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REACTION OF 1,3-BENZODITHIOL-2-YLIDENES WITH ELEMENTAL SULFUR AND SELENIUM: A CONVENIENT PREPARATION OF 2-THIOXO- AND 2-SELENOXO-1,3-BENZODITHIOLES

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Summary: A variety of 1,3-benzodithiol-2-ylidene carbenes react with elemental sulfur and selenium to give 2-thioxo- and 2-selenoxo-1,3-benzodithioles in good yields.

Although reactions of carbenes with molecular oxygen ($^3O_2$) both in a solution and a gas phase have attracted much attention, those with elemental sulfur[1] and selenium[2] have been scarcely studied, and moreover, to our knowledge, those with tellurium have never been reported. Sulfur, selenium, and tellurium all react with strong carbon-nucleophiles such as Grignard and organolithium reagents, and therefore nucleophilic carbenes would be expected to be capable of reacting with these elements. In this belief, 1,3-benzodithiol-2-ylidene (1a) is a carbene chosen by us for the present study because 1,3-dithiol-2-ylidenes having a cyclic 6 π-electron system like cycloheptatrienylidenes are known to be nucleophilic.[3,4]

Three methods for generating 1a in a solution are available: Method A; thermal dissociation of 2-isopentyloxy-1,3-benzodithiole (2a)[5] into 1a and isoamyl alcohol,[6] Method B; deprotonation of 1,3-benzodithiolium tetrafluoroborate (3) by treatment with base,[7] and Method C; cycloaddition of benzyne with carbon disulfide.[4] Thus the reaction of 1a with elemental sulfur was first investigated by using each method.

A mixture of 2a (5 mmol) and elemental sulfur (0.17 g, 5.3 mg-atoms of S) in *o*-dichlorobenzene (15 ml) was refluxed for 4 h. Workup of the mixture by column chromatography gave 2-thioxo-1,3-benzodithiole (4a, 86%) and dibenzotetrathiafulvalene (6, 3%).

A mixture of 3 and elemental sulfur in pyridine (base) was refluxed for 1 h. Workup of the mixture gave 4a (70%) and 6 (22%).

A mixture of benzenediazonium-2-carboxylate (precursor of benzyne prepared from 10 mmol of anthranilic acid),[8] carbon disulfide (10 ml), and an excess of elemental sulfur in dichloromethane (100 ml) was refluxed for 1 h. Workup of the mixture gave 4a (9%) and 6 (4%).

In every case, the common and main product is consistently compound **4a**. This undoubtedly indicates that **4a** arises from the reaction of **1a** with elemental sulfur. The formation of **6** also provides an additional evidence for the intermediacy of **1a** in these systems.

Since **1a** satisfactorily reacted with elemental sulfur, its reaction with elemental selenium was examined next. Thus **1a** generated from **2a** in refluxing *o*-dichlorobenzene reacted with elemental selenium to give 2-selenoxo-1,3-benzodithiole (**5a**, 87%) and **6** (5%). Similarly, **1a** generated from **3** in boiling pyridine reacted with selenium yielding **5a** (29%) and **6** (32%).

The above results show that **1a** generated from **2a** most effectively reacts with elemental sulfur and selenium. Accordingly, a variety of derivatives of **1a** having a substituent on the benzene ring were generated from the corresponding derivatives of **2a** and allowed to react with elemental sulfur and selenium. Results summarized in Table show that the reaction is quite general

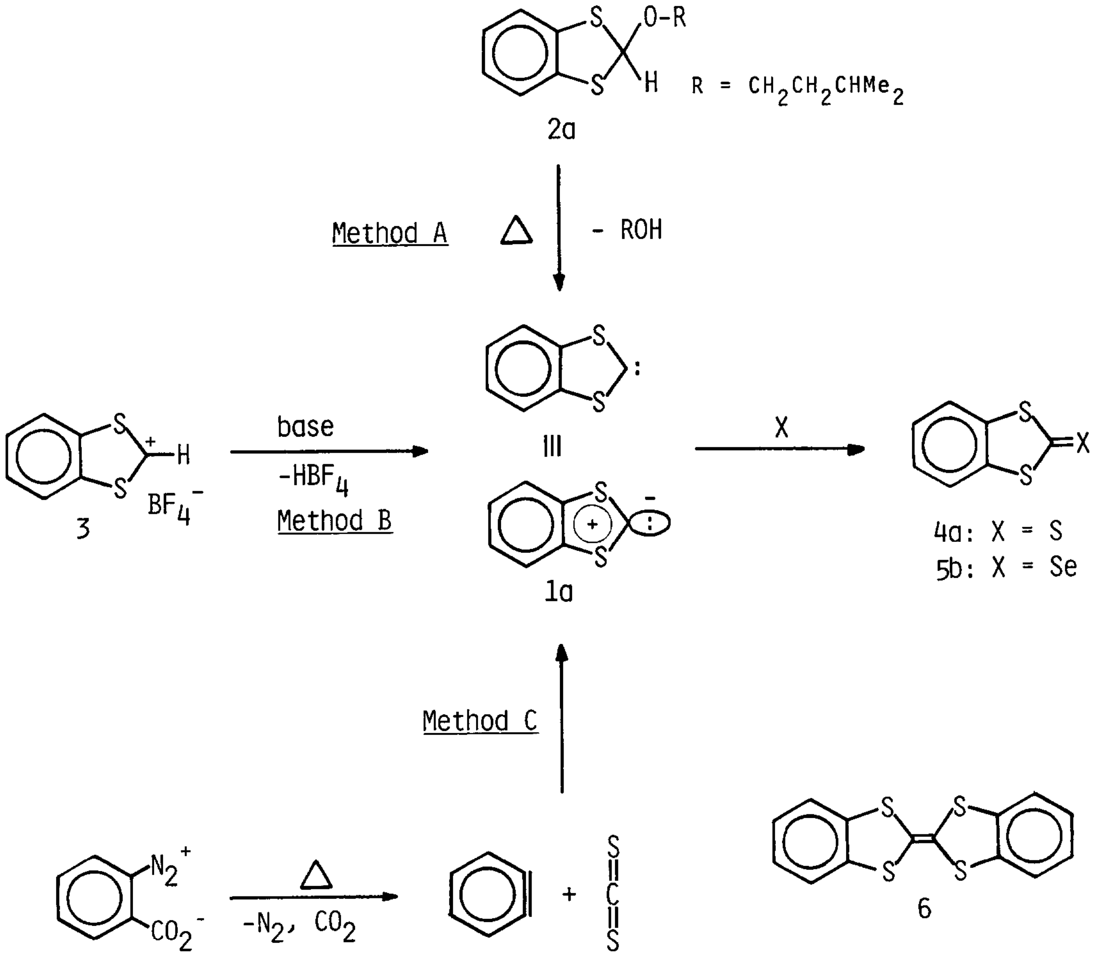
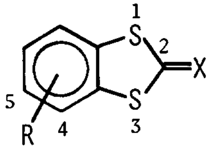


Table Preparation of 2-Thioxo- and 2-Selenoxo-1,3-benzodithioles (**4** and **5**)[a]



4: X = S
5: X = Se

Method for Generation of Carbenes	X	R	Conditions	Yield (%) of **4** or **5**	mp (°C)
A	S	H	reflux, 4 h *o*-dichlorobenzene	86	165-166[b]
B	S	H	reflux, 1 h pyridine	70	
C	S	H	reflux, 1 h dichloromethane	9	
A	S	4-Me	reflux, 4 h *o*-dichlorobenzene	95	83-84
A	S	5-Me	reflux, 4 h *o*-dichlorobenzene	89	84.5[b]
A	S	5-Cl	reflux, 5 h *o*-dichlorobenzene	70	120.5-121[b]
A	S	5-NO_2	reflux, 6 h *o*-dichlorobenzene	55	184-186[b]
A	Se	H	reflux, 4 h *o*-dichlorobenzene	87	214-216[b]
B	Se	H	reflux, 1 h pyridine	29	
A	Se	4-Me	reflux, 4 h *o*-dichlorobenzene	64	106-108
A	Se	5-Me	reflux, 4 h *o*-dichlorobenzene	73	102-103
A	Se	5-Cl	reflux, 10 h *o*-dichlorobenzene	43	148-149.5

[a] In all of the cases, dibenzotetrathiafulvalenes were produced as by-products. [b] These are known compounds.

and more nucleophilic carbenes having an electron-donating substituent on the benzene ring generally give better yields of 2-thioxo- and 2-selenoxo-1,3-benzodithioles (**4** and **5**).

Despite the satisfactory results of reaction of **1a** with sulfur and selenium, all attempts to obtain 2-telluroxo-1,3-benzodithiole by reaction of **1a** with elemental tellurium were fruitless.

2-Thioxo-1,3-benzodithioles (**4**) are synthetically important compounds, considering their role as precursors of 1,2-benzenedithiols, a plethora of 1,3-benzodithiolium and 1,3-benzodithiole derivatives, and dibenzotetrathiafulvalenes,[9] but their synthesis is tedious.[10] No general synthetic method for 2-selenoxo-1,3-benzodithioles (**5**) is available. The advantage of the present reaction from a synthetic point of view is that it can be done in a large scale and that in a simple procedure using easily accessible **2a**.[5] The following is typical.

A mixture of **2a** (72 g, 0.3 mol) and sulfur (9.9 g) in *o*-dichlorobenzene (900 ml) was refluxed for 4 h. The mixture was concentrated to ca. 300 ml, and the resulting crystalline precipitate was collected and washed with carbon tetrachloride (50 ml) to give 44.2 g (80%) of practically pure **4a**.

In summary, we found that a variety of 1,3-benzodithiol-2-ylidenes react with elemental sulfur and selenium to give 2-thioxo- and 2-selenoxo-1,3-benzodithioles (**4** and **5**) in good yields, thus providing the most straightforward synthetic method for these synthetically useful compounds.

References and Notes

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