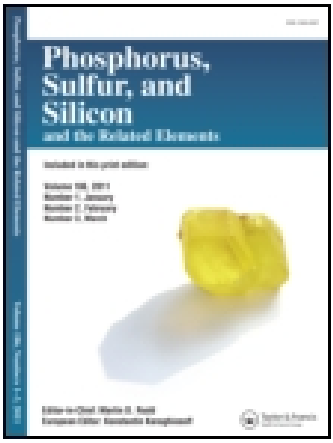


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gpss20

Reaction of Selenoketones with Propiolic Acid

Kentaro Okuma [a], Masahiro Koda [a] & Toshiyuki Shigetomi [a]
[a] Department of Chemistry, Faculty of Science, Fukuoka University, Jonan-ku, Fukuoka, Japan
Published online: 29 Oct 2008.

To cite this article: Kentaro Okuma, Masahiro Koda & Toshiyuki Shigetomi (2008) Reaction of Selenoketones with Propiolic Acid, Phosphorus, Sulfur, and Silicon and the Related Elements, 183:4, 1057-1060, DOI: 10.1080/10426500801901103

To link to this article: http://dx.doi.org/10.1080/10426500801901103

Phosphorus, Sulfur, and Silicon, 183:1057–1060, 2008

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500801901103

Reaction of Selenoketones with Propiolic Acid

Kentaro Okuma, Masahiro Koda, and Toshiyuki Shigetomi
Department of Chemistry, Faculty of Science, Fukuoka University, Jonan-ku, Fukuoka Japan

The reaction of di-tert-butyl selenoketone with propiolic acid gave 2H,6H-1,3-oxaselenin-6-one in 78% yield, whereas the reaction of di-tert-butyl thioketone with propiolic acid recovered starting thioketone almost quantitatively. On the other hand, the reaction of selenofenchone with propiolic acid gave 2H,6H-1,3-oxaselenin-6-one and Wagner-Meerwein rearranged product in good yields.

Keywords Propiolic acid; selenodioxenone; selenoketone; Wagner-Meerwein rearrangement

INTRODUCTION

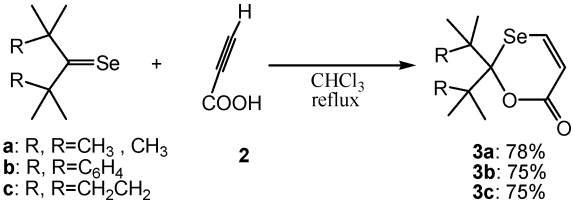
The reaction of selenocarbonyl compounds (**1**) is of current interest.[1] Recently, we have found that isolable thioketones reacted with propiolic acid (**2**) to give 2*H*,6*H*-1,3-oxathiin-6-ones (thiodioxenone).[2] The Wagner-Meerwein rearrangement is a popular acid catalyzed reaction. Martinez et al. have reported the reaction of fenchone with trifluoromethanesulfonic anhydride, which led to the Wagner-Meerwein rearranged products.[3] These results prompted us to investigate the possibility of the formation of 2*H*,6*H*-1,3-oxaselenin-6-ones (selenodioxenone) (**3**) and Wagner-Meerwein rearranged products (**4**) in the reaction of selenoketones **1** with propiolic acid **2**. We report herein the isolation of **3** and **4** from **1** and **2**.

RESULTS AND DISCUSSION

Treatment of di-*tert*-butyl selenoketone (**1a**) with **2** resulted in the formation of 2,2-di-*tert*-butyl-2*H*,6*H*-1,3-oxaselenin-6-one (**3a**)

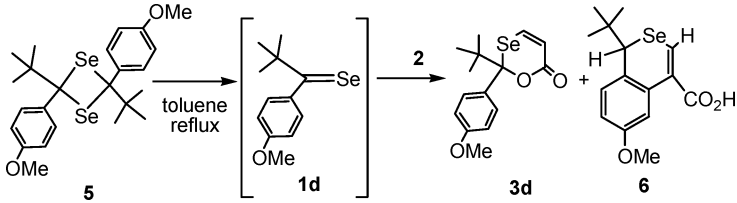
Address correspondence to Kentaro Okuma, Department of Chemistry, Faculty of Science, Fukuoka University, Jonan-ku, Fukuoka 814-0180, Japan. E-mail: kokuma@fukuoka-u.ac.jp

in 78% yield. 1,1,3,3-Tetramethylindan-2-selone (**1b**) and 2,2,5,5-tetramethylcyclopentane-1-selone (**1c**) also reacted with **2** to give the corresponding selenodioxenones (**3b,c)** (Scheme 1).



SCHEME 1

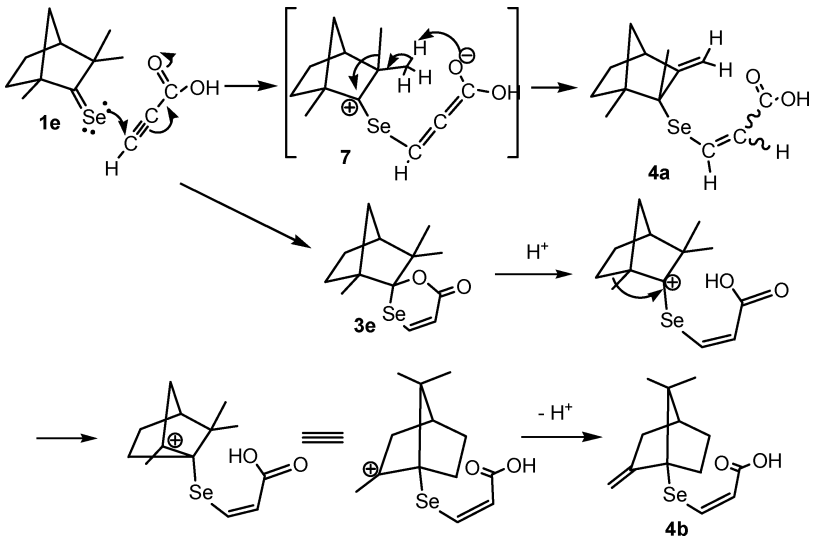
Since diselenetane (**5**) undergoes the thermal cycloreversion to give 4′-methoxyselenopivalophenone (**1d**), the reaction with **2** was carried out in refluxing toluene.[4] The obtained products were selenodioxenone (**3d**) and 4′-methoxypivalophenone in 25% and 15% yields, respectively (Scheme 2). A small amount of 1-(4′-methoxyphenyl)-6-methoxy-1*H*-isoselenochromene-4-carboxylic acid (**6**) was formed, whereas analytically pure sample was not obtained. Due to the low reactivity of **1d** toward **2**, **1d** was easily oxidized to give 4′-methoxypivalophenone.



SCHEME 2

We then tried the reaction of selenofenchone (**1e**) with **2**. Treatment of **1e** with **2** (2 eq) in refluxing chloroform for 16h resulted in the formation of corresponding selenodioxenone (**3e**) along with side product (**4**). As to the structure of **4**, its proton NMR showed two methyl (0.93 and 1.12 ppm), exo-methylene (4.94 and 5.03 ppm), and alkene signals (6.35 and 7.82 ppm) along with norbornane's proton signals. The coupling constant between these alkene signals (10 Hz) suggested that this product has *Z*-configuration. We initially thought that the reaction proceeded through carbocation intermediate (**7**), methyl migration of which led to **4a**. However, a small correlation between exomethylene protons and methylene protons was observed in its H-H cosy

spectrum, suggesting that the correct structure is not **4a** but a Wagner-Meerwein rearranged product (**4b**) (Scheme 3). Recently,



SCHEME 3

Mloston et al. have reported the reaction of thiocamphor or thiofenchone with sulfenyl chlorides, which led to Wagner-Meerwein rearranged products.[5] The present method provides the first example of Wagener-Meerwein rearrangement reaction of selenofenchone. The result is quite different from the reaction of selones with benzyne, which led to the methyl migrated products along with [2 + 2] cycloadducts.[6]

To confirm this reaction mechanism, the reaction was carried out under solvent-free conditions, only the rearranged product **4b** was obtained in 97% yield. Additionally, the reaction of selenodioxenone with propiolic acid or acetic acid gave **4b** in almost quantitative yields.

The difference in the reactivity between thiones and selones **1** might be due to their carbon-heteroatom bond lengths. Bond lengths of thiones are in the range of 1.630–1.661 Å, whereas those of selones are in the range of 1.774–1.790 Å. Thus, selones are more reactive than the corresponding thiones toward alkenes or other dienophiles.

EXPERIMENTAL

Reaction of Selenofenchone 1d with Propiolic Acid 2

To a solution of **1d** (2 mmol) in chloroform was added **2** (4 mmol). After refluxing for 16 h, the reaction mixture was evaporated to afford pale yellow oil, which was chromatographed over silica gel by elution

with hexane and dichloromethane-ethyl acetate (3:1) to afford selenodioxenone **3e** (0.89 mmol) and the rearranged product **4b** (0.25 mmol).

3e

134.5–135.8°C: ^{1}H NMR ($CDCl_3$) δ = 1.22 (s, 6H, 2 Me), 1.29 (s, Me), 1.20–1.66 (m, 5H, CH_2), 1.77 (br, 1H, CH), 2.20 (br d, J = 11 Hz, CHH), 6.32 (d,J = 10 Hz,=CH), 7.82 (d, J = 10 Hz, =CH). ^{13}C NMR ($CDCl_3$)δ 19.00 (Me), 25.27 (CH_2), 28.45 (Me), 29.69 (Me), 32.04 (CH_2), 40.32 (CH_2), 51.79 (q-C), 55.76 (q-C), 106.46 (q-C), 118.20 (=CH), 140.20 (=C), 164.12 (C=O).

4b

M.p. 156–158°C; ^{1}H NMR ($CDCl_3$) δ = 0.93 (s, 3H, Me), 1.12 (s, 3H, Me), 1.36 (m, 1H, CHH), 1.73 (m, 1H, C<u>H</u>H), 1.85–1.97 (m, 2H, CH and C<u>H</u>H), 2.00–2.12 (m, 2H, C<u>H</u>H), 2.56 (br d, 1H, J = 16 Hz, C<u>H</u>H), 4.94 (dd, 1H, J = 1 and 2 Hz, =CH_2), 5.03 (dd, 1H, J = 1 and 2 Hz, =CH_2), 6.35 (d, 1H, J = 10 Hz, =CH_2) 7.82 (d, 1H, J = 10 Hz, =CH).

^{13}C NMR ($CDCl_3$) δ = 20.16 (Me), 20.97 (Me), 28.62 (CH_2), 35.51 (CH_2), 37.36 (CH_2), 43.79 (CH), 50.70 (q-C), 63.08 (q-C,J_{Se-C} = 43 Hz), 107.33 (=CH_2), 116.11 (=CH), 149.84 (=CH, J_{Se-C} = 80 Hz), 154.08 (=C), 172.49 (C=O).

REFERENCES AND NOTES

[1] (a) For reviews, see F. S. Guziec, Jr., In *Organoselenium Chemistry,* D. Liotta, Ed. (Wiley, New York, 1987), p 277 ; (b) F. S. Guziec, Jr. and L. J. Guziec, In *Comprehensive Organic Functional Group Transformations*, F. S. Katritky, O. M-Cohn, C. W. Rees, and G. Pattenden Group, Eds. (Pergamon, Cambridge, 1995), Vol. 3. 3.09.

[2] (a) K. Okuma, S. Maekawa, S. Shibata, K. Shioji, T. Inoue, T. Kurisaki, H. Wakita, and Y. Yokomori, *Eur. J. Org. Chem*., **2003,** 3727 (2003); (b) K. Okuma, M. Koda, S. Maekawa, K Shioji, T. Inoue, T. Kurisaki, H. Wakita, and Y. Yokomori, *Org. Biomol. Chem*., **4,** 2745 (2006).

[3] A. G. Martinez, E. T. Vilar, A. G. Fraile, S. de la M. Cerero, and B. L. Maroto, *Tetrahedron Lett.,* **42,** 6359 (2001).

[4] K. Okuma and T. Kubota, *Tetrahedron Lett*., **42,** 3881 (2001).

[5] A. Majchrzak, G. Mloston, A. Linden, and H. Heimgartner, *Helvetica Chim. Acta,* **87,** 790 (2004).

[6] K. Okuma, A. Okada, Y. Koga, and Y. Yokomori, *J. Amer. Chem. Soc.*, **123,** 7166 (2001).