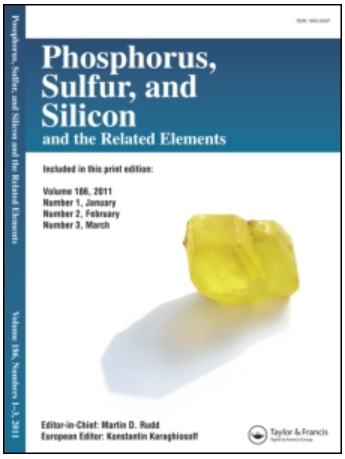


Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

On the Positional Reactivity Order in the Sulfonation of Biphenyl and a Series of Oxy Derivatives

Hans Cerfontain[a]; Yousi Zou[ab]; Bert H. Bakker[a]
[a] Laboratory of Organic Chemistry, University of Amsterdam, Amsterdam, The Netherlands [b] Department of Chemical Engineering, Xiamen University, Xiamen, Fujian, P.R.C.

To cite this Article Cerfontain, Hans , Zou, Yousi and Bakker, Bert H.(1994) 'On the Positional Reactivity Order in the Sulfonation of Biphenyl and a Series of Oxy Derivatives', Phosphorus, Sulfur, and Silicon and the Related Elements, 92: 1, 231 — 237
To link to this Article: DOI: 10.1080/10426509408021477
URL: http://dx.doi.org/10.1080/10426509408021477

Phosphorus, Sulfur, and Silicon, 1994, Vol. 92, pp. 231-237
Reprints available directly from the publisher
Photocopying permitted by license only

Communication

ON THE POSITIONAL REACTIVITY ORDER IN THE SULFONATION OF BIPHENYL AND A SERIES OF OXY DERIVATIVES[1,2]

HANS CERFONTAIN,* YOUSI ZOU† and BERT H. BAKKER
Laboratory of Organic Chemistry, University of Amsterdam, Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands

(Received June 16, 1994; in final form July 21, 1994)

The sulfonation of biphenyl (**1**) and its 2- and 4-methoxy, 3,3'- and 4,4'-dimethoxy, and 4,4'-dimesyloxy derivatives with sulfur trioxide in dichloromethane as solvent at 22°C has been studied. Sulfonation of biphenyl leads to the subsequent formation of the 4-sulfonic acid (4-S), 4,4'-S_2, 2,4,4'-S_3 and traces of 2,4,2',4'-S_4. The sulfonation of the oxy substituted biphenyls also occurs successively in the one phenyl and then in the other. In case of the asymmetrical 2- and 4-methoxybiphenyl the substitution starts in the anisyl moiety.

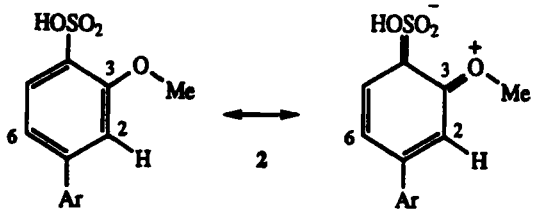
Key words: Sulfur trioxide sulfonation, biphenyl, 2- and 4-methoxybiphenyl, 3,3'- and 4,4'-dimethoxybiphenyl, 4,4'-dimesyloxybiphenyl, steric inhibition of resonance.

INTRODUCTION

As counterpart of extensive studies on the sulfonation of biphenyl and derivatives with concentrated sulfuric acid,[4-8] we now report results on the sulfur trioxide sulfonation of biphenyl and a series of methoxy and mesyloxy derivatives.

RESULTS AND DISCUSSION

Upon reaction of biphenyl (**1**) with 1.0 and 2.0 mol-equiv. of SO_3 in dichloromethane as solvent at 22 ± 2°C for 30 min and subsequent quenching of the heterogeneous reaction mixtures with water, followed by neutralization with an



Ar = 3'-MeO-4'-$SO_3HC_6H_3$-

†Present address: Department of Chemical Engineering, Xiamen University, Xiamen, Fujian, P.R. China.

TABLE I

Sulfonation of biphenyl and a series of oxy derivatives with SO_3 in dichloromethane at 22°C

Substituents	SO_3 (equiv, ± 0.1)	Reactn time (min)	Sulfo product mixture composition[a] (%, ±3)				
-	1.0	30	4-S (38)	4,4'-S_2 (62)			
	2.0	30	4-S (32)	4,4'-S_2 (68)			
	4.0	30	4-S (9)	4,4'-S_2 (91)			
	7.0	1260	-	4,4'-S_2 (90)	2,4,4'-S_3 (10)		
	12.0	1080		4,4'-S_2 (77)	2,4,4'-S_3 (21)	2,4,2',4'-S_4 (2)	
2-OMe	1.0	30	5-S (42)	5,4'-S_2 (58)			
	2.0	30	5-S (18)	5,4'-S_2 (76)	3,5,4'-S_3 (6)		
	4.0	30	-	5,4'-S_2 (91)	3,5,4'-S_3 (9)		
	8.0	30		5,4'-S_2 (78)	3,5,4'-S_3 (22)		
4-OMe	1.0	30	3-S (23)	3,4'-S_2 (74)	3,5,4'-S_3 (3)		
	2.0	30	3-S (17)	3,4'-S_2 (80)	3,5,4'-S_3 (3)		
	4.0	30	3-S (6)	3,4'-S_2 (84)	3,5,4'-S_3 (10)		
	6.0	1035	-	3,4'-S_2 (60)	3,5,4'-S_3 (27)	3,5,2'4'-S_4 (13)	
	10.0	1080		-	3,5,4'-S_3 (77)	3,5,2'4'-S_4 (21)	3,5,2'4',6'-S_5 (2)
3,3'-$(OMe)_2$	1.0	60	4-S (31)	4,4'-S_2 (39)	4,6,4'-S_3 (16)	4,6,4'6'-S_4 (3)	2,4,6,4',6'-S_5 (11)
	2.0	60	4-S (13)	4,4'-S_2 (45)	4,6,4'-S_3 (17)	4,6,4'6'-S_4 (4)	2,4,6,4',6'-S_5 (21)
	4.0	60	-	4,4'-S_2 (6)	4,6,4'-S_3 (16)	4,6,4'6'-S_4 (20)	2,4,6,4',6'-S_5 (58)
	6.0	1010		-	4,6,4'-S_3 (8)	4,6,4'6'-S_4 (17)	2,4,6,4',6'-S_5 (75)

	12.0	1080			4,6,4'-S_3 (6)	4,6,4',6'-S_4 (19)	2,4,6,4',6'-S_5 (75)
4,4'-$(OMe)_2$	1.0	30	3-S (20)	3,3'-S_2 (80)			
	2.0	30	3-S (7)	3,3'-S_2 (93)			
	4.0	30	-	3,3'-S_2 (95)	3,5,3'-S_3 (5)		
	7.0	195		3,3'-S_2 (67)	3,5,3'-S_3 (17)	3,5,3',5'-S_4 (16)	
4,4'-$(OSO_2Me)_2$	1.0	120	3-S (66)	3,3'-S_2 (29)	3,5,3'-S_3 (5)		
	2.0	120	3-S (62)	3,3'-S_2 (33)	3,5,3'-S_3 (5)		
	4.0	120	3-S (39)	3,3'-S_2 (39)	3,5,3'-S_3 (15)	3,5,3',5'-S_4 (7)	
	8.0	120	-	3,3'-S_2 (27)	3,5,3'-S_3 (63)	3,5,3',5'-S_4 (10)	
	12.0	1220		3,3'-S_2 (14)	3,5,3'-S_3 (41)	3,5,3',5'-S_4 (45)	

[a] S stands for $SO_3^-K^+$.

aqueous KOH solution, a mixture of biphenyl-4-sulfonate (**1**-4-S^-) and **1**-4,4'-$(S^-)_2$ is obtained (Table I).

Further sulfonation of **1**-4,4'-disulfonic acid (**1**-4,4'-S_2) affords **1**-2,4,4'-S_3 and even some **1**-2,4,2',4'-S_4. In a given unsubstituted phenyl ring, the degree of *para*-substitution is >97%, indicating very substantial interphenyl conjugative stabilization of the corresponding σ-complex.[9] The relatively very low degree of *ortho*-substitution (<3%) is ascribed to steric hindrance. Catalin-Stuart type of molecular models reveal that the conversion of the σ-complex for *ortho*-sulfonation into **1**-2-S is the step which encounters severe steric hindrance. In fact, the Stuart molecular model showed the interphenyl dihedral angle of the resulting 2-S to be ≈60°.

With 2-methoxybiphenyl the 2-methoxy and 1-phenyl substituents are competitive. Molecular models show that the interphenyl dihedral angle is ≈35° larger for 2-methoxybiphenyl than biphenyl, and accordingly the interphenyl conjugative stabilization will be substantially less for 2MeO-**1** than **1**. Monosulfonation of 2-MeO-**1** gives the 5-S, illustrating that the directing effect of the 2-methoxy substituent dominates over that of the 1-phenyl. The subsequent sulfonation occurs in the non-substituted phenyl at the 4'-position—and not at the 3-position—to form 5,4'-S_2; apparently the desactivation by the 5-sulfo substituent dominates over the activating effect of the 2-methoxy group, preventing substitution at C(3). Thereupon sulfonation occurs again at the 2-methoxyphenyl moiety to give 2-MeO-**1**-3,5,4'-S_3.

Sulfonation of 4-MeO-**1** similarly gives initially 3-S, subsequently 3,4'-S_2, thereupon 3,5,4'-S_3, and finally 4-MeO-**1**-3,5,2',4'-S_4 with traces of 3,5,2',4',6'-S_5. The lower degree of sulfonation of the phenyl group of 2-MeO-**1** is due to the enhanced steric inhibition of resonance for the sulfonation of the 2- as compared with the 4-MeO-**1**.

The sulfonation pattern of the symmetrical 3,3'- and 4,4'-dimethoxy-, and 4,4'-dimesyloxy-biphenyl is dominated by the oxy substituents. The 3- and 3'-methoxyphenyl groups both direct the sulfonation of 3,3'-$(MeO)_2$-**1** to occur at C(4) and subsequently at C(4'), giving 3,3'-$(MeO)_2$-**1**-4,4'-S_2. Further sulfonation takes place at C(6) and C(6'), the substitution at C(2) and C(2') being sterically hindered by the 3-MeO methyl, which in view of conjugative stabilization between the 3-methoxy and 4-sulfo groups requires the methyl carbon to be positioned in the plane through the phenyl moiety. This can only be effected when the methyl is directed to H(2), as is shown in structure **2**. Moreover, for sulfonation with SO_3 as sulfonating reagent, the 3-MeO substituent is electronically predominantly *para*-directing.[12] Eventually, one of the remaining *ortho*-hydrogens of 3,3'-$(MeO)_2$-**1**-4,6,4',6'-S_4 is replaced by a sulfo group to give the corresponding 2,4,6,4',6'-S_5.

Sulfonation of 4,4'-$(MeO)_2$-**1** yields initially 3-S, then 3,3'-S_2, and subsequently 3,5,3'-S_2 and 3,5,3',5'-S_4. No penta-sulfonation was observed; apparently the two sulfo groups in each of the two 3,5-disulfo-4-methoxyphenyl moieties both strongly deactivate the available *ortho*-positions. The substitution pattern of 4,4'-dimesyloxy-**1** is similar to that of 4,4'-dimethoxy-**1**.

EXPERIMENTAL

The substrates were obtained commercially from Aldrich and used as such, except for 4,4'-dimesyloxybiphenyl which was synthesized from 4,4'-dihydroxybiphenyl by reaction with methanesulfonyl chloride.[14]

TABLE II

^{1}H-NMR data of the biphenyl derivatives and their sulfo products

Biphenyl substituents[a]	Solvent	δ (ppm, ± 0.03)[b]									
		2	3	4	5	6	2'	3'	4'	5'	6'
	$CDCl_3$	7.62	7.47	7.38							
4-S	D_2O	7.72 (7.67)	7.84 (7.82)				7.67 (7.61)	7.48 (7.43)	7.48 (7.39)		
4,4'-S_2	D_2O	7.77 (7.63)	7.87 (7.75)								
2,4,4'-S_3	D_2O		8.27 (8.12)		8.14 (8.12)	8.02 (7.70)	7.81 (7.65)	7.95 (7.73)			
2-OMe	$CDCl_3$		6.99	7.33	7.03	7.33	7.53	7.41	7.33		
5-S	D_2O		7.08 (7.02)	7.67 (7.73)		7.72 (7.71)		7.38 (7.29)	7.38 (7.30)		
5,4'-S_2	D_2O		7.17 (6.95)	7.79 (7.67)		7.74 (7.75)	7.58 (7.50)	7.83 (7.61)			
3,5,4'-S_3	D_2O			8.25 (8.12)		8.00 (8.04)	7.54 (7.42)				
4-OMe	$CDCl_3$	7.52	6.97				7.54	7.42	7.29		
3-S	D_2O	8.03 (7.90)				7.62 (7.47)	7.50 (7.49)				
3,4'-S_2	D_2O	8.06 (7.86)			7.26 (6.93)	7.85 (7.43)	7.76 (7.51)	7.85 (7.62)			
3,5,4'-S_3	D_2O	8.16 (7.78)					7.78 (7.43)	7.87 (7.47)			
3,5,2',4'-S_4	D_2O	7.95 (7.80)									7.57 (7.50)
3,5,2',4',6'-S_5	D_2O	8.35 (7.82)						8.49 (8.21)			
3,3'-$(OMe)_2$	$CDCl_3$	7.11		6.89	7.34	7.17					
4-S	D_2O				7.43 (7.69)	7.24 (7.22)			6.25 (6.91)	6.72 (7.30)	
4,4'-S_2	D_2O	7.25 (7.12)			7.77 (7.62)						

TABLE II (*Continued*)

Biphenyl substituents[a]	Solvent	δ (ppm, ± 0.03)[b]									
		2	3	4	5	6	2'	3'	4'	5'	6'
4,6,4'-S_3	D_2O				7.93 (7.99)						
4,6,4',6'-S_4	D_2O	7.27 (7.21)			8.26 (7.97)						
2,4,6,4',6'-S_5	D_2O				8.36 (8.34)					7.18 (7.23)	
4,4'-$(OMe)_2$	$CDCl_3$	7.47	6.95								
3-S	D_2O	7.96 (7.85)			7.01 (6.98)	7.53 (7.42)					
3,3'-S_2	D_2O	8.01 (7.77)			7.21 (6.83)	7.76 (7.34)					
3,5,3'-S_3	D_2O	8.25 (7.69)					8.07 (7.69)			7.27 (6.83)	7.82 (7.26)
3,5,3',5'-S_4	D_2O	8.29 (7.61)									
4,4'-$(OSO_2Me)_2$	$CDCl_3$	7.57	7.36								
3-S	D_2O	7.48 (7.95)			6.70 (7.39)						
3,3'-S_2	D_2O	7.80 (7.87)			6.70 (7.39)	7.48 (7.44)					
3,5,3'-S_3	D_2O	7.93 (7.79)									7.02 (7.24)
3,5,3',5'-S_4	D_2O	7.99 (7.71)									

[a] S stands for $SO_3^-K^+$. [b] The data between brackets are calculated values using the substituent shift data collected in Table III.

TABLE III

^{1}H-substituent chemical-shift of the $SO_3^-K^+$ group[a]

Biphenyl substituent	δ (ppm, ± 0.02)							
	2	3	4	5	6	2'	3'	4'
2-$SO_3^-K^+$		0.37	0.31	0.37	0.07	0.02	-0.02	0.07
3-$SO_3^-K^+$	0.35		0.37	0	-0.08	-0.08	-0.15	-0.06
4-$SO_3^-K^+$	0.02	0.32		0.32	0.02	-0.04	-0.07	0.02

[a] Calculated from the chemical shifts of the substituted biphenyl in $CDCl_3$ as solvent, and of the 2-, 3- and 4-$SO_3^-K^+$ mono-substituted biphenyl in D_2O. The chemical shifts for biphenyl in D_2O were calculated from the observed data of biphenyl in $CDCl_3$ and of benzene in both $CDCl_3$ and D_2O.

Sulfonation Procedures and Analyses

Sulfonation reactions of the substrates with variable amounts of SO_3 in dichloromethane, the subsequent working-up, and ^{1}H-NMR analyses of the resulting potassium sulfonate product mixtures in D_2O were carried out, as described before.[3] The ^{1}H-NMR spectra were recorded on Bruker AC-200, WM-250 and ARX-400 spectrometers. The assignments of the potassium sulfonate products are collected in Table II.

REFERENCES AND NOTES

1. Aromatic sulfonation part 125. For part 124, see Reference 3.
2. For reasons of consistency, the sulfonic acid products have been numbered as for the starting substrate.
3. H. Cerfontain, Y. Zou and B. H. Bakker, *Recl. Trav. Chim. Pays-Bas*, **113**, 403 (1994).
4. T. A. Kortekaas and H. Cerfontain, *J. Chem. Soc. Perkin Trans.*, **2**, 1560 (1977).
5. T. A. Kortekaas and H. Cerfontain, *J. Chem. Soc. Perkin Trans.*, **2**, 742 (1978).
6. T. A. Kortekaas, H. Cerfontain and J. M. Gall, *J. Chem. Soc. Perkin Trans.*, **2**, 445 (1978).
7. H. Cerfontain, T. A. Kortekaas and A. Koeberg-Telder, *Recl. Trav. Chim. Pays-Bas*, submitted for publication.
8. T. A. Kortekaas, Thesis (in English), University of Amsterdam, 1976, Chapter 8.
9. The dihedral angle of biphenyl in heptane as solvent is ≈20°.[10] Biphenyl in the crystalline state is planar.[11]
10. H. Suzuki, *Bull. Chem. Soc. Jpn.*, **32**, 1340 (1960).
11. A. Hargreaves, S. Hozan Risvi and J. Trotter, *Proc. Chem. Soc.*, 122 (1961).
12. The monosulfonation of anisole with SO_3 at 35°C gives >98% of the 4-sulfonic acid.[13]
13. H. D. Goossens, H. J. A. Lambrechts, H. Cerfontain and P. de Wit, *Recl. Trav. Chim. Pays-Bas*, **107**, 426 (1988).
14. A. Vogel, "Practical Organic Chemistry" (Longmans, Green and Co. Ltd., London, 1978), 3rd ed., p. 684.