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

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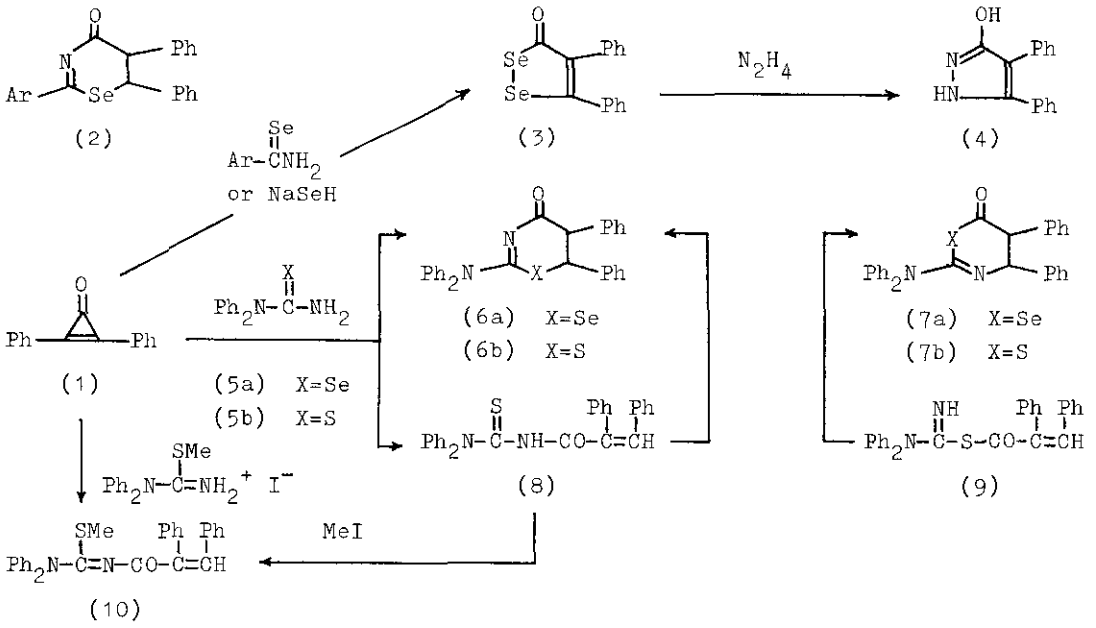
Abstract - Reaction of diphenylcyclopropenone (1) with selenoamides or sodium hydrogen selenide afforded 3,4-diphenyl-1,2-diselenol-5-one (3), which was transformed into 4,5-diphenyl-3-hydroxypyrazole (4) on treatment with hydrazine. On the other hand, reaction of 1 with N,N-diphenylselenourea gave 2-(N,N-diphenylamino)-5,6-diphenyl-5,6-dihydro-4H-1,3-selenazin-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



hydrazine hydrate in refluxing methanol, 3 afforded the known compound, 4,5-diphenyl-3-hydroxypyrazole (4)[6] in 42% yield. Similar transformation of 1,2-dithiol-5-ones and -5-thiones into pyrazole has been described.[7]

Although 3 was also obtained in 4% yield on treatment of 1 with N,N-diphenylselenourea (5a) in a methanolic solution, reflux of a chloroform solution of 1 and 5a for 24 h gave 1,3-selenazine in 38% yield. But, since the spectral and analytical data could not distinguish between 1,3-selenazin-4-one (6a) and its regiosomer, 1,3-selenazin-6-one (7a), preparation of the sulfur analogue 6b was attempted to assign the structure by comparison of the spectral data with those of 1,3-selenazine. Thus, when a methanolic solution of 1 and N,N-diphenylthiourea (5b) was heated for 12 h, a ring-opened product was obtained in 75% yield. The structure of the product was proved not to be S-(2-phenylcinnamoyl) derivative (9) but 1,1-diphenyl-3-(2-phenylcinnamoyl)-2-thiourea (8)[8] as follows; treatment of 1 with 2-methyl-1,1-diphenylisothiourea hydroiodide in the presence of potassium carbonate in ethanol afforded 2-methyl-1,1-diphenyl-3-(2-phenylcinnamoyl)isothiourea (10)[9] in 17% yield, which was identical with the product prepared in 49% yield on treatment of 8 with methyl iodide in the presence of potassium carbonate in acetonitrile. Reflux of a chloroform solution of 8 gave 2-(N,N-diphenylamino)-5,6-diphenyl-5,6-dihydro-

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 $NaBH_4$ (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 atomospher. The mixture was stirred at room temperature for 24 h, and the precipitates collected by filtration were extracted with $CHCl_3$ (50 ml). After the $CHCl_3$ 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 $CHCl_3$ (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 $CHCl_3$ (5 ml) was refluxed for 24 h under a nitrogen atomospher. 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).

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References and Notes

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5) Compound 3: mp 134-136°C (MeOH-$CHCl_3$). IR (KBr) cm^{-1}: 1645 1630 1540 1480 1440. NMR ($CDCl_3$) 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-$CHCl_3$). 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).

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8) Compound 8: mp 157-159°C ($CHCl_3$-hexane). IR (KBr) cm^{-1}: 3330 1710 1610 1505 1485. NMR ($CDCl_3$) δ: 7.67 (s, 1H, C<u>H</u>Ph) 7.27-6.93 (m, 20H, ArH). UV (MeOH) nm (log ε): 297 (4.44).

9) Compound 10: mp 115-118°C ($CHCl_3$-hexane). IR (KBr) cm^{-1}: 1635 1616 1590 1550 1490. NMR ($CDCl_3$) δ: 7.57 (s, 1H, C<u>H</u>Ph) 7.27-7.07 (m, 20H, 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-$CHCl_3$). IR (KBr) cm^{-1}: 1648 1590 1465 1445 1348. NMR ($CDCl_3$) δ: 7.33-6.88 (m, 20H, ArH) 4.83 (d, 1H, J=4.4 Hz, C<u>H</u>Ph) 4.12 (d, 1H, J=4.4 Hz, C<u>H</u>Ph). UV (MeOH) nm (log ε): 270 (4.21).

11) Compound 6a: mp 183-185°C (MeOH-$CHCl_3$). IR (KBr) cm^{-1}: 1640 1588 1470 1450 1345. NMR ($CDCl_3$) δ: 7.53-6.87 (m, 20H, ArH) 4.93 (d, 1H, J=4.5 Hz, C<u>H</u>Ph) 4.24 (d, 1H, J=4.5 Hz, C<u>H</u>Ph). UV (MeOH) nm (log ε): 273 (4.25).

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