# Aromatic Sulphonation. Part XXXVI.[1] The Sulphuric Acid Sulphonation of Some *o*-Dialkylbenzenes, Benzocycloalkenes, and their 4-Sulphonic† Acids. Formation of Polyxylylene from Benzocyclobutene

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Isomer distributions for the sulphonation of two *o*-dialkylbenzenes, indane, tetralin, and 6,7,8,9-tetrahydro-5*H*-benzocycloheptene with concentrated aqueous sulphuric acid have been determined. The 3-:4-sulphonic † acid ratio decreases in the order tetralin > indane > *o*-xylene > 6,7,8,9-tetrahydro-5*H*-benzocycloheptene > *o*-diethylbenzene. The partial rate factors for 3-substitution by the $H_2S_2O_7$ sulphonation mechanism exhibit the order tetralin ≃ indane > *o*-xylene > *o*-diethylbenzene ≃ 6,7,8,9-tetrahydro-5*H*-benzocycloheptene. The results of tetralin and indane are accounted for by means of a theory recently advanced to explain the Mills–Nixon effect for, *e.g.*, protiodetritiation. The reversed order of indane and *o*-xylene for sulphonation as compared with protiodetritiation is ascribed to hyperconjugative stabilization of the transition state for sulphonation of indane at the 3-position. Both the lower 3 : 4 ratio and the lower $f_3$ of *o*-diethylbenzene than of *o*-xylene and of the benzocycloheptene than of tetralin are ascribed to steric hindrance in the case of the former substrates. Sulphonation of the corresponding arene-4-sulphonic acids leads to the sole formation of the arene-3,5-disulphonic acids. In *ca.* 100% $H_2SO_4$ the rate order is rather similar to that of the parent hydrocarbons. The reaction of benzocyclobutene with 81—98% $H_2SO_4$ yields polyxylylene.

THE Mills–Nixon effect [2] was originally observed in the azo-coupling and bromination of β-hydroxybenzocycloalkenes. In view of the renewed interest in the electrophilic substitution of both benzocycloalkenes [3] and β-hydroxybenzocycloalkenes [2,4] and as an extension of our study on monoalkylbenzenes,[5] we now report on the sulphonation of two *o*-dialkylbenzenes, benzocycloalkenes and their 4-sulphonic acids.†

The high-temperature sulphonation of indane [6] and tetralin [7] has been studied before. Both yield a mixture of mostly 4- and some 3-sulphonic acid; with indane the 4 : 3 ratio increases with increasing temperature, possibly as a result of isomerization (*cf.* ref. 8).

## RESULTS

*Hydrocarbons.*—Varying amounts of a given *o*-dialkylbenzene or benzocycloalkene were sulphonated at 25 °C with various concentrations of sulphuric acid ranging from 80·9 to 98·3% $H_2SO_4$. For all substrates, the ratio of 3- to 4-sulphonic acid decreases with increasing amounts of sulphonated substrate. The ratios of 3- to 4-substitution under conditions of homogeneous sulphonation were obtained by graphical extrapolation to zero substrate conversion.[5] The results are in Table 1. The data for *o*-xylene are in agreement with those obtained by multicomponent u.v. analysis.[9] For a given substrate the ratio of 3- to 4-substitution increases with increasing sulphuric acid concentration to decrease again, except for 6,7,8,9-tetrahydro-5*H*-benzocycloheptene, at acid concentrations >95% $H_2SO_4$. At a given acid concentration the ratio of 3- to 4-sulphonic acid decreases in the orders: *o*-xylene > *o*-diethylbenzene, and tetralin > indane > *o*-xylene > the benzocycloheptene.

The rate of sulphonation of the hydrocarbons was determined in 84·7% $H_2SO_4$ at 25 °C. The overall pseudo-first-order rate constants and the derived rate constants for sulphonation at the 3- and 4-position are in Table 2. The accuracy of the data is less for the benzocycloalkenes than for the *o*-dialkylbenzenes because of the lower solubility of the former in sulphuric acid.

The monosulphonation mixtures in 98·3% $H_2SO_4$ were further sulphonated by addition of 65% oleum to yield 11% oleum solutions. The n.m.r. spectra of the disulphonation mixtures obtained with *o*-xylene, *o*-diethylbenzene, indane, tetralin, and the benzocycloheptene all exhibit an AX absorption pattern for the aromatic hydrogens with $J_{AX}$ 1·5—2·0 Hz and $\delta_A - \delta_X =$ *ca.* 0·31, 0·29, 0·18, 0·34, and 0·35 p.p.m. respectively, two slightly overlapping, symmetrically broadened absorption peaks for the benzylic hydrogens with $\Delta\delta = 0·19$, 0·24, 0·21, 0·22, and 0·22 p.p.m. respectively,[10a] and one broad peak for the remaining carbon-bonded hydrogens.‡ These spectra demonstrate the sole

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† The aromatic ring positions of the benzocycloalkenesulphonic acids have been numbered for reasons of convenience such that the alkyl substituents are at C-1 and -2.

‡ With indane the two benzylic hydrogen peaks are in fact two broadened, not completely resolved, triplets. With *o*-diethylbenzene, only the high-field benzylic hydrogen absorption is a resolved quartet; the two β-methyl groups exhibit two overlapping triplets with $\Delta\delta = 0·04$ p.p.m., each with *J ca.* 7 Hz.

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[2] W. H. Mills and I. G. Nixon, *J. Chem. Soc.*, 1930, 2510.

[3] (*a*) G. Berthier and A. Pullman, *Bull. Soc. chim. France*, 1950, 88; (*b*) R. Granger, H. Orzalesi, and A. Muratelle, *Compt. rend.*, 1959, **249**, 2337; 1961, **252**, 1478; (*c*) R. Granger and H. Orzalesi, *ibid.*, 1959, **249**, 2782; (*d*) F. R. Jensen and G. Maciel, *J. Org. Chem.*, 1960, **25**, 640; (*e*) H. Tanida and R. Muneyuki, *J. Amer. Chem. Soc.*, 1965, **87**, 4794; (*f*) J. Vaughan, G. J. Welch, and G. J. Wright, *Tetrahedron*, 1965, **21**, 1665; (*g*) J. Vaughan and G. J. Wright, *J. Org. Chem.*, 1968, **33**, 2580; (*h*) A. R. Bassindale, C. Eaborn, and D. R. M. Walton, *J. Chem. Soc.* (*B*), 1969, 12; (*i*) R. Taylor, *Chimia*, 1968, **22**, 1; (*j*) R. D. Rieke, *J. Org. Chem.*, 1971, **36**, 227; (*k*) R. Taylor, *J. Chem. Soc.* (*B*), 1971, 536.

[4] (*a*) O. S. Pascual, *Chem. Abs.*, 1964, **60**, 10,516; (*b*) J. L. G. Nilsson, H. Selander, H. Sievertsson, I. Skånberg, and K. G. Svensson, *Acta Chem. Scand.*, 1971, **25**, 94.

[5] H. de Vries and H. Cerfontain, *Rec. Trav. chim.*, 1967, **86**, 873.

[6] W. Borsche and M. Pommer, *Ber.*, 1921, **54**, 102.

[7] G. Schroeter, *Annalen*, 1921, **426**, 17, 83.

[8] A. Koeberg-Telder, A. J. Prinsen, and H. Cerfontain, *J. Chem. Soc.* (*B*), 1969, 1004.

[9] A. J. Prinsen and H. Cerfontain, *Rec. Trav. chim.*, 1969, **88**, 833.

[10] (*a*) *Cf.* C. Ris, forthcoming thesis (in English), University of Amsterdam, chap. 2; (*b*) M. P. Cava and D. R. Napier, *J. Amer. Chem. Soc.*, 1958, **80**, 2255.

presence of the 3,5-disulphonic acid, the ratio of the peak areas being the appropriate one for all the substrates studied.

*Benzocyclobutene*.—The reaction of this hydrocarbon with 81—98% $H_2SO_4$ leads to the sole formation of a sulphuric acid-insoluble polymer.[10b] The n.m.r. spectrum revealed that no organic material was present in the sulphuric acid phase. The n.m.r. spectrum of the polymer in $CDCl_3$ exhibits a singlet absorption at $\delta = 2{\cdot}85$ p.p.m. and a not completely resolved doublet with maxima at 7·11 and 7·20 p.p.m. The absorption-area ratio of benzylic to aromatic hydrogens is 0·96. The structure assigned to the polymer is polyxylylene $(\text{-}C_6H_4{\cdot}CH_2{\cdot}CH_2\text{-})_n$.

TABLE 1

Isomer distribution in the homogeneous sulphonation at 25·0 °C

| $H_2SO_4$ wt % (±0·2) | 3-$ArSO_3H$ : 4-$ArSO_3H$ [a] *o*-Xylene (±0·03) | *o*-Xylene U.v. anal.[9] (±0·01) | *o*-Diethylbenzene (±0·05) | Indane (±0·06) | Tetralin (±0·08) | 6,7,8,9-Tetrahydro-5*H*-benzocycloheptene (±0·05) |
|---|---|---|---|---|---|---|
| 98·3 | 0·66 | 0·73 | 0·25 | 0·64 | 1·05<br>(0·90 ± 0·12) | 0·58 |
| 95·2 | 0·74 | 0·79 | 0·35 | 0·90 | 1·38 | 0·48 |
| 90·0 | 0·65 | 0·68 | 0·27 | 0·77 | 1·10 | 0·41 |
| 85·4 | 0·53 | 0·48 | 0·22 | 0·67 | 0·94 | |
| 84·7 | | | | | | 0·27 |
| 80·9 | 0·29 | 0·27 | 0·16 | 0·55 | 0·66 | |

[a] The data were obtained from the n.m.r. analysis of the benzylic hydrogen pattern; the datum in parentheses refers to analysis of the aromatic hydrogen pattern.

TABLE 2

Pseudo-first-order rate constants for sulphonation in 84·7% $H_2SO_4$ at 25·0 °C

| Substrate | λ/nm [a] | $10^3k_1/s^{-1}$ | $\frac{3\text{-}SO_3H}{4\text{-}SO_3H}$ [b] | $10^3\,{}_3k_1/s^{-1}$ | $10^3\,{}_4k_1/s^{-1}$ |
|---|---|---|---|---|---|
| *o*-Xylene | 277 | 2·94 ± 0·08<br>2·98 ± 0·08 [c] | 0·44 ± 0·01 | 0·45 ± 0·02 | 1·03 ± 0·03 |
| *o*-Diethylbenzene | 231 | 2·57 ± 0·08 | 0·21 ± 0·03 | 0·23 ± 0·03 | 1·06 ± 0·03 |
| Indane [d] | 231 | 3·9 ± 0·6 [d] | 0·65 ± 0·04 | 0·77 ± 0·10 [d] | 1·18 ± 0·20 [d] |
| Tetralin | 231 | 3·4 ± 0·5 | 0·89 ± 0·05 | 0·80 ± 0·12 | 0·90 ± 0·13 |
| 6,7,8,9-Tetrahydro-5*H*-benzocycloheptene | 231 | 2·0 ± 0·4 | 0·27 ± 0·03 | 0·21 ± 0·05 | 0·79 ± 0·15 |

[a] Wavelength at which the rate measurement was made. [b] Data obtained from Table 1. [c] Ref. 8. [d] With indane some polymerization (*ca.* 10%) takes place in concurrence with the sulphonation. The actual sulphonation rate constants are therefore *ca.* 10% smaller than listed here.

TABLE 3

Pseudo-first-order rate constants for sulphonation of arenesulphonic acids at 25·0 °C

| Substrate * | $10^4k_1/s^{-1}$ [a] 99·97% $H_2SO_4$ | $10^4k_1/s^{-1}$ [a] 100·12% $H_2SO_4$ |
|---|---|---|
| 3,4-Dimethylbenzenesulphonic acid | 1·5 (290 nm) | 46 (287 nm) |
| 3,4-Diethylbenzenesulphonic acid | | 26 (268 nm) |
| Indane-5-sulphonic acid | 18 (290 nm) | 380 (297; 301 nm) |
| Tetralin-6-sulphonic acid | 11 (290 nm) | 300 (297 nm) |
| 6,7,8,9-Tetrahydro-5*H*-benzocycloheptene-2-sulphonic acid | 1·6 (290 nm) | 51 (297 nm) |

[a] The data in parentheses refer to the wavelength at which the rate measurement was made.

* Named systematically.

*Arene-4-sulphonic Acids*.—The pseudo-first-order rate constants for the sulphonation of the *o*-dialkylbenzene-4-sulphonic acids and 4-sulphobenzocycloalkenes are given in Table 3.

DISCUSSION

*Isomer Distribution*.—The sequence of the ratio of 3- to 4-substitution ($k_3 : k_4$) of *o*-xylene, indane, tetralin, and the benzocycloheptene is similar for the sulphonation with, *e.g.*, 95·2% $H_2SO_4$ (0·79, 0·90, 1·38, 0·48), as well as for the chloromethylation (0·22, 0·24, 0·32, 0·05 [3a,b]) and possibly for nitration with mixed acid in nitromethane [1·22 (without solvent)[11], 1·00, 1·07, —[3e]]. On the other hand, for protiodetritiation (0·71, 0·25, 0·92, —[3g]), protiodesilylation,[3h] and bromination[3f] $k_3 : k_4$ follows the order indane < *o*-xylene < tetralin, *i.e.*, the sequence of *o*-xylene and indane is reversed. Let us compare the sulphonation and protiodetritiation reactions.

Protiodetritiation is a reaction of minimal steric requirements.[12] The steric hindrance for sulphonation of *o*-xylene at the 3-position with 95·2% $H_2SO_4$, *i.e.*, by the $H_2S_2O_7$ mechanism,[13] is only very small at most.[8] Thus the reverse order of $k_3 : k_4$ for indane and *o*-xylene cannot be explained in terms of differences in steric hindrance for the two different substitution reactions.

The observed $k_3 : k_4$ order of *o*-xylene and the benzo-

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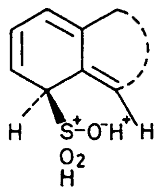
[11] G. A. Olah, S. J. Kuhn, S. H. Flood, and J. C. Evans, *J. Amer. Chem. Soc.*, 1962, **84**, 3687.

[12] R. Baker, C. Eaborn, and R. Taylor, *J. Chem. Soc.*, 1961, 4927.

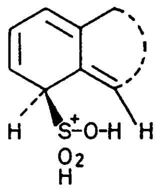
[13] H. Cerfontain and C. W. F. Kort, *Internat. J. Sulfur Chem.* (*C*), 1971, **6**, 123.

cycloalkenes in protiodetritiation was explained by Vaughan and Wright,[3f] and later by Eaborn and his co-workers[3h] and Taylor *et al.*[3i,14] in terms of a bond-order argument. They pointed out that in the Wheland intermediate for 3-substitution, the bond common to both rings has $\frac{2}{3}$ double-bond character, whereas for 4-substitution it has $\frac{1}{3}$ double-bond character. This tends to decrease the length of this bond in the formation of the transition state for 3-substitution, but to increase it for 4-substitution. For indane this will lead to an increased strain in the fused ring for 3-substitution and decreased strain for 4-substitution, thus leading to a lower $k_3 : k_4$ ratio than with *o*-xylene. For tetralin, however, any strain will be decreased in the formation of the transition state for 3-substitution and increased in the case of 4-substitution, leading to a higher $k_3 : k_4$ ratio than with *o*-xylene.

With sulphonation, additional canonical structures can be formulated for the Wheland intermediate for 3-substitution but not for that for 4-substitution. These hyperconjugative structures [(A) and (B)] illustrate a stabilizing electrostatic proximity effect between one of the electron-rich oxygen atoms of the incoming $SO_3H^+$ group and the hydrogen atoms of the *ortho*-benzylic methylene or methyl group. For the sulphonation of *o*-xylene by the $H_2S_2O_7$ mechanism, this stabilizing proximity effect is virtually absent.[9] In the case of the benzocycloalkenes, the contributions of the structures (A) and (B) tend to lower the double-bond character of the bond common to both rings but to increase that of the exocyclic bond *ortho* to the reaction centre. If, for example, equal contributions of (A), (B), and the three common canonical structures are assumed, this leads to $\frac{2}{5}$ double-bond character of both the bond common to both rings and the exocyclic bond *ortho* to the reaction centre. Provided that this Wheland intermediate has a lower enthalpy of formation with indane than with *o*-xylene, possibly for geometric reasons,[3d,15,16] this would lead to a higher $k_3 : k_4$ for indane than for *o*-xylene, as observed.

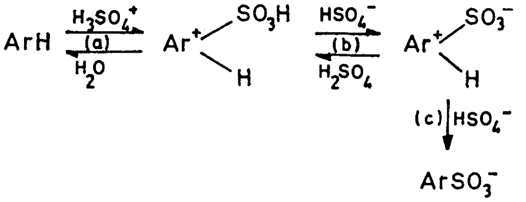


(A)

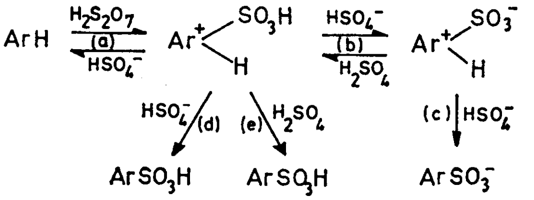


(B)

For a given hydrocarbon $k_3 : k_4$ increases upon varying the acid concentration from 80 to 95% $H_2SO_4$. This is due to the occurrence of two sulphonation mechanisms. At low sulphuric acid concentrations the sulphonation proceeds by mechanism (1) whereas at high acid concentrations up to *ca.* 100% $H_2SO_4$ it proceeds by mechanism (2).[13] With mechanism (2) up to *ca.* 95% $H_2SO_4$ and with mechanism (1), the formation of the areniumsulphonic acid intermediate is rate-limiting. With *o*-xylene the changeover from the $H_3SO_4^+$ to the $H_2S_2O_7$ mechanism takes place at a lower acid concentration for the 3- than for the 4-substitution.[9] The observed maximal 3- to 4-substitution ratio gives the $_{2a}k_3 : {}_{2a}k_4$ ratio. The lower $k_3 : k_4$ ratio at 98·3% $H_2SO_4$ for all hydrocarbons, except the benzocycloheptene, may be explained in terms of a higher $_{-2a}k : {}_{2c}k$ for 3- than for 4-substitution, probably as a result of steric hindrance in the proton-abstracting step for substitution *ortho* to the alkyl or methylene group. With the benzocycloheptene $k_3 : k_4$ ratio is higher for 98·3 than 95·2% $H_2SO_4$. This may be explained in terms of a lower rate for the proton-removing step (c) in the case of the benzocycloheptene than the other hydrocarbons as a result of a greater steric hindrance encountered by the sulphonate group upon entering the plane of the aromatic ring.



(1)



(2)

*Partial Rate Factor* $f_3$.—The sulphonation partial factors were determined for the highest acid concentration at which relatively accurate rate data could be obtained, *viz.*, 84·7% $H_2SO_4$ (Table 4). At that acid concentration, the sulphonation of both benzene and the 3-position of *o*-xylene proceeds by mechanism (1), whereas the sulphonation at the 4-position of *o*-xylene is effected by both mechanisms (1) and (2) in about equal

TABLE 4

Partial rate factors for sulphonation in 84·7% $H_2SO_4$ at 25·0 °C

| Substrate | $f_3$ $H_2S_2O_7$ mechanism | $f_4$[a] |
|---|---|---|
| *o*-Xylene | 180 ± 10 | 410 ± 20 |
| *o*-Diethylbenzene | 92 ± 10 | 420 ± 20 |
| Indane | 280 ± 50 | 420 ± 80 |
| Tetralin | 320 ± 50 | 360 ± 60 |
| 6,7,8,9-Tetrahydro-5*H*-benzocycloheptene | 84 ± 20 | 320 ± 60 |

[a] $f_4$ Is a composite quantity, see text.

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[14] R. Taylor, G. J. Wright, and A. J. Holmes, *J. Chem. Soc.* (*B*), 1967, 780.

[15] W. R. Moore, E. Marcus, S. E. Fenton, and R. T. Arnolds, *Tetrahedron*, 1959, **5**, 179.

[16] W. R. Jackson and C. H. McMullen, *J. Organometallic Chem.*, 1965, **4**, 392.

amounts. As an increase in the size of an alkyl substituent *ortho* to the reaction centre tends to lower the sulphuric acid concentration at which the changeover from the $H_2S_2O_7$ to the $H_3SO_4^+$ mechanism takes place,[13] the $f_3$ data are all taken to refer to mechanism (2) with step (a) as rate-limiting step. The $f_4$ data do not refer to one and the same mechanism and will not be discussed.*

The $f_3$ follows the order *o*-xylene $<$ indane $\simeq$ tetralin. This order indicates that the higher $k_3 : k_4$ for indane than for *o*-xylene originates in a higher rate of 3-substitution, as was presumed in the foregoing discussion on the isomer ratios.

For tetralin $f_3$ is higher than for *o*-xylene. This may be explained in terms of the cycloalkene bond order–strain argument given before and in addition in terms of the highly favourable alignment for hyperconjugation of the pseudoaxial benzylic carbon–hydrogen bond *ortho* to the reaction centre in the case of tetralin.[3d,15,17] With *o*-xylene, the most stable conformations probably have one hydrogen atom of each methyl group in the plane through the aromatic ring.[18] The alignment of the bonds between the benzylic carbon atom and the two other hydrogens is then not so favourable for hyperconjugation.

The values of $f_3$ and $k_3 : k_4$ are smaller for *o*-diethylbenzene than for *o*-xylene. This difference may be explained in terms of the larger steric requirements of the ethyl than the methyl group. $f_3$ and $k_3 : k_4$ are also smaller for the benzocycloheptene than for tetralin. The (most) stable conformation of benzocycloheptene is the chair form.[19] The lower values with this substrate may be explained in terms of substantial steric hindrance for the formation of one of the two Wheland intermediates for 3-substitution, *viz.*, the one in which the $SO_3H$ group and the two β-methylene groups are at the same side of the plane through the cyclohexadienyl ring. The steric requirements for the formation of the other Wheland intermediate (with those groups on the same side) are according to model studies comparable with those of *o*-xylene.

The rate constants for sulphonation at the 6-position of the *o*-dialkylbenzene-4-sulphonic acids and 4-sulphobenzocycloalkenes in *ca.* 100% $H_2SO_4$ show a variation similar to those for sulphonation of the 3-position of the corresponding hydrocarbons. With sulphuric acid of a composition close to 100% $H_2SO_4$, the sulphonation mechanism differs from the $H_2S_2O_7$ mechanism for the sulphonation of the hydrocarbons in that it now proceeds by steps (a), (d), and (e) of mechanism (2).

*Polyxylylene.*—The formation of polyxylylene from benzocyclobutene in the presence of sulphuric acid can be explained by the following reaction steps: (1) protonation of benzocyclobutene at a bridgehead carbon atom; (2) an $S_N2$ reaction between this arenium ion and another molecule of benzocyclobutene; (3) proton removal from the adduct by $HSO_4^-$ with formation of mainly 4- with probably only a negligible amount of 3-(2-phenylethyl)-benzocyclobutene;[3h,20] (4) protonation at one of the bridgehead carbon atoms of the benzocyclobutene moiety of the dimer; (5) reaction of this protonated dimer with a molecule of benzocyclobutene, and so on. With regard to the fourth step, the protonation will take place at C(1) rather than at C(2) because of hyperconjugative stabilization of the transition state for C(1) protonation. The major part of the ethylene bridges between the phenyl groups in the polymer will thus have *para*-orientation, and the remaining part will have *meta*-orientation.

## EXPERIMENTAL

*Materials.*— 6,7,8,9-Tetrahydro-5*H*-benzocycloheptene was obtained by Wolff–Kishner reduction of 6,7,8,9-tetrahydro-5*H*-benzocyclohepten-5-one (Aldrich). The other aromatic hydrocarbons were commercial. The potassium arene-4-sulphonates were obtained by sulphonation of the the hydrocarbons with chlorosulphuric acid in either carbon tetrachloride or chloroform, subsequent hydrolysis of the sulphonyl chloride with alcoholic potassium hydroxide, and recrystallization of the potassium sulphonates from ethanol. The sulphonates gave satisfactory elemental analysis; their isomeric purity was established by n.m.r.

*Spectrometers.*—A Zeiss PMQ-2 u.v. spectrophotometer and a Varian HA 100 n.m.r. spectrometer were used.

*Procedures.*—The monosulphonation of aromatic hydrocarbons has been described;[5,9] the rate measurements of the benzocycloalkenes were made in cuvettes with a path-length of 2·0—5·0 cm. The disulphonation mixtures were obtained by addition of 65% oleum (1·5 ml) to the monosulphonation mixtures which resulted from the reaction of 0·4 ml of substrate with 4·0 ml 98·3% $H_2SO_4$. With indane some insoluble material was formed which was filtered off before the n.m.r. spectra were recorded.

For a given sulphuric acid concentration, the rate measurements of the hydrocarbons and their 4-sulphonic acids were taken in acid samples, all originating from one stock solution, in accordance with standard procuedures.[9,21]

*N.m.r. Analysis.*—For *o*-xylene, the n.m.r. spectra of the monosulphonation mixtures exhibit two methyl singlet absorptions with a difference in chemical shift of 0·20 p.p.m. (Figure). After the spectra had been compared with those of authentic samples, the low-field singlet was attributed to

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* It is remarkable that the $k_3 : k_4$ ratio for the sulphonation of an *o*-dialkylbenzene in 84·7% $H_2SO_4$ (0·44 ± 0·04 for R = Me and 0·22 ± 0·03 for R = Et) is equal to $R_{f_o}/R_{f_p}$ for that of the corresponding monoalkylbenzene in 89·1% $H_2SO_4$ (0·44 ± 0·04 for R = Me and 0·20 ± 0·05 for R = Et). This equality would only be expected if the sulphonations of the various substrates proceed by one and the same mechanism with the restriction that the principle of additivity of substituent effects holds.

[17] H. V. Ansell and R. Taylor, *Tetrahedron Letters*, 1971, 4915.

[18] K. S. Pitzer and D. W. Scott, *J. Amer. Chem. Soc.*, 1943, **65**, 813; R. v. Helden, P. E. Verkade, and B. M. Webster, *Rec. Trav. chim.*, 1954, **73**, 39.

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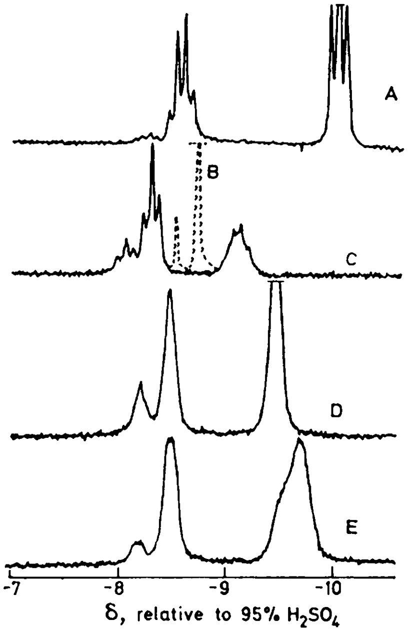
[20] J. B. Lloyd and P. A. Ongley, *Tetrahedron*, 1964, **20**, 2185; 1965, **21**, 245; A. Streitwieser, G. R. Ziegler, P. C. Mowery, A. Lewis, and R. G. Lawler, *J. Amer. Chem. Soc.*, 1968, **90**, 1357.

[21] A. J. Prinsen, A. Koeberg-Telder, and H. Cerfontain, *Tetrahedron*, 1970, **26**, 1953.

the methyl group of *o*-xylene-3-sulphonic acid *ortho* to the sulphonic acid group, the high-field singlet to the other methyl group of *o*-xylene-3-sulphonic acid, and the two methyl groups of *o*-xylene-4-sulphonic acid.



Alkyl n.m.r. absorption patterns of the sulphonation mixtures of some *o*-dialkylbenzenes and benzocycloalkenes in 95·2% sulphuric acid: A, *o*-diethylbenzene; B, *o*-xylene; C, indane; D, tetralin; E, 6,7,8,9-tetrahydro-5*H*-benzocycloheptene

For *o*-diethylbenzene the monosulphonation n.m.r. spectra exhibit two only very slightly overlapping quartets of the benzylic hydrogens with $\Delta\delta = 0{\cdot}25$ p.p.m. and one triplet for all the methyl groups. For indane the spectra exhibit two slightly overlapping triplets of the benzylic hydrogens with $\Delta\delta = 0{\cdot}24$ p.p.m., and a broadened absorption peak of the remaining methylene group. For tetralin and the benzocycloheptene the n.m.r. spectra of the monosulphonation mixtures exhibit two diffuse broadened peaks of the benzylic hydrogens with $\Delta\delta = 0{\cdot}28$ and 0·30 p.p.m. respectively. The non-benzylic methylene groups exhibit one broadened singlet for tetralin and two overlapping broadened singlets for the benzocycloheptene. The isomeric assignment of the two benzylic hydrogen absorption patterns for all these arenesulphonic acids is similar to that given for the *o*-xylenesulphonic acids (see the Figure).

For the *o*-dialkylbenzenes and benzocycloalkenes the ratio of 3- to 4-sulphonic acid was determined by n.m.r. Equation (3) can be derived [in the absence of 3,5-disulphonic acid which shows an isolated absorption of H(4) at $\delta = 8{\cdot}20$ p.p.m.], where $A$ and $B$ are the areas of the low-

$$3\text{-ArSO}_3\text{H}/4\text{-ArSO}_3\text{H} = 2A/(B - A) \qquad (3)$$

and high-field benzylic hydrogen absorption patterns respectively. For tetralin, the ratio of 3- to 4-sulphonic acid was also determined by n.m.r. from the aromatic hydrogen absorption pattern, similar absorption patterns being assumed for the two tetralin sulphonic acids and the corresponding *o*-xylenesulphonic acids.[10] The analysis is based on the observation [10] that the H(4) absorption of the 3-sulphonic acid is shifted 0·14 and 0·20 p.p.m. downfield relative to the absorption of H(3) and H(5) respectively of the 4-sulphonic acid.

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