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Aromatic Hydrocarbon-Catalyzed Direct Reaction of Sulfur and Sodium in a Heterogeneous System: Selective and Facile Synthesis of Sodium Monosulfide and Disulfide

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Sodium disulfide and monosulfide were selectively formed via the direct reaction of sulfur and an equimolar amount of sodium in 1,2-dimethoxyethane at 70 °C in the presence of a catalytic amount of aromatic hydrocarbons and ketone.

Sodium oligosulfide, generally prepared by the reaction of elemental sulfur with sodium sulfide, is a key intermediate for the synthesis of a variety of organic oligosulfanes.[1] While sodium sulfide is available as hydrate, its dehydration requires immense heating to prepare anhydrous sodium sulfide.[2] The reduction of sodium sulfate with carbon also requires considerable heating.[3] Although the laboratory scale synthesis of anhydrous sodium sulfide in liquid ammonia has been reported, this method has not been practically applied because of the use of liquid ammonia.[4] Access to anhydrous sodium oligosulfides has been rather difficult, and the preparation of moisture sensitive organic oligosulfanes has shown practical problems.[5] Although the direct reaction of molten sulfur and sodium has been used industrially,[6] the solution state synthesis of oligosulfides is desirable for further use of sodium oligosulfide to prepare organic oligosulfanes. Recently, we developed a reaction of elemental sulfur and sodium metal in organic solvent that ensures easy access to anhydrous sodium oligosulfides.[7] However, it has not yet been possible to control the number of sulfur atoms in the oligosulfides. Thus, a great deal of effort was put into the selective preparation of sodium oligosulfides. In this paper, the selective synthesis of anhydrous sodium disulfide and monosulfide is reported. Further, a novel catalyst system for the reaction of elemental sulfur and sodium metal is also described.

The reaction of sodium dispersion and powdery sulfur was carried out in anhydrous 1,2-dimethoxyethane (DME) in accordance with our previous report.[7] For a prompt and simple evaluation of the yield and composition of sodium oligosulfides, and to confirm their applicability to the synthesis of organic oligosulfanes, the reaction mixture was quenched by slight excess of benzyl chloride to convert sodium oligosulfide into dibenzyl oligosulfane.[8] The organic product was analyzed by GC−MS and ^{1}H NMR spectra to determine the yield and composition of the oligosulfanes.

Scheme 1

$$2\mathrm{Na} + (n/8)\mathrm{S}_8 \xrightarrow[\text{DME, 70 °C}]{} \mathrm{Na}_2\mathrm{S}_n \xrightarrow[\text{rt, 1 h}]{\mathrm{PhCH_2Cl}} \mathrm{PhCH}_2\mathrm{S}_n\mathrm{CH}_2\mathrm{Ph}$$

Although a mixture of oligosulfanes in which the average sulfur content corresponded to the feed ratio of sulfur to sodium (n) was obtained, most of our attempts to obtain oligosulfide selectively were unsuccessful. However, when sulfur was reacted with 1.1 atom equiv of sodium, dibenzyl disulfane was obtained selectively. Namely, disulfane was

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(8) The conversion of inorganic oligosulfide to organic oligosulfane was investigated by various electrophiles including benzyl chloride, benzyl bromide, methyl iodide, and propyl bromide, and no difference was observed in the composition of oligosulfanes. Therefore, it was assumed that the composition of dibenzyl oligosulfanes obtained by the trapping experiments by benzyl chloride is well corresponded to the composition of sodium oligosulfides in the solution. Further, the yield of sodium oligosulfide can be evaluated by the yield of benzyl oligosulfane because of both the high nucleophilicity of sulfur anion and the high electrophilicity of benzyl chloride.

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Table 1. Preparation of Sodium Disulfide[a]

run	temp/°C	time/h	catalyst[b]	yield[c]/% $n = 1$	yield[c]/% $n = 2$	selectivity of disulfide/%
1	70	2	none	1	25	95
2	70	4	none	2	40	96
3	70	8	none	4	64	94
4	70	12	none	3	66	96
5	70	24	none	2	20	92
6	70	4	naphthalene	4	78	91
7	70	4	anthracene	6	73	92
8	70	4	phenanthrene	1	82	99
9	70	4	benzophenone	2	83	98
10	rt	4	none	3	5	63
11	rt	4	anthracene	6	65	92

[a] Elemental sulfur was reacted with 1.1 atom equiv of sodium dispersion in DME before treatment with 1.5 equiv of benzyl chloride at room temperature for 1 h. [b] 0.18 equiv toward sodium. [c] Yields of sodium oligosulfides were evaluated after benzylation followed by GC analyses using tetradecane as an internal standard.

Table 2. Preparation of Sodium Monosulfide[a]

catalyst[b]	yield[c]/% $n = 1$	yield[c]/% $n = 2$	selectivity of monosulfide/%
none	21	44	32
naphthalene	41	5	89
anthracene	13	4	76
phenanthrene	68	3	96
benzophenone	26	30	46
phenanthrene	87[d]	<1	>99

[a] Elemental sulfur was reacted with 2.2 atom equiv of sodium dispersion in DME before treatment with 1.5 equiv of benzyl chloride at room temperature for 1 h. [b] 0.18 equiv toward sodium. [c] Yields of sodium oligosulfides were evaluated after benzylation followed by GC analyses using tetradecane as an internal standard. [d] Reaction with benzyl chloride was carried out under reflux for 5 h.

obtained with a small amount of dibenzyl sulfane (selectivity ~96%) as shown in Table 1. Only traces of oligosulfanes with three or more sulfur atoms were detected. Since heterogeneous reaction conditions were used to suppress the explosive direct reaction of sodium and sulfur, the reaction proceeded rather slowly. The yield of disulfane gradually increased up to 66% in 12 h while selectivity remained high, but the prolonged reaction decreased both yield and selectivity (runs 1−5). The reaction with solvent may cause the decomposition of sodium disulfide.

Since a similar reaction in liquid ammonia gave sodium sulfide in quantitative yield,[4] effective electron transfer from sodium to sulfur is presumably necessary to enhance the reaction. Therefore, additives that can mediate the electron transfer from sodium were explored. It was found that aromatic hydrocarbons and ketone such as naphthalene, anthracene, phenanthrene, and benzophenone showed high catalytic activity to facilitate the formation of sodium disulfide without decreasing selectivity (runs 6−9). Thus, 83% yield of disulfane was obtained with 98% selectivity when a catalytic amount of benzophenone was added to the system. Although only a 5% yield of disulfane was obtained with 63% selectivity when the reaction was carried out at room temperature without a catalyst, a 65% yield of disulfane was obtained with 92% selectivity in the presence of anthracene as a catalyst (runs 10, 11). Encouraged by the effective catalytic activity of the aromatic compounds, we further investigated the synthesis of sodium monosulfide by the direct reaction method. When elemental sulfur was reacted with 2.2 atom equiv of sodium at 70 °C for 4 h, dibenzyl sulfane and disulfane were obtained in 21% and 44% yields, respectively, after treatment with benzyl chloride. The reduction of disulfide to monosulfide was thus very slow. However, when the reaction was carried out in the presence of phenanthrene (18 mol % toward sodium), 68% of dibenzyl sulfane was obtained with 96% selectivity. To further increase the selectivity, the reaction with benzyl chloride was carried out in refluxing DME for 5 h. Monosulfane was obtained in 87% yield, and only traces of disulfane were observed (selectivity >95%). Because of the low solubility of sodium sulfide in DME, the yield of sulfane increased under refluxing conditions.

The reduction potential of sulfur to sulfide and disulfide anions is reported to be −0.476 and −0.428 V, respectively.[9] Although the reduction potential of oligosulfides with three or more sulfur atoms is unknown, it is expected to be higher in accordance with the number of sulfur atoms, because of reduced electrostatic repulsion between two negative charges in oligosulfides. Therefore, not only the atom ratio of sodium to sulfur but the gaps of reduction potential between these oligosulfides were attributed to the selective reduction of sulfur to disulfide and monosulfide. Thus, selective reduction to either disulfide or sulfide was achieved in this system because the gaps of reduction potential between sulfide, disulfide, and oligosulfides are rather big. Meanwhile, aromatic compounds were reduced by sodium to form radical anions that then reduced sulfur. The aromatic compounds mediated the electron transfer between the solid substrates to reveal remarkable catalytic activity. The difference in catalytic activity among the aromatic compounds tested can presumably be accounted for by the electron-releasing ability of the radical anion formed as an intermediate and its interacting ability with the sulfur molecule or oligosulfide anions.

In summary, we have demonstrated the selective synthesis of sodium disulfide and monosulfide by the direct reaction of elemental sulfur and sodium metal in organic solvent under heterogeneous conditions. We evaluated the yields of sodium disulfide and monosulfide by reacting these products with benzyl chloride in order to convert them to the corresponding organic di- and monosulfanes. Aromatic hydrocarbons and ketone were quite effective catalysts to enhance both the yield and the selectivity of sodium oligosulfides. The advantage of the present method is the simple and direct preparation of anhydrous sodium oligosulfides as a solution in organic solvent under mild conditions. While organic disulfanes have been prepared via the oxidation of thiols, the alkylation of sodium disulfide has not been paid much attention.[10] However, the method described above was proven as simple and effective as the conventional oxidation method. This

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method's strong feature is that it does not require stinky thiol for the preparation of disulfane.

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