

Selenium Heterocycles XIV. (1)
2,6-Diaryltetrahydro-selenopyran-4-ones

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In our previous communications, we have reported that selenium heterocycles could be easily obtained either by using selenium dioxide (3) or by selenium (4). In continuation of our studies on the synthesis and chemistry of selenium heterocycles, it was of interest to use aluminum selenide as the precursor of selenium in the preparation of selenium heterocycles.

Hydrogen sulfide is widely used for the introduction of the sulfur atom in sulfur heterocycles. The preparation of the geometric isomers of 2,6-diphenyltetrahydrothiopyran-4-one was first described in 1925 (5). The configuration and the conformation of this compound as well as its oxygen heterocyclic analogue have recently been reported (6). 2,6-Diphenyltetrahydrothiopyran-4-one has been prepared by interaction of hydrogen sulfide and dibenzylideneacetone in aqueous alcohol containing sodium acetate (5-7). On the basis of this reaction, the preparation of 2,6-diaryltetrahydro-selenopyran-4-one was attempted.

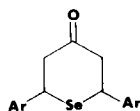
Due to the poisonous character and unpleasant odor of hydrogen selenide as well as its instability, the use of this compound in organic reactions is not convenient. Therefore, it was decided to use aluminum selenide lumps in aqueous ethanol containing sodium acetate in order to generate hydrogen selenide which would in turn react with

the dibenzylideneacetone present in the medium. Since release of hydrogen selenide in boiling aqueous ethanol is slow, three hours refluxing would be necessary to give high yields of 2,6-diphenyltetrahydro-selenopyran-4-one.

Lower yields were obtained when sodium acetate was replaced by acetic acid. Substituted dibenzylideneacetones behaved similarly and afforded high yields of the corresponding 2,6-diphenyltetrahydro-selenopyran-4-ones (See Table I).

The compounds were crystallized from a mixture of benzene-*n*-hexane (50:50) and had sharp melting points without appreciable decomposition. At the temperature 50° or more above the melting point, selenium separated as black microneedles. The structural elucidation of the decomposition product is under investigation. In accordance with this observation, the mass spectra of the compounds showed the abundant fragment ($M - 79$)⁺ resulting

Table I



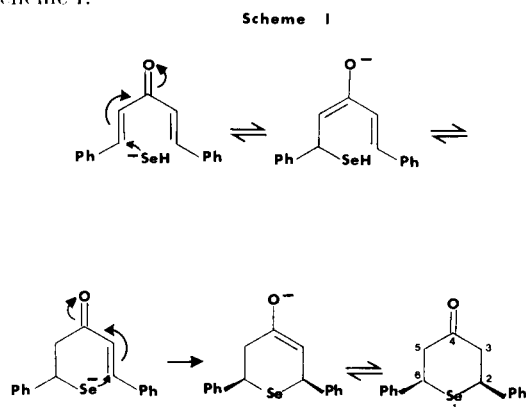
Ar	M.P. °C (a)	Yield %	Formula	C%		H%	
				Calcd.	Found	Calcd.	Found
C ₆ H ₅	108-109	78	C ₁₇ H ₁₆ OSe	64.76	64.81	5.07	4.98
<i>p</i> -ClC ₆ H ₄	138-140	73	C ₁₇ H ₁₄ Cl ₂ OSe	53.12	53.15	3.64	3.68
<i>o</i> -CH ₃ OC ₆ H ₄	122-124	60	C ₁₉ H ₂₀ O ₃ Se	60.80	60.95	5.33	5.41
<i>p</i> -CH ₃ OC ₆ H ₄	168-171	68	C ₁₉ H ₂₀ O ₃ Se	60.80	60.89	5.33	5.29
3,4-OCH ₂ OC ₆ H ₃	188-191	59	C ₁₉ H ₁₆ O ₅ Se	56.57	56.50	3.97	4.01

(a) All compounds were recrystallized from benzene-*n*-hexane (50:50), and had the expected molecular weight by mass spectroscopy.

from the elimination of selenium.

Examination of the nmr spectra of 2,6-diaryltetrahydro-selenopyran-4-ones showed two sets of complex multiplets corresponding to methylene and methine groups in accordance with a nonplanar structure of this new ring system. In contrast to its oxygen and sulfur heterocyclic analogues, fractional crystallization or tlc of 2,6-diaryltetrahydro-selenopyran-4-ones did not show the existence of two geometric isomers. Qualitative kinetic study of the reaction also revealed that only one isomer was formed. A molecular model of 2,6-diphenyltetrahydro-selenopyran-4-one shows clearly that the most stable conformation is a chair ring with both phenyl groups in *cis* and equatorial positions. The coupling constants $J_{2,3ax} = J_{5,6ax} = 12$ cps and $J_{2,3eq} = J_{5,6eq} = 5$ cps between methylene and methine protons are in accordance with the suggested structure.

A possible mechanism for this reaction is demonstrated in Scheme I.



EXPERIMENTAL

Melting points were taken on a Kofler hot stage microscope and are uncorrected. Ir spectra were obtained on a Leitz Model III spectrograph. Mass spectra were recorded on a Varian Mat 111

spectrometer. Nmr spectra were taken on a Varian A60A instrument using tetramethylsilane as the internal standard. Uv spectra were taken on a Varian Techtron 635 spectrometer.

2,6-Diphenyltetrahydro-selenopyran-4-one.

To a refluxing mixture of 4.68 g. (0.02 mole) of pure dibenzylideneacetone and 5.44 g. (0.02 mole) of hydrated sodium acetate in 60 ml. of 90% aqueous ethanol was added 3.5 g. (0.012 mole) of aluminum selenide lumps. After 3 hours under reflux, the reaction mixture was diluted with 400 ml. of water and stored in an ice box for 12 hours. The crude precipitate was filtered, washed with cold water and dried. Purification was achieved by dissolving the crude product in 50 ml. of hot benzene, decolorizing with charcoal to obtain a pale yellow liquid, evaporating 25 ml. of solvent, adding 25 ml. of *n*-hexane and refrigerating until crystallization was complete. The cream colored fine needles (3.2 g.) has a melting point 106-108°. A second crop weighing 1.7 g. was obtained by further addition of 25 ml. of *n*-hexane to the filtrate to give a total 78% yield. Analytically pure 2,6-diphenyltetrahydro-selenopyran-4-one was obtained by repeated crystallization from benzene-*n*-hexane (50:50) m.p. 108-109°. Molecular weight by mass spectrometer *m/e* 315; calculated 315. Uv max (methanol): 222 nm (ϵ 27255). Ir, ν max (potassium bromide): 3335, 1707, 1641, 1496, 1459, 1386, 1245, 1192, 1085, 1027, 807, 762 and 698 cm^{-1} ; nmr τ (deuteriochloroform): 6.82 (m, 4H, CH_2), 4.1 (m, 2H, CH) with coupling constants $J_{2,3ax} = J_{5,6ax} = 12$ cps and $J_{2,3eq} = J_{5,6eq} = 5$ cps; and 2.69 (s, 10H, C_6H_5).

All other 2,6-diaryltetrahydro-selenopyran-4-ones were prepared similarly.

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