decrease in that of hydrogen at position 3. The inversion reaction may be followed through the change in the resonance bands of (*c*) hydrogen at positions 5 and 6, (*d*) hydrogen at position 4, and (*e*) hydrogens at position 7. The accuracy of the integrated intensities depends on the shape of the resonance band and on the vicinity of other absorption peaks. In order to compare the reliability of the methods, all of them were first employed to measure the rate constants k_{H-D} and k_{inv} of compound (I): the results are shown in Tables 1 and 2.

TABLE 1.

First-order rate constants of exchange (10^3k_1, hr.$^{-1}$) of compound (I) in D_2O at 25·0°; $C_{OD^-} = 0{\cdot}40$M.

Method (*a*): 26·1 ± 2·3, 23·9 ± 3·6
,, (*b*): 25·5 ± 1·1, 23·7 ± 0·6

TABLE 2.

First-order rate constants of inversion (10^3k_1, hr.$^{-1}$) of compound (I) at 25·0°; $C_{OD^-\,(OH^-)} = 0{\cdot}40$M.

	Method				Method		
Solvent	(*c*)	(*d*)	(*e*)	Solvent	(*c*)	(*d*)	(*e*)
D_2O	1·63 ± 0·05	1·68 ± 0·12	1·77 ± 0·07	H_2O	1·29 ± 0·05	1·20 ± 0·11	1·50 ± 0·12
D_2O	1·57 ± 0·04	1·80 ± 0·09	1·70 ± 0·06	H_2O	1·22 ± 0·08	0·89 ± 0·19	1·50 ± 0·09
D_2O	1·75 ± 0·05	1·78 ± 0·13	1·81 ± 0·07	H_2O	1·10 ± 0·07	1·07 ± 0·10	1·28 ± 0·12
D_2O	1·69 ± 0·08	1·77 ± 0·11	1·77 ± 0·06				

Representative examples of the exchange and inversion rates of compound (I) are plotted in Figs. 2 and 3, respectively. It appears that, in principle, each method can be used, since

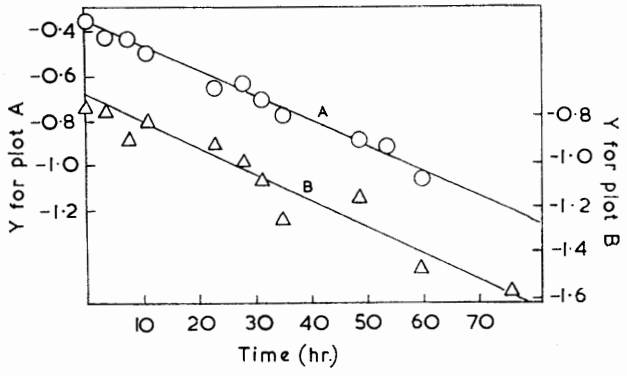


FIG. 2. H–D Exchange for sulphone (I) in 0·40N-NaOD–D_2O at 25°. Y is the kinetic expression on p. 973 [(A) method (*a*); (B) method (*b*)].

all give approximately the same rate constants. For the other *cis-endo*-acids (IV) and (V) we restricted ourselves to method (*b*) for exchange and method (*c*) for inversion, since for these the determination of the spectral areas presents only minor difficulties. Experimentally the measurements in protium oxide were more difficult than those in deuterium oxide, on account of the broad resonance peak of the solvent in the first case.

The results for the exchange and inversion reaction of compound (III) are given in Table 3.

TABLE 3.

First-order rate constants of exchange and inversion (10^3k_1, hr.$^{-1}$) of compound (III) at 25·0°; $C_{OD^-\,(OH^-)} = 0{\cdot}40$M.

	In D_2O	In H_2O
Inversion	7·05 ± 0·30, 6·56 ± 0·38	5·28 ± 0·43, 5·05 ± 0·41
Exchange	23·5 ± 0·9, 24·7 ± 1·1	

Some experiments were carried out with the 2,3-dideutero-*cis-endo*-acid (IV), since it was easier to prepare * than the 3-deutero-acid. Compound (IV) was obtained as follows:

$$H{\cdot}C{\equiv}C{\cdot}CO_2^- + OD^- \rightleftharpoons D{\cdot}C{\equiv}C{\cdot}CO_2^- + OH^-$$

$$D{\cdot}C{\equiv}C{\cdot}CO_2^- + PhS^- + D_2O \longrightarrow cis\text{-}PhS{\cdot}CD{=}CD{\cdot}CO_2^- + OD^-$$

$$\longrightarrow cis\text{-}Ph{\cdot}SO_2{\cdot}CD{:}CD{\cdot}CO_2H \longrightarrow (IV)$$

The inversion rates of compound (IV) are given in Table 4.

TABLE 4.

First-order rate constants of inversion † (10^3k_1, hr.$^{-1}$) of compound (IV) at 25·0°; $C_{OD^-\ (OH^-)}$ = 0·40M.

In D_2O, 1·73 ± 0·07; in H_2O, 1·23 ± 0·10, 1·41 ± 0·10

† The H–D exchange in H_2O could not be followed as the broad H_2O band partly overlaps the 3(*ex*)-proton peak.

In the *trans*-compounds (II), (V), and (VI) inversion does not occur, so only H–D exchange was measured (Table 5). The standard deviations in the rate constants for compounds (II)

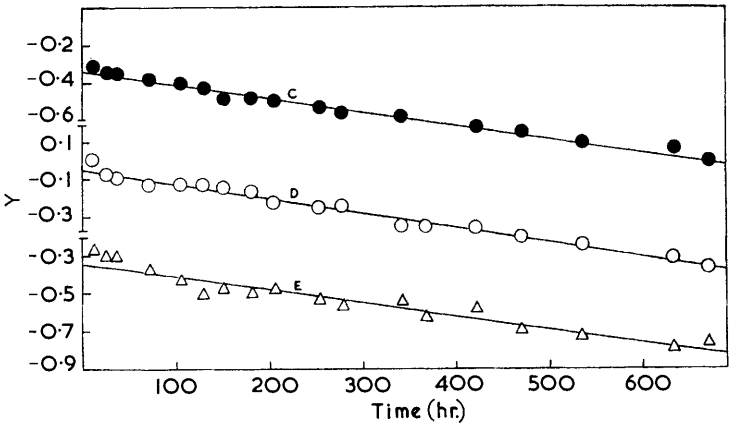


FIG. 3. Inversion at the centre carrying the phenylsulphonyl group in sulphone (I) in 0·40N-NaOD–D_2O at 25°. For kinetic expressions Y see p. 973 [plots (C), (D), and (E) refer to expressions (*c*), (*d*), and (*e*), respectively].

and (VI) are high (30%), owing to the composite structure of the peaks and, in one case, also to the presence of the broad H_2O band.

TABLE 5.

First-order rate constants of exchange (10^3k_1, hr.$^{-1}$) of compounds (II), (V), and (VI) at 25·0°; $C_{OD^-\ (OH^-)}$ = 0·40M.

Compound	In H_2O	Compound	In D_2O	Compound	In D_2O
(II)	0·59 ± 0·19, 0·63 ± 0·21	(V)	1·69 ± 0·08, 1·70 ± 0·14	(VI)	0·35 ± 0·09

The reactions, all of the first order in the bicyclic compound, were generally followed to 50—80% conversion. The concentration of the substrate was 0·43M, except in the case of the *cis-exo*-acid (III) (0·20M) on account of its low solubility in the alkaline solution. No correction

* Attempts to prepare the intermediate *cis*-acid, $Ph{\cdot}SO_2{\cdot}CD{:}CH{\cdot}CO_2H$, by nucleophilic addition of thiophenol to methyl deuteropropiolate with a catalytic amount of cyclohexyldimethylamine in tetrahydrofuran, followed by oxidation to the sulphone, resulted in a mixture of *cis*- and *trans*-isomers. An analogous reaction in ethanol (not used here so as to avoid H–D exchange) is known [17] to proceed by a stereospecific *trans*-addition. However, after this study was completed, a very simple way to prepare *cis*-β-deutero-β-phenylsulphonylacrylic acid was found, *i.e.*, by base-catalysed H–D exchange of *cis*-β-phenylsulphonylacrylic acid.

[17] Montanari, *Tetrahedron Letters*, 1960, **4**, 18.

for the small change in isotopic composition of the solvent was necessary, as the amount of the exchangeable hydrogen or deuterium in the bicyclic compounds is negligible compared with that of the solvent (D_2O or H_2O). Measurements of the areas of all the peaks for the bicyclic compounds showed that the only H–D exchange occurs in position 3.

Discussion

Carbanion Structure and Stability.—The sensitivity to solvent effect of the ratio k_{H-D}/k_{rac} for optically active 1-methylheptyl phenyl sulphone has been attributed to differences in asymmetric solvation, which is high in associating and low in dissociating solvents.[3,4,6] It was suggested [4] that the " intrinsic asymmetry of the sulphine anion is responsible for values of k_{H-D}/k_{rac} as high as 10 " (in $CH_3{\cdot}OH$–$CH_3{\cdot}OK$ as base–solvent system), " whereas those parts of the values in excess of 10 are due to asymmetric solvation." In our solvent–base systems, H_2O–NaOH and D_2O–NaOD asymmetric solvation is unlikely.

In the *cis-endo*-acid (I) (Tables 1 and 2) the ratio k_{H-D}/k_{inv} is 15. This requires that exchange occurs largely with retention of configuration at the carbanion. It may be observed that this value is lower than any previously found.* Very probably this occurs because of the rigid structure of the bicyclic compound, in which steric and electronic interactions exist between the phenylsulphonyl group and the carboxyl anion. [The repulsion between CO_2^- and $Ph{\cdot}SO_2$ has previously [18] been evaluated through the acidity constants of the *cis*- and *trans*-acids; pK_a (1 : 1 EtOH–H_2O) = (I) 6·23, (III) 6·03, (V) 5·25, and (VI) 5·36]. Such interactions would operate as driving forces for the inversion at the centre carrying the phenylsulphonyl substituent. Nonetheless, the rate of exchange still exceeds that of inversion by a factor of 15, which might carry some implications for the structure of the intermediate sulphonyl carbanion. In fact, if the carbanion had a planar structure (sp^2-hybridisation), roughly equal values of k_{H-D} and k_{inv} would be expected. This is so because interaction between the substituents would prevent formation of the pre-existing configuration (which implies an increase in the repulsion energy) and would cause the phenylsulphonyl group to move to the *trans*-position so as to decrease the repulsion energy.

It could be objected that the sulphonyl-carbanion might be planar, and that in the *cis*-series the ratio k_{H-D}/k_{inv} (larger than 1) depends on a sterically favoured direction of electrophilic attack by the solvent on the carbanion. For example, in the case of the *cis*-derivatives, (I) (*endo*) and (III) (*exo*), this preferred direction of attack should be, respectively, *exo* and *endo*. However, it seems difficult to believe that steric effects are sufficiently effective to overcome the electrostatic repulsion by CO_2^-, discussed above. Therefore, an sp^3-hybridisation of the carbanion (or at least a configuration with predominant sp^3-character) seems to explain better the experimental results.

For the *cis-exo*-compound (III) the ratio k_{H-D}/k_{inv} is 4 (Table 3). As the k_{H-D} values for both *cis*-compounds (I) and (III) are equal, the difference in structure is reflected in k_{inv}. In other words, the free energies of activation for the formation of both carbanions are equal, while the optical stabilities are different. A similar situation is found [19] for the *p*-chlorophenyl acids. It should be noted that the pK_a of the *cis-exo*-compound (III) is lower than that of the *cis-endo*-compound (I), so that the increase in k_{inv} cannot be explained only on the basis of the repulsion between the two substituents. Possibly

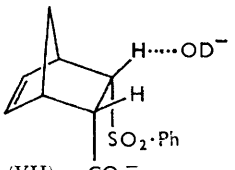
* In a comparable system, 2 : 1 EtOD–D_2O (OD^- as catalyst) a value of 41 was found [3] for k_{H-D}/k_{rac} of 1-methylheptyl phenyl sulphone. Although the authors [3] did not believe asymmetric solvation to be important, it seems to us that it may not be negligible because of the presence of significant amounts of EtOD.

In the present paper k_{H-D}/k_{inv} is considered, while in the previous ones [3,4,6] the ratio $k_{H-D}/k_{rac} = k_{H-D}/2k_{inv}$ was used.

[18] Hogeveen and Montanari, *J.*, 1963, 4864.
[19] Hogeveen, Maccagnani, Montanari, and Taddei, *Boll. sci. Fac. Chim. ind. Bologna*, 1963, **21**, 255.

steric interaction of the phenylsulphonyl group with one of the hydrogen atoms of the methylene bridge has to be taken into account.*

Interesting differences are observed (Tables 1, 3, and 5) between the exchange rates of *cis*- and *trans*-acids. Both *cis*-acids (I) and (III) undergo replacement of hydrogen



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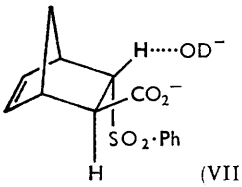


(VIII)

by deuterium about 14 and 70 times, respectively, faster than the *trans*-acids (V) and (VI). This can be interpreted on the basis of electrostatic repulsion between the carboxyl anion and the catalytic species OD^-, which is obviously greater for the *trans*-acids [see (VII) and (VIII)]. [Alternatively it might be supposed that the formation of the carbanion occurs by intramolecular nucleophilic attack of the CO_2^- on the proton, even though the basicity of CO_2^- is much lower than that of OH^-. Such a mechanism would be sterically favoured either by direct attack of a carboxyl-oxygen, or by indirect attack through a solvent shell. In fact, the rates of H–D exchange of the *trans*-sulphones, lower than those of the *cis*-sulphones, correspond to lower basicity of the carboxyl anion in the first case, as can be inferred from pK_a data.[18] However, if steric factors play a leading role in a mechanism of this kind, the exchange should be faster in the *trans*-series, where the relative spatial arrangement of the carboxyl group and the proton at position 3 (both *endo* or *exo*) is much more favourable. This is not observed; therefore the hypothesis of catalysis by OH^- (OD^-) ions seems more reasonable.]

The difference between the exchange rates of compounds (V) and (VI) (Table 5) is more difficult to explain. Although electronic and steric effects might be tentatively considered, they cannot be used to interpret the results for the *cis*-compounds (I) and (III).

Isotope Effects and Reaction Mechanism.—It is well known [21] that kinetic isotope effects may yield information on the rate-determining step of a reaction. The ratio k^H_{inv}/k^D_{inv} for compound (I) in H_2O (Table 2) and compound (IV) in D_2O (Table 4) amounts to 0·7.† This value lies in the region of isotope effects (0·3—1·9) for the racemisation of 1-methylheptyl phenyl sulphone.[3,4] The mechanistic implication is that the slow step of the inversion does not involve carbon–hydrogen bond breaking, because that should require a primary kinetic isotope effect of at least 3. Virtually the same isotope effect (0·8) is found for the inversion of compounds (I) and (IV), in D_2O and H_2O (Tables 2 and 4). In fact, exchange is about 15 times faster than inversion and consequently most of the molecules become isotopically homogeneous with the solvent before inversion is detectable. Also the *cis-exo*-compound (III) shows an isotope effect of 0·7 for inversion (Table 3).

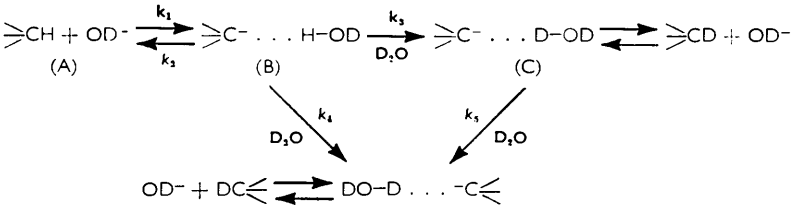
An approximate isotope effect for the exchange could be obtained only by comparing the rates for compounds (II) and (VI) (Table 5): $k^H_{H-D}/k^D_{H-D} = 0·6$. Isotope effects for the exchange of 1-methylheptyl phenyl sulphone in organic solvents lie [4] between 0·5

* A somewhat analogous explanation, based on steric effects of hydrogen at positions 5 and 6 has been invoked [20] to account for the difference in rates of solvolysis of *exo*- and *endo*-norbornyl toluene-*p*-sulphonate.

† This is a composite isotope effect. The kinetic deuterium isotope effect can be estimated by allowing for the isotope effect of the solvent–catalyst. The assumption has been made [22] that OD^- ions (in D_2O) remove protons 39% faster than do OH^- ions (in H_2O): therefore, the kinetic deuterium isotope effect is about 1. A secondary isotope effect of deuterium in position 2 is within the experimental errors.

[20] Brown, in " The Transition State," *Chem. Soc. Special Publ.* No. 16, 1962, p. 140.
[21] Wiberg, *Chem. Rev.*, 1955, **55**, 713.
[22] Hine and Burche, *J. Amer. Chem. Soc.*, 1956, **78**, 3337.

and 1·5. Hine and Ramsay[23] obtained a k^{H}_{H-D}/k^{D}_{H-D} of 2·4 for exchange in *cis*-2-methoxycyclohexyl *p*-tolyl sulphone in 1 : 1 dioxan–water. In our case the low value for the isotope effect does not allow breaking of the carbon–hydrogen bond in the slow step of the reaction. Therefore the mechanistic scheme proposed by Corey and Kaiser,[3] LSH $\rightleftharpoons$ LS^- $\rightleftharpoons$ DS^- $\rightleftharpoons$ DSH, which is not applicable to the results of Cram and his co-workers,[4] does not apply to our results either. The existence of a pre-equilibrium before the exchange step seems more likely, and the following reaction scheme is proposed:



The rate of exchange is $v_{H-D} = k_3C_B + k_4C_B$. Application of the steady-state assumption for (B), $dC_B/dt = 0$, gives:

$$C_B = \frac{k_1C_A}{k_2 + k_3 + k_4} \text{ and } v_{H-D} = \frac{k_1(k_3 + k_4)C_A}{k_2 + k_3 + k_4}$$

As k_3 and k_4 will be much smaller than k_2, the rate equation becomes:

$$v_{H-D} = (k_1/k_2)(k_3 + k_4)C_A.$$

Isotope effects on the rate constants in this equation will be small: k_1/k_2 corresponds to an equilibrium constant, and $(k_3 + k_4)$ deals with processes where no covalent bond is formed or broken.

The rate of inversion can be written as $v_{inv} = k_4C_B + k_5C_C$. If we assume that $dC_B/dt = 0$, and that $dC_C/dt = 0$, it follows * that

$$v_{inv} = \frac{k_1k_4C_A}{k_2 + k_3 + k_4} + \frac{k_1k_5C_A}{k_2 + k_3 + k_4} = \frac{k_1(k_4 + k_5)C_A}{k_2 + k_3 + k_4}$$

As k_3 and $k_4 \ll k_2$, $v_{inv} = (k_1/k_2)(k_4 + k_5)C_A$ and also the rate equation for inversion is consistent with small isotope effects.

For the *cis-exo*-compound (III) we have

$$\frac{k_{H-D}}{k_{inv}} = \frac{\frac{k_1}{k_2}(k_3 + k_4)}{\frac{k_1}{k_2}(k_4 + k_5)} = 4.$$

As k_4 and k_5 will be virtually equal, it follows that $k_3 = 7k_4$. In other words, one in every eight carbanions (B) is deuterated with inversion, while the other seven are first deuterated *via* carbanions (C) and subsequently inverted. The *cis-endo*-acid (I) is deuterated with a higher degree of retention of configuration: only one in every thirty carbanions (B) is inverted with simultaneous deuteration.

Experimental

Compounds.—The *cis-* and *trans*-sulphones (I), (III), (V), and (VI) were prepared as previously described.[15]

2,3-*Dideutero*-3-endo-*phenylsulphonylbicyclo*[2,2,1]*hept*-5-*ene*-2-endo-*carboxylic Acid* (IV).—A solution of propiolic acid (0·70 g.) in a 2N-solution of sodium deuteroxide in deuterium oxide

* From the steady-state assumption alone, it follows that C_B = Constant × C_C. The constant is assumed to be 1, as (B) and (C) are almost identical structures.

[23] Hine and Ramsay, *J. Amer. Chem. Soc.*, 1962, **84**, 973.

(5 ml.) was heated for 2 hr. on a steam-bath. Thiophenol (1·1 g.) in the same alkaline solution (7 ml.) was then added, and heating continued for 1·5 hr. The mixture was acidified and extracted with chloroform. The chloroform layer was extracted with aqueous sodium hydrogen carbonate, and the latter acidified to yield *cis*-αβ-dideutero-β-phenylthioacrylic acid (1 g.), m. p. 100—104°. A mixed m. p. with the non-deuterated parent compound (m. p. 105·5—106·5°) [24] showed no depression.

Oxidation of the sulphide (1 g.) with an excess of peracetic acid, followed by evaporation, yielded *cis*-αβ-dideutero-β-phenylsulphonylacrylic acid (0·8 g.), m. p. 160—163°. A mixed m. p. with the non-deuterated parent compound (m. p. 164—166°) [24] showed no depression.

A benzene solution of the crude sulphone and an equal amount of freshly distilled cyclopentadiene was boiled for 1 hr. Extraction with aqueous sodium carbonate and acidification of the aqueous layer yielded the deuterated acid (IV) (0·9 g.), m. p. 200—201° (from ethanol). A mixed m. p. with 3-*endo*-phenylsulphonylbicyclo[2,2,1]hept-5-ene-2-*endo*-carboxylic acid (I) (m. p. 198—199°) [15] showed no depression. The proton magnetic resonance spectrum in NaOD–D_2O showed the absence of protons in position 2 and 3 (peaks [16] at −121·8 and −161·9 c./sec.).

3-*Deutero*-3-exo-*phenylsulphonylbicyclo*[2,2,1]*hept*-5-*ene*-2-endo-*carboxylic Acid* (II).—3-*endo*-2-Phenylsulphonylbicyclo[2,2,1]hept-5-ene-2-*endo*-carboxylic acid (I) (1·3 g.), dissolved in 0·9N-sodium deuteroxide (10 ml.) was heated for 3 hr. on a steam-bath. Acidification yielded almost quantitatively the deuterated acid (II), m. p. 179·5—181° (from benzene). A mixed m. p. with 3-*exo*-phenylsulphonylbicyclo[2,2,1]hept-5-ene-2-*endo*-carboxylic acid (VI) (m. p. 183°) [15] showed no depression. The proton magnetic resonance spectrum in NaOD–D_2O solution showed the absence of the peak at −123·5 c./sec., corresponding to the proton in position 3 of compound (VI).[16]

Kinetics.—$0{\cdot}46 \times 10^{-3}$ Mole of the compound was dissolved in 0·98 ml. of a 0·91N-sodium deuteroxide (or hydroxide) solution in deuterium (or protium) oxide. Kinetic measurements were made on 0·2 ml. of this solution, kept in a sealed proton magnetic resonance tube at 25° ± 0·05°. Recording of the spectrum and integration of the peak areas, made at 23° with a Varian D.P. 60 spectrometer operating at 56·4 Mc./sec., required about 10 min., which is a short time in comparison with the half-life of the reaction (20—1800 hr.). Band integration was performed by a Varian 3521 integrator and was repeated six times. The concentration of OD^- (OH^-) was computed by taking into account the increase in volume caused by dissolving the bicyclic compound. In the calculation of the rate constants the integrated first-order rate equation $\log (a - x)/a = -0{\cdot}43kt$ was applied, the term $(a - x)/a$ being replaced by the intensities A of the peaks. The rate constants were computed by least-squares analysis. The chemical shifts of the protons [16] used in the kinetic formulæ are given in Table 6.

TABLE 6.

Chemical shifts * (c./sec.) used in the kinetic formulæ.

Compound	H-1	H-2	H-3	H-4	H-5	H-6	H-7α	H-7β
(I)			−161·9	−80·0	−275·3	−296·8	0·0	0·0
(II)	−109·8	−109·8		−105·9	−276·6	−276·6	−10·6	−35·0
(III)		−76·3	−124·4		−258·0	−284·2	−5·7	−65·1
(IV)					−279·1	−298·6		
(V)		−70·4	−168·0		−274·2	−292·8	−15·7	−15·7
(VI)	−108·8	−108·8	−123·5	−108·8	−276·1	−276·1		

* In NaOD–D_2O; internal standard, *t*-butyl alcohol.[16]

Kinetic formulæ. Those used were as follows:

Compound (I), exchange (Table 1):

$$(a) \qquad \log \frac{A^{\infty}(H_2O)}{A^{\infty}(\text{H-5, H-6})} - \frac{A(H_2O)}{A(\text{H-5, H-6})} = -0{\cdot}43k_{H-D}t + \text{Constant.}$$

$\frac{A^{\infty}(H_2O)}{A^{\infty}(\text{H-5, H-6})}$ refers to infinity (actually, ten half-lives).

[21] Montanari and Negrini, *Gazzetta*, 1957, **87**, 1073.

The H_2O peak lies at *ca.* −190 c./sec.

(*b*) $$\log A(\text{H-3})/A(\text{H-5,H-6}) = -0{\cdot}43k_{\text{H-D}}t - \log 2.$$

Compound (I), inversion (Table 2):

(*c*) $$\log A\{\text{H-6(I)}\}/A(\text{H-5, H-6}) = -0{\cdot}43\,k_{\text{inv}}t - \log 2.$$

(*d*) $$\log A\{\text{H-4(I)}\}/A(\text{H-5, H-6}) = -0{\cdot}43\,k_{\text{inv}}t - \log 2.$$

(*e*) $$\log \frac{A\{\text{H-7}\alpha\text{,(I), H-7}\beta\text{(I), H-7}\alpha\text{(II)}\} - A\{\text{H-7}\beta\text{(II)}\}}{A(\text{H-7}\alpha\text{, H-7}\beta)} = -0{\cdot}43k_{\text{inv}}t.$$

The bands of protons H-7α(I), H-7β(I), and H-7α(II) partially overlap.
Compound (II), exchange (Table 5):

$$\log \left\{2 - \frac{A(\text{H-1,H-2,H-3,H-4})}{A(\text{H-5,H-6})}\right\} = -0{\cdot}43k_{\text{H-D}}t - \log 2.$$

The bands of protons H-1, H-2, H-3, and H-4 partially overlap in compound (VI).
Compound (III), inversion (Table 3):

$$\log \frac{2A\{\text{H-2(III), H-7}\beta\text{(III), H-2(V)}\} - A\{\text{H-7}\alpha\text{(III), H-7}\alpha\text{(V), H-7}\beta\text{(V)}\}}{A(\text{H-2,H-7}\alpha\text{,H-7}\beta)} = -0{\cdot}43k_{\text{inv}}t.$$

The bands of protons H-2(III), H-7β(III), and H-2(V), and those of protons H-7α(III), H-7α(V), and H-7β(V) partially overlap.
Compound (III), exchange (Table 3):

$$\log A(\text{H-3})/A(\text{H-5,H-6}) = -0{\cdot}43k_{\text{H-D}}t - \log 2.$$

Compound (IV), inversion (Table 4):

$$\log A\{\text{H-6(IV)}\}/A(\text{H-5,H-6}) = -0{\cdot}43k_{\text{inv}}t - \log 2.$$

Compound (V), exchange (Table 5):

$$\log A(\text{H-3})/A(\text{H-5,H-6}) = -0{\cdot}43k_{\text{H-D}}t - \log 2.$$

Compound (VI), exchange (Table 5):

$$\log \left\{\frac{2A(\text{H-1,H-2,H-3,H-4})}{A(\text{H-5,H-6})} - 3\right\} = -0{\cdot}43k_{\text{H-D}}t.$$

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(M. F.) Istituto di Chimica Organica dell'Università, Modena, Italy.
(H. H., F. T.) Istituto di Chimica Industriale dell'Università,
Laboratorio C.N.R., V Gruppo di Ricerca,
Bologna, Italy.

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