

THE FORMATION OF 1,2-DISELENOL-5-ONE AND 5,6-DIHYDRO-4H-1,3-SELENAZIN-4-ONE DERIVATIVES FROM DIPHENYLCYCLOPROPENONE

Masahiko Takahashi*, Shin-ichi Watanabe, and Tohru Kasai
 Department of Industrial Chemistry, Faculty of Engineering,
 Ibaraki University, Hitachi, Ibaraki 316

Abstract - Reaction of diphenylcyclopropenone (1) with selenoamides or sodium hydrogen selenide afforded 3,4-diphenyl-1,2-diselenol-5-one (3), which was transformed into 4,5-diphenyl-3-hydroxypyrazole (4) on treatment with hydrazine. On the other hand, reaction of 1 with N,N-diphenylselenourea gave 2-(N,N-diphenylamino)-5,6-diphenyl-5,6-dihydro-4H-1,3-selenazin-4-one (6a).

The reaction of diphenylcyclopropenone (1) with carboxamides has been reported to give ring-opened products, O-(2-phenylcinnamoyl)amide derivatives.¹⁾ On the other hand, the reaction of 1 with thioamides gave cyclized products, 5,6-dihydro-4H-1,3-thiazin-4-ones.²⁾ No reaction, however, concerning selenoamides and related compounds has been known. We wish to report the transformation of cyclopropenone into selenium heterocycles by the reaction of 1 with selenoamides and related compounds.

Selenoamides are anticipated to react with 1 in the similar way as thioamides to give 1,3-selenazin-4-ones (2). Unexpectedly, however, two selenium atoms were incorporated into cyclopropenone ring to yield 1,2-diselenole.³⁾ Treatment of 1 with benzoselenoamide or p-methylbenzoselenoamide in refluxing benzene formed the same product in 22% and 27% yields, respectively, which was prepared more conveniently and in better yield (45%) by treating 1 with sodium hydrogen selenide⁴⁾ in ethanol at room temperature. The structure of 3,4-diphenyl-1,2-diselenol-5-one (3)⁵⁾ was elucidated on the basis of the spectral and analytical results. Additional support for the structure 3 was derived from its ring transformation into pyrazole. Upon reaction with

4H-1,3-thiazin-4-one (6b)¹⁰⁾ in 31% yield, which was also obtained directly in 51% yield by refluxing a mixture of 1 and 5b in chloroform. The similarity of the spectral data of 6b to those of 1,3-selenazine mentioned above indicates that its structure is 2-(N,N-diphenylamino)-5,6-diphenyl-5,6-dihydro-4H-1,3-selenazin-4-one (6a).¹¹⁾

Experimental

3,4-Diphenyl-1,2-diselenol-5-one (3). To the ethanolic solution (40 ml) of NaSeH prepared from powdered Se (2.0 g, 25 mmol) and NaBH₄ (1.1 g, 10 mmol) according to the literature,⁴⁾ an ethanolic solution (10 ml) of 1 (2.1 g, 10 mmol) was added under a nitrogen atmosphere. The mixture was stirred at room temperature for 24 h, and the precipitates collected by filtration were extracted with CHCl₃ (50 ml). After the CHCl₃ solution was concentrated and diluted with MeOH, the precipitates formed were collected by filtration to give 3 (1.8 g, 45% yield).

4,5-Diphenyl-3-hydroxypyrazole (4). A methanolic solution (20 ml) of 3 (360 mg, 1.0 mmol) and 100% hydrazine hydrate (100 mg, 2.0 mmol) was refluxed for 5 h. After the precipitates were removed by filtration, the filtrate was evaporated to give solid residue. It was dissolved into CHCl₃ (20 ml) and then the solution was added with a small amount of petroleum ether to give precipitates, which were collected by filtration to give 4 (100 mg, 42% yield).

2-(N,N-Diphenylamino)-5,6-diphenyl-5,6-dihydro-1,3-selenazin-4-one (6a). A mixture of 1 (206 mg, 1.0 mmol) and 5a (275 mg, 1.0 mmol) in CHCl₃ (5 ml) was refluxed for 24 h under a nitrogen atmosphere. After cooling, a small amount of insoluble materials was removed by filtration and the solvent was evaporated. The oily residue was triturated with a small amount of MeOH and the resulting precipitates were filtered off to give 6a (184 mg, 38% yield).

Acknowledgement

The authors are very grateful to Sankyo Co., Ltd., for the mass measurements.

References and Notes

- 1) F. Toda, T. Kataoka, and K. Akagi, Bull. Chem. Soc. Jpn., 44, 244 (1971).
- 2) W. Walter and J. Krohn, Liebigs Ann. Chem., 752, 136 (1971).
- 3) The chemistry of 1,2-diselenole has been scarcely known; R. B. Silverman, "Organic Selenium Compounds: Their Chemistry and Biology", eds. by D. L. Klayman and W. H. H. Gunther, Wiley Interscience, New York, 1973, p. 535.
- 4) D. L. Klayman and T. S. Griffin, J. Amer. Chem. Soc., 95, 197 (1973).
- 5) Compound 3: mp 134-136°C (MeOH-CHCl₃). IR (KBr) cm⁻¹: 1645 1630 1540 1480 1440. NMR (CDCl₃) δ: 7.23 (s, ArH). UV (MeOH) nm (log ε): 224 (sh, 4.30) 272 (4.27) 356 (3.69). MS m/e: 366 (M⁺).
- 6) Compound 4: mp 236-238°C (AcOEt-CHCl₃). IR (KBr) cm⁻¹: 3420 3240 2600 (broad) 1610 1510. UV (MeOH) nm (log ε): 238 (4.16) 264 (sh, 4.06). MS m/e: 236 (M⁺). The mp and spectral data are consistent with those of the literatures; a) P. Gruenanger and P. V. Finzi, Atti Accad. Nazl. Lincei, 31, 128 (1961); Chem. Abstr., 58, 516 (1963). b) D. S. Matterson, J. Org. Chem., 27, 4293 (1962).
- 7) D. S. Breslow and H. Skolnik, "The Chemistry of Heterocyclic compounds", ed. by A. Weissberger, Interscience Publishers, New York, 1966, Vol 21, Part I, p. 403.
- 8) Compound 8: mp 157-159°C (CHCl₃-hexane). IR (KBr) cm⁻¹: 3330 1710 1610 1505 1485. NMR (CDCl₃) δ: 7.67 (s, 1H, CHPh) 7.27-6.93 (m, 2OH, ArH). UV (MeOH) nm (log ε): 297 (4.44).
- 9) Compound 10: mp 115-118°C (CHCl₃-hexane). IR (KBr) cm⁻¹: 1635 1616 1590 1550 1490. NMR (CDCl₃) δ: 7.57 (s, 1H, CHPh) 7.27-7.07 (m, 2OH, ArH) 2.30 (s, 3H, SMe). UV (MeOH) nm (log ε): 222 (sh, 4.44) 250 (sh, 4.29) 308 (4.33).
- 10) Compound 6b: mp 197-198°C (MeOH-CHCl₃). IR (KBr) cm⁻¹: 1648 1590 1465 1445 1348. NMR (CDCl₃) δ: 7.33-6.88 (m, 2OH, ArH) 4.83 (d, 1H, J=4.4 Hz, CHPh) 4.12 (d, 1H, J=4.4 Hz, CHPh). UV (MeOH) nm (log ε): 270 (4.21).
- 11) Compound 6a: mp 183-185°C (MeOH-CHCl₃). IR (KBr) cm⁻¹: 1640 1588 1470 1450 1345. NMR (CDCl₃) δ: 7.53-6.87 (m, 2OH, ArH) 4.93 (d, 1H, J=4.5 Hz, CHPh) 4.24 (d, 1H, J=4.5 Hz, CHPh). UV (MeOH) nm (log ε): 273 (4.25).

Received, 28th July, 1980