Two New Oxaselenoles from Desyl Selenocyanate

Joyce Gramza,[1] R. B. Mitchell, and D. C. Dittmer*

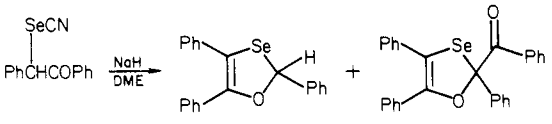
Department of Chemistry, Syracuse University, Syracuse, New York 13210

Received November 29, 1983

Few 1,3-oxaselenoles are known. Among these are 2-(acylimino)-1,3-oxaselenoles which were prepared in 38–56% yield by reaction of *gem*-dicyano epoxides with potassium selenocyanate.[2] Several spirooxaselenoles have been obtained by treatment of cyclic diones or triones with selenium dioxide at low pH.[3–7] The sulfur analogues, 1,3-oxathioles, are much more common.[8] 2,4,5-Triphenyl-2*H*-1,3-oxathiole and 2-benzoyl-2,4,5-triphenyl-1,3-oxathiole have been prepared by treatment of desyl thiocyanate (1,2-diphenyl-2-thiocyanatoethanone) with sodium hydride.[9–11]

Air-sensitive desyl selenocyanate (1,2-diphenyl-2-selenocyanatoethanone) was prepared in 48% yield by refluxing a solution of desyl chloride and potassium selenocyanate in acetone. A single, sharp absorption attributed to the selenocyano group is observed at 2160 cm^{-1} in the infrared and is comparable to the absorption of benzyl selenocyanate at 2158 cm^{-1}.[12] The isomer, desyl isoselenocyanate, is not obtained since isoselenocyanates show two broad absorptions in the region 2000–2200 cm^{-1}.[13] The ^{77}Se NMR chemical shift is 395 ppm relative to external Me$_2$Se and is at lower field than that of benzyl selenocyanate (291 ppm[14]). A secondary external standard, diphenyl diselenide, was used whose shift is 481 ppm downfield from dimethyl selenide.[15]

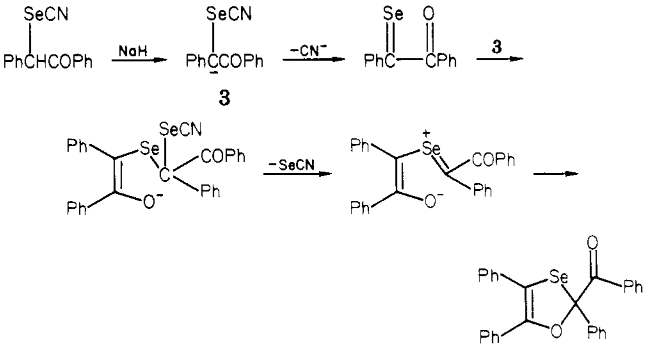
Treatment of desyl selenocyanate with a 1.7-fold excess of sodium hydride in dimethoxyethane (DME) gave 2,4,5-triphenyl-2*H*-1,3-oxaselenole, **1**, in 66% yield. When approximately equimolar amounts of selenocyanate and sodium hydride were used, 2-benzoyl-2,4,5-triphenyl-1,3-oxaselenole, **2**, was obtained (39% yield).



1 **2**

The ^{77}Se NMR chemical shifts for **1** and **2**, relative to external Me$_2$Se, are 544 and 622 ppm, respectively. A selenium–C-2 proton coupling of 15 Hz is observed in the proton-coupled spectrum of **1**; this C-2 proton is not resolved in the ^{1}H NMR spectrum since its absorption lies in the aromatic region. The magnitude of this two-bond Se–H coupling constant is similar to that for other selenium compounds.[14,16] The ^{77}Se chemical shifts of 544 and 622 ppm are comparable to those reported (δ 378–595) for several spirooxaselenoles,[17] as are the ^{13}C NMR chemical shifts.[3] The ^{13}C chemical shifts for **2** are comparable with those of the sulfur analogue.[10] The ultraviolet spectra of **1** and **2** also are similar to those of their sulfur analogues although a band around 300 nm seems characteristic for the selenium compounds.[9–11] Oxaselenole **1** fluoresces moderately at 531 and 584 nm and strongly at 298 nm when excited at 262 nm, and **2** fluoresces at 480 nm and weakly at 355 and 715 nm when excited at 235 nm. In the mass spectra of **1** and **2** the major ion corresponds to PhCO$^+$, and an ion corresponding to diphenylacetylene also is prominent. An ion corresponding to the loss of benzaldehyde is observed in the mass spectrum of **1**.

The formation of **1** may be rationalized similarly to the formation of the corresponding oxathiole.[9] The formation of **2** may proceed via monoselenobenzil and the anion of the selenocyanate (**3**).



Experimental Section

^{77}Se NMR spectra were obtained on a 250-MHz spectrometer equipped with Fourier transform capability and operating at 47.7 MHz. Diphenyl diselenide was used as an external standard resonating at 481 ppm relative to dimethyl selenide.[15] ^{13}C NMR spectra were obtained either on a Bruker WM360 spectrometer operating at 90.56 MHz or a 250-MHz spectrometer operating at 62.90 MHz. ^{1}H NMR spectra were obtained on a Varian T-60 spectrometer, and mass spectra (electron impact, solid probe) were obtained on a Finnegan 4000 MS/GC/DS spectrometer. Fluorescence spectra were recorded on a Perkin-Elmer Model 650-10S spectrometer. UV spectra were obtained on a Carey 219 spectrometer. Dimethoxyethane was dried over calcium hydride for 48 h and distilled under nitrogen as needed.

Desyl Selenocyanate (1,2-Diphenyl-2-selenocyanatoethanone). Desyl chloride (63.6 g, 0.276 mol) in acetone (250 mL) was added to potassium selenocyanate (43.2 g, 0.299 mol) in hot acetone (120 mL) under nitrogen. The reaction mixture was stirred and refluxed for 4.5 h and filtered while hot. Benzene (100 mL) was added to the orange filtrate. Inorganic salts were removed by washing with water (3 × 100 mL). The yellow organic layer was dried over molecular sieves, and the benzene solvent was removed on a rotary evaporator. The residue was dissolved in methylene chloride and filtered, and hexane was added. The solution was concentrated and chilled to give air-sensitive desyl selenocyanate (39.6 g, 0.132 mol, 47.8%): mp 121–123 °C; IR (CHCl$_3$) 2160 (SeCN), 1664 (CO) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.8 (m, 2 H), 7.35 (m, 8 H), 6.4 (s, 1 H); ^{13}C NMR (360 MHz, CDCl$_3$) δ 194.3 (CO), 135.8, 134.5, 132.8, 129.6, 129.4, 128.9, 128.3, 103.5, 60.7 (^{77}Se satellite), 60.5; ^{77}Se NMR (CDCl$_3$) δ 395 (relative to dimethyl selenide); MS (70 eV), *m/e* (relative abundance) 301 (3, M$^+$), 195 (61, M$^+$ − SeCN), 167 (93, Ph$_2$CH$^+$), 152 (33, C$_{12}$H$_8$$^+$), 105 (100, PhCO$^+$). Anal. Calcd for C$_{15}H_{11}$NOSe: C, 60.01; H,

---

(1) Syracuse University Summer Undergraduate Research Scholar.

(2) Robert, A.; LeMarechal, A. *J. Chem. Soc., Chem. Commun.* **1978**, 447.

(3) Laitalainen, T.; Simonen, T.; Kivekas, R.; Klinga, M. *J. Chem. Soc., Perkin Trans. 1* **1983**, 333.

(4) Laitalainen, T. *Ann. Acad. Sci. Fenn., Ser. A2*, **1982**, *195*.

(5) Laitalainen, T.; Simonen, T.; Kivekas, R. *Tetrahedron Lett.* **1978**, 3079.

(6) Laitalainen, T.; Simonen, T.; Klinga, M.; Kivekas, R. *Finn. Chem. Lett.* **1979**, 145.

(7) Laitalainen, T. *Finn. Chem. Lett.* **1982**, 10.

(8) Elliott, A. J. In "Comprehensive Heterocyclic Chemistry"; Pergamon: Oxford, 1983; Vol. 6.

(9) Dittmer, D. C.; Kuhlmann, G. E. *J. Org. Chem.* **1969**, *34*, 2006.

(10) Jacobsson, U.; Kempe, T.; Norin, T. *J. Org. Chem.* **1974**, *39*, 2722.

(11) Dittmer, D. C.; Levy, G. C. *J. Org. Chem.* **1965**, *30*, 636.

(12) Maartmann-Moe, K.; Sanderud, K. A.; Songsted, J. *Acta Chem. Scand., Ser. B* **1982**, *B36*, 211.

(13) Franklin, W. J.; Werner, R. L.; Ashby, R. A. *Spectrochim. Acta, Part A* **1974**, *30A*, 1293.

(14) Christiaens, J.-L.P.; Laitem, L.; Baiwir, M.; Denoel, J.; Llabres, G. *Org. Magn. Reson.*, **1976**, *8*, 354.

(15) Odom, J. D.; Dawson, W. H.; Ellis, P. D. *J. Am. Chem. Soc.* **1979**, *101*, 5815.

(16) McFarlane, W.; Rycroft, D. S. *J. Chem. Soc., Chem. Commun.* **1973**, 10.

(17) Laitalainen, T.; Rahkamoa, E. *Org. Magn. Reson.* **1982**, *20*, 102.

0022-3263/84/1949-2057$01.50/0 © 1984 American Chemical Society

3.69; N, 4.67. Found: C, 59.96; H, 3.52; N, 4.59.

2,4,5-Triphenyl-2-benzoyl-2*H*-1,3-oxaselenole. Sodium hydride (2.05 g, 57% dispersion in oil, 0.049 mol) was washed with hexane several times under nitrogen and finally with dry dimethoxyethane. It was combined with dry dimethoxyethane (30 mL) in a flask cooled in an ice–salt bath. A chilled solution of desyl selenocyanate (15 g, 0.05 mol) in dry dimethoxyethane (80 mL) was added in one portion to the stirred suspension of sodium hydride, resulting in the vigorous evolution of hydrogen. The reaction mixture exhibited a series of color changes from yellow to red and finally to red-orange. Inorganic salts were removed by filtration; ether was added to the filtrate, and this solution was washed with water. The orange organic layer was separated and dried over $MgSO_4$. Ether was removed under reduced pressure to give a red-orange oil, which was recrystallized from methanol to give the bright yellow oxaselenole (9.1 g, 0.02 mol, 39%), mp 96–103 °C. Further recrystallizations from methanol gave a sample: mp 111–114 °C; IR ($CHCl_3$) 1690 (s), 1230 (s) cm^{-1}; UV (CH_3CN) 230 (ϵ 21 400), 300 (5600), 336 (3980) nm; fluorescence emission (CH_3CN, excitation at 235 nm) 242, 355, 479, 715 nm; ^1H NMR ($CDCl_3$) δ 7.0–7.8 (m); ^{13}C NMR ($CDCl_3$) δ 194.7 (CO), 143.3 (C-5), 139.9, 133.5, 133.3, 132.9, 130.7, 130.2, 129.4, 129.0, 128.9, 128.6, 128.3, 128.1, 128.0, 127.6, 125.8, 109.8 (C-4), 99.1 (C-2); ^{77}Se NMR ($CDCl_3$) δ 622 (relative to dimethyl selenide); MS (70 eV), *m/e* (relative abundance) 468 (17, M^+), 363 (41.5, $M^+ - PhCO$), 178 (32.8, $PhC{\equiv}CPh$) 105 (100, PhCO), 77 (50, Ph). Anal. Calcd for $C_{28}H_{20}O_2Se$: C, 71.95; H, 4.31. Found: C, 72.03; H, 4.22.

2,4,5-Triphenyl-2*H*-1,3-oxaselenole. The procedure for the synthesis of the preceding oxaselenole was followed except that an excess of sodium hydride (2.3 g, 57% in oil, 0.053 mol) in dimethoxyethane (40 mL) was used. Desyl selenocyanate (10 g, 0.033 mol) in dimethoxyethane (80 mL) was added as before to give after workup and recrystallization from methanol the yellow-orange product (8.0 g, 0.022 mol, 66%), mp 70–73 °C. Further recrystallizations give orange crystals: mp 72–73 °C; IR ($CHCl_3$) 1220 (s) cm^{-1}; UV (CH_3CN) 226 (ϵ 24 270), 304 (6500), 358 (3400) nm; fluorescence emission (CH_3CN, excitation at 262 nm) 267, 298, 531, 584 nm; ^1H NMR ($CDCl_3$) δ 7.05–7.85 (m); ^{13}C NMR ($CDCl_3$) δ 143.7 (C-5), 140.8, 134.2, 129.4, 128.7, 128.62, 128.59, 128.2, 128.0, 125.8, 109.3 (C-4), 82.2 (C-2); ^{77}Se NMR ($CDCl_3$) δ 543.8 (relative to dimethyl selenide) ($^2J_{SeH}$ = 15 Hz); MS (70 eV), *m/e* (relative intensity) 364 (19.9, M^+), 258 (18.6, $M^+ - PhCHO$), 178 (96.9, $PhC{\equiv}CPh$), 105 (100 , PhCO), 77 (37, Ph). Anal. Calcd for $C_{21}H_{16}OSe$: C, 69.42; H, 4.44. Found: C, 69.51; H, 4.54.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the partial support of this research. We are grateful to Anirban Banerjee for assistance in obtaining the ^{77}Se and ^{13}C NMR spectra.

Registry No. 1, 89936-26-5; 2, 89936-27-6; PhCH(SeCN)COPh, 89936-28-7; PhCHClCOPh, 447-31-4; KSeCN, 3425-46-5; NaH, 7646-69-7.

---

^{1}H NMR Spectrum of Hexa-*n*-propylbenzene

Marc D. Radcliffe and Kurt Mislow*

Department of Chemistry, Princeton University, Princeton, New Jersey 08544

Received December 8, 1983

The markedly asymmetric pattern of ^1H NMR resonances in hexa-*n*-propylbenzene (1) has been attributed to hindered rotation of the *n*-propyl groups which destroys the equivalence of the α-methylene protons.[1] Our recent findings[2] that ethyl group rotation in hexaethylbenzene and its transition-metal complexes requires activation barriers of less than 12 kcal mol^{-1} seemed inconsistent with this interpretation. We have therefore reinvestigated this problem.

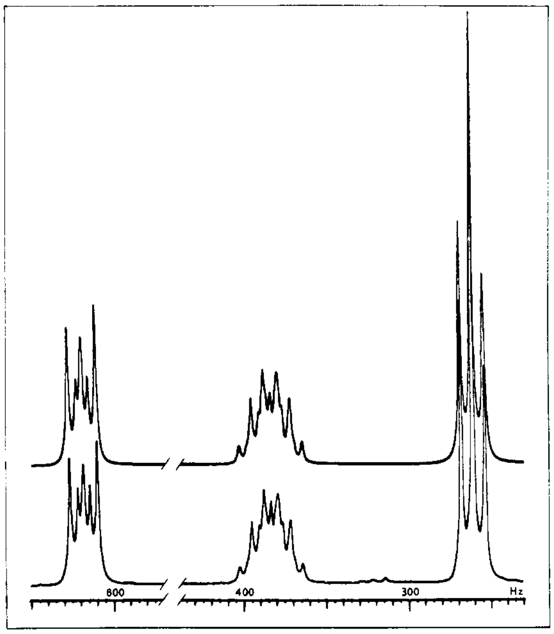


Figure 1. Lower trace: observed 250-MHz ^1H NMR spectrum of 1 in $CDCl_3$ at ambient temperature. The scale is divided into 5-Hz increments. Upper trace: simulated spectrum, $AA'BB'C_3$ spin system.

Table I. ^{1}**H NMR Spectral Parameters for 1 and 2 at Room Temperature**[a]

	δ_A	δ_B	δ_C	$J_{AA'}$	$J_{BB'}$	$J_{AB'}$	J_{AB}	J_{BC}	J_{AC}
1	2.47	1.53	1.04	−13.57	−13.75	12.18	4.82	7.26	<1
2	2.57	1.63	0.93	−12.8	−12.6	8.99	6.26	7.37	<1

[a] Chemical shifts (δ) in ppm relative to Me_4Si. Coupling constants (*J*) in hertz. Subscripts refer to α-methylene (A, A′), β-methylene (B, B′), and methyl (C) protons.

The analysis of $AA'BB'C_3$ spin systems for *n*-propyl derivatives[3,4] is directly applicable to 1 and *n*-propylbenzene (2). The spin system of the *n*-propyl groups in 1 and 2 is described by three chemical shifts and six coupling constants (Table I),[5] and the spin-simulated ^1H NMR spectrum of 1 matches the experimentally observed spectrum (Figure 1). The spectrum of 1 is therefore fully accounted for by the *magnetic* nonequivalence of the α- and β-methylene protons, and there is no need to invoke hindered rotation.[7]

---

(1) Hopff, H.; Gati, A. *Helv. Chim. Acta* **1965**, *48*, 509.

(2) Iverson, D. J.; Hunter, G.; Blount, J. F.; Damewood, J. R., Jr.; Mislow, K. *J. Am. Chem. Soc.* **1981**, *103*, 6073. Hunter, G.; Blount, J. F.; Damewood, J. R., Jr.; Iverson, D. J.; Mislow, K. *Organometallics* **1982**, *1*, 448. Blount, J. F.; Hunter, G.; Mislow, K. *J. Chem. Soc., Chem. Commun.* **1984**, 170. Hunter, G.; Mislow, K. *Ibid.* **1984**, 172.

(3) Schrumpf, G. *J. Magn. Reson.* **1972**, *6*, 243.

(4) Aksnes, D. W.; Støgård, J. *Acta Chem. Scand.* **1973**, *27*, 3277.

(5) Data for the analysis of the $AA'BB'C_3$ spin systems were obtained from degassed $CDCl_3$ (Me_4Si) solutions on a JEOL FX-90Q spectrometer (1 and 2) and on a Bruker WM 250 spectrometer (1). Spin simulations were performed by using the Bruker PANIC simulation program and were iteratively fitted by using several dozen lines. Geminal coupling constants were taken to be negatively signed[6] and were strongly interdependent. The magnitude of the geminal coupling constants was fixed by the observation and assignment of small-intensity lines occurring about the α- and β-methylene signals. J_{AC} as well as any long-range couplings among the six *n*-propyl groups was assumed to be negligible ($J \approx 0$).

(6) Hirst, R. C.; Grant, D. M. *J. Chem. Phys.* **1964**, *40*, 1909 and references therein.

0022-3263/84/1949-2058$01.50/0 © 1984 American Chemical Society