Aromatic Sulphonation. Part 66.[1] Sulphonation of Some Biphenyl Derivatives

By **Theodorus A. Kortekaas** and **Hans Cerfontain,*** Laboratory for Organic Chemistry, University of Amsterdam, Nieuwe Achtergracht 129, Amsterdam, The Netherlands

The sulphonation of a number of biphenyl derivatives, *viz.* 2,2′-Me_2, 3,3′-Me_2, 4,4′-Me_2, 3,5-Ph_2, 2,2′-$(SO_3H)_2$, 2,4′-$(SO_3H)_2$, 4,4′-$(SO_3H)_2$, 2,2′-SO_2-, 2,2′-$(NO_2)_2$, and 2,4,6-$(NO_2)_3$ in sulphuric acid at 25 °C has been studied; product analysis was by multicomponent ^1H n.m.r. analysis. Sulphonation of 2,2′-dimethylbiphenyl resulted in a 5 : 19 : 76 mixture of the 3,3′-, 3,5′-, and 5,5′-disulphonic acids. Further sulphonation yielded the 3,3′,5,5′-tetrasulphonic acid. 3,3′-Dimethylbiphenyl yielded a 52 : 48 mixture of the 4,4′- and 4,6′-disulphonic acid. Further sulphonation of each of the disulphonic acids yielded the 4,4′,6,6′-tetrasulphonic acid. 4,4′-Dimethylbiphenyl yielded a 34 : 66 mixture of the 2,3′- and 3,3′-disulphonic acids. Further sulphonation of the latter yielded the 3,3′,5,5′-tetrasulphonic acid. 1,3,5-Triphenylbenzene gave exclusively the 4′,4″,4‴-trisulphonic acid, which could not be further sulphonated. Biphenyl-2,4′- and -4,4′-disulphonic acid both yielded the 2,2′,4,4′-tetrasulphonic acid, which is *not* obtained from biphenyl-2,2′-disulphonic acid. Dibenzothiophen 5,5-dioxide gave the 3,7-disulphonic acid. 2,2′-Dinitrobiphenyl yielded the 4,4′-disulphonic acid, but 2,4,6-trinitrobiphenyl only a mixture of monosulphonic acids which contained 88% of the 4′-acid.

In addition to the sulphonation of biphenyl[2] and the biphenylmonosulphonic acids[3] and in the absence of literature information, the sulphonation of the symmetrical bitolyls, 1,3,5-triphenylbenzene, biphenyl-2,2′-, -2,4′-, and -4,4′-disulphonic acid, dibenzothiophen 5,5-dioxide, 2,2′-dinitrobiphenyl, and 2,4,6-trinitrobiphenyl has been investigated. de la Mare *et al.* have extensively studied the chlorination in acetic acid of the symmetrical bitolyls,[4,5] and the results of iodination and bromination of 3,3′-dimethylbiphenyl in acetic acid have also been reported.[6]

Numerous reports on aromatic substitution of 1,3,5-triphenylbenzene are available.[7-16] Chlorination, bromination, benzoylation, and nitration of this compound take place on the central ring in 76, 91, 90, and 62—70% yields, respectively. Substitution on the central ring is favoured over that at the peripheral rings, despite steric hindrance. The only reaction leading to exclusive peripheral (and *para*)-substitution is Friedel–Crafts acylation in nitrobenzene as solvent.[16]

RESULTS

2,2′-Dimethylbiphenyl.—This compound was sulphonated heterogeneously with a large excess of 98.4 wt % H_2SO_4 at 25 °C to yield a homogeneous colourless solution within 18 h.

TABLE 1

Isomer distributions of the disulphonic acids obtained upon sulphonation of the dimethylbiphenyls with 98.4 wt % H_2SO_4 at 25 ± 3 °C

Substrate	Disulphonic acid	Relative amount (% ±3)	
2,2′-Dimethylbiphenyl	3,3′	5	
	3,5′	19	29[a]
	5,5′	76	71[a]
3,3′-Dimethylbiphenyl	4,4′	52	
	4,6′	48	
4,4′-Dimethylbiphenyl	2,3′	34	
	3,3′	66	

[a] Neglecting the presence of any 3,3′-disulphonic acid.

The product composition was determined from the ^1H n.m.r. spectrum of the reaction mixture. This spectrum can be interpreted in two different ways: first, it may be attributed to the presence of a mixture of 2,2′-dimethylbiphenyl-3,5′- and -5,5′-disulphonic acids, and secondly, to the presence of a mixture of the 3,3′-, 3,5′-, and 5,5′-disulphonic acids. The disulphonic acid isomer distributions are given in Table 1. Isolation of any of these compound failed. Further homogeneous sulphonation of the sulphonic acid mixture was effected by sulphur trioxide addition and resulted in the formation of one single compound, *viz.* 2,2′-dimethylbiphenyl-3,3′,5,5′-tetrasulphonic acid.

3,3′-Dimethylbiphenyl.—This compound was also sulphonated heterogeneously with an excess of 98.4 wt % H_2SO_4 at 25 °C to yield a homogeneous solution within 18 h, the composition of which is given in Table 1. Addition of a few drops of water to the sulphonation mixture resulted in the slow precipitation of the 4,4′-disulphonic acid. After removal of this acid the ^1H n.m.r. spectrum of the remaining sulphuric acid solution was attributed to one compound, 3,3′-dimethylbiphenyl-4,6′-disulphonic acid.[†] The relative amounts of the two disulphonic acids were determined from the ^1H n.m.r. spectrum of the reaction mixture before the addition of water and are given in Table 1.

Further sulphonation of the isolated 4,4′-disulphonic acid resulted in the formation of 3,3′-dimethylbiphenyl-4,4′,6,6′-tetrasulphonic acid. The 4,6′-disulphonic acid yields the same tetrasulphonic acid upon further sulphonation.

4,4′-Dimethylbiphenyl.—This substrate was sulphonated heterogeneously in an excess of 98.4 wt % H_2SO_4 at 25 °C for 18 h, during which time the substrate dissolved and a precipitate was formed. The ^1H n.m.r. spectrum of the isolated precipitate (in D_2O) could be attributed to 4,4′-dimethylbiphenyl-3,3′-disulphonic acid. The ^1H n.m.r. spectrum of the remaining sulphuric acid solution was interpreted in terms of the presence of 4,4′-dimethylbiphenyl-2,3′-disulphonic acid. The isomer ratio is given in Table 1. Further sulphonation of the isolated 3,3′-disulphonic acid

[†] Alternatively the spectrum can be attributed to a mixture of the 4,6′- and 6,6′-disulphonic acids and a quantity of disulphonic acids equal to that of the 6,6′-disulphonic acid, in which the two methyls are both *ortho* to a sulpho group, *i.e.* the 2,2′-, 2,4′-, and 4,4′-disulphonic acid. The presence of a large amount of the 6,6′-disulphonic acid is however very unlikely in view of the observation that biphenyl in 96.8% H_2SO_4 at 25 °C does not yield any 2,2′-disulphonic acid.[2] This renders the alternative attribution highly unlikely.

yielded one compound, 4,4′-dimethylbiphenyl-3,3′,5,5′-tetrasulphonic acid.

1,3,5-*Triphenylbenzene*.—This compound was sulphonated heterogeneously in an excess of 98.4 wt % H_2SO_4 at 25 °C. The end of the reaction was difficult to observe, because the reaction product(s) proved to be insoluble in 98.4% H_2SO_4. After five days a precipitate was isolated and its ^1H n.m.r. spectrum (in D_2O) assigned to one compound, 1,3,5-triphenylbenzene-4′,4″,4‴-trisulphonic acid. The remaining sulphuric acid did not show any ^1H n.m.r. absorption signal due to dissolved organic materials. Attempts to sulphonate the trisulphonic acid further, even in 114.6 wt % H_2SO_4, failed.

Biphenyl-2,4′- *and* -4,4′-*disulphonic Acids*.—These disulphonic acids were sulphonated homogeneously in 114.6 wt % H_2SO_4 at 25 °C for two weeks. The ^1H n.m.r. spectra, recorded for *ca.* 99% H_2SO_4 solutions have both been attributed unambiguously to biphenyl-2,2′,4,4′-tetrasulphonic acid.

Dibenzothiophen 5,5-*Dioxide*.—This compound in 98.4 wt % H_2SO_4 only dissolved, but was not sulphonated at all after seven weeks. Sulphonation was accomplished in 111 wt % H_2SO_4 at 25 °C yielding a precipitate. The ^1H n.m.r. spectrum of the precipitate in D_2O was attributed to 5,5-dioxobenzothiophen-3,7-disulphonic acid. The remaining sulphuric acid did not show any ^1H n.m.r. absorption signal. Attempts to achieve further sulphonation of the 3,7-disulphonic acid in 114.6 wt % H_2SO_4 proved unsuccessful.

2,2′-*Dinitrobiphenyl*.—This compound has been sulphonated in an excess of 114.6 wt % H_2SO_4 at 25 °C during three weeks. The ^1H n.m.r. spectrum of a *ca.* 98% H_2SO_4 solution was attributed to 2,2′-dinitrobiphenyl-4,4′-disulphonic acid.

2,4,6-*Trinitrobiphenyl*.—This substrate was sulphonated heterogeneously in an excess of 98.4 wt % H_2SO_4 at 25 °C for 10 days. The ^1H n.m.r. spectrum of the sulphonation mixture was attributed to the presence of a mixture of monosulphonic acids which contained 88% 2′,4′,6′-trinitrobiphenyl-4-sulphonic acid. Attempts to achieve further sulphonation of this compound in 114.6 wt % H_2SO_4 for one week were unsuccessful.

^1H *N.m.r. Data*.—The ^1H n.m.r. data of the various biphenylsulphonic acids are given in Table 2. The spectrum of isolated dipotassium 5,5-dioxodibenzothiophen-3,7-disulphonate in D_2O exhibits a singlet (δ 8.46) and an AB pattern [δ 8.42 and 8.06 (*J* 8.0 Hz)].

TABLE 2

^1H N.m.r. data of the biphenyl derivatives

		δ of H or Me									
Substituents	Solvent	2	2′	3	3′	4	4′	5	5′	6	6′
2,2′,4,4′-$(SO_3^-)_4$	66% H_2SO_4			8.80 (s)	8.80 (s)			8.65 (d) [a]	8.65 (d) [a]	8.39 (d) [a]	8.39 (d) [a]
2,2′-Me_2-3,5′-$(SO_3H)_2$	97% H_2SO_4	2.79 (s)	2.79 (s)		8.04 (d)	8.60—8.25 (m)	8.36 (d)	7.95—7.70 (m)		7.95—7.70 (m)	8.15 (d)
2,2′-Me_2-5,5′-$(SO_3H)_2$	97% H_2SO_4	2.59 (s)	2.59 (s)	8.04 (d)	8.04 (d)	8.36 (d)	8.36 (d)			8.15 (s)	8.15 (s)
2,2′-Me_2-3,3′,5,5′-$(SO_3H)_4$	99% H_2SO_4	3.05 (s)	3.05 (s)			9.34 (s) [b]	9.34 (s) [b]			8.76 (s) [b]	8.76 (s) [b]
3,3′-Me_2-4,4′$(SO_3^-)_2$	D_2O	7.34 (s) [c]	7.34 (s) [c]	2.90 (s)	2.90 (s)			8.15 (d) [d]	8.15 (d) [d]	7.38 (d) [c,d]	7.38 (d) [c,d]
3,3′-Me_2-4,4′-$(SO_3H)_2$	97% H_2SO_4	8.06 (s) [c]	8.06 (s) [c]	3.18 (s)	3.18 (s)			8.48 (d) [d]	8.43 (d) [d]	8.03 (d) [c,d]	8.03 (d) [c,d]
3,3′-Me_2-4,6′-$(SO_3H)_2$	97% H_2SO_4	8.05 ↔	7.55 (m)	3.15 (s)	2.90 (s)		8.05—7.55 (m)	8.55 ↔	8.37 (m)	8.05—7.55 (m)	
3,3′-Me_2-4,4′,6,6′-$(SO_3^-)_4$	D_2O	7.52 (s)	7.52 (s)	3.06 (s)	3.06 (s)			8.37 (s)	8.37 (s)		
4,4′-Me_2-2,3′-$(SO_3H)_2$	97% H_2SO_4		8.45 (s)	8.40 (s)		2.96 (s)	3.19 (s)	8.00 (m)	7.77 (d) [e]	7.95 (d)	8.05 (m) [e]
4,4′-Me_2-3,3′-$(SO_3^-)_2$	D_2O	8.51 (s) [f]	8.51 (s) [f]			3.02 (s)	3.02 (s)	7.77 (d) [g]	7.77 (d) [g]	8.00 (d) [f,g]	8.00 (d) [f,g]
4,4′-Me_2-3,3′,5,5′-$(SO_3H)_4$	99% H_2SO_4	9.05 (s)	9.05 (s)			3.55 (s)	3.55 (s)			9.05 (s)	9.05 (s)
3,5-Ph_2-4′,4″,4‴-$(SO_3^-)_3$ [h]	D_2O	7.56 (s)	7.04 (d) [i]		8.16 (d) [i]	7.56 (s)			8.16 (d) [i]	7.56 (s)	7.64 (d) [i]
2,2′-$(NO_2)_2$-4,4′-$(SO_3H)_2$	98% H_2SO_4			9.43	9.43			8.90 [j]	8.90 [j]	8.16 [j]	8.16 [j]
2,4,6-$(NO_2)_3$-4′-SO_3^-	70% H_2SO_4		6.71 [k]	8.31	7.21 [k]			8.31	7.21 [k]		6.71 [k]

[a] $J_{5,6} = J_{5',6'} = 8.0$ Hz. [b] $J_{4,6} = J_{4',6'} = 1.5$ Hz. [c] $J_{2,6} = J_{2',6'} = 2.0$ Hz. [d] $J_{5,6} = J_{5',6'} = 7.5$ Hz. [e] $J_{5',6'} = 7.5$ Hz. [f] $J_{2,6} = J_{2',6'} = 1.5$ Hz. [g] $J_{5,6} = J_{5',6'} = 8.0$ Hz. [h] The chemical shifts of the corresponding protons of the three peripheral rings are the same. [i] $J_{2',3'} = J_{5',6'} = J_{2'',3''} = J_{5'',6''} = J_{2''',3'''} = J_{5''',6'''} = 8.0$ Hz. [j] $J_{5,6} = J_{5',6'} = 8.0$ Hz. [k] $J_{2',3'} = J_{5',6'} = 8.0$ Hz.

DISCUSSION

The disulphonic acid isomer distribution of the symmetrical bitolyls allows a discussion on the competition of the directing effects of the methyl and tolyl substituent.

With 2,2′-dimethylbiphenyl the directing influence of the methyl substituent is completely dominant, as *only* disulphonic acids containing the sulpho groups *ortho* and/or *para* to the methyl substituent are observed, and no products with the sulpho groups *ortho* and/or *para* to the *o*-tolyl substituent. This is easily understood since the two phenyls of 2,2'-dimethylbiphenyl are close to perpendicular.[17] This excludes any inter-ring mesomeric stabilization of the σ-complexes leading to 4-(or 4'-) and 6-(or 6'-)substitution.

With 3,3'-dimethylbiphenyl it is *a priori* impossible to discriminate between the directing effects of the methyl and *m*-tolyl substituents, because the positions which are *ortho* to the methyl are *ortho* or *para* to the *m*-tolyl group, and those which are *para* to the methyl are *ortho* to the *m*-tolyl group. However, in comparison with *e.g.* biphenyl a relatively large amount of the 6'-sulpho product is formed, the *ortho*/*para* substitution ratios of biphenyl[2] and 3,3'-dimethylbiphenyl being 0.04 and 0.32 respectively, where *ortho* and *para* now refer to the inter-ring C–C bond. This clearly reveals the *para* directing effect of the methyl substituent.

Upon sulphonation of 4,4'-dimethylbiphenyl the 2,3'- and 3,3'-disulphonic acids are obtained in a ratio of 34 : 66. Thus 17% of the sulpho groups are introduced at the 2-position and 83% at the 3-position. With biphenyl the degree of 2- and 3-substitution amounts only to 6.3 and 2.4% respectively.[2] These observations illustrate the dominating influence of the methyl substituent at the 4-position which stabilizes hyperconjugatively the σ-complex leading to 3-substitution. The further sulphonation of the disulphonic acids of the three symmetrical bitolyls proceeds always *meta* to the sulpho group already present, which is also *ortho* or *para* to the methyl substituents.

On comparing the results of this study with those of the chlorination studies made by de la Mare *et al.*[4,5] there appears to be satisfactory agreement for the two types of substitution, but for 2-substitution of 3,3'- and 4,4'-dimethylbiphenyl. For these bitolyls de la Mare reported the formation of 18% 2-chloro-3,3'- and 78% 2-chloro-4,4'-dimethylbiphenyl, respectively. The degree of 2-substitution for sulphonation is considerably less: with 3,3'-dimethylbiphenyl no 2-substituted product was detected and with 4,4'-dimethylbiphenyl only 17% of the sulpho groups are introduced at the 2-position. These differences are very well explained in terms of the larger steric requirements for the introduction of a sulpho as compared with a chloro group. In accordance with this explanation, the 2- to 4-substitution ratio of biphenyl itself is 0.6 for chlorination [18,19] and only 0.07 for sulphonation with 96.8% sulphuric acid.[2]

Upon sulphonation of 1,3,5-triphenylbenzene, the only reaction product is the 4',4'',4'''-trisulphonic acid. No central ring substitution is observed, as occurs with other electrophilic substitutions.[7-15] The angle between the planes of the peripheral phenyl rings and the plane of the central ring in 1,3,5-triphenylbenzene is 38°.[20] From a study of Stewart molecular models it followed that the formation of the σ-complex and especially its conversion to the 2-sulphonic acid will encounter strong steric hindrance, and apparently will not occur.

The sulphonation of biphenyl-2,4'- and -4,4'-disulphonic acids requires highly concentrated fuming sulphuric acid, illustrating the strong deactivation by the original sulpho substituents. The formation of the 2,2',4,4'-tetrasulphonic acid further illustrates the predominantly *meta*-directing effect of that substituent, especially since the sulphonation at the 2- and 2'-position is sterically strongly retarded.[2] It must be stressed here that biphenyl-2,2'-disulphonic acid in fuming sulphuric acid is rapidly converted, but does not yield the 2,2',4,4'-tetrasulphonic acid.[21] This stands unexplained, especially since 2,2'-dinitrobiphenyl yields the 4,4'-disulphonic acid.

Dibenzothiophen 5,5-dioxide (*i.e.* a sulphone) upon sulphonation in fuming sulphuric acid yields the 3,7-disulphonic acid. The substitution pattern is that to be expected on the basis of the presence of both the biphenyl moiety, which undergoes sulphonation *para* to the inter-ring C–C bond and the sulphone moiety, which is *meta*-directing.

For the sulphonation of 2,4,6-trinitrobiphenyl the main product is the 4'-sulphonic acid. This fact and the absence of the 3'-sulphonic acid prompted us to the conclusion that there must be a considerable mesomeric stabilization of the σ-complex and accordingly the two phenyl rings of the σ-complex are not perpendicular, possibly because the nitro groups at positions 2 and 6 have rotated along the C–N bond out of the plane of the attached phenyl group (*cf.* ref. 3). A similar conclusion was drawn for 2-nitrobiphenyl.[3]

EXPERIMENTAL

Apparatus and Materials.—The ^1H n.m.r. spectra were 100 MHz spectra recorded on a Varian HA 100 spectrometer, using (neat) tetramethylsilane, sealed capillary, as an external reference for both the sulphuric acid and the deuterium oxide solutions. Sulphuric acid (AnalaR; *d* 1.84) was obtained from B.D.H., fuming sulphuric acid (minimum 65% SO_3) from Merck, and sulphur trioxide from Hardman and Holden Ltd. Sulphuric acid with a concentration of between 98.4 and 114.6 wt % H_2SO_4 was obtained by mixing the desired amounts of 98.4% sulphuric acid and sulphur trioxide. 3,3'-Dimethylbiphenyl was obtained from EGA-Chemie KG, 2,2'- and 4,4'-dimethylbiphenyl from K and K Laboratories, 1,3,5-triphenylbenzene (purum) from Fluka, and dibenzothiophen 5,5-dioxide and 2,2'-dinitrobiphenyl from Aldrich. Biphenyl-2,4'- and -4,4'-disulphonic acid were described before.[2,22]

Sulphonation Procedure.—Substrate (100 mg) and sulphuric acid (1.0 ml) of the desired strength were added to a test tube. The stoppered test tube was shaken mechanically in a thermostatically controlled room kept at 25 ± 3 °C for a period of time sufficiently long to bring about the desired conversion. In cases where the products proved to be insoluble the precipitate was filtered off, dissolved in deuterium oxide, and an ^1H n.m.r. spectrum recorded. Homogeneous mixtures were directly transferred from the test tube into an n.m.r. tube and recorded as such. The dimethylbiphenyldisulphonic acids which did not precipitate from the sulphuric acid solutions were further sulphonated by adding sulphur trioxide (1.0 ml) and leaving the resulting oleum solution at 25 ± 3 °C for 48 h. In order to obtain resolved ^1H n.m.r. spectra all oleum solutions were diluted with a few drops of water to a concentration just below 100% H_2SO_4.

^{1}H *N.m.r. Spectra*.—The spectra of all the sulphonation mixtures are reproduced in the thesis of one of us.[22]

Analyses.—The ratios of the isomeric sulphonic acids in the sulphonation mixtures were determined by multicomponent ^{1}H n.m.r. analysis.[23] For the 2,2′-dimethylbiphenyldisulphonic acid mixture, two calculations were made, one based on the presence of only the 3,5′- and 5,5′-disulphonic acids, and the other considering the presence of the 3,3′-, 3,5′-, and 5,5′-disulphonic acids. For the latter calculation the fraction of the 3,3′-disulphonic acid formed was taken to be p, and the ratio of substitution *para* and *ortho* to the methyl in a given phenyl group q. On the assumption that q is the same for the introduction of the first and second sulpho groups, it then follows that the fractions of the 3,3′-, 3,5′-, and 5,5′-disulphonic acid will be p, qp, and q^2p respectively. The ratio of the methyls *para* and *ortho* to a sulpho group will be equal to the ratio of the area of the two methyl singlets A_p/A_o. Thus equations (1) and (2) apply. By solving these two equations the

$$p + qp + q^2p = 1 \qquad (1)$$

$$(2\,q^2p + qp)\,(qp + 2p) = A_p/A_o \qquad (2)$$

relative amounts of the three disulphonic acids were obtained.

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