Direct Preparation of Anhydrous Sodium Oligosulfides from Metal Sodium and Elemental Sulfur in Aprotic Organic Media Directed toward Synthesis of Silane Coupling Agent

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Anhydrous sodium oligosulfide was prepared by the heterogeneous reaction of metal sodium and elemental sulfur in aprotic solvents. The oligosulfide consisted of a mixture of several Na_2S_n ($n = 2 - 8$). Organic oligosulfides (R_2S_n, $n \geq 2$) including moisture-sensitive one were synthesized by the reaction with organic halides in high yeilds under mild conditions.

Anhydrous sodium oligosulfide (Na_2S_n)[1] is a key compound for preparation of a variety of industrially important materials such as the silane coupling agent (bis(3-(triethoxysilyl)propyl) tetrasulfide)), an essential additive for energy-saving tire,[2] of which positive use is strongly desired, for the solution of the world wide resources and environmental problems. Much effort has been devoted so far to obtain anhydrous Na_2S_n by simple procedure under mild conditions. Among several synthetic methods of anhydrous Na_2S_n,[1] direct synthesis from metal sodium and elemental sulfur in molten state[1] or in liquid ammonia[3] is most straightfoward. However, the methods hitherto reported are suffered from difficulties in procedure, purification, successive reaction, cost, and so on. Anhydrous Na_2S_n can also be obtained by the reaction of anhydrous sodium sulfide (Na_2S) with elemental sulfur in dry alcohol.[4] Although it displays obvious advantages in application and operation, it is rather difficult to obtain Na_2S in anhydrous state.[1,5–7] Therefore, development of efficient, practical, and high-yielding processes for the preparation of anhydrous Na_2S and Na_2S_n has been a current subject to be solved. We have recently succeeded in developing a novel practical synthetic method of anhydrous sodium oligosulfide by the direct reaction of Na and S_8 in aprotic organic media, with which organic oligosulfides including the silane coupling agent are prepared, which is disclosed in this paper.

Our hypothesis was that the direct reaction of metal Na and solid S_8 is most promising and would proceed to be controlled when an appropriate solvent is chosen. First were examined solvents capable of partially dissolving elemental sulfur such as aromatic hydrocarbons (benzene, toluene, xylene, and so on), but all attempts were in vain.[8] Second were examined solvents probably capable of dissolving the produced Na_2S_n by chelation. They were tetrahydrofuran (THF), dimethoxyethane (DME), and related solvents all of which have high donor number. Interestingly, a heterogeneous mixture of Na and S_8 in dry DME immediately turned dark brown at room temperature, and by heating at 60–75 °C both Na and S_8 were smoothly exhausted and almost disappeared in a few hours to give a homogeneous solution. In dioxane, the reaction was sluggish and incomplete for a prolonged reaction time, whereas THF and diglym were similar to DME.

To determine the structure of the product benzyl chloride, 1.5 equiv) was added to the reaction mixture to convert inorganic oligosulfides to organic ones [eq (1)]. High nucleophilicity of thiolate anion made the conversion of Na_2S_n to RS_nR nearly complete.[9] The organic product obtained by extraction from the resulting mixture (83% yield, Table 1, run 3)[10] was a mixture of oligosulfides (R_2S_n) with $n = 2 - 8$ as identitied by GC, GC-MS, and HPLC analyses, in accordance with the results of the ^{1}H NMR. As shown in Figure 1, the products derived by the quenching with benzyl chloride and their ratio could be determined readily by the ^{1}H NMR spectrum. The averaged number of sulfur atoms incorporated (n) was calculated as 3.61. The n value was sometimes sensitive toward the reaction conditions so that the ratio varied in a certain degree (within ca. ±10%) (Table 1, runs 3 and 4). With typical electrophiles such as

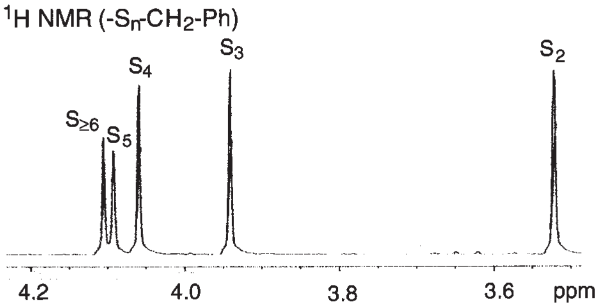

Figure 1. Partial ^{1}H NMR spectrum of the product (a mixture of benzyl oligosulfides $PhCH_2-S_n-CH_2Ph$) obtained in the reaction of run 5 of Table 1 (270 MHz, $CDCl_3$, 27 °C).

Table 1. Composition of dibenzyl oligosulfides obtained by the reaction of benzyl chloride with anhydrous Na_2S_n directly prepared from Na and S_8 in DME[a]

Run	Na : S[c]	Time /h	Yield /%)	Composition/%[b]					S content
				S_2	S_3	S_4	S_5	$S_{\geq 6}$	
1	2 : 2	3	65	64	24	8	4	0	—
2	2 : 3	3	79	39	28	18	5	10	3.19[d]
3	2 : 4	3	83	28	23	23	12	14	3.61[e]
4	2 : 4	3	81	25	29	23	8	15	3.63[e]
5	2 : 5	3	77	17	31	26	9	17	3.78[e]
6	2 : 2	17	82	>99	0	0	0	0	2.00
7	2 : 3	16	76	29	36	21	4	10	3.30[d]

[a]Reaction conditions (1st step: Na(small pieces): 25 mg-atom, S_8: 25–125 mg-atom, solvent: dry DME 10 mL, Ar atmosphere, 70 °C. 2nd step: benzyl chloride: 37.5 mmol, room temperature). [b]Determined by the ^{1}H NMR integration. [c]Feed ratio (g-atom/g-atom). [d]A small amount of sodium was recovered. [e]A small amout of elemental sulfur was recovered.

methyl iodide, similar results were obtained.

$$2\,\mathrm{Na} + n\,\mathrm{S} \xrightarrow[\text{DME, 70 °C, 3 h}]{\text{Ar}} \mathrm{Na_2S_n} \xrightarrow[\text{RT - reflux}]{\text{2 R-X}} \mathrm{R\text{-}S_n\text{-}R} \quad (1)$$

Feed ratio change of Na and S resulted in the shift of the oligomer distribution as expected (Table 1, runs 1–5). It is known that trisulfide and higher oligosulfides are in equilibrium with the related higher and lower oligosulfides in solution.[12] Therefore, the products obtained by this method also displayed a certain oligosulfide distribution. An initial distribution observed in the case of 2 : 2 ratio (Table 1, run 1) are changed to be astringent to disulfide by the prolonged reaction (run 6). This result is consistent with that the equilibrium of the oligosulfide interconversion takes some time to be settled. Meanwhile, similar experiment with 2 : 3 ratio of Na and S did not cause such astringency even by prolonged reaction (runs 2 and 7), being consistent with the typical behavior of oligosulfide in solution.[12] The results obtained suggest the possible selective synthesis of disulfides.

Several organic halides such as ester and allyl group-containing halides as well as simple primary and secondary alkyl halides were promptly converted to the respective oligosulfides with Na_2S_n (averaged n = 4.0) (Figure 2).

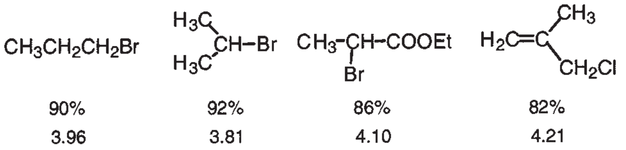

Figure 2. Substrate (top), yield (middle) and averaged S-content (bottom).

With anhydrous Na_2S_n by the present method, synthesis of the silane coupling agent was carried out. To a Na_2S_n (averaged n = 4.0) solution in dry DME freshly prepared using S_8 and sodium dispersion was added an equivalent of 3-(triethoxysilyl)-propyl chloride. The mixture was refluxed for 1 h. The pale yellow product[13] obtained quantitatively by filtration had 98% purity as determined by HPLC and ^{1}H NMR. Content of free sulfur in the product was also determined by HPLC to be less than 1%. There was no gelated product which would be derived by influence of water contaminated in the system, indicating the formation of completely dry Na_2S_n. Large scale synthesis (more than 1 kg) with sodium dispersion[14] was readily accomplished in similar yield, purity, and oligomer distribution.

$$\mathrm{(EtO)_3Si(CH_2)_3Cl} + \mathrm{Na_2S_n} \xrightarrow[\text{DME, reflux, 1 h}]{} \mathrm{(EtO)_3Si(CH_2)_3S_n(CH_2)_3Si(OEt)_3} \quad (2)$$

(averaged n = 4.0)

In summary, we have demonstrated the novel practical synthetic method of anhydrous sodium oligosulfides from metal and elemental sulfur, with which various organic oligosulfides were synthesized in high yields. The method can be characterized by the simple procedure, high yield, large scale synthesis, easy successive reaction, and so on. This development would be indebt to the unprecedent choice of ethereal (aprotic) solvent, which unambiguously promotes the reaction progress due to the clean and reactive solid surface kept by dissolving the product Na_2S_n formed on the surface.[15]

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8 Notice: The violent explosive reaction took place, when the mixture of Na and S_8 in most solvents was heated over or around the melting point of Na.

9 The initial mixture of oligosulfides moves to a mixture with an appropriate distribution during the equilibrium in solution. The result obtained by quenching with organic electrophiles to organic oligosulfides should reflect the distribution of Na_2S_n in solution, because the product ratio was not largely changed by the concentration change of the electrophile added, and further the nucleophilic substitution with thiolate anion is sufficiently fast compared to the "slow" equilibrium between the oligosulfides.

10 Both the reaction yielding Na_2S_n (step 1) and the reaction with electrophile (step 2) are very clean and the yield should be nearly quantitative, like the case of the silane coupling agent. The reduced yield in the case of benzyl chloride would be attributed to the occurrence of the oversulfurization reaction[11] and/or some secondary reaction of oligosulfides with benzyl halide forming sulfonium species. In fact, treatment of benzyl chloride with excess Na_2S_n (averaged n = 3.8) in DME afforded high yield of dithiobenzoate. No attempt is done to collect the sulfonium derivatives at present time.

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13 The structure of the silane coupling agent and its oligomer distribution were determined by the ^{1}H NMR in comparison with the authentic samples. All oligomers ($n = 2 - 8$) were separable by HPLC.

14 Very small amount of sodium or sulfur remained unreacted at the end of the reaction. Therefore, sodium dispersion prepared in toluene was used for the preparation of oligosulfides. Actually, the consumption of both solid materials was somewhat accelerated and the yield of the product was improved by a few percent.

15 The mechanism of the formation of Na_2S_n can be simply explained by the successive one-electron reduction of sulfur with sodium causing the S_8 ring cleavage in a random fashion leading to the formation of a variety of Na_2S_n. On the other hand, Na_2S_n thus formed can attack nucleophilically at sulfur atom of S_8 bringing about the ring cleavage and eventually yields higher sulfur-content Na_2S_n.