

Thermal reactions of organyl chalcogenides with α,β -unsaturated aldehydes

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Thermal gas-phase reactions of acrolein, cinnamaldehyde, and benzaldehyde with diorganyl chalcogenides and diorganyl dichalcogenides were studied. Acrolein does not react with chalcogenides at 300–600 °C but completely decomposes under reaction conditions. At 600–650 °C, cinnamaldehyde reacts only with diorganyl selenides and diselenides to give benzoselenophene. Its highest yield (53%) is achieved in the reaction with dimethyl diselenide at 630 °C and at an equimolar ratio of the reactants. The gas-phase reactions of benzaldehyde at 400–500 °C afford chalcogen-containing derivatives of several types, among which thioanisole and its selenium or tellurium analogs predominate. The mechanisms of the above reactions were discussed in terms of homolytic substitution of the formyl group at unsaturated carbon atoms by chalcogenyl radicals.

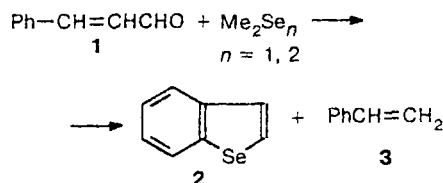
Key words: gas-phase reactions, cinnamaldehyde, benzaldehyde, chalcogenyl radicals, benzo[*b*]selenophene, selenoanisole, telluroanisole.

Chalcogenyl radicals are generated upon thermolysis of organyl chalcogenides. Whereas organic derivatives of sulfur decompose at 300–600 °C, diorganyl deselenides dissociate at the Se–Se bond even on heating to 100–200 °C in the liquid phase. Organyl tellurides are extremely unstable and usually eliminate the tellurium atom on heating.^{1,2} Systematic studies dealing with thermal reactions of organyl chalcogenides with several substrates allowed us to find efficient "traps" for various types of chalcogenyl radicals and to formulate some rules characterizing their reactivity: vinylthiyl and arylthiyl radicals react efficiently with haloarenes, haloolefins, and acetylene; their selenium and tellurium analogs react only with acetylene and its derivatives, whereas in the case of alkylthiyl and alkylselenyl radicals, no appropriate chemical traps other than dimethylenecyclobutanes have been found for thermal reactions.³

To continue the studies on the thermal reactions of organyl chalcogenides, we investigated for the first time their gas-phase reactions with α,β -unsaturated aldehydes, viz., acrolein, cinnamaldehyde (**1**), and benzaldehyde. The α -C atom in these compounds carries an increased electron density and, hence, it can be attacked by electrophilic chalcogenyl radicals. This might result in the replacement of the formyl group by the chalcogenide group, by analogy with reactions of haloarenes and haloolefins.^{1,2}

We found that thermal reactions of acrolein with Me_2S_2 , All_2S_2 , and Me_2Se_2 in the 300–600 °C temperature range do not afford the expected products;⁴ instead, they involve extensive thermolysis of the starting compounds accompanied by gas evolution and resinification.

The thermal reactions of compound **1** with dimethyl selenide and dimethyl diselenide at 600–650 °C give benzoselenophene (**2**), whose yield reaches 53%, and styrene (**3**).



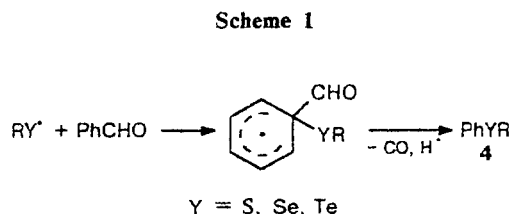
Toluene, benzene, and naphthalene are formed as by-products (Table 1).

The yield of benzoselenophene **2** and the selectivity of this reaction (the ratio of products **2** and **3**) depend markedly on the reaction temperature, the ratio of the reactants, and the duration of their contact.

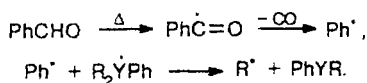
The highest yield of compound **2** is attained in the reaction between equimolar quantities of aldehyde **1** and Me_2Se_2 at 630 °C. When an excess of compound **1** is used, the yield of styrene (**3**) increases, whereas an excess of the diselenide results in lower yields of both major products.

Styrene (**3**) does not react with Me_2Se_2 under these conditions; when there is a deficiency of Me_2Se_2 , aldehyde **1** is mostly (53%) converted into hydrocarbon **3**. Therefore, compound **2** results most likely from the replacement of the formyl group by electrophilic selenyl radicals due to the primary attack of these radicals on the C(2) atom of the double bond (located in the β -position with respect to the phenyl ring), which car-

replacement of the formyl group by alkylchalcogenyl radicals, according to Scheme 1.

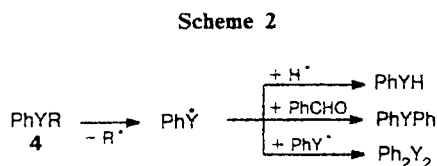


The alternative mechanism consisting of homolytic substitution at the chalcogen atom in the initial mono- and dichalcogenides also cannot be ruled out.



However, this mechanism is less probable, because it is thermodynamically more favorable for the phenyl radical to be converted into benzene than into unstable intermediates and relatively unstable chalcogenides 4.

Other products formed in the reaction of PhCHO result from secondary thermal transformations of chalcogenides 4 into chalcogenophenols, diphenyl chalcogenide, and diphenyl dichalcogenide involving phenylchalcogenyl radicals generated upon cleavage of the PhY—Alk bond (Scheme 2):



The methylselenyl radicals generated from dimethyl diselenide react most readily according to Scheme 1.

Sulfides and selenides 4 are most stable at 450 °C, and tellurides 4 are most stable at 350 °C. In turn, the PhY· radicals resulting from the cleavage of the PhY—R bond in chalcogenides 4 are also capable of replacing the formyl group in PhCHO to give diphenyl chalcogenides in accordance with Scheme 2. This is indicated by the reaction of PhCHO with Ph₂Se₂ serving as the source of phenylselenyl radicals, which gives diphenyl selenide at 450–500 °C (Table 3). The yield of the latter can be as high as 85%. This product can be formed only by Scheme 2, since pyrolysis of Ph₂Se₂ under these conditions affords diphenyl selenide (see Table 1). Similarly, the reaction with thiophenol used as the source of phenylthiyl radicals affords diphenyl sulfide and diphenyl disulfide, although this occurs at substantially higher temperatures (630–690 °C) (Table 3). Phenylselenyl radicals react most efficiently, whereas phenylthiyl radicals exhibit the lowest reactivity. Benzene, toluene, and diphenyl are products of the thermal destruction of PhCHO according to the Schemes given above. The use of dimethyl sulfide in the reaction with PhCHO is accompanied by the predominant formation of benzene and toluene, while in the case of dimethyl telluride, diphenyl is formed. In the absence of organyl chalcogenides, PhCHO starts to decompose at 400 °C to give benzene.

Thus, alkyl- and phenylchalcogenyl radicals, generated by thermolysis of the corresponding organyl chalcogenides are able to replace the formyl group at the sp²-hybridized carbon atom during gas-phase reactions and, in terms of reactivity, they can be arranged in the following series:



Previously, alkylchalcogenyl radicals have been involved only in gas-phase reaction with dimethylenecyclobutanes,³ while alkylselenyl radicals have been involved, in addition, in liquid-phase thermal reactions with allyl and benzyl halides.⁶ Unlike phenylthiyl radicals, phenylselenyl and phenyltelluryl radicals do not

Table 3. Thermal reaction of benzaldehyde with thiophenol and Ph₂Se₂^a

Chalco- genide	T/°C	Conversion (%)		Reaction products and their yields (%) ^b				
		PhCHO	Chalco- genide	PhSeH	PhPh	PhSePh	PhSPh	Ph ₂ S ₂
Ph ₂ Se ₂	450	—	67.1	—	5.2	84.5		
Ph ₂ Se ₂	500	—	88.6	19.4	3.3	64.8		
Ph ₂ Se ₂	520	—	87.1	5.9	9.5	55.2		
Ph ₂ Se ₂	550	—	94.5	—	6.5	26.2		
PhSH	480	66.4	13.5				—	65.2
PhSH	530	90.6	11.0				21.6	31.8
PhSH	630	100.0	61.6		3.1		20.4	2.2
PhSH	690	95.1	66.4		14.5		19.8	10.2
PhSH	740	79.8	79.8		30.0		2.0	17.4

^a The ratio Ph₂Se₂ : PhCHO = 1 : 4 and PhSH : PhCHO = 1 : 1.

^b Based on converted chalcogenide.

react with haloarenes or haloolefins in the gas phase. From the preparative viewpoint, the reaction of **1** with Me_2Se_2 can be used for the synthesis of benzo-selenophene, while the reaction of PhCHO with R_2Y_n can be used for the synthesis of seleno- and telluro-anisoles, as well as diphenyl selenide.

Experimental

Liquid reaction products were analyzed by GLC using a LKhM-8MD-2 chromatograph, a 2 m-long column with a diameter of 3 mm, DS 550 liquid phase, 5% on Chromaton N-AW-HMDS, helium as the carrier gas, and linear temperature programming in the column. GC/MS analysis was carried out using an LKB-2091 GC/MS spectrometer (a capillary column, SE-30 phase, linear programming of the temperature in the column from 135 to 240 °C at a rate of 8°/min). The ionization energy was 70 eV. ^1H NMR spectra were recorded on a Tesla BS 567 A instrument (100 MHz) in deuteriochloroform (HMDS).

Thermal reactions of cinnamaldehyde (1) and benzaldehyde (general procedure). The reactions were carried out in the gas phase in tubular hollow quartz reactors (30 × 650 mm) heated in tubular electric furnaces. Mixtures of aldehydes with chalcogenides (Table 1 and 3) were delivered to the reactor in a nitrogen stream (4–5 L h⁻¹). Liquid reaction products were condensed in cooled traps, and the condensates were analyzed by GLC and GC/MS. The target products were isolated by distillation of the reaction mixtures. The yields of the products are listed in Tables 1–3.

Benzo[b]selenophene (**2**) was isolated by distillation of the reaction mixtures resulting from the interaction of **1** with

Me_2Se_2 . The fraction boiling at 90 °C (5 Torr) contained 93% **2** and 7% naphthalene. The product was purified from naphthalene by column chromatography on silica gel using petroleum ether as the eluent, m.p. 48–50 °C; parameters of the ^1H NMR spectrum corresponded to the published data.^{7,8}

Benzo[b]tellurophene was identified only by GC/MS analysis: M^+ for ^{130}Te , 182 m/z .

The products of the reaction of PhCHO with chalcogenides R_2Y_n were identified by GLC using comparison with authentic samples and also by GC/MS.

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