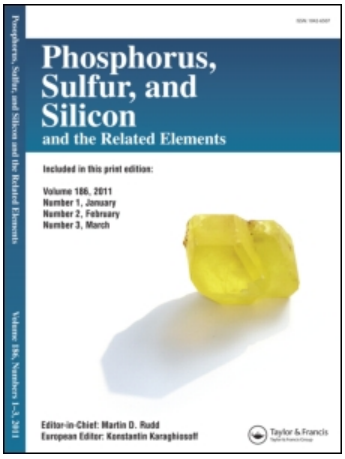


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

HIGH TEMPERATURE SULPHONATION OF BENZENEPHOSPHONIC ACID IN LIQUID SULPHUR TRIOXIDE

Enzo Montoneri[a]
[a] Dipartimento di Chimica Industriale e Ingegneria Chimica Giulio Natta, da Vinci, Milano, Italy

To cite this Article Montoneri, Enzo(1991) 'HIGH TEMPERATURE SULPHONATION OF BENZENEPHOSPHONIC ACID IN LIQUID SULPHUR TRIOXIDE', Phosphorus, Sulfur, and Silicon and the Related Elements, 55: 1, 201 — 204
To link to this Article: DOI: 10.1080/10426509108045941
URL: http://dx.doi.org/10.1080/10426509108045941

Phosphorus, Sulfur, and Silicon, 1991, Vol. 55, pp. 201–204
Reprints available directly from the publisher
Photocopying permitted by license only

HIGH TEMPERATURE SULPHONATION OF BENZENEPHOSPHONIC ACID IN LIQUID SULPHUR TRIOXIDE

ENZO MONTONERI

Dipartimento di Chimica Industriale e Ingegneria Chimica Giulio Natta, Politecnico di Milano, Pz. L. da Vinci 32-20133 Milano, Italy

(Received March 1, 1990; in final form April 16, 1990)

The reaction of benzenephosphonic acid (**I**) and SO_3 in the absence of solvent, at $2.2 \leq SO_3$:**I** mole ratio ≤ 12.7 and at $170 \leq T(°C) \leq 240$, yields benzenephosphono-3-sulphonic acid (**II**) and benzenephosphono-3,5-disulphonic acid (**III**):

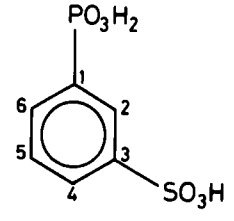
$$\mathbf{I} \xrightarrow{SO_3} \mathbf{II} \xrightarrow{SO_3} \mathbf{III}.$$

In the reaction performed at atmospheric pressure (SO_3:**I** $\simeq 2.4$), substantial dephosphonation occurs. Under autogenous pressure ($5.2 \leq SO_3$:**I** ≤ 12.7), complete conversion of **I** to **III** and no dephosphonation are observed.

Key words: Sulphonation; benzenephosphono-3-sulphonic acid; benzenephosphono-3,5-disulphonic acid

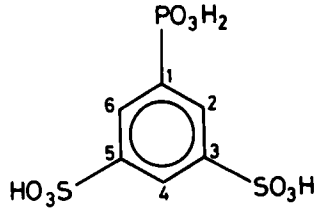
The sulphonation of aromatic compounds to the corresponding sulphonic acids is carried out with various reagents such as concentrated sulphuric acid, oleum, chlorosulphonic acid[1,2] and sulphur trioxide diluted in a solvent.[3,4] Problems that are often encountered in this reaction are the formation of product mixtures which are difficult to separate and the formation of undesired sulphones. To the author's knowledge there are no previous examples of sulphonation of a solid compound with liquid sulphur trioxide in the absence of solvent. Yet, for the sulphonation of benzenephosphonic acid (**I**) to benzenephosphono-3-sulphonic acid (**II**)

II



and to benzenephosphono-3,5-disulphonic acid (**III**)

III



these experimental conditions were found necessary and gave surprising excellent results. As organosulphur phosphorus polyacids, these compounds are new and are desirable as intermediates for the synthesis of materials which are useful in the field of metal ion exchange, coordination chemistry and Brønsted acid catalysis.[5,6]

Table I reports the experimental conditions and the products yields for 23 reactions (identified by the reaction number RN) between **I** and SO_3. The general procedure involves the addition of freshly distilled[4] SO_3 to **I** (Fluka commercial product) kept at 0°C under nitrogen. The use of diluting solvents in this reaction is superfluous, since upon addition of SO_3 to **I** a viscous liquid phase forms and this is not miscible with any of the commonly used SO_3 uncomplexing solvents (i.e., liquid SO_2 or halogenated aliphatic compounds).[3,4,7] Other more polar solvents (i.e., dioxane or amines) were not considered because they lower the reactivity of SO_3 and are not indicated for the sulphonation of the deactivated phenyl ring as in **I**. The runs performed at atmospheric pressure (RN 1–16, 23) were carried out in a glass flask equipped with a reflux condenser. The runs performed at SO_3:**I** mole ratio ≥ 5.2 (RN 17–22) were carried out in a sealed glass bottle. The product yields (relatively to the initial benzenephosphonic acid) in Table I have been cal-

TABLE I

Product yields in the reaction of benzenephosphonic acid (**I**) and SO_3

RN[a]	SO_3:I mol/mol	T °C	t[b]	Yield, mole/mole II	III	H_3PO_4	n.i.[c]
1	1.2	16	0	9			
2	1.2	16	8d	9			
3	1.2	115	50m	12			
4	1.2	145	100m	24			
5	1.2	180	12h	63		6	
6	1.2	180	24h	63		13	
7	1.2	180	5d	64		24	
8	2.4	16	24h	30			
9	2.4	16	20d	46			
10	2.4	84	24h	100			
11	2.4	170	18h	100			
12	2.4	200	4d	93	7		
13	2.4	200	7d	76	24		
14	2.4	240	12d		83	9	8
15	2.4	230	10d		81	12	7
16	2.4	230	21d		61	36	3
17	7.0	120	11d	80	20		
18	12.7	120	18d	74	26		
19	12.7	140	28d	33	67		
20	12.7	180	35d		100		
21	12.7	190	53d		100		
22	5.2	240	13d		100		
23[d]		260	71d			100	

[a] Reaction number.

[b] Reaction time in minutes (m), hours (h) or days (d).

[c] Unidentified compound.

[d] Reaction performed by refluxing 19 days at atmospheric pressure the following mixture: **III** 21.8, SO_3 19, H_2SO_4 58.2 and Hg 1% w/w.

culated from proton decoupled ^{31}P N.m.r. spectra, which were recorded after keeping the reaction sample in D_2O for 24 hours. The N.m.r. signals observed for the reaction samples were assigned based on the coincidence of the chemical shifts with those of the authentic compounds (δ = 17.9 ppm for **I** and − 0.2 ppm for H_3PO_4) and of the new products (δ = 14.9 ppm for **II** and 12.3 ppm for **III**), as isolated from the reaction mixtures according to the procedure given below. The spectra contained also a fourth signal at δ = 11.3 ppm, which was assigned to the unidentified product mentioned in Table I. The products **II** and **III** recovered from the reaction mother liquor are solid compounds. They were found, by visual observation in a Buchi melting point apparatus and by TGA-DTA scanning in N_2 up to 200°C, to melt at 164°C (**II**) and at 146°C (**III**); the weight loss was negligible for **II** or ca. 3.73 % for **III**. The structures of these products were assigned based on the elemental analysis and on N.m.r. spectroscopy (Table II).

The reaction data show that the 1.2 mole ratio between **I** and SO_3 is negligible at 16°C (RN 1–2). At the same temperature, but at higher mole ratio (RN 8–9), some improvement is obtained. When compared with the nearly quantitative reaction of SO_3 and diphenyl sulfide to the 4-sulphonic acid at the same temperature and reagents mole ratio,[4] the data in Table I appear consistent with strong deactivation of the aromatic ring in benzenephosphonic acid by the electron-withdrawing $-PO_3H_2$ functional group. A significant reaction with formation of **II** in 63–64% yield is observed at 1.2 mole ratio and at 180°C (RN 5–7). However, the presence of phosphoric acid in the reaction mixture reveals that either **I** and/or **II** are not

TABLE II

Data from the elemental analysis and from the ^{13}C N.m.r. spectra of compounds **II** and **III**

Compound	% w/w[a]				H^+ meg/g[b]
	C	H	P	S	
II[c] found	29.9	3.1	13.0	13.2	12.4
II[c] theor.	30.3	3.0	13.0	13.5	12.6
III[d] found	21.4	2.9	9.1	19.1	12.0
III[d] theor.	21.4	2.7	9.2	19.1	11.9

	^{13}C N.m.r. spectra[e]						
	C_n[f]:	C_1	C_2	C_3	C_4	C_5	C_6
II	δ[g]:	132.2	127.3	142.8	128.9	129.6	133.4
II	$J_{C,P}$[h]:	132.3	12.0	14.8	2.6	14.5	10.3
III	δ[g]:	133.5	129.8	143.7	125.8	143.7	129.8
III	$J_{C,P}$[h]:	182.3	10.9	14.8	n.o.[i]	14.8	10.9

[a] Elemental analysis data.
[b] Product acid equivalent concentration by alkali titration.
[c] Anhydrous.
[d] Monohydrated.
[e] Recorded in D_2O at 50.12 MHz and 298 K.
[f] Carbons numbered as in **II** and **III**.
[g] Chemical shifts (ppm from Me_4Si) assigned on the basis of the additivity of substituent effects,[8] taking **I** as reference compound (δ: C_1 132.7, C_2 and C_6 133.1, C_3 and C_5 131.3, C_4 135 ppm).
[h] Carbon-phosphorus coupling constant (Hz).
[i] Not observed.

stable under these conditions. The best operational conditions for the synthesis of **II** are a mole ratio of 2.4 and a temperature range of 84–170°C (RN 10–11).

The formation of **III** occurs at mole ratio ≥ 2.4 and at 180–240°C. At 2.4 mole ratio and 240°C the presence of phosphoric acid in the reaction mixture (RN 14–16) is consistent with the results obtained in runs 5–7. Surprisingly, at higher mole ratio and under autogenous pressure, no formation of phosphoric acid is observed and very high yields of **III** are achieved (RN 20–22). These results seem really very peculiar. It should also be observed that the synthesis of the analogous tri-substituted acid compound, benzene trisulphonic acid,[9] is known to occur also under very drastic experimental conditions: i.e., benzene in oleum, with Hg catalyst, at 275°C. However, under similar conditions, compound **III** is very unstable (RN 23).

The mechanistic aspects of the above described phenomena are not clear. From the practical standpoint of view, the high reagents conversion and product selectivity obtained under the optimum experimental conditions in Table I has some significant advantages and prospects. In the case of runs 10, 11, 20–23 where, together with unreacted SO_3, either **I** or **II** are largely the main components, sulphur trioxide may be eliminated by distillation and recovered for other batch reactions. Residual SO_3 may be eliminated as barium sulphate by taking up the reaction mixture with water and adding aqueous HCl and $BaCl_2$. Excess barium chloride is removed afterwards by concentration, filtration of the saturated solution and ion-exchanging of the residual barium ions on Dowex 50W-X8, H^+ form resin. The resin eluate is finally concentrated and dried at 80°C under vacuum (1 mmHg) to yield the solid products **II** or **III**. The yields of the products recovered by this procedure have been found close to those determined from the ^{31}P spectra of the raw reaction mixture.

Although here limited to the case of benzenephosphonic acid, the described sulphonation procedure offers scope for investigating the reaction with other compounds having strongly deactivated aromatic rings and for the synthesis of new sulphonic acids.

REFERENCES

1. H. H. Roth, *Ind. Eng. Chem.*, **49**, 1820–1822 (1957).
2. F. A. Tubak, *Ind. Eng. Chem. Prod. Res. Dev.*, **1**, 275–278 (1962).
3. J. K. Bosscher, and H. Cerfontain, *Tetrahedron*, **24**, 6543–6555 (1968).
4. E. Montoneri, L. Giuffré, and G. C. Pappalardo, *Gazz. Chim. Ital.*, **114**, 543–545 (1984).
5. G. Alberti, and U. Costantino, *J. Mol. Catalysis*, **27**, 235–250 (1984).
6. G. Alberti, U. Costantino, J. Kornyei, and M. L. Luciani Giovagnotti, *Reactive Polymers*, **4**, 1–10 (1985).
7. E. Montoneri, M. Fornaroli, L. Giuffré, E. Tempesti, and G. Sioli, *J. Chem. Soc., Perkin Trans.* **2**, 1784–1789 (1976).
8. E. Montoneri, M. Gleria, G. Ricca, and G. C. Pappalardo, *Makromol. Chem.*, **190**, 191–202 (1989).
9. C. M. Suter, and G. H. Harrington, *J. Amer. Chem. Soc.*, **59**, 2575–2578 (1937).