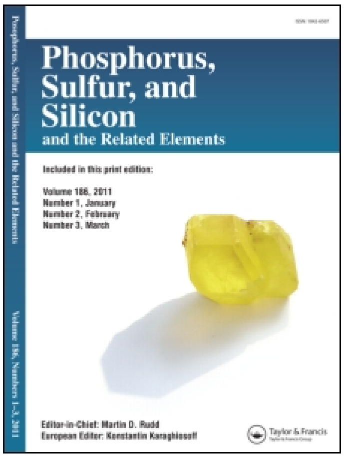

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Communication

SELENOBENZOPHENONES AND DIAZOALKANES: REACTION AND MECHANISTIC ELUCIDATION

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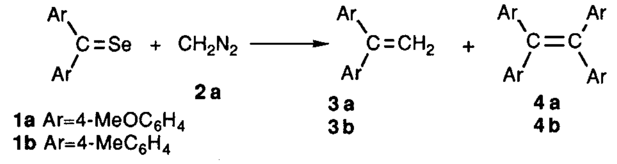
The reaction of selenobenzophenones with diazomethane afforded the corresponding diarylethylenes and symmetrical olefins. The reaction with other diazoalkanes gave three different types of olefins. This reaction proceeded through selenadiazoline intermediates and retrocyclization was observed.

Key words: Selenobenzophenone; diazoalkane, selenadiazoline; episelenide; olefin

Recently, much attention has been paid to the chemistry of carbon-selenium double bond because of their unique and interesting reactivity.[1,2] The reactions of thioketones with diazoalkanes were well studied.[3] However, there are relatively few reports on the reaction of selenoketones with diazoalkanes.[4] Recently, we have isolated 4,4′-disubstituted selenobenzophenones in moderate yields by the reaction of Wittig reagents with elemental selenium.[5] These findings prompted us to investigate the reaction of selenobenzophenones with diazoalkanes. In this communication, we would like to report the results of this reaction and its mechanistic investigation.

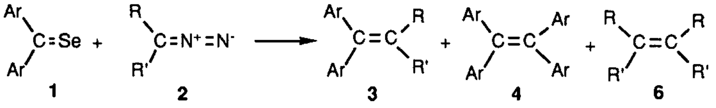
When 4,4′-dimethoxyselenobenzophenone (**1a**) was allowed to react with diazomethane at room temperature, 1,1-4,4′-dimethoxydiphenylethylene (**3a**) and tetra(4-methoxyphenyl)ethylene (**4a**) were obtained in 50 and 5% yields, respectively.



Scheme 1

Thiobenzophenone was found to react with diazomethane to give the corresponding thiirane and 1,3-dithiorane.[6–8] Recently, Kawashima *et al.* found that the reaction of sterically hindered thioaldehyde with diazoalkanes also afforded the corresponding thiiranes.[9] As to the formation of olefins **3**, the reaction might proceed through the similar episelenide intermediates. First, the reaction of selone **1** with diazomethane afforded the corresponding selenadiazolines (**5a** and **5b**), which converted into the corresponding episelenides. Since episelenides are unstable, they decomposed to selenium and olefins **3**.

However, this mechanism cannot explain the formation of symmetrical olefins **4**. Thus, another mechanism must have been operative. Back *et al.* found that the reaction of di-*t*-butylselenoketone with diphenyldiazomethane afforded 5,5-diphenyl-2,2-di-*t*-butyl-Δ^3-1,3,4-selenadiazoline (**5c**) in 73% yield.[4] The stability of this compound might be attributed to steric hindrance. In view of the formation of the readily isolable selenadiazoline and mechanistic investigation of the above reaction, the reactions of selenobenzophenones with diazoalkanes were carried out at low temperature. Treatment of 4,4′-dimethoxyselenobenzophenone with diphenyldiazomethane at −78°C resulted in the formation of tetraphenylethylene (**6b**) and 1,1(4,4′-dimethoxydiphenyl)-2,2′-diphenylethylene (**3d**) in 33 and 34% yields, respectively. At −78°C, nitrogen evolution was not observed in this reaction, nitrogen was evolved at −40°C, however, and at −20°C the precipitation of red selenium was observed. The investigated reactions are summarized in Table I.



Scheme 2

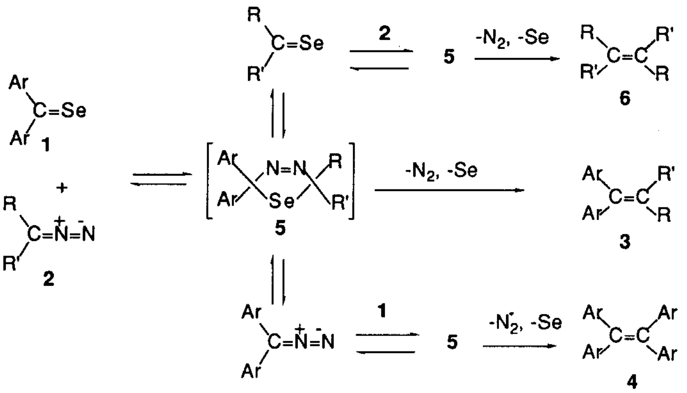
Besides the expected olefins **3** the symmetrical olefins **4** and **6** were also obtained. Thus, the reaction might proceed as follows. Selenobenzophenones reacted with diazoalkanes to give the corresponding selenadiazoline **5**, which equilibrated to a mixture of three selenadiazolines followed by elimination of nitrogen to form episelenide, and finally elemental selenium precipitated to give the olefins **3**, **4**, and **6** (Scheme 3).

The present reaction involving selenobenzophenone is quite different from the reaction of thiobenzophenone with diazomethane. Huisgen *et al.* found that this reaction afforded tiiranes, 1,3-dithianes, and 1,4-dithianes.[8] However, they did not observe the thiadiazoline retrocyclization. Since thiocarbonyl ylide is a plausible intermediate in this reaction. To check this assumption, the reaction of selenobenzophenone with diazomethane and dimethyl acetylenedicarboxylate was carried out. However, the obtained products were only the corresponding olefins. This result suggests that the equilibrium of episelenide and selenocarbonyl ylide is not observed.

TABLE I

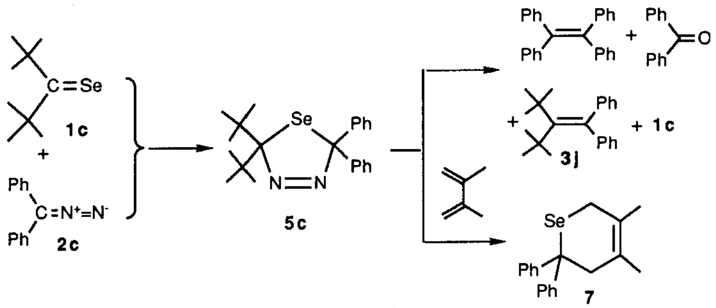
Reaction of selenobenzophenones with diazoalkanes

	Diazoalkane			Conditions	Products (Yield/%)		
1	R	R'	eq	Temperature/°C	3	4	6
1a	Me_3Si	H	3	rt	**3c** 62	**4a** 26	**6a** --
1a	Ph	Ph	1	-78	**3d** 34	**4a** 0	**6b** 33
1a	4-Tol	4-Tol	1	-78	**3e** 76	**4a** 0	**6c(4b)** 22
1a	4-Tol	4-Tol	1	rt	**3e** 54	**4a** 0	**6c(4b)** 10
1a	4-MeOC_6H_4	4-MeOC_6H_4	1	-45	**3f(4a)**	84	
1b	Me_3Si	H	3	rt	**3g** 9	**4b** 31	**6a** --
1b	Ph	Ph	1.5	rt	**3h** 26	**4b** 31	**6b** 29
1b	4-Tol	4-Tol	1	rt	**3i(4b,6c)**	75	



Scheme 3

The existence of retrocyclization was supported by the following results. The reaction of di-*t*-butylselenoketone with diphenyldiazomethane gave the selenadiazoline **5c**. Thermolysis of **5c** afforded tetraphenylethylene (12%) and benzophenone (55%) along with the expected decomposition products (**3j**, **1c**). Treatment of **5c** with excess of 2,3-dimethylbutadiene afforded the corresponding Diels-Alder adduct (**7**) in 62% yield.



Scheme 4

Back *et al.* found that thermolysis of **5c** afforded only the normal decomposition products along with di-*t*-butylselenoketone.[4] The present result is quite different from theirs. However, retrocyclization of extremely sterically hindered selenoketones was observed by Guziec *et al.*[10] Since, selenadiazolines **5**, are generally unstable, the retrocyclization might be a reasonable step in this reaction. This represents another example of a retrocyclization by a selenadiazoline.

Reaction of **1a** *with 4,4'-ditolyldiazomethane* (**2b**). To a solution of **1a** (152 mg, 0.50 mmol) in THF (5 mL) was added a solution of **2b** (110 mg, 0.50 mmol) in THF via syringe at −78°C. The reaction mixture was stirred for 1 h and warmed up to rt. The resulting solution was evaporated and chromatographed over silica gel by elution with hexane-dichloromethane and afforded **3e** (161 mg, 0.38 mmol) and **6c** (42 mg, 0.11 mmol) in 76 and 22% yields, respectively.[11]

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REFERENCES

1. For reviews, see R. Okazaki, *Yuki Gosei Kagaku Kyokaishi* **46,** 1149 (1988). F. Guziec, Jr., Organoselenium Chemistry, Ed. by D. Liotta, pp. 58–83, John Wiley & Sons (1987).
2. H. Fischer, K. Treier and J. Hofmann, *J. Organomet. Chem.*, **384,** 305 (1990). M. Segi, T. Koyama, Y. Takata, T. Nakajima and S. Suga, *J. Am. Chem. Soc.*, **111,** 8749 (1989). G. M. Li, M. Segi and T. Nakajima, *Tetrahedron Lett.*, **33,** 3515 (1992). H. Fischer, *J. Organomet. Chem.*, **345,** 65 (1988). J. Nakayama and Y. Sugihara, *J. Phys. Org. Chem.*, **1,** 59 (1988). P. T. Meinke and G. A. Krafft, *J. Am. Chem. Soc.*, **110,** 8671 and 8679 (1988). G. W. Kirby and A. N. Trethewey, *J. Chem. Soc., Perkin Trans. 1*, 7 (1988). K. Okuma, Y. Komiya, I. Kaneko, Y. Tachibana, E. Iwata and H. Ohta, *Bull. Chem. Soc. Jpn.*, **63,** 1653 (1990). K. Okuma, I. Kaneko, H. Ohta and Y. Yokomori, *Heterocycles,* **31,** 2107 (1990). A. Krief, M. Trabelsi and W. Dumont, *SYNLETT*, 638 (1992). Y. Takikawa, A. Uwano, H. Watanabe, M. Asanuma and K. Shimada, *Tetrahedron Lett.*, **30,** 6047 (1989). K. Shimada, N. Jin. M. Fujiwara, Y. Nagano, E. Kudoh and Y. Takikawa, *Chem. Lett.*, 1843 (1992).
3. A. Shönberg, B. König and E. Singer, *Chem. Ber.*, **100,** 767 (1967). A. Shönberg, W. Knöfel, E. Frese and K. Praefcke, *Chem. Ber.*, **103,** 938 (1970) and references cited therein.
4. T. G. Back, D. H. R. Barton, M. R. Britten-Kelly and F. S. Guziec, Jr., *J. Chem. Soc., Chem. Commun.*, 539 (1975). T. G. Back, D. H. R. Barton, M. R. Britten-Kelly and F. S. Guziec, Jr., *J. Chem. Soc., Perkin Trans. 1*, 2079 (1976).
5. K. Okuma, K. Kojima, I. Kaneko and H. Ohta, *Chem. Lett.*, 1053 (1991). K. Okuma, K. Kojima, I. Kaneko and H. Ohta, *Tetrahedron Lett.*, **33,** 1333 (1992). See also, G. Erker, R. Hock, C. Krüger, S. Werner, F.-G. Klärmer and U. Artschwager-Perl, *Angew. Chem. Int. Ed. Engl.*, **29,** 1067 (1990).
6. A. Schönberg, D. Cernik and W. Urban, *Ber. Dtsch. Chem. Ges.*, **64,** 2577 (1931).
7. H. Staudinger and J. Siegwart, *Helv. Chim. Acta,* **3,** 833 (1920).
8. I. Kalwinsch, L. Xingya, J. Gottstein and R. Huisgen, *J. Am. Chem. Soc.*, **103,** 7032 (1981).
9. T. Kawashima, S. Watanabe and R. Okazaki, *Chem. Lett.*, 1603 (1992).
10. J. F. S. Guziec, L. J. SanFilippo, C. J. Murry, C. A. Moustakis and E. R. Cullen, *Tetrahedron,* **41,** 4843 (1985).
11. Satisfactory of elemental analyses or mass spectra were obtained for all new compounds. Spectral data of **3e**: ^{1}H NMR ($CDCl_3$) δ = 2.25 (s, 6H, TolMe), 3.73 (s, 6H, MeO), 6.63 (d, 4H, Ar), 6.89 (s, 8H, Tol), 6.93 (d, 4H, Ar). ^{13}C NMR ($CDCl_3$) δ = 21.15 (TolMe), 55.05 (MeO), 112.70, 128.33, 130.95, 132.50, 135.52, 136.77, 139.09, 141.45, 157.85: Mp 180–181°C.