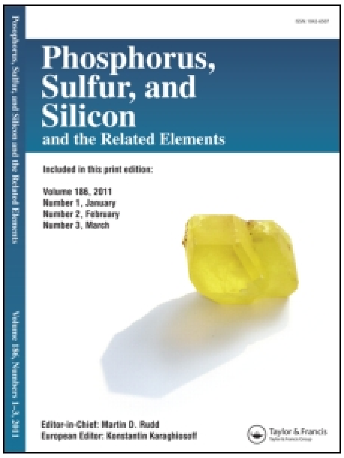


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

A CONVENIENT SYNTHESIS OF POLYSULFIDES BY PHASE TRANSFER CATALYSIS

D. Roberts[a]; M. Born[b]; J. L. Mieloszynski[a]; D. Paquer[a]
[a] Laboratoire de Chimie Organique, Université de Metz Ile du Saulcy, Metz, France [b] Institut Français du Pétrole, Rueil-Malmaison

To cite this Article Roberts, D. , Born, M. , Mieloszynski, J. L. and Paquer, D.(1993) 'A CONVENIENT SYNTHESIS OF POLYSULFIDES BY PHASE TRANSFER CATALYSIS', Phosphorus, Sulfur, and Silicon and the Related Elements, 83: 1, 49 — 51

To link to this Article: DOI: 10.1080/10426509308034346

URL: http://dx.doi.org/10.1080/10426509308034346

Phosphorus, Sulfur, and Silicon, 1993, Vol. 83, pp. 49–51
Reprints available directly from the publisher
Photocopying permitted by license only

A CONVENIENT SYNTHESIS OF POLYSULFIDES BY PHASE TRANSFER CATALYSIS

D. ROBERTS,[a] M. BORN,[b] J. L. MIELOSZYNSKI[a] and D. PAQUER[a]*
[a]*Laboratoire de Chimie Organique, Université de Metz Ile du Saulcy 57045, Metz, France,* [b]*Institut Français du Pétrole, Avenue de Bois-Préau 92506, Rueil-Malmaison*

(Received July 22, 1993; in final form August 5, 1993)

The synthesis of symmetric polysulfides using phase transfer catalysis (PTC) by reaction of chlorosulfides with sodium polysulfide (Na_2S_x; x = 1, 2) is presented and discussed.

Key words: Chlorosulfide; iodosulfide; sulfide; ^1H NMR; ^{13}C NMR.

INTRODUCTION

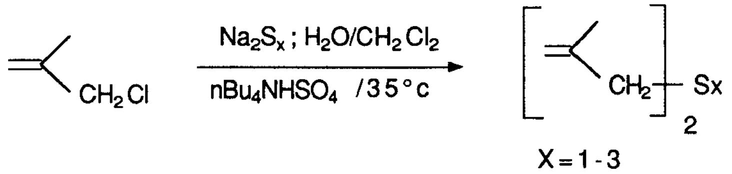
Many petroleum additives include heteroatoms, particularly sulfur.[1] In this report we present the synthesis of symmetrical polysulfides containing three to four sulfur atoms. The compounds are prepared from chlorides by phase transfer catalysis[2] in a two phases system with the use of sodium polysulfide. Nevertheless, in some cases the chloride atom is not enough reactive and must be transformed to the corresponding iodide. The reaction is shown below:

$$R{-}S{-}(CH_2)_n{-}Cl \xrightarrow[KI/CTP]{Na_2S_x} [R{-}S{-}(CH_2)_n]_2 Sx$$

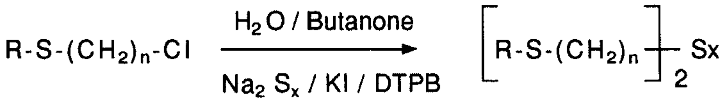
In a previous communication we have reported the synthesis of methallyl polysulfides by reaction of methallyl chloride with Na_2S_x systems.[3] The reaction is realized in PTC in a two phases system (H_2O/CH_2Cl_2) with tetrabutylammoniumhydrogenosulfate (nBu_4NHSO_4) as catalyst and provides good yields (>90%) (Scheme I).

The same reaction applied to 2-hydroxyethyl methallyl sulfide and 3-hydroxypropyl methallyl sulfide[4] doesn't give the pure desired sulfides but a mixture of mono, di and and trisulfides and that in low conversion. The change of solvent (chloroform, toluene) doesn't give better results.

The failure of the reaction is certainly due to the weak reactivity of the chloride atom previously observed in this type of compounds.[5]



SCHEME I



$$R\text{-}S\text{-}(CH_2)_n\text{-}Cl \xrightarrow[Na_2S_x\,/\,KI\,/\,DTPB]{H_2O\,/\,Butanone} \left[R\text{-}S\text{-}(CH_2)_n\right]_2 Sx$$

compounds a to h

R = t.Bu	n = 2; x = 1	**a**	R = Methallyl	n = 2; x = 1	**e**
	n = 2; x = 2	**b**		n = 2; x = 2	**f**
	n = 3; x = 1	**c**		n = 3; x = 1	**g**
	n = 3; x = 2	**d**		n = 3; x = 2	**h**

SCHEME II

Thus we have modified the procedure by transforming "*in situ*" the chloride into the iodide by addition of potassium iodide. The reaction is run in butanone and among all the catalysts tested, dodecyltributylphosphonium bromide (DTPB) gives the best results (Scheme II).

EXPERIMENTAL

^{13}C NMR and ^{1}H NMR spectra were obtained on a Jeol PMX 60 spectrometer in $CDCl_3$ using tetramethylsylane (TMS) as internal standard and the GC/MS spectra on Hewlett Packard 5971.

General Procedure: To a solution of butanone (100 ml) and potassium iodide (16 mmol) is added dodecyltributyl phosphonium chloride (1.6 mmol). The chloride derivative (32 mmoles) is introduced dropwise at 75°C. Then Na_2S_x system (16 mmol) is added and the mixture is held at this temperature for 48 hours. After cooling and removing the solvent, chloroform is added. The organic layer is washed with water and dried over Na_2SO_4. Chloroform is evaporated under reduced pressure and the (poly)sulfide is purified by chromatography on silica gel with a mixture of petroleum/ether (98/2) as eluent.

Compound **a**: ^{1}H NMR (CCl_4): δ 1.3s (t.Bu), 2.6m (CH_2). ^{13}C NMR ($CDCl_3$): δ 31.7 ($C(\underline{C}H_3)_3$), 42.5 ($\underline{C}(CH_3)_3$), 32.7 (CH_2S_x), 28.7 (Ch_2S). IC-MS: m/z(%) 266 (M^+, 1), 209 (m^+-t.Bu, 15), 57 (t.Bu^+, 100).

Compound **b**: ^{1}H NMR (CCl_4): δ 1.3s (t.Bu), 2.8m (CH_2). ^{13}C NMR ($CDCl_3$): δ 31.1 ($C(\underline{C}H_3)_3$), 42.9 ($\underline{C}(CH_3)_3$), 39.1 (CH_2S_x). IC-MS: m/z(%) 298 (M^+, 1), 117 (t.$BuSCH_2CH_2^+$, 100). $C_{12}H_{26}S_4$ (298.448)

Calcd. C: 48.25 H: 8.78 S: 42.97
Found C: 48.01 H: 8.81 S: 43.24

Compound **c**: ^{1}H NMR (CCl_4): δ 1.3s (t.Bu), 2.6t (CH_2S), 1 = .9m (CH_2). ^{13}C NMR ($CDCl_3$): δ 31.0 ($C(\underline{C}H_3)_3$), 42.0 ($\underline{C}(CH_3)_3$), 32.7 (CH_2S_x), 29.7 (CH_2S_x). IC-MS: m/z(%) 294 (M^+, 1), 237 (M^+-t.Bu, 30), 57 (t.Bu^+, 100).

Compound **d**: ^{1}H NMR (CCl_4): δ 1.3s (t.Bu), 2.0m (CH_2), 2.6t (CH_2S); 2.9 (CH_2S_x). ^{13}C NMR ($CDCl_3$): δ 31.0 ($C(\underline{C}H_3)_3$), 42.0 ($\underline{C}(CH_3)_3$), 37.8 (CH_2S_x). IC-MS: m/z(%) 326 (M^+, 1), 163 (t.$BuSCH_2CH_2CH_2S^+$, 95).

Compound **e**: ^{1}H NMR (CCl_4): δ 1.8s (CH_3), 2.9m (CH_2S), 3.1 (CH_2S_x), 4.8 ($CH_2{=}$) ^{13}C NMR ($CDCl_3$) δ 140.8 ($CH_2{=}\underline{C}$), 112.9 ($\underline{C}H_2{=}C$), 29.1 (CH_2S_x). IC-MS: m/z(%) 262 (M^+, 1), 147 ($CH_2{=}C(CH_3)CH_2SCH_2CH_2^+$, 12), 87 ($CH_2{=}C(CH_3)CH_2S^+$, 100).

Compound **f**: ^{1}H NMR (CCl_4): δ 1.8s (CH_3), 2.9 to 3.4 (CH_2S_x), 4.8 ($CH_2{=}$). ^{13}C NMR ($CDCl_3$): δ 140.8 ($CH_2{=}\underline{C}$), 113.8 ($\underline{C}H_2{=}C$), 39.2 (CH_2S_x). IC-MS: m/z(%) 294 (M^+, 1), 147 ($CH_2{=}C(CH_3)CH_2SCH_2CH_2^+$, 5), 87 ($CH_2{=}C(CH_3)CH_2S^+$, 95).

Compound **g**: ^{1}H NMR (CCl_4): δ 1.8 s (CH_3), 4.8 s (CH_2S), 2.5t (SCH_2), 2.1m (CH_2), 2.6t (CH_2S_x). ^{13}C NMR ($CDCl_3$): δ 141.0 ($CH_2{=}\underline{C}$), 113.4 ($\underline{C}H_2{=}C$), 32.5 (CH_2S_x), 39.2 (CH_2S), 29.4 (SCH_2), 31.3 (CH_2), 20.4 (CH_3). IC-MS: m/z(%) 290 (M^+, 1), 55 ($CH_2{=}C(Me)^+$, 52), 129 ($CH_2{=}C(Me)CH_2S(CH_2)_3^+$, 100), 235 ($M^+{-}CH_2{=}C(Me)CH_2$, 35).$C_{14}H_{26}S_4$ (322.448)

Calcd. C: 52.10 H: 8.13 S: 39.77
Found C: 51.92 H: 8.10 S: 40.01

Compound **h**: ^1H NMR (CCl_4): δ 1.8s (CH_3), 4.8s (CH_2S), 2.6t (SCH_2), 2.1m (CH_2), 2.7m (CH_2S_x). IC-MS: m/z(%) 322 (M^+, 1), 55 ($CH_2{=}C(Me)^+$, 50), 161 ($CH_2{=}C(Me)CH_2S(CH_2)_3S^+$, 100).

REFERENCES

1. W. Davey and E. D. Edwards, *wear*, **1**, 291 (1957).
2. E. V. Dehmlov and S. S. Dehmlov, "Phase Transfer Catalysis," Verlag Chemie Gmbh, D-6940 Weinhelm, 1980.
3. J. M. Castex, J. F. Roussel, G. Parc, J. L. Mieloszynski, G. Kirsch and D. Paquer, *Sulfur Letters*, **2**, 77 (1984).
4. O. Aberkane, J. L. Mieloszynski, D. Robert, M. Born and D. Paquer, *Phosphor, Sulfur and Silicon* (in press).
5. M. Cerf, J. L. Mieloszynski and D. Paquer, *Fr. Patent*: 90/08 109 (1990)—Norsolor CA: P 129 845 I.