

Aromatic Isomerization Reactions. Part 5.¹ Isomerization of Some Biphenyldisulphonic Acids in Aqueous Sulphuric Acid at Elevated Temperatures

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

The isomerization of six biphenyldisulphonic acids, containing one sulpho-group per phenyl ring, in 75 wt. % sulphuric acid at 140 and 180 °C has been studied. At 140 °C biphenyl-2,2'- and -2,4'-disulphonic acid isomerize to biphenyl-4,4'-disulphonic acid within 96 h, whereas biphenyl-2,3'-disulphonic acid isomerizes to biphenyl-3,4'-disulphonic acid within 24 h. Biphenyl-3,3'-, -3,4'-, and -4,4'-disulphonic acid do not show any isomerization at 140 °C after 96 h. At 180 °C all biphenyldisulphonic acids are eventually converted into the 3,4'-isomer, which remained unchanged. The reactivity order for the isomerization of the biphenyldisulphonic acids is 2,3' > 2,2' > 2,4' ≧ 4,4' > 3,3'.

IN connection with our study on the sulphonation of biphenyl² and its monosulphonic acids,³ the isomerization of the biphenyldisulphonic acids has been investigated. The isomerization of arenesulphonic acids was studied previously, but the reports only refer to

¹ Part 4, E. G. Willard and H. Cerfontain, *Rec. Trav. chim.*, 1973, **92**, 739.

substituted benzenesulphonic and substituted and unsubstituted naphthalenesulphonic acids.

In the isomerization of the alkylbenzenesulphonic acids, the most extensively studied substrates are the

² T. A. Kortekaas and H. Cerfontain, *J.C.S. Perkin II*, 1977, 1560.

³ T. A. Kortekaas, H. Cerfontain, and J. M. Gall, *J.C.S. Perkin II*, 1978, 445.

toluenesulphonic acids.⁴ Muramoto^{5a} and Spryskov *et al.*^{5b} studied the isomerization of ethylbenzenesulphonic acids. The isomerization of *o*- and *m*-xylenesulphonic acids was examined by Cerfontain *et al.*^{6a} and Gnedin *et al.*,^{6b} while the isomerization of *t*-butylbenzenesulphonic acids was investigated by Cerfontain and Arends.⁷ Reports are available on the isomerization of the chlorobenzenesulphonic acids,^{8,9} bromobenzenesulphonic acids,^{9,10} hydroxybenzenesulphonic acids,¹¹ sulphobenzoic acids,¹² benzenedisulphonic acids,¹³ and orthanilic acid.¹⁴ The isomerization of naphthalene-1-sulphonic acid into its 2-isomer was investigated¹⁵ and also the isomerization of some substituted naphthalenesulphonic acids.¹⁶ The isomerization of various naphthalenetrisulphonic acids was examined by Karavaev.¹⁷

RESULTS

The isomerizations were carried out in 75% sulphuric acid at both 140 and 180 °C. The isomerization was followed by recording the ¹H n.m.r. spectra of the (cooled) sulphuric acid samples as such and comparing them with the spectra of the pure biphenyldisulphonic acids in the same sulphuric acid solvent.

Biphenyl-2,2', -2,3', and -2,4'-disulphonic acids in 75% sulphuric acid at 140 °C and a reaction time of 1 h did not show any isomerization. For a reaction time of 24 h isomerization was complete for the 2,3'-disulphonic acid, substantial for the 2,2'-isomer (65–75%), and had only just started for the 2,4'-isomer. For a reaction time of 96 h the conversion of the 2,2'- and 2,3'-disulphonic acid was >90%, whereas the 2,4'-isomer was only 50–60% converted. From the ¹H n.m.r. spectra it appeared that both the 2,2'- and 2,4'-disulphonic acids were eventually completely converted into the 4,4'-isomer, and that the 2,3'-disulphonic acid was completely converted into the 3,4'-isomer. The conversion of the 2,2'- into the 4,4'-disulphonic acid is thought to proceed *via* the 2,4'-isomer as intermediate. Biphenyl-3,3', -3,4', and -4,4'-disulphonic acids in 75% sulphuric acid at 140 °C for 96 h did not show any isomerization.

⁴ (a) A. F. Holleman and P. Caland, *Ber.*, 1911, **44**, 2504; (b) E. A. Shilov and F. M. Vainshtein, *Ukraine Khim. Zhur.*, 1955, **21**, 58 (*Chem. Abs.*, 1955, **49**, 8845b); (c) Y. K. Syrkin, V. I. Yakerson, and S. E. Shnol, *Zhur. obshchei Khim.*, 1955, **29**, 187; (*Chem. Abs.*, 1959, **53**, 21764g); (d) A. C. M. Wanders and H. Cerfontain, *Proc. Chem. Soc.*, 1963, 174; A. C. M. Wanders, H. Cerfontain, and C. W. F. Kort, *Rec. Trav. chim.*, 1967, **86**, 301; (e) A. A. Spryskov and V. A. Kozlov, *Izvest. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol.*, 1969, **12**, 166 (*Chem. Abs.*, 1969, **70**, 114,361u).

⁵ (a) Y. Muramoto, *Kagaku To Kogyo Osaka*, 1959, **33**, 259 (*Chem. Abs.*, 1960, **54**, 12,041b); (b) E. N. Krylov, V. A. Kozlov, and A. A. Spryskov, *Izvest. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol.*, 1975, **18**, 58 (*Chem. Abs.*, 1975, **82**, 11,1348g).

⁶ (a) A. Koeberg-Telder, A. J. Prinsen, and H. Cerfontain, *J. Chem. Soc. (B)*, 1969, 1004; (b) B. G. Gnedin and T. A. Baranova, *Otkrytiya, Izobret., Prom. Obratzy, Tovarnye Znaki*, 1974, **51**, 64 (*Chem. Abs.*, 1974, **80**, 120,540z).

⁷ H. Cerfontain and J. M. Arends, *Rec. Trav. chim.*, 1966, **85**, 358.

⁸ O. I. Kachurin and A. A. Spryskov, *Izvest. V. Sh. Khimiya i Khim. Tekhnologii*, 1958, **5**, 52 (*Chem. Abs.*, 1959, **53**, 11,285d).

⁹ H. Cerfontain, A. Koeberg-Telder, and W. A. Zwartvoorspuj, *Canad. J. Chem.*, 1972, **50**, 1574.

¹⁰ T. I. Potapova, A. A. Spryskov, and E. P. Kukushkin, *Izvest. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol.*, 1968, **11**, 904 (*Chem. Abs.*, 1969, **70**, 64,135a).

At 180 °C isomerization was already apparent after 1 h for biphenyl-2,2', -2,3', -2,4', and -4,4'-disulphonic acids. It was complete after 24 h for the 2,2'- and 2,3'-isomer (>90%), whereas the isomerization of the 2,4'-isomer (50–60%) and the 4,4'-isomer (40–50%) was not yet completed. After 116 h the latter two disulphonic acids had also reached the equilibrium composition. From the ¹H n.m.r. spectra obtained after 1 h it again appeared that the initial conversion of the 2,2'- and 2,4'-disulphonic acid is into the 4,4'-disulphonic acid, and that the 2,3'-disulphonic acid is converted into the 3,4'-isomer.

The ¹H n.m.r. spectra of the isomerization samples of biphenyl-3,3', -3,4', and -4,4'-disulphonic acid recorded after 116 h^{18a} showed only some changes in the peak heights with the reaction time. On comparison of the peak height ratios of these spectra with those of the pure disulphonic acids (Table 1), it was tentatively concluded that after

TABLE 1

¹H N.m.r. peak height ratios of the biphenyl-3,3', -3,4', and -4,4'-disulphonic acids and their isomerization mixtures in 75% H₂SO₄

Neat disulphonic acid	Disulphonic acid isomerized for 116 h at 180 °C	Peak height ratio ^a		
		A : B	A : C	A : D
3,3' ^b		1.76	0.79	2.18
		±0.11	±0.03	±0.10
3,4' ^b		1.13	0.88	1.84
		±0.03	±0.02	±0.09
4,4' ^b		0.78	0.81	1.40
		±0.05	±0.08	±0.10
	3,3'	0.96	0.94	1.50
	3,4'	1.07	0.99	1.80
	4,4'	1.19	0.96	2.14

^a Peaks A–D are in the order of increasing magnetic field.

^b Average value of three independently recorded spectra.

116 h at 180 °C the 3,3'- and 4,4'-isomer had completely isomerized to the 3,4'-isomer which proved to be stable.

¹¹ (a) G. T. Moody, *Chem. News*, 1893, **67**, 34; (b) A. A. Spryskov and N. A. Ovsyankina, *Zhur. obshchei Khim.*, 1954, **24**, 1810 (*Chem. Abs.*, 1955, **49**, 12,342e); (c) E. A. Shilov, M. N. Bogdanov, and A. E. Shilov, *Doklady Akad. Nauk. S.S.S.R.*, 1953, **92**, 93 (*Chem. Abs.*, 1954, **48**, 10,695e); R. N. Khelevin and A. A. Spryskov, *Izvest. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol.*, 1968, **11**, 1139 (*Chem. Abs.*, 1969, **70**, 114,756b).

¹² J. Maarse, *Rec. Trav. chim.*, 1914, **33**, 207; J. S. Reese, *J. Amer. Chem. Soc.*, 1932, **54**, 2009.

¹³ R. Behrend and M. Mertelmann, *Annalen*, 1911, **378**, 352; S. P. Starkov and A. A. Spryskov, *Zhur. obshchei Khim.*, 1957, **27**, 3067 (*Chem. Abs.*, 1958, **52**, 8072).

¹⁴ (a) E. Bamberger and J. Kunz, *Ber.*, 1897, **30**, 2274; (b) W. J. Spillane and F. L. Scott, *Tetrahedron*, 1968, **24**, 5011; W. J. Spillane and F. L. Scott, *Internat. J. Sulfur Chem. C*, 1970, **5**, 59.

¹⁵ S. E. Shnol, Ya. K. Syrkin, V. I. Yakerson, and L. A. Blyumenfel'd, *Doklady Akad. Nauk. S.S.S.R.*, 1955, **101**, 1075 (*Chem. Abs.*, 1956, **50**, 3354h); F. M. Vainshtein and E. A. Shilov, *Zhur. obshchei Khim.*, 1957, **27**, 2559 (*Chem. Abs.*, 1958, **52**, 7246c); N. N. Vorozhtsov, jun., V. A. Koptyug and A. M. Komagorov, *Zhur. Vsesoyuz. Khim. Obshchestva im. D.I. Mendeleeva* 1960 **5**, 232 (*Chem. Abs.*, 1960, **54**, 20,997e).

¹⁶ P. B. Fischer and H. Zollinger, *Helv. Chim. Acta*, 1970, **53**, 1306; T. Kagaya, *J. Soc. Org. Synth. Chem. Japan*, 1955, **13**, 216 (*Chem. Abs.*, 1955, **51**, 2682f); V. V. Kozlov, *J. Gen. Chem. U.S.S.R.*, 1957, **27**, 1229; V. V. Kozlov and G. G. Yakobson, *ibid.*, p. 1238.

¹⁷ B. I. Karavaev and A. A. Spryskov, *Zhur. obshchei Khim.*, 1956, **26**, 2002 (*Chem. Abs.*, 1957, **51**, 5018c); B. I. Karavaev and V. E. Egorov, *Tr. Ivanov. Khim. Tekhnol. Inst.*, 1969, **11**, 49 (*Chem. Abs.*, 1971, **74**, 12,877g).

¹⁸ T. A. Kortekaas, Thesis (in English), University of Amsterdam, 1976 (a) p. 79; (b) pp. 81–83; (c) ch. 2.

The preliminary conclusion of the ^1H n.m.r. studies was that all the biphenyldisulphonic acids at 180 °C are eventually converted into the 3,4'-isomer.

In order to obtain further information, the isomerization of biphenyl-3,3'-, -3,4'-, and -4,4'-disulphonic acid was followed by recording ^{13}C n.m.r. spectra of the (cooled) sulphuric acid samples as such and comparing them with the ^{13}C n.m.r. spectra of the pure biphenyldisulphonic acids in the same sulphuric acid solvent (Table 2). The spectra of the isomerization mixtures^{18b} clearly showed that biphenyl-3,3'- and -4,4'-disulphonic acid both isomerize completely into the 3,4'-isomer. Biphenyl-3,4'-disulphonic acid did not isomerize.

The origin of the small, additional absorption signals (*cf.* Table 2) present in the ^{13}C n.m.r. spectra obtained after

TABLE 2

^{13}C N.m.r. chemical shifts (p.p.m.) of the absorption signals of biphenyl-3,3'-, -3,4', and -4,4'-disulphonic acid in 75 wt. % H_2SO_4 before and after isomerization

Before isomerization			After isomerization ^a		
3,3'	3,4'	4,4'	3,3'	3,4'	4,4'
141.0	144.3	144.5	144.2	144.4	144.2
140.6	140.8	139.4	140.9	140.9	140.9
132.8	140.5	129.1	140.6	140.0	140.4
131.3	139.1	127.6	139.2	138.6	139.3
126.5	132.7		132.6	132.9	132.7
125.1	131.2		131.2	131.2	131.2
	128.8		128.9	128.8	128.8
	127.5		127.4	127.6	127.5
	126.7		126.6	126.6	126.6
	125.2		125.1	125.1	125.1

^a Additional absorptions with a higher intensity than the weakest of the (resulting) 3,4'-isomer were found on starting with the 3,3'-isomer at δ 144.1, 140.8, 139.4, 128.8, 126.4, and 125.0, on starting with the 4,4'-isomer at δ 140.8, 139.0, and 126.5 p.p.m., and none on starting with the 3,4'-isomer.

isomerization at 180 °C of especially the 3,3'-disulphonic acid is not clear. The possibility of the presence of other isomers in the isomerization samples can be excluded, because the two most probable isomers, *viz.* the 3,3'- and 4,4'-compounds, have their absorption signals at other chemical shifts. The possibility of the presence of the monosulphonic acid (obtained after desulphonation) in the isomerization samples was ruled out by recording the ^{13}C n.m.r. spectrum of pure biphenyl-3-sulphonic acid (the most probable monosulphonic acid intermediate) dissolved in the same sulphuric acid solvent. The additional absorption signals are therefore tentatively ascribed to the presence of decomposition product(s) in the isomerization samples which were heated at 180 °C for 116 h (!) in 75% sulphuric acid.

The isomerization results are summarized in Table 3.

TABLE 3

Main products resulting from the isomerization of the biphenyldisulphonic acids in 75% sulphuric acid at 140 and 180 °C

Biphenyldisulphonic acid substrate	Predominant isomer eventually present	
	140 °C	180 °C
2,2'	4,4' ^a	3,4'
2,3'	3,4' ^a	3,4'
2,4'	4,4' ^a	3,4'
3,3'	<i>b</i>	3,4' ^c
3,4'	<i>b</i>	3,4' ^{b,c}
4,4'	<i>b</i>	3,4' ^c

^a Determined by ^1H n.m.r. spectroscopy. ^b No isomerization products were detectable. ^c Determined by ^{13}C n.m.r. spectroscopy.

It appeared that the reactivity order of the biphenyldisulphonic acids is: 2,3' > 2,2' > 2,4' \gg 4,4' > 3,3'.

DISCUSSION

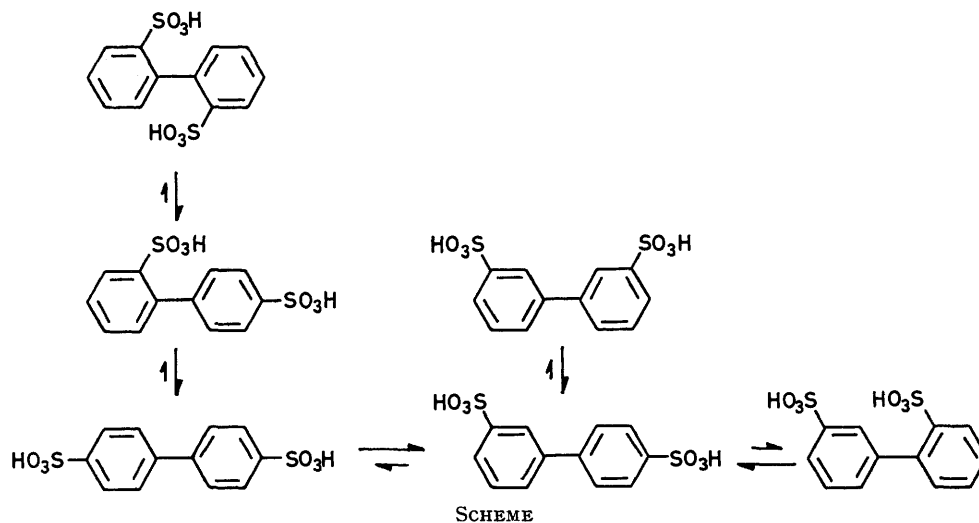
At 140 °C only the *ortho*-substituted biphenyldisulphonic acids undergo isomerization, whereas the *meta*- and *para*-substituted acids appear to be stable. With the three *ortho*-substituted biphenyldisulphonic acids the only sulpho-transfer observed is that from the *ortho*- to the *para*-position. This is in agreement with the behaviour of other monosubstituted benzenesulphonic acids,^{4b, 5a, 8, 9, 11b, 12, 13, 14a} insofar as the initial *ortho-para* isomerization is concerned. If the assumption is made that the mechanism of isomerization consists of desulphonation followed by resulphonation, then this transfer is easily understood. Desulphonation of an *o*-sulpho-group is accompanied by release of steric strain (the biphenyl system will become more planar, leading to an increase in mesomeric stabilization between the two phenyl rings) and will thus be faster than that of a *p*-sulpho-group. The resulphonation will not take place at the *o*-position,^{2,3} because of the steric hindrance caused by the *o*-hydrogen atom(s) of the other sulphophenyl ring. This would, on formation of the *o*- σ -complex intermediate, force the other phenyl ring out of the plane, thus preventing inter-ring mesomeric stabilization.

At 180 °C the biphenyl-2,2'-, -2,3'-, and -2,4'-disulphonic acids rapidly isomerize to yield the biphenyl-4,4'-, -3,4'-, and -4,4'-disulphonic acid respectively. Subsequently the 4,4'-disulphonic acid isomerizes in a slower process to the 3,4'-disulphonic acid. The initial isomerization of the 2,2'-, 2,3'-, and 2,4'-disulphonic acids thus appears to be migration of the sulpho-group(s) from the *ortho*- to the *para*-position(s) with formation of the 4,4'-disulphonic acid. The slower subsequent isomerization then yields the thermodynamically more stable 3,4'-isomer. In fact, the 3,4'-disulphonic acid itself in 75% sulphuric acid at 180 °C appears to be stable. Accordingly, biphenyl-3,4'-disulphonic acid is thermodynamically the most stable compound of the series of biphenyldisulphonic acid studied and the equilibria represented in the Scheme are far to the side of the 3,4'-isomer.

The isomerization is supposed to proceed by desulphonation followed by resulphonation (see before). The alternative mechanism, *viz.* sulphonation (resulting in a trisulphonic acid) followed by desulphonation seems very unlikely in view of the strong deactivation by the sulpho substituents in the presumed trisulphonic acid intermediate for the then required (electrophilic) protio-desulphonation. Another argument against the reverse mechanism is found in the fact that the sulpho-substituents already present exert a *meta*-directing influence. Thus the trisulphonic acid obtained from the 3,3'- and 4,4'-disulphonic acid would be the 3,3',5- and 2,4,4'-trisulphonic acid respectively, neither of which would yield the actual product upon desulphonation, *viz.* the 3,4'-disulphonic acid.

The isomerization of substituted benzenesulphonic acids in aqueous sulphuric acid at elevated temperatures leads in most cases to a mixture of *meta*- and *para*-isomers. With the toluene- and ethylbenzene-sulphonic

scale using $\delta_{[^2\text{H}_6]\text{acetone}}$ 29.2. The ^2H resonance of hexadeuterioacetone was used as field-frequency lock. A high power pulse amplifier supplied 90° radiofrequency pulses of 27 μs . The free inductive decays were averaged in a



acids there is also a small amount of *ortho*-substituted arenesulphonic acid present in the isomerization mixture.^{4a, 4, 5b} In most isomerizations studied the relative amount of the *meta*-isomer is slightly $>50\%$ and that of the *para*-isomer slightly $<50\%$. Regarding the eventual isomerization product of all the biphenyldisulphonic acids, biphenyl-3,4'-disulphonic acid, as substituted 50% *meta* and 50% *para*, then our results are in line with those obtained previously.

EXPERIMENTAL

Apparatus and Materials.— ^1H N.m.r. spectra were recorded on a Varian HA 100 spectrometer, using tetramethylsilane as external reference. ^{13}C N.m.r. spectra were taken on a Varian XL 100 Fourier transform spectrometer in 12 mm tubes at 37°C at 25.2 MHz with proton noise decoupling. Chemical shifts (δ) were determined relative to external hexadeuterioacetone (5 mm concentric tube in 12 mm sample tube) and converted to the tetramethylsilane

Varian 620i computer, employing 5 000 Hz sweep width in 8 192 data points.

The synthesis of the dipotassium biphenyldisulphonates has been described.^{2, 18c} Sulphuric acid (AnalaR; d 1.84; B.D.H.) was diluted with demineralized water to a concentration of 75%.

Procedure.—The isomerizations were performed in test tubes containing the appropriate dipotassium biphenyldisulphonate (50 mg) and 75 wt. % sulphuric acid (0.5 ml). The stoppered test tubes were heated on a thermostatted oil-bath kept at 140 or 180°C . In case of heating at 140°C , the test tubes were removed after 1, 24, and 96 h, at 180°C , after 1, 24, and 116 h, and cooled in ice. The cooled contents of the test tubes were transferred into n.m.r. tubes and the ^1H n.m.r. spectra recorded as such.

For ^{13}C n.m.r. analysis the procedure was similar to that for the ^1H n.m.r. spectra, but 300 mg of the appropriate dipotassium biphenyldisulphonate were used in 75 wt. % sulphuric acid (3.0 ml).

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