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REACTION OF SULFUR YLIDES WITH ELEMENTAL SULFUR AND SELENIUM. ASPECTS AND MECHANISTIC CONSIDERATIONS

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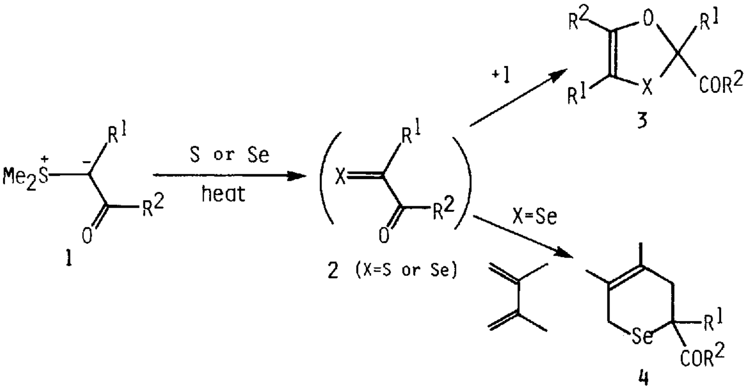
ABSTRACT

The reaction of sulfur ylides with elemental sulfur or selenium initially affords thio- or seleno-carbonyl compounds, which then react with starting ylides to give episulfides or episelenides from which the heteroatom (sulfur or selenium) is extruded to give olefins as the final product. In the case of carbonyl-stabilized ylides, the resulting thio- or seleno-carbonyl compounds react with starting ylides to afford 1,3-oxathioles or 1,3-oxaselenoles as previously reported. Supporting evidence for the intermediacy of thio(seleno)-carbonyl compounds and episulfides (episelenides) is presented.

We have recently reported that carbonyl-stabilized sulfur ylides (**1**) react with elemental sulfur and selenium to afford 1,3-oxathiole and 1,3-oxaselenole derivatives (**3**), respectively, in good yields.[1] The mechanism proposed by us involves the initial formation of α-oxo thio- or seleno-carbonyl compounds (**2**) as intermediates, which then react with starting ylides to give the final products **3**. Indeed, when the reaction of ylides **1** with selenium was carried out in the presence of a 1,3-diene, the resulting seleno-carbonyl compounds **2** (X = Se) could be effectively trapped by Diels–Alder reaction to give selenium-containing heterocyclic compounds (**4**).[2] We have now applied the reaction to other ylides to know more about its scope and mechanism.



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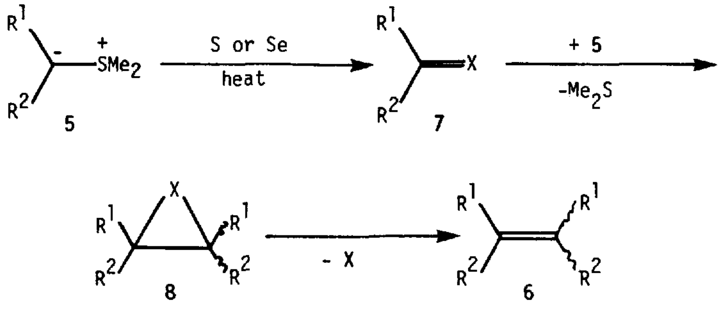
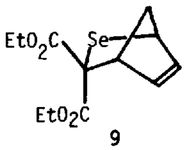
Heating dimethylsulfonium dicyanomethylide (**5a**) with sulfur (1·5 equiv.) in refluxing *o*-dichlorobenzene for 1·5 h unexpectedly afforded tetracyanoethylene (**6a**) with elimination of dimethyl sulfide (run 1 in Table 1). Since any products containing sulfur were not formed, the net result of the above transformation is a sulfur-catalyzed olefin-forming reaction from the ylide. Actually the use of a catalytic amount of sulfur (0·1 equiv.) effected this conversion quantitatively (run 2). The thermolysis of **5a** carried out under the same conditions, but in the absence of sulfur, gave only 12% of **6a** along with other products with recovery of 57% of the ylide (run 3).[3] In these cases the yield of **6a** was estimated by determining the intensity of the charge transfer band between **6a** and *o*-dichlorobenzene which occurs at 380 nm, since the volatile and sublimative nature of **6a** made its isolation difficult. However, when the reaction was carried out without solvent in a sublimation apparatus under reduced pressure, **6a** was easily isolated by sublimation nearly quantitatively regardless of the amount of sulfur used (runs 4 and 5).

Elemental selenium also effects this conversion (runs 6–9). In this case the use of a catalytic amount of selenium without solvent gives the decreased yield (64%) of **6a** probably because selenium cannot work effectively whilst the system is heterogeneous (run 9).



a: $R^1=R^2=CN$, b: $R^1=R^2=CO_2Et$, c: $R^1=CO_2Et$, $R^2=H$



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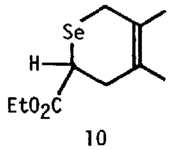

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Heating the ylide **5b** with sulfur (1·5 equiv.) in refluxing *o*-chlorotoluene for 4 h afforded the olefin **6b** quantitatively. Selenium (1·5 equiv.) brought about the same conversion quantitatively in refluxing *o*-chlorotoluene for 2 h. The ylide **5c**, when heated with selenium (1·5 equiv.) in refluxing chloroform for 3 h, gave the olefin **6c** in 92% yield (*E*:*Z* = 2·3:1).*

The mechanism we propose for this olefin-forming reaction again involves the initial formation of thio- or seleno-carbonyl compounds **7**. Compounds **7** then react with starting ylides **5** to give episulfides or episelenides **8**. The formation of **8** is analogous to that of epoxides by reaction of carbonyl compounds with sulfur ylides.[4] These three-membered heterocycles thus formed would be unstable under the conditions and eliminate sulfur or

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*The reaction of **5c** with sulfur affords a complex mixture containing 2,3-bis(ethoxycarbonyl)thiirane.

Table 1. Sulfur(selenium)-catalyzed decomposition of dimethylsulfonium dicyanomethylide yielding tetracyanoethylene (TCNE)

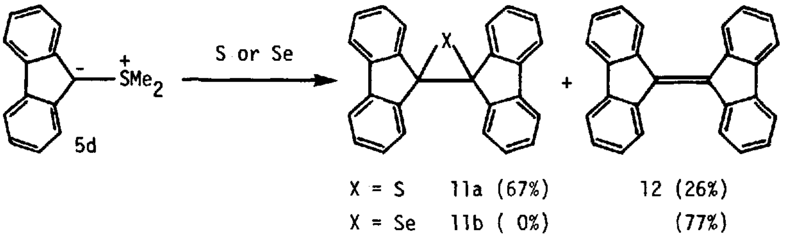
run	additive (equiv.)	solvent	temperature	time (h)	yield of TCNE (%)
1	sulfur (1·5)	*o*-dichlorobenzene	reflux	1·5	~ 100
2	sulfur (0·1)	*o*-dichlorobenzene	reflux	1·5	~ 100
3	none	*o*-dichlorobenzene	reflux	1·5	12[a]
4	sulfur (1·5)	none	130 °C	0·5	99
5	sulfur (0·1)	none	120 °C	0·7	~ 100
6	selenium (1·5)	*o*-dichlorobenzene	reflux	0·5	99
7	selenium (0·1)	*o*-dichlorobenzene	reflux	1·0	99
8	selenium (1·5)	none	110 °C	0·5	92
9	selenium (0·1)	none	110 °C	3·0	64[b]

[a] The ylide (57%) was recovered along with a few unidentified products.

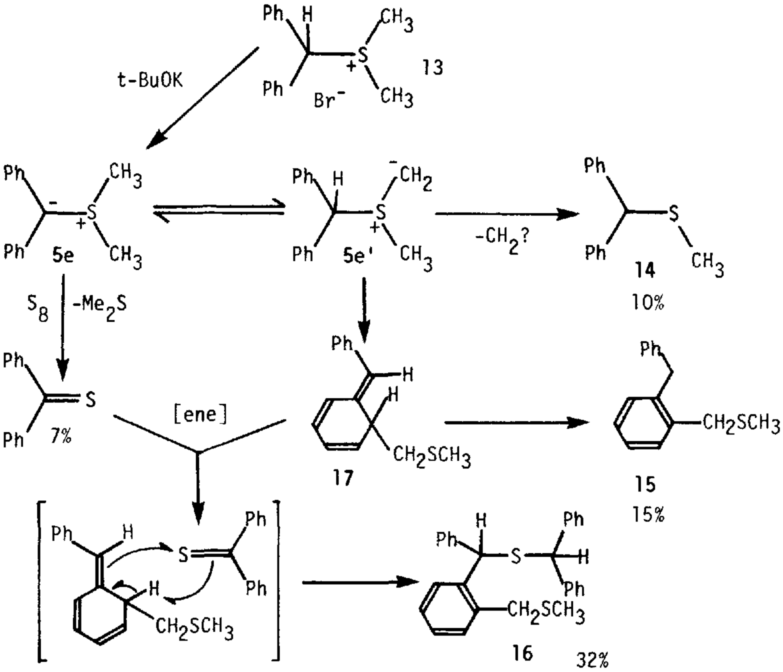
[b] A small amount of the ylide was recovered along with unidentified products.

selenium to give the olefins. The proposed intermediates, seleno-carbonyl compounds **7** (X = Se), could be satisfactorily trapped by Diels–Alder reaction, when the reaction was carried out in the presence of a 1,3-diene. Thus, heating the ylide **5b** with selenium in the presence of dicyclopentadiene in refluxing *o*-dichlorobenzene gave the Diels–Alder adduct **9** (adduct of the corresponding seleno-carbonyl compound with cyclopentadiene formed *in situ* by thermal dissociation of dicyclopentadiene) in 78% yield. The reaction of the ylide **5c** with selenium in the presence of 2,3-dimethyl-1,3-butadiene in refluxing chloroform gave the adduct **10** in 26% yield.

Supporting evidence for the intermediacy of episulfides (episelenides) comes from the following observations. The reaction of the ylide **5d** with sulfur (1·5 equiv.) in methylene chloride at room temperature for 1·5 h affords the episulfide **11a** (67%) along with bifluorenylidene **12** (26%).[5] Meanwhile, the reaction of **5d** with selenium under similar conditions yields **12** (77%) exclusively, thus providing a convenient synthesis of **12**. The isolation of **11a** provides direct evidence for the intermediacy of episulfides. Episelenides are more labile than the corresponding episulfides. (The first synthesis of an isolable episelenide has recently appeared.[6]) This is probably responsible for the failure of the isolation of the episelenide **11b**



The reaction of the ylide **5e**, which was generated *in situ* by treatment of the sulfonium salt **13** with potassium *t*-butoxide, with sulfur (1·5 equiv.) in toluene at room temperature affords thiobenzophenone (7%) and three sulfides **14** (10%), **15** (15%), and **16** (32%). The formation of thiobenzophenone provides supporting evidence for the intermediacy of thio-carbonyl compounds in the foregoing olefin-forming reaction. The sulfide **15** is the product of Sommelet–Hauser rearrangement of the ylide **5e′** which was formed from **5e** by hydrogen transfer,[7] while **14** might be formed from **5e′** by loss of methylene. Of particular interest is the formation of **16** which corresponds to the ene reaction product of thiobenzophenone with the exo-methylene compound **17** which is the intermediate of the Sommelet–Hauser rearrangement of **5e′** to **15**. In fact, the reaction of the ylide **5e** with thiobenzophenone in toluene at room temperature gave the sulfide **16** (19%) along with **14** and **15**. To our knowledge this is the first example that the non-aromatized intermediate of Sommelet–Hauser rearrangement could be chemically trapped. (The exo-methylene compounds are stable enough to isolate when the allylic hydrogen is replaced by an alkyl group.[8])



It is thus concluded that the reaction of sulfur ylides with sulfur or selenium initially affords thio- or seleno-carbonyl compounds, which then react with starting ylides usually to give episulfides or episelenides from which the heteroatom (sulfur or selenium) is extruded to give olefins,[9] while, in the case of carbonyl-stabilized ylides, the resulting thio- or seleno-carbonyl compounds react with starting ylides to give 1,3-oxathioles or 1,3-oxaselenoles.

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