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Reaction of 2,4,6-Tri-*t*-butylselenobenzaldehyde with Sterically Crowded Diazo Compounds. Formation of Seleniranes

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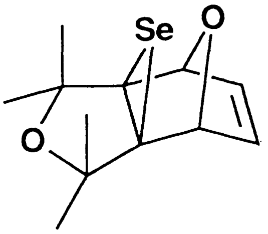
Reaction of the title stable selenoaldehyde with di-*t*-butyldiazomethane and 2-diazo-1,1,3,3-tetramethylindan at -50 °C in the presence of a catalytic amount of CuCl resulted in the formation of the corresponding seleniranes.

Oxiranes[1)] and thiiranes[2)] have been extensively studied as a result of their interesting structural and chemical features. Conversely, chemistry of seleniranes is very little known because attempted synthesis of seleniranes always results in the formation of the corresponding olefins by loss of selenium although only one example of stable selenirane **1** with an exotic structure has been reported.[3)]



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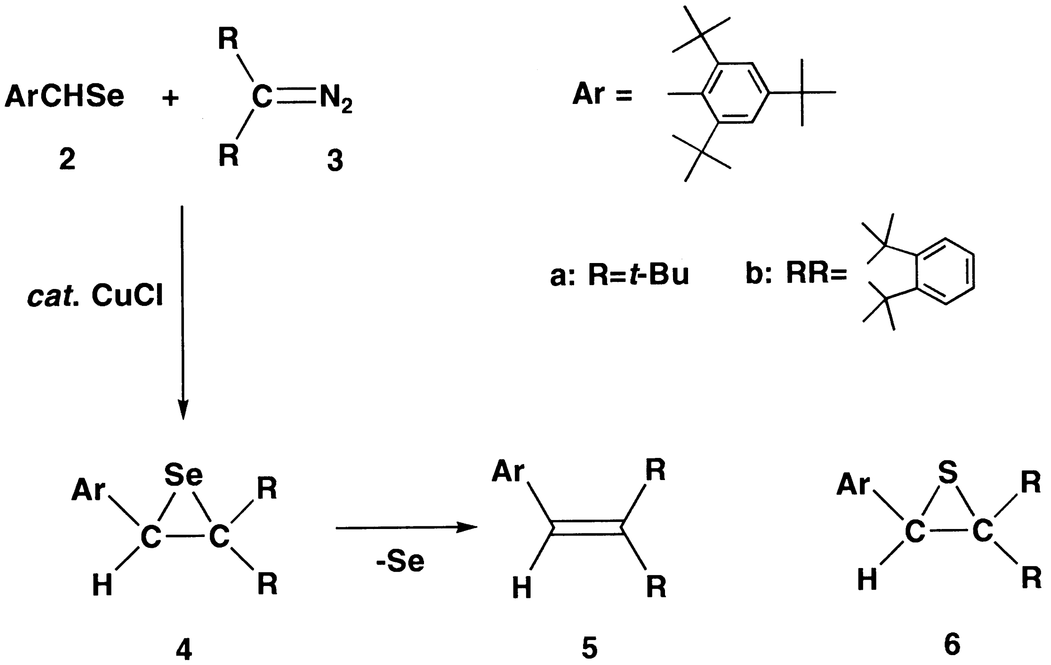
Recently we reported the synthesis of the first stable selenoaldehyde **2** taking advantage of kinetic stabilization by a bulky group, 2,4,6-tri-*t*-butylphenyl.[4)] We became interested in the use of this selenoaldehyde for the synthesis of highly unstable compounds otherwise difficult to obtain. Here we describe the formation of stable seleniranes **4** from the reaction of **2** with sterically crowded diazo compounds **3**.

Reaction of selenoaldehyde **2** with di-*t*-butyldiazomethane **3a**[5)] in the presence of a catalytic amount of CuCl(I) was carried out in THF at -50 °C for 3 h. The reaction mixture, which was obtained by the filtration of CuCl through celite followed by evaporation of the solvent at -50 °C, was dissolved in acetone-d_6 and analyzed



by NMR at the same temperature. The ^{1}H- and ^{13}C-NMR spectra are shown in Fig. 1 and Fig. 2, respectively, along with those for the corresponding thiirane **6a**. Signals marked with "O" in Fig. 1 can be assigned as those for olefin **5a**$^{6)}$ from comparison with an authentic sample, whereas signals marked with "S" can be attributed to selenirane **4a** because they are very similar to those for the corresponding thiirane **6a**, although the sp^3 methine H_a in **5a** is much deshielded compared to that in **6a**. A similar conclusion can be drawn from ^{13}C-NMR (Fig. 2). Here again, the signal due to C_a is deshielded than that in the corresponding thiirane **6a**. Monitoring by ^{1}H-NMR indicates that **4a** is stable even at room temperature although the signals due to **4a** gradually disappear during one hour to change into those for **5a**. The formation of selenirane **4a** was also confirmed by measuring the mass spectrum of the reaction solution showing the parent peak (*m/z* 464).

The observed stability of **4a** prompted us to purify the reaction mixture by low temperature flash chromatography (SiO_2, pentane, -50 ℃). Selenirane **4a** was found to survive the chromatography, thus indicating **4a** is stable at room temperature even in the solid state. However, very similar chromatographic behavior of **4a** and olefin **5a** did not allow us to isolate pure **4a**. The stability of **4a** is noteworthy in view of the fact that **4a** is a tri-substituted selenirane unlike **1** which is tetra-substituted.

A similar reaction of selenoaldehyde **2** with 2-diazo-1,1,3,3-tetramethylindan **3b**$^{7)}$ gave selenirane **4b** along with **5b**$^{6)}$ as evidenced by ^{1}H- and ^{13}C-NMR monitoring. The stability of **4b** is approximately the same

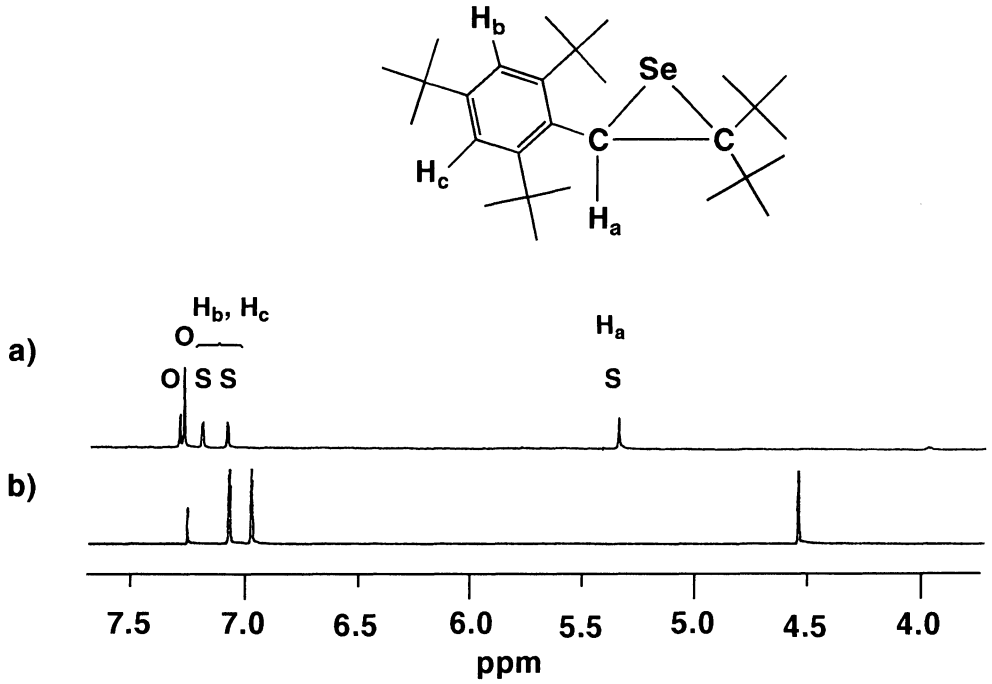


Fig. 1. a) The ^{1}H-NMR spectrum of the reaction mixture of selenoaldehyde **2** and di-*t*-butyldiazomethane (**3a**) in acetone-d_6 at -50 ℃. b) The ^{1}H-NMR spectrum of thiirane **6a** in deuteriochloroform at room temperature.

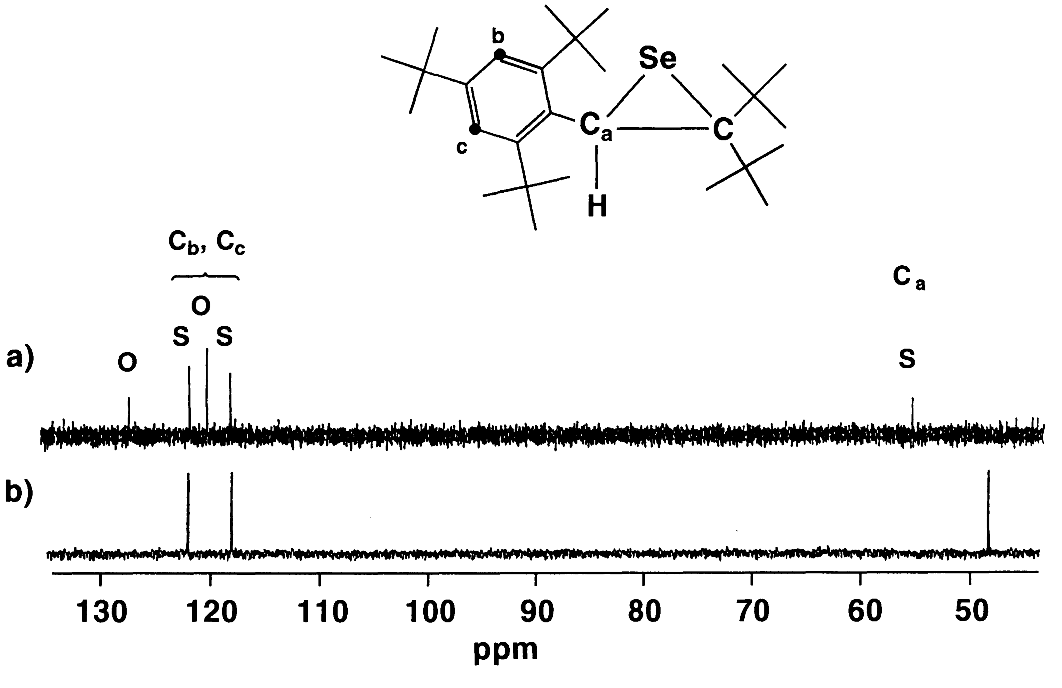


Fig. 2. a) The ^{13}C-NMR spectrum of the reaction mixture of selenoaldehyde **2** and di-*t*-butyldiazomethane (**3a**) in acetone-d_6 at -50 ℃. b) The ^{13}C-NMR (DEPT) spectrum of thiirane **6a** in deuteriochloroform at room temperature.

as that of **4a**; **4b** is stable at -40 °C for long time, but is converted to **5b** at room temperature during about 2 h.

In summary, we have found that the stable selenoaldehyde **2** reacts with sterically crowded diazo compounds to afford tri-substituted seleniranes which are stable at room temperature.

References

1) E. G. Lewars, "Oxiranes and Oxirenes," in "Comprehensive Heterocyclic Chemistry," ed by A. R. Katritzky and C. W. Rees, Pergamon Press, New York (1984), Vol. 7, pp. 95-130.

2) D. C. Dittmer, "Thiiranes and Thiirenes," in "Comprehensive Heterocyclic Chemistry," ed by A. R. Katritzky and C. W. Rees, Pergamon Press, New York (1984), Vol. 7, pp. 131-184.

3) W. Ando, Y. Kumamoto, and N. Tokitoh, *Tetrahedron Lett.*, **28**, 2867 (1987); *J. Phys. Org. Chem.*, **1**, 317 (1988).

4) R. Okazaki, N. Kumon, and N. Inamoto, *J. Am. Chem. Soc.*, **111**, 5949 (1989).

5) T. G. Back, D. H. R. Barton, M. R. Britten-Kelly, and F. S. Guziec, Jr., *J. Chem. Soc., Perkin Trans. 1*, **1976**, 2079.

6) Physical and spectral data of **5a** and **5b** are as follows. **5a**: white crystals; mp 105.8-107.5 °C; ^{1}H-NMR($CDCl_3$): δ=0.88 (9H, s), 1.29 (9H, s), 1.40 (18H, s), 1.41 (9H, s), 7.20 (2H, s), and 7.21(1H, s); ^{13}C-NMR ($CDCl_3$): δ=31.54 (q), 32.02 (q), 32.74 (q×2), 33.57 (q), 34.59 (s), 37.53 (s×2), 38.46 (s), 40.08 (s), 120.98 (d×2), 128.17 (d), 136.98 (s), 146.78 (s×2), 146.92 (s), and 148.40 (s). **5b**: white crystals; mp 132.0-133.0 °C; ^{1}H-NMR($CDCl_3$): δ=0.93 (6H, s), 1.33 (9H, s), 1.36 (18H, s), 1.55 (6H, s), 6.98 (1H, m), 7.11 (1H, s), 7.15-7.20 (3H, m), and 7.26 (2H, s); ^{13}C-NMR ($CDCl_3$): δ=30.62 (q×2), 31.30 (q×2), 31.52 (q), 33.85 (q×2), 34.57 (s), 38.17 (s×2), 46.72 (s), 48.01 (s), 121.16 (d×2), 121.92 (d), 122.38 (d), 125.57 (d), 126.64 (d), 126.93 (d), 131.49 (s), 147.50 (s), 148.54 (s×2), 148.77 (s), 150.81 (s), and 152.67 (s).

7) F. S. Guziec, Jr., L. J. SanFilippo, C. J. Murphy, C. A. Moustakis, and E. R. Cullen, *Tetrahedron*, **41**, 4843 (1985); F. S. Guziec, Jr., C. J. Murphy, and E. R. Cullen, *J. Chem. Soc., Perkin Trans. 1*, **1985**, 107.

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