FACILE FORMATION OF CYCLIC POLYSULFIDES BY A NEW GENERATION METHOD FOR DIATOMIC SULFUR

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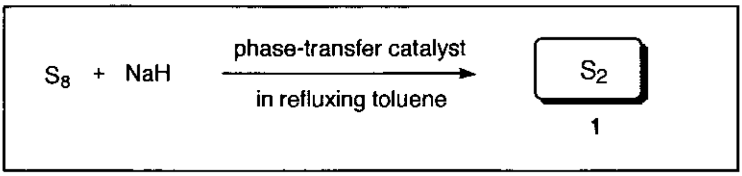
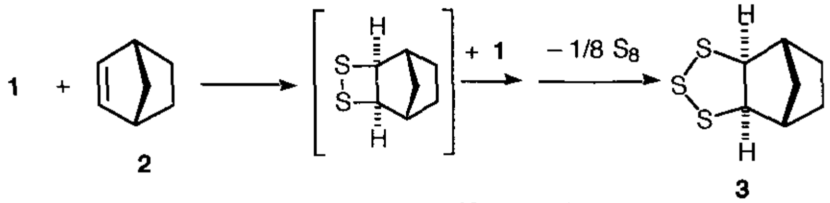
Abstract—A new generation of diatomic sulfur (**1**) has been achieved in a remarkably simple process by treatment of elemental sulfur with sodium hydride in the presence of phase-transfer catalysts. This facile generation of **1** has been trapped with olefins, diene, and triene to give cycloadducts as the form of cyclic sulfides in high yields.

Keen interest has been paid to the generation of singlet diatomic sulfur since the first discovery by Steliou *et al.*[1,2] Bartlett and Ghosh also found that thermolysis of elemental sulfur in DMF (100°C) generated active sulfur, which further reacted with norbornene (**2**) to give the corresponding trisulfide (**3**).[3] Sato *et al.* reported that the thermolysis of pentathiocin or tetrathiepin in DMSO (120°C) generated active sulfur which further reacted with dienes to give the corresponding cycloadducts.[4] In most cases, however, diatomic sulfur (**1**) has been generated from complicated precursors which are designed specifically. This paper offers a new and efficient generation method of diatomic sulfur (S_2, **1**) *in a remarkably simple procedure* using elemental sulfur (S_8), sodium hydride and a phase-transfer catalyst.



Scheme 1. A facile generation of diatomic sulfur (**1**)

We have attempted to generate diatomic sulfur (**1**) from the reaction of elemental sulfur (S_8) with sodium hydride under the presence of norbornene (**2**) as a trapping reagent. However, the corresponding adducts could not be obtained. Searching experimental conditions precisely, we have succeeded in a facile and efficient generation of **1** and trapped with norbornene (**2**), when the reaction has been performed in the presence of a phase-transfer catalyst (1 mol %), 15-crown-5 or tris[2-(2-methoxyethoxy)ethyl]amine[5] (TDA-1) (Scheme 1). Scheme 2 shows the trapping experiment of **1** with the olefin (**2**) to give trisulfide (**3**), which is the same product as that in the first generation of singlet diatomic sulfur from the reaction of silyl- and germanium-protected trisulfides by Steliou *et al.*[1,6]



Scheme 2. Trapping of diatomic sulfur (**1**) with norbornene (**2**).

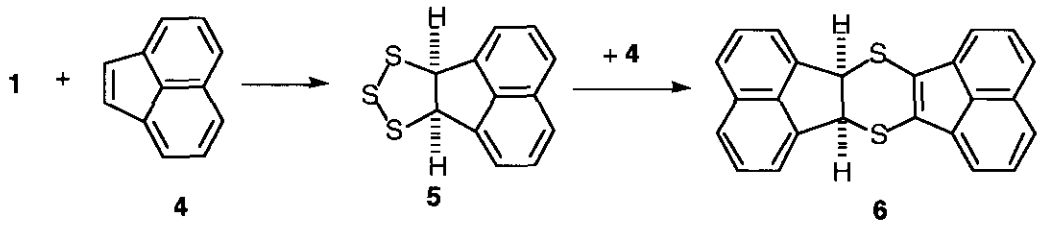
Table 1 summarizes the experimental results for trapping of **1** with **2**. The reaction has been performed in the presence of 15-crown-5 (1 mol %) as a partner of NaH, to give an adduct,[3] a trisulfide (trithiolane) (**3**) in moderate yield (Entry 2 in Table 1). Instead of the crown ether, TDA-1 has brought us an improved generation of **1** leading to the optimum yield (70 %) of the adduct (**3**) (Entry 3 in Table 1). Thus, the experimental results show that the reaction generated **1** predominantly among the other active sulfur species.

Table 1. Trapping Experiments of Diatomic Sulfur (**1**) with Norbornene (**2**).

	Reaction conditions						Product
Entry	Solvent	PT[a] catalyst	Sulfur (equiv.)	Base (equiv.)	Time (h)	Temp. (°C)	Yield[b] (%)
1	toluene	none	3	NaH (0.01)[c]	6	110	**3** (0)
2	toluene	15-Crown-5	3	NaH (0.01)	6	110	**3** (57)
3[d]	toluene	TDA-1	3	NaH (0.01)	6	110	**3** (70)
4	benzene	TDA-1	4	NaH (0.01)	24	80	**3** (66)
5	THF	TDA-1	4	NaH (0.01)	24	65	**3** (46)
6	toluene	none	3	Et_3N (0.2)	6	110	**3** (11)

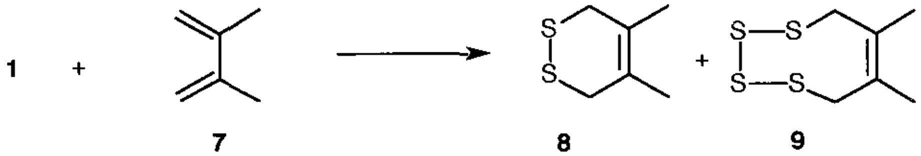
[a] Phase transfer catalyst. [b] Yields isolated are based on trapping reagent, **2**. [c] The 0.1-mol base was used. [d] The optimum conditions for the generation of **1**.

Under similar conditions (in refluxing toluene for 5 h), trapping of diatomic sulfur (**1**) with acenaphtylene (**4**) led to the formation of dinaphtho[1,8-*b*:1',8'-*e*]-2,3-dihydro-1,4-dithiine (**6**) in 65% yield.[7] At an early stage of the reaction in quenching experiment of **1**, a small amount of trisulfide, acenaphto[1,2-*d*]-1,2,3-trithiolane (**5**),[4] has been isolated as an intermediate which was further subjected to the reaction under the similar conditions to afford **6**. The intermediate (**5**) would be further oxidized to form a dithione which cycloadded to the another molecule of **4** giving the product (**6**).



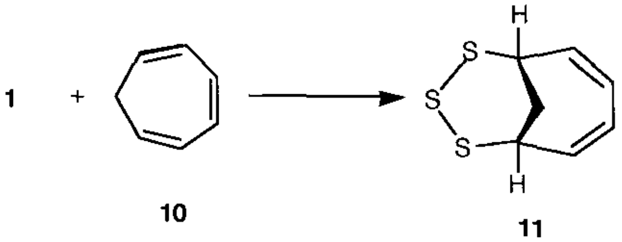
Scheme 3. Quenching diatomic sulfur (**1**) with acenaphtylene (**4**).

Scheme 4 shows that a further trapping of diatomic sulfur (**1**) with a diene, 2,3-dimethylbutadiene (**7**), has led to the predominant formation of a Diels–Alder cycloadduct, disulfide (**8**),[1] and tetrasulfide (**9**) suggesting the generated S_2 species. The disulfide (**8**) is a direct 1:1 cycloadduct between **1** and **7**, and has been isolated as a stable compound (Table 2-A). The formation of tetrasulfide (**9**) was confirmed in the reaction mixture by HPLC and ^{1}H NMR (7 %). However, upon isolation by distillation, tetrasulfide (**9**) was converted to disulfide (**8**).



Scheme 4. Trapping of diatomic sulfur (**1**) with 2,3-dimethylbutadiene (**7**)

As a triene, cycloheptatriene (**10**) was subjected to the reaction with **1** under the similar conditions to give the predominant product, bicyclo[4.1.3]heptadienetrisulfide[6] (**11**), showing again the generation of **1** to be successful (Table 2-B).



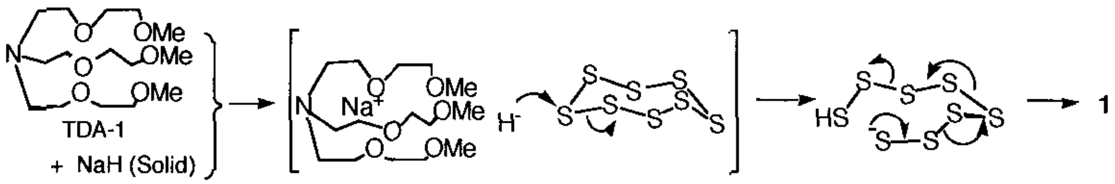
Scheme 5. Trapping of diatomic sulfur (**1**) with cycloheptatriene (**10**).

Table 2. Trapping Reaction of 1 with 2,3-Dimethyl-1,3-butadiene (**7**) and Cycloheptatriene (**10**).

Entry	Trapping reagent	Reaction conditions: Solvent	PT catalyst	Sulfur (equiv.)	Base (equiv.)	Time (h)	Temp. (°C)	Product: Yield[a] (%)
(A) Trapping with diene, 2,3-dimethyl-1,3-butadiene (**7**)[b]								
1	**7**	toluene	TDA-1	3	NaH (0.01)	3	110	**8** (45)
2	**7**	toluene	TDA-1	3	NaH (0.01)	2	110	**8** (36)
3	**7**	benzene	TDA-1	3	NaH (0.01)	3	80	**8** (32)
(B) Trapping with triene, cycloheptatriene (**10**)								
4	**10**	toluene	TDA-1	4	NaH (0.01)	6	110	**11** (36)
5	**10**	toluene	TDA-1	4	NaH (0.01)	15	110	**11** (23)[c]

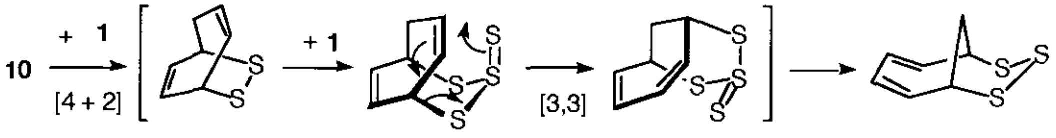
a) Yields isolated are based on trapping reagents, **7** and **10**. b) The product is accompanied with a small amount of unidentified complex mixture. c) Prolonged heating under these conditions resulted in the formation of ditropyl as a byproduct.

How do we account for the formation of diatomic sulfur under these conditions? Phase-transfer catalyst makes sodium hydride soluble in refluxing THF, benzene, or toluene. The hydride anion in non polar solvent attacked S_8 to give initially formed HS_8^-, which further separated more stable diatomic sulfur (**1**) as shown in Scheme 6.



Scheme 6. Formation of **1** using TDA-1 and NaH.

Viewing the product structures (1,4- and 1,6-adducts) in Schemes 4 and 5, the reaction of **1** with triene (**10**) seems to be different entirely from that with the diene (**7**). However, the formation of 1,6-adduct (**11**) from the reaction is interpretable when we take into account a [3,3] sigmatropic (thio-Cope) rearrangement as is illustrated in Scheme 7.[6,8]



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Scheme 7.

In summary, we have succeeded in a new and predominant generation of diatomic sulfur (**1**) in a simple procedure using a phase-transfer catalyst and sodium hydride in refluxing toluene, benzene or THF. Trapping of **1** with strained olefins forms trisulfide, while that with a diene gives disulfide of a [4 + 2] cycloadduct. We have demonstrated a facile formation of cyclic polysulfides by a simple method.

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6. K. Steliou, Y. Gareau, G. Milot, and P. Salama, *J. Am. Chem. Soc.*, 1990, **112**, 7819.
7. Acenaphtylene dithiine (**6**): Reddish orange needles, mp 216–217 °C, ^{1}H NMR ($CDCl_3$) δ 5.59 (s, 2 H, C*H*), 7.5–7.8 (complex m, 12 H, Ar). Dinaphtho[1,8-*b*:1',8'-*d*]thiophene was obtained as a side product after prolonged reaction time at this temperature. Thermolysis of **6** in refluxing DMF gave dinaphto[1,8-*b*:1',8'-*d*]thiophene in quantitative yield.
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