

**789. Carbanions. Part II.<sup>1</sup> Electronic Effect of Substituents on the Configurational Stability of Sulphone-stabilised Carbanions in the Norbornene System.<sup>2</sup>**

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The rates of the base-catalysed H-D exchange in the 3-arylsulphonyl-bicyclo[2,2,1]hept-5-ene-2-carboxylic acids, (*cis*) (I), (IV), and (*trans*)-(II), and of the base-catalysed inversion of the arylsulphonyl group in *cis*-compounds (I) and (IV) have been measured. The data from the reaction series [exchange in compounds (I), exchange in compounds (II), inversion in compounds (I)] fit into the Hammett equation with a high degree of correlation. The results show that the substituent effect on the rate of exchange is larger than on that of inversion. External steric and electrostatic factors are discussed and shown to be similar for all *cis*-compounds (I). The observed trends in the ratio  $k_{\text{H-D}}/k_{\text{inv}}$  have been related to a change in charge transfer from the doubly occupied carbon orbital to a vacant 3*d* orbital of sulphur. The hybridisation of open-chain sulphone-stabilised carbanions is likely to be essentially  $sp^3$ .

As far as the intrinsic optical stability of sulphone-stabilised carbanions is concerned, two extreme explanations have been offered for their structure:<sup>1</sup> (i) planar carbanions ( $sp^2$  hybridised), with the 2*p*-orbital containing the lone pair electrons in the CSC-plane; (ii) non-planar carbanions ( $sp^3$  hybridised), with the doubly occupied  $sp^3$ -orbital overlapped to a vacant 3*d*-orbital of sulphur. The latter interpretation seems to be more likely: however, a definitive answer to the problem has not yet been given.<sup>1</sup>

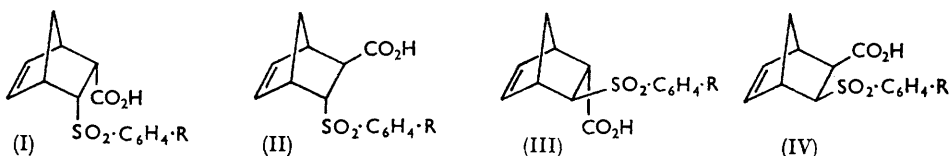
One way to obtain information about these carbanions is comparison of the rates of hydrogen-deuterium exchange and those of inversion (racemisation) in optically active sulphones. In the present paper the influence of substituents on both rates is examined. The compounds investigated were the bicyclic sulphones (I), (II), and (IV), obtained by Diels-Alder reaction between cyclopentadiene and β-arylsulphonylacrylic acids.<sup>3,4</sup>

<sup>1</sup> Part I, Hogeveen, Montanari, and Taddei, *J.*, 1964, 965.

<sup>2</sup> Presented, in part, at the XIXth International Congress Pure Appl. Chem., July 1963, London; preliminary communication: Hogeveen, Maccagnani, Montanari, and Taddei, *Boll. sci. Fac. Chim. ind. Bologna*, 1963, **21**, 259.

<sup>3</sup> Albera, Luciani, and Montanari, *Boll. sci. Fac. Chim. ind. Bologna*, 1960, **18**, 52.

<sup>4</sup> Hogeveen, *Rec. trav. chim.*, in the press.



R (I, II, III) = *p*-CH<sub>3</sub>O, *p*-CH<sub>3</sub>, H, *p*-Cl, *m*-NO<sub>2</sub>, *p*-NO<sub>2</sub>; R (IV) = H, *p*-Cl.

In the *cis*-sulphones, (I) and (IV), both hydrogen–deuterium exchange and arylsulphonyl inversion occur, leading respectively to the deuterated *trans*-compounds (III) and (II). In the *trans*-sulphones (II) only the hydrogen–deuterium exchange is observed and the final products are still in the *trans*-configuration (thermodynamically more stable). Both reactions were carried out in 0.40N-NaOD–D<sub>2</sub>O solution at 25° and studied concurrently with nuclear magnetic resonance spectroscopy, as previously<sup>1</sup> described for the unsubstituted compounds. The rate constants of the reactions are given in Table 1, and the values of the ratio  $k_{\text{H-D}}/k_{\text{inv}}$  for compounds (I) in Table 2.

TABLE 1.

First order rate constants of exchange and inversion ( $10^3 k_1 \text{ hr.}^{-1}$ ) of compounds (I) and (II) at 25°;  $c_{\text{OD}^-} = 0.40\text{M}$  in D<sub>2</sub>O solution.

R	Exchange (I)	Inversion (I)	Exchange (II)
<i>p</i> -OMe .....	4.30 ± 0.22 <sup>a</sup> 4.70 ± 0.21	0.41 ± 0.01 0.39 ± 0.02	0.45 ± 0.02
<i>p</i> -Me .....	8.84 ± 0.42 9.26 ± 0.45	0.63 ± 0.05 0.63 ± 0.05	0.91 ± 0.06 1.01 ± 0.07
H .....	24.6 <sup>b</sup> ± 0.6	1.66 <sup>b</sup> ± 0.03	1.70 <sup>b</sup> ± 0.08
<i>p</i> -Cl .....	54.2 ± 2.0 56.1 ± 2.8	3.09 ± 0.13 3.16 ± 0.16	5.05 ± 0.27 6.26 ± 0.54
<i>m</i> -NO <sub>2</sub> .....	1870 <sup>c</sup> ± 350	50.2 ± 1.3 47.0 ± 1.3	127 ± 21 133 ± 38 116 ± 11 139 ± 15
<i>p</i> -NO <sub>2</sub> .....	5400 <sup>c</sup> ± 1500	126 ± 13 134 ± 11	215 ± 20 175 ± 20 250 ± 35

<sup>a</sup> Standard deviation; <sup>b</sup> taken from ref. 1; <sup>c</sup> on account of the relatively high rate, the rate constant was derived from three independent kinetic runs; the high standard deviation is due also to the proximity of the absorption band of H-3 to that of H<sub>2</sub>O.

TABLE 2.

Effect of substituent on the ratio  $k_{\text{H-D}}/k_{\text{inv}}$  for compounds (I).

Subst. ....	<i>p</i> -OMe	<i>p</i> -Me	H	<i>p</i> -Cl	<i>m</i> -NO <sub>2</sub>	<i>p</i> -NO <sub>2</sub>
Ratio $k_{\text{H-D}}/k_{\text{inv}}$ ...	11.3 ± 0.7 <sup>a</sup>	14.4 ± 1.4	14.8 ± 0.6	17.6 ± 1.1	39 ± 8	42 ± 14

<sup>a</sup> Standard deviation.

The effect of structure on the rate constants of exchange and inversion of compounds (I) and on those of exchange of compounds (II) have been analysed by the Hammett equation,  $\log k = \rho\sigma + \text{constant}$ . The results of the correlations are shown in Table 3, and the corresponding Hammett plots in Figs. 1, 2, and 3.

TABLE 3.

Correlation with the Hammett equation.

	$\rho^a$	$s^b$
Exchange compounds (I) .....	2.81	0.992
Inversion compounds (I) .....	2.29	0.992
Exchange compounds (II) .....	2.53	0.997

<sup>a</sup> Correlation coefficient, ref. 5; <sup>b</sup> standard deviation of reaction constant  $\rho$ . The normal  $\sigma$ -values are taken from Hine, "Physical Organic Chemistry," McGraw-Hill, New York, 2nd edn., 1962, p. 87.

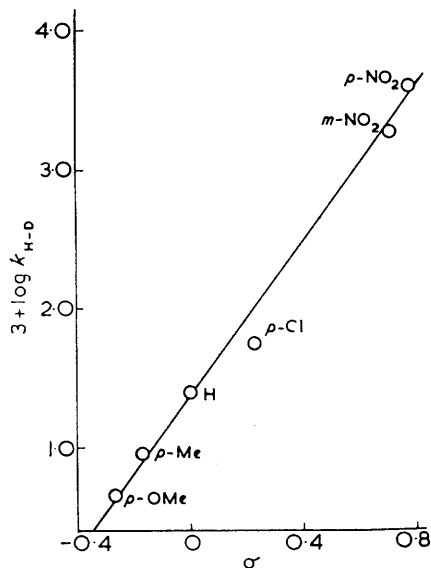


FIG. 1. Relation between the rate of the hydrogen-deuterium exchange and substituent constants in compounds (I).

FIG. 2. Relation between the rate of inversion and substituent constants in compounds (I).

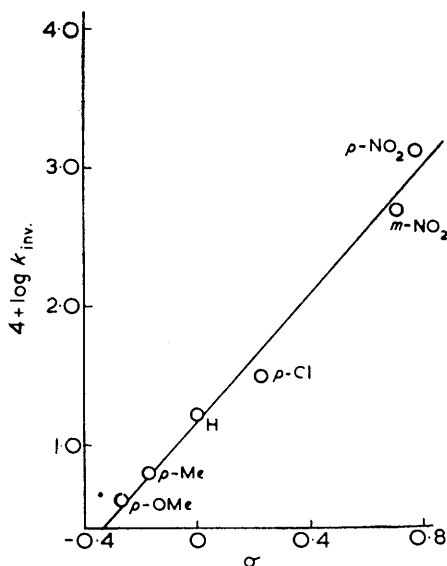
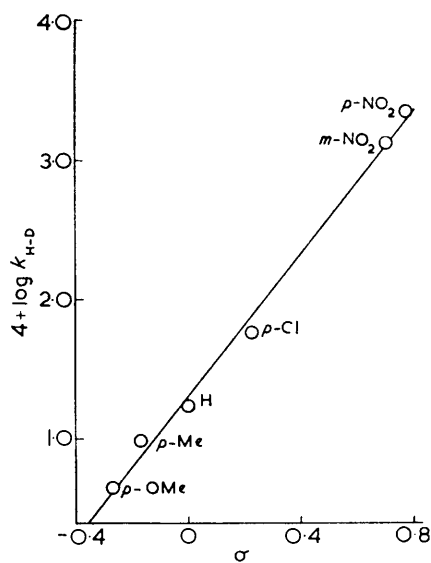


FIG. 3. Relation between the rate of hydrogen-deuterium exchange and substituent constants in compounds (II).

In the *cis-exo* series (IV) the rate constants of exchange and inversion have been measured only for R = H and *p*-Cl (Table 4).

TABLE 4.  
First-order rate constants of exchange and inversion ( $10^3 k_1 \text{ hr.}^{-1}$ ) of compounds (IV) at 25°;  $c_{\text{OD}^-} = 0.40\text{M}$  in  $\text{D}_2\text{O}$  solution.

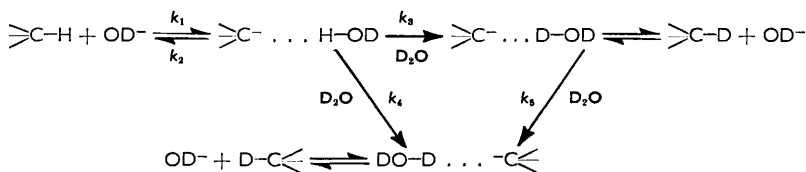
Substituent	Exchange	Inversion	Ratio $k_{\text{H-D}}/k_{\text{inv.}}$
H .....	$24.1^a \pm 0.7^b$	$6.81^a \pm 0.24$	$3.54 \pm 0.23$
<i>p</i> -Cl .....	$47.9 \pm 2.7$	$8.74 \pm 0.35$	$5.59 \pm 0.46$
	$47.2 \pm 3.2$	$8.28 \pm 0.54$	

<sup>a</sup> Taken from ref. 1; <sup>b</sup> standard deviation.

### DISCUSSION

Some observations made in Part I for the unsubstituted compounds (I), (II), and (IV), R = H are confirmed here for the substituted compounds. As shown in Table 1, the rate of the hydrogen-deuterium exchange is always lower for the *trans*-compounds (II) than for the corresponding *cis*-isomers (I). This is due to differences in electrostatic repulsion between the carboxylic anion and the catalytic species,  $\text{OD}^-$ . Obviously, this repulsion is larger for the *trans*-compounds and consequently the rates are lower.<sup>1</sup> In compounds (I), the rate of inversion of the arylsulphonyl group is lower than that of the hydrogen-deuterium exchange, but the degree of retention of configuration (defined as the ratio  $K_{\text{H-D}}/K_{\text{inv.}}$ ) is variable (see below). Furthermore, the rates of exchange in *cis-exo*-sulphones (IV) (Table 4) are nearly the same as those of the corresponding *cis-endo*-sulphones (I), but the rates of inversion are higher in the former series. This means that the free energy of activation in the formation of the sulphone-stabilised carbanions is the same in both series, while the optical stability is different.<sup>1</sup> Also for the *cis-exo*-sulphones (IV) the ratio  $k_{\text{H-D}}/k_{\text{inv.}}$  is not constant.

The most interesting point arising from the present investigation is the variation of  $k_{\text{H-D}}/k_{\text{inv.}}$  with the substituent R in the phenyl ring: increasing electron-withdrawing power corresponds to an increase of this ratio (from 11 to 42, Table 2). The observed values are conveniently discussed by analysing separately both  $k_{\text{H-D}}$  and  $k_{\text{inv.}}$  through a Hammett equation. The results obtained (Table 3) show that the fit to a linear free energy relationship of this type is excellent<sup>5</sup> in both cases (correlation coefficients > 0.99). The same holds for the correlation of the rate constants of hydrogen-deuterium exchange in *trans*-compounds (II). The reaction constants  $\rho$  for exchange in both series (I) and (II) are practically the same (within the combined standard deviations) (Table 3). This would be expected since the structural difference between the *cis*-series (I) and the *trans*-series (II) is the same for every pair of *cis-trans* isomers [in other words, the difference in free energy of activation between the exchange reaction of the *cis*-compounds (I) and that of the *trans*-compounds (II) is not affected by the substituents]. The fact that all three  $\rho$ -values (Table 3) are positive is in agreement with the occurrence of a negatively charged reaction centre in the transition states. The significant difference (0.52) between the reaction constants of hydrogen-deuterium exchange and of inversion in compounds (I) indicates that the exchange reaction is more subject to structural changes than the inversion reaction. The few data available for the *cis-exo* isomers (IV) (Table 4) are in agreement with this observation. In terms of the previously<sup>1</sup> suggested reaction scheme



<sup>5</sup> Jaffé, *Chem. Rev.*, 1953, **53**, 191.

the variation of the ratio  $k_{\text{H-D}}/k_{\text{inv.}}$  can be discussed on the basis of the following equation:

$$\frac{k_{\text{H-D}}}{k_{\text{inv.}}} = \frac{k_1(k_3 + k_4)}{k_2} \bigg/ \frac{k_1(k_4 + k_5)}{k_2} = \frac{(k_3 + k_4)}{(k_4 + k_5)} \quad (1)$$

Now,  $k_4$  and  $k_5$  are virtually equal and  $k_3 \gg k_4$  for the *cis-endo*-compounds (I) ( $k_3 = 21 k_4$  for *p*-OMe, and  $k_3 = 81 k_4$  for *p*-NO<sub>2</sub>), so that

$$k_{\text{H-D}}/k_{\text{inv.}} = k_3/2k_4 \quad (2)$$

Substitution of (2) in the combined Hammett equation,

$$\log k_{\text{H-D}}/k_{\text{inv.}} = (\rho_{\text{H-D}} - \rho_{\text{inv.}}) \sigma + \text{constant}, \quad (3)$$

where  $\rho_{\text{H-D}} - \rho_{\text{inv.}} = 0.52$ , yields equation (4):

$$\log (k_3/k_4) = 0.52 \sigma + \text{constant}. \quad (4)$$

The substituent constant  $\sigma$  is thus directly related to the ratio of the rate constants  $k_3$  and  $k_4$ , and proportional to the difference in free energy content of the corresponding transition states.

The variation in the ratio  $k_{\text{H-D}}/k_{\text{inv.}}$ , *i.e.*, in  $\Delta F_{\text{H-D}}^\ddagger - \Delta F_{\text{inv.}}^\ddagger$ , may give indications for the structure of the intermediate sulphone-stabilised carbanions. This is possible if the ratio  $k_{\text{H-D}}/k_{\text{inv.}}$  is not influenced by external factors. These might be the following:

(i) *Change of steric factors in the deuteration of the carbanions.* Zimmermann has shown that the protonic attack on carbanions, stabilised by carbonyl,<sup>6,7</sup> nitro-,<sup>8</sup> or sulphone groups,<sup>9</sup> is subject to steric hindrance. The system which he used was *cis*-2-substituted 1-phenylcyclohexane, and the ratio of *cis*- and *trans*-isomers obtained by protonation of the carbanions varied with the steric requirements of the proton donor.<sup>9</sup> In the bicyclic system, used in the present study, the variation of substituents takes place in the *para*- and *meta*-position of the phenyl-ring, and steric interactions with the reaction centre are excluded. As the deuterium-donor is always the same, *i.e.*, the solvent D<sub>2</sub>O, for compounds (I), a possible preferred direction of electrophilic attack on the carbanions<sup>1</sup> affects in the same way the inversion of configuration for all compounds.

(ii) *Change in electrostatic interaction between the carboxylate anion and the sulphonyl-oxygens.* The electrostatic interaction through space (field effect) between the carboxylate anion and the sulphonyl group was recently<sup>10</sup> invoked to explain the low acidities of *cis-endo*- and *cis-exo*-3-phenylsulphonylbicyclo[2,2,1]hept-5-ene-2-carboxylic acids (I) and (IV), R = H. The same interaction was assumed to act as a driving force for the base-catalysed phenylsulphonyl inversion in the same compounds.<sup>1</sup> It might be therefore that the variation in ratio  $k_{\text{H-D}}/k_{\text{inv.}}$  is due to variation in the magnitude of this force. This is not unreasonable because electron-withdrawing substituents in the phenyl ring will increase the positive charge on the sulphonyl-sulphur atom,<sup>11</sup> which in turn will affect to some extent the negative charge on the sulphonyl-oxygens. As the field effect is a function of this negative charge, electron-withdrawing substituents ought to decrease the rate of inversion compared with that of exchange. However, as recently shown<sup>4</sup> from the acidity constants of the series of *cis*-compounds (I) and *trans*-compounds (II), no change in the electrostatic intramolecular interaction is detectable. There is one example in the literature supporting the idea that the ratio  $k_{\text{H-D}}/k_{\text{inv.}}$  is really characteristic of the substituent (see below). Goering, Towns, and Dittmar<sup>12</sup> measured the relative rates of base-catalysed racemisation and deuterium exchange in phenyl and *p*-tolyl 2-deutero-2-octyl

<sup>6</sup> Zimmermann and Cutshall, *J. Amer. Chem. Soc.*, 1958, **80**, 2893.

<sup>7</sup> Zimmermann, *J. Org. Chem.*, 1955, **20**, 549.

<sup>8</sup> Zimmermann and Nevins, *J. Amer. Chem. Soc.*, 1957, **79**, 6559.

<sup>9</sup> Zimmermann and Thyagarajan, *J. Amer. Chem. Soc.*, 1958, **80**, 3060.

<sup>10</sup> Hogeveen and Montanari, *J.*, 1963, 4864.

<sup>11</sup> Meyers, Moretti, and Maioli, *J. Org. Chem.*, 1962, **27**, 625.

<sup>12</sup> Goering, Towns, and Dittmar, *J. Org. Chem.*, 1962, **27**, 736.

sulphone, and found  $k_{H-D}/k_{rac.} = 17$  and  $14$ , respectively. This is the same behaviour observed in Tables 2 and 4.

In view of these observations it is very likely that the trend in  $k_{H-D}/k_{inv.}$  is essentially due to a change in charge transfer between the carbon orbital containing the lone pair and a vacant  $3d$  orbital of sulphur. The variation in positive charge on sulphur due to the electron-withdrawing power of the substituent will in fact increase the electronegativity of the vacant  $3d$  orbital of sulphur, resulting in a stabilisation of the carbanion.

In the case of an  $sp^2$ -hybridised carbon, a greater charge delocalisation lowers the free energy of activation for the carbanion formation. As, in the reaction steps (3) (exchange) and (4) (inversion), both the common initial state and the two transition states are planar, one expects the influence of substituents to be about the same in the two steps. This means that the exchange and the inversion rates should vary equally, so the ratio  $k_{H-D}/k_{inv.}$  will be constant for all compounds (I). In the case of  $sp^3$  hybridisation, the structure of the carbanion in the initial state and in the transition state of reaction step (3) (exchange) is essentially the same (apart from differences in hydrogen bonding), but it differs in the reaction step (4) (inversion), being non-planar in the initial state and planar in the transition state. This implies that the increase in coupling of the  $sp^3$  orbital containing the lone pair electrons with the  $3d$  orbitals of sulphur will make the inversion more difficult relatively to the exchange, and therefore will increase the ratio  $k_{H-D}/k_{inv.}$ \*

We may conclude that the present results afford strong evidence that sulphone-stabilised carbanions in open chain (cyclic sulphone-carbanions may be different<sup>13</sup>) are essentially  $sp^3$ -hybridised.

#### EXPERIMENTAL

*Compounds.*—The syntheses of the bicyclic sulphones have been recently described.<sup>3,4</sup>

*Kinetics.*— $0.46 \times 10^{-3}$  Mole of the compound was dissolved in 0.98 ml. of a 0.91N-sodium deuterioxide solution in deuterium oxide. Kinetic measurements were made on 0.2 ml. of this solution, kept in a sealed proton magnetic resonance tube at  $25 \pm 0.05^\circ$ . Recording of the spectrum and integration of the peak areas, made at room temperature ( $24^\circ$ ) with a Varian D.P. 60 spectrometer operating at 56.4 Mc./sec., required about 10 min. Band integration, performed by a Varian 3521 integrator, was repeated six times (except in the case of hydrogen-deuterium exchange of the *m*- and *p*-nitro-substituted compounds (I), for which the results are less accurate because of the relatively high rate). The concentration of  $OD^-$  was calculated taking into account the increase in volume caused by dissolving the bicyclic compound. The reactions were followed to 50–70% conversion and showed first order kinetics. The first order rate constants were computed by least squares analysis. The exchange reaction was followed kinetically by measuring the decrease in area of the resonance peak belonging to proton at position-3, and the inversion reaction by the change in the resonance bands of the ethylenic protons at positions-5, and -6, as previously described in more detail.<sup>1</sup>

When the reaction was completed, the products were isolated by precipitation with dilute sulphuric acid. The yields were always higher than 90%. Deuterated *trans*-isomers (II) were obtained starting from both non-deuterated *trans*- and *cis*-isomers (II) and (IV), and deuterated *trans*-isomers (III) from non-deuterated *cis*-isomers (I); mixed m. p. were not depressed.

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\* An explanation in terms of electrostatic repulsion between the lone-pair electrons and the sulphonyl-oxygens in the transition state of the inversion does not seem correct, since this repulsion is expected to be less for compounds with electron-withdrawing substituents than those with electron-donor substituents, and the trend in ratio  $k_{H-D}/k_{inv.}$  would be the opposite of that observed.

<sup>13</sup> Cram and Wingrove, *J. Amer. Chem. Soc.*, 1963, **85**, 1100.