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GENERATION AND DIENOPHILIC REACTIVITY OF α-OXOSELENOALDEHYDES AND KETONES

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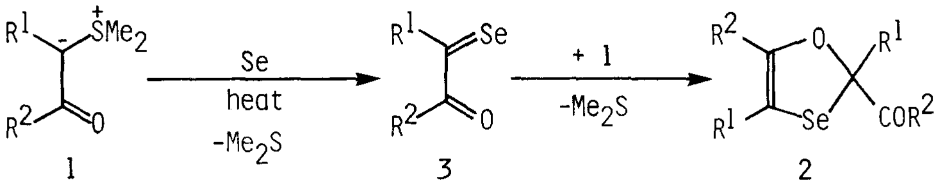
Summary: The reaction of elemental selenium with sulfur ylides stabilized by electron-withdrawing substituent(s) affords a facile method for generation of functionalized selenocarbonyl compounds, which can be effectively trapped by Diels-Alder reaction with 1,3-dienes.

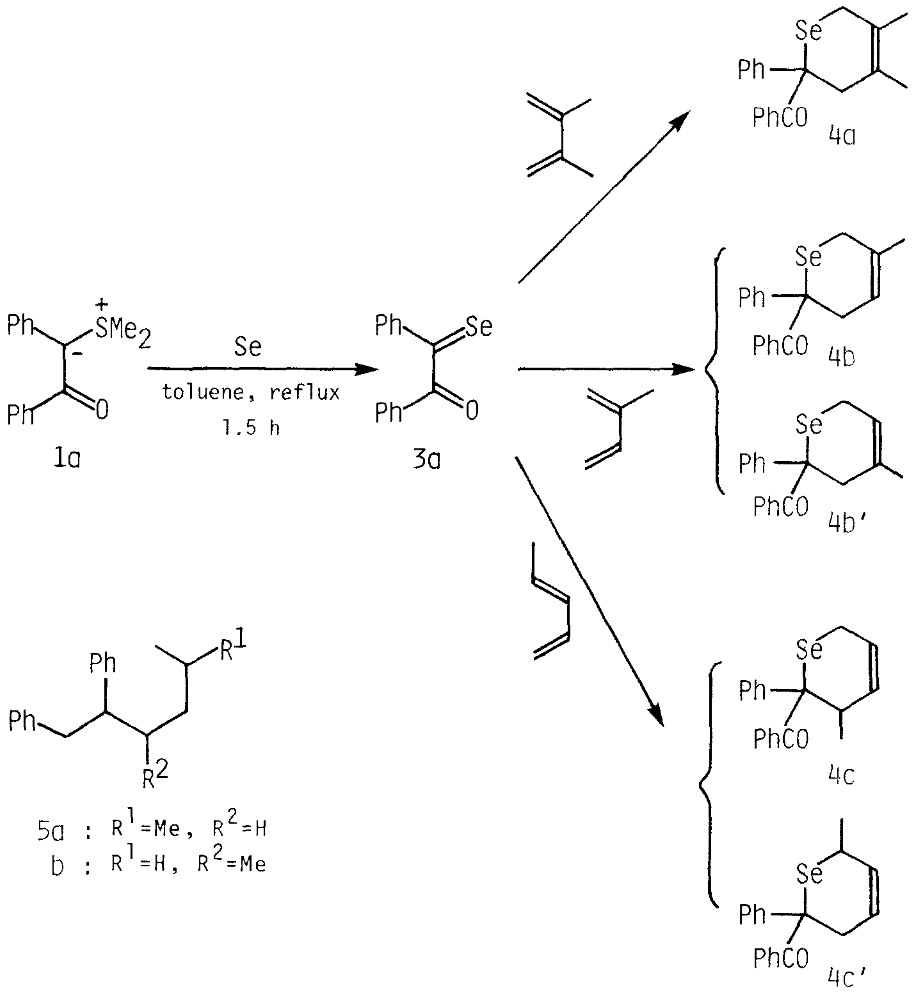
We previously reported that a series of carbonyl-stabilized sulfur ylides (1) react with elemental selenium to afford 1,3-oxaselenoles (2) in good yields.[1,2] The proposed mechanism by us involves the initial formation of α-oxoselenocarbonyl compounds (3), which react with 1 to produce the final products 2. We now succeeded in the trapping of 3 by Diels-Alder reaction and show that the reaction of sulfur ylides with selenium provides an effective method for generation of hitherto unknown α-oxoselenoaldehydes and ketones.[3-6]



1 3 2

a : R^1=R^2=Ph
b : R^1=H, R^2=Ph
c : R^1=COMe, R^2=Me
d : R^1=CO_2Et, R^2=Me

Heating the ylide 1a with elemental selenium[7] (1.5 equiv) in the presence of excess 2,3-dimethylbutadiene (8 equiv) in refluxing toluene for 1.5 h afforded compound 4a as crystals in 89% yield, while the reaction in the absence of the diene gave the oxaselenole 2a (82%) as the sole product. Compounds 4a corresponds to the Diels-Alder adduct of hitherto unknown monoselenobenzil 3a[8] and the diene. Similarly the reaction in the presence of isoprene (10 equiv) afforded the adducts 4b and 4b' in 74% yield in the ratio of 2:1 along with 2a (10%). The major regioisomer 4b could be isolated in a pure crystalline form. Treatment of 4b with freshly prepared Raney nickel W-2 in refluxing ethanol resulted in deselenation, hydrogenation of the double bond, and reduction of the carbonyl to methylene simultaneously, to give 1,2-diphenyl-5-methylhexane (5a) in 72% yield. The reaction in the presence of <u>trans</u>-piperylene



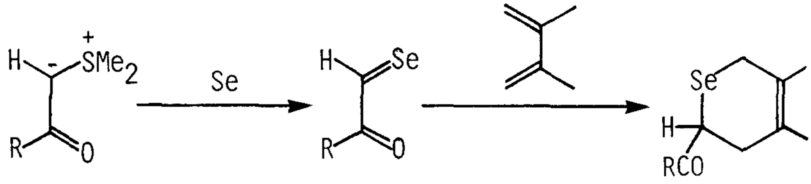
5a : R^1=Me, R^2=H
b : R^1=H, R^2=Me

(8 equiv) produced the adducts 4c and 4c' in 73% yield in the ratio of 6:1 along with 2a (22%) Both 4c and 4c' are mixtures of cis:trans isomers in the same ratio of 3:2.[9] The major regioisomer 4c isolated as a mixture of cis:trans isomers gave 1,2-diphenyl-3-methylhexane (5b) in 57% yield on treatment with Raney nickel. Structure of 5b was established by an independent synthesis.[10] The observed regiochemistry in the Diels-Alder reaction, especially predominant formation of sterically disfavored isomer 4c over 4c', shows that the selenium of 3a is electronically positively charged as expected.[11]

Monoselenophenylglyoxal 3b could be also satisfactorily generated. The reaction of the ylide 1b with elemental selenium in the presence of 2,3-dimethylbutadiene in refluxing toluene for 1.5 h afforded the adduct 4d (45.5%) along with the oxaselenole 2b (13%), while the reaction without the diene gave only 2b in 43.5% yield. The selenoaldehyde 3c, formation of which was previously reported by Kirby,[5] was also produced by the present method. Heating the ylide 1c and selenium in the presence of 2,3-dimethylbutadiene provided the adduct 4e in 26% yield and 1,2-bis(ethoxycarbonyl)ethylene in 26% yield in the cis:trans ratio 3:1. The reaction in the absence of the diene afforded the bis(ethoxycarbonyl)ethylene in 92% yield in the cis:trans ratio 5:2. The ethylene must be formed by extrusion of selenium from the labile selenirane intermediate 6 which is produced from 3c and 1c.[12]

Generation of monoselenoketone such as 3d can also be effected by the present method and trapped by cyclopentadiene produced in situ by thermal dissociation of dicyclopentadiene. Thus heating the ylide 1d and selenium in the presence of excess dicyclopentadiene in refluxing o-dichlorobenzene for 1 h afforded the adduct 4f in 43% yield. The reaction of 1d with selenium without dicyclopentadiene afforded the oxaselenole 2c in 91% yield. Similarly selenoketones 3e and 3f were generated from the ylides 1e and 1f in refluxing o-dichlorobenzene and trapped by cyclopentadiene to give the adducts 4g and 4h in 78 and 38% yields, respectively. The endo:exo ratio of 4h was 1:1.[13] In reactions carried out without dicyclopentadiene, 1e afforded tetrakis(ethoxycarbonyl)ethylene quantitatively, while 1f gave the oxaselenole 2d in 94% yield.[12]

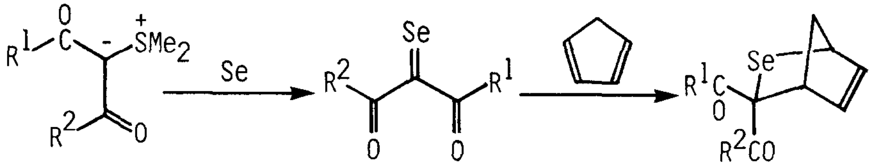
A wide variety of sulfur ylides can be easily prepared by diverse methods. Accordingly the reaction developed here provides a novel facile method for generation of functionalized selenocarbonyl compounds which are otherwise difficult to generate.



1b : R = Ph
c : R = OEt

3b : R = Ph
c : R = OEt

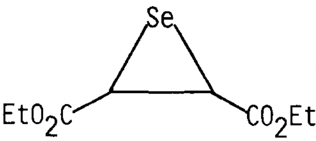
4d : R = Ph
e : R = OEt



1d : $R^1=R^2=Me$
e : $R^1=R^2=OEt$
f : $R^1=Me, R^2=OEt$

3d : $R^1=R^2=Me$
e : $R^1=R^2=OEt$
f : $R^1=Me, R^2=OEt$

4f : $R^1=R^2=Me$
g : $R^1=R^2=OEt$
h : $R^1=Me, R^2=OEt$



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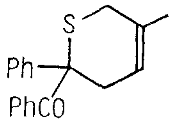
References and Notes

1. J. Nakayama, H. Sugiura, M. Hoshino, and H. Kobayashi, Tetrahedron Lett., 26, 2201 (1985).
2. *Elemental sulfur similarly reacts with 1 to give 1,3-oxathioles in good yields.*[1]

3. This work was presented at the 14th Symposium on Organic Sulfur and Phosphorus Chemistry, January 1986, Urawa, Japan.
4. For generation and reactions of α-oxothioaldehydes, see E. Vedejs, T. H. Eberlein, D. J. Mazur, C. K. McClure, D. A. Perry, R. Ruggeri, E. Schwartz, J. S. Stults, D. L. Varie, R. G. Wilde, and S. Wittenberger, *J. Org. Chem.*, **51**, 1556 (1986) and references cited therein. For monothiobenzil, see, for example, (a) D. C. Dittmer and G. E. Kuhlmann, *J. Org. Chem.*, **35**, 4224 (1970) and references cited therein; (b) M. J. Loadman, B. Saville, M. Steer, and B. K. Tidd, *J. Chem. Soc., Chem. Commun.*, 1167 (1972); (c) C. Bak, and K. Praefcke, *Chemiker-Ztg.*, **102**, 456 (1978).
5. It is very recent that simple selenoaldehydes including selenoformaldehyde, which had been elusive compounds by virture of high reactivity and difficulty of preparation,[6] was satisfactorily generated by the fluoride-induced elimination of cyanide from α-silyl selenocyanates and could be trapped by Diels-Alder reaction with cyclopentadiene: G. A. Krafft and P. T. Meinke, *J. Am. Chem. Soc.*, **108**, 1314 (1986). Generation of $RO_2CCH=Se$ by base-induced 1,2-elimination from selenenyl derivatives was also very recently reported: G. W. Kirby and A. N. Trethewey, *J. Chem. Soc., Chem. Commun.*, 1152 (1986). For possible intermediacy of 2,4,6-tri-*t*-butylselenobenzaldehyde, see R. Okazaki, A. Ishii, and N. Inamoto, *J. Chem. Soc., Chem. Commun.*, 71 (1986).
6. See references cited by Krafft and Meinke.[5]
7. Selenium powder was used as purchased from Wako Pure Chemical Industries, Ltd.
8. Formation of 4-methoxymonoselenobenzil was previously suggested as intermediate: C. Bak and K. Praefcke, *Chemiker-Ztg.*, **102**, 361 (1978).
9. Both ratios of **4c** and **4c'** and of cis:trans isomers were determined by ^1H-NMR, but which is which could not be determined by spectroscopic methods.
10. Prepared starting from reaction of $PhCOCH(CH_3)C_3H_7$ with benzylmagnesium chloride.
11. The reaction of **1a** with elemental sulfur (1.5 equiv) in the presence of isoprene (10 equiv) was carried out in refluxing toluene in order to compare the reactivity of **3a** with monothiobenzil.[2] The cycloadducts **7** and **7'** of monothiobenzil and isoprene were obtained in low yield (2.4%) in the ratio 3:2, the major product being 2-benzoyl-2,4,5-triphenyl-1,3-oxathiole (87%). Thus, monselenobenzil seems to be stronger than monothiobenzil in dienophilic reactivity, though regioselectivity of the both compounds in Diels-Alder reaction seems to be comparable.



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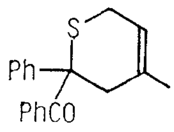

7'

12. These results show that the formation of 1,3-oxaselenoles requires the presence of ketonic carbonyl. Thus, dimethylsulfonium dicyanomethylide and dimethylsulfonium 9-fluorenylide afford tetracyanoethylene and 9,9'-bifluorenylidene, respectively, in excellent yields on reaction with selenium.
13. The endo:exo ratios of cycloadducts of simple selenoaldehydes with cyclopentadiene range from 2.3:1 to 9.0:1.[5]

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