Preparation and some properties of 3,5-disubstituted tetrahydro-1,3,5-selenodiazine-2-selenones

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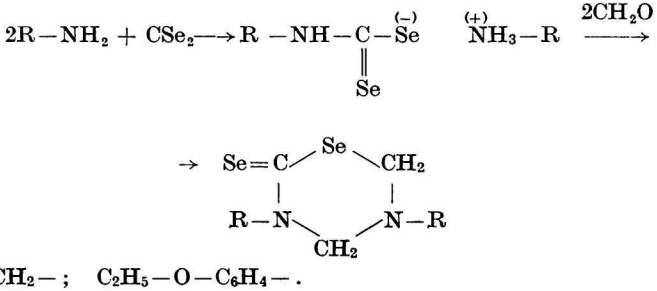
3,5-Disubstituted tetrahydro-1,3,5-selenodiazine-2-selenones have been synthesized from primary amines, carbon diselenide, and formaldehyde. Infrared, ultraviolet, and nuclear magnetic resonance spectra of the title compounds are discussed.

In search for new routes to isoselenocyanates we have focused our attention also on the nucleophilic addition of carbon diselenide to amines. *Barnard* and *Woodbridge* [1] described the preparation of dialkyldiselenocarbamates as the final products of the reaction of carbon diselenide with secondary amines in dioxan at −10°C. The preparation of 1,3-diphenyl selenourea in low yield by the addition of aniline to carbon diselenide was described by *Grimm* and *Metzger* [2]. Higher yields were obtained by *Warner* [3] who treated primary amines with carbon diselenide at reflux.

The synthesis of 3,5-disubstituted tetrahydro-1,3,5-thiadiazine-2-thiones was described by *Ainley* [4] and *Rieche* [5, 6]. These syntheses were based on the addition of carbon disulfide to an amine to give dithiocarbamic acid which was cyclized with another molecule of amine and two molecules of formaldehyde. It was assumed therefore that carbon diselenide might react with primary amines in a similar manner and, consequently, selenodiazines would be formed.

In the present work the conditions of preparation and physicochemical properties of 3,5-disubstituted tetrahydro-1,3,5-selenodiazine-2-selenones have been studied. The synthesis of the compounds under investigation has been realized following the route



R = $C_6H_5-CH_2-$; $C_2H_5-O-C_6H_4-$.

Experimental

Carbon diselenide (b.p. 46°C/51 torr) was prepared according to [7].

Infrared spectra were measured at 3600 − 700 cm^{-1} using a double-beam spectrophotometer UR-20 (Zeiss, Jena). Concentration of the samples in sodium chloride cells

(thickness 0.26 and 0.4 mm) was 0.02 and 0.1 mol l^{-1}. The instrument was calibrated against a polystyrene foil. Ultraviolet spectra (210—400 nm) were measured at 20 ±1°C in a 10-mm cell using a Perkin—Elmer spectrophotometer Model 402. Concentration of the solutes in methanol, acetonitrile, and *n*-heptane was 6×10^{-5} mol l^{-1}. Nuclear magnetic resonance spectra were obtained with a Tesla BS 487 A spectrometer (at 80 MHz in $CDCl_3$) using hexamethyldisiloxane as the internal standard.

3,5-Disubstituted tetrahydro-1,3,5-selenodiazine-2-selenones

Amine (0.01 mole) in benzene (100 ml) was poured under nitrogen into a three-necked flask (250 ml) equipped with a condenser and mechanical stirrer. The flask was cooled with tap water and under vigorous stirring carbon diselenide (0.85 g; 0.005 mole) in benzene (50 ml) was added. Some turbidity and discolouration of the reaction mixture had developed during the addition and when this was complete, formaldehyde (2.4 g; 0.03 mole, 37% water solution) was added and stirring was continued for 1 hr at room temperature. The solution was filtered off, dried with anhydrous sodium sulfate, and concentrated. The product was purified by elution from a column of alumina using petroleum ether—chloroform 4 : 1. Crystallization from chloroform—petroleum ether gave 3,5-dibenzyltetrahydro-1,3,5-selenodiazine-2-selenone (0.7 g, 34.3%); m.p. 122—123°C.

For $C_{17}H_{18}N_2Se_2$ (408.3) calculated: 50.01% C, 4.44% H, 6.86% N; 49.64% C, 4.21% H, 6.84% N.

3,5-Di-(4-ethoxyphenyl)tetrahydro-1,3,5-selenodiazine-2-selenone (0.15 g, 6.5%) was prepared in a similar manner and had m.p. 135—136°C.

For $C_{19}H_{22}N_2O_2Se_2$ (468.3) calculated: 48.73% C, 4.69% H, 5.98% N; found: 48.99% C, 4.72% H, 6.12% N.

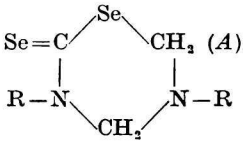
Discussion

The method of *Rieche et al.* [5, 6], when applied to the selenium analogs, gives much lower yields of the desired products than was the case with 3,5-disubstituted tetrahydro-1,3,5-thiadiazine-2-thiones. This is caused, on the one hand, by the polymerization of carbon diselenide and, on the other one, by instability of the diselenocarbamate salt which readily decomposes to give isoselenocyanate, amine, and hydrogen selenide. Isoselenocyanate formed may then react with amine to give selenourea. We have therefore modified Rieche's method by conducting the reaction in an inert atmosphere and by using dilute solution of carbon diselenide. Under these conditions it was possible to isolate 34% of 3,5-dibenzyltetrahydro-1,3,5-selenodiazine-2-selenone. The yield of the corresponding 4-ethoxy derivative was only 6.5% of the theory. Aromatic amines bearing electron-withdrawing substituents (4-nitroaniline, 4-aminoacetophenone, 4 bromoaniline) were used in the synthesis; however, only negative results were obtained.

The skeleton characteristic of 3,5-disubstituted tetrahydro-1,3,5-selenodiazine-2-selenones manifests itself in the i.r. spectrum as three intense absorption bands. These, by analogy to the corresponding sulfur derivatives [8, 9] correspond to $=N-C(=Se)-$ arrangement (Table 1; Fig. 1). Ultraviolet spectra of the compounds under investigation show an absorption maximum at 330 nm shifted bathochromically as compared to the thiadiazines [10], the difference in the case of the benzyl derivative being 42 nm. The bathochromic effect is obviously attributed to different electronegativity and polarizability of the atoms of selenium and sulfur and thus to facilitated excitability of the

Table 1

Spectral data of 3,5-disubstituted tetrahydro-1,3,5-selenodiazine-2-selenones



(*A*)

(*B*)

R	$\nu(>N-C=Se)$ [cm^{-1}]	λ_{max}/log ε [nm] MeOH	CH_3CN	n-C_7H_{16}	δ
$C_6H_5-CH_2-$ (C_1, C_2)	1505 (*I*) 1330 (*II*) 1110 (*III*)	 329 3.92	 331 3.88	 339 3.79	4.47 (*A*) 4.24 (*B*) 5.40 (C_1), 3.7 (C_2)
$C_2H_5O-C_6H_4-$ (*D*)	1530 (*I*) 1315 (*II*) 1121 (*III*)	 335 3.82	 337 3.88		5.04 (*A*) 5.00 (*B*) 3.97, 1.33 (*D*)

chromophoric $-C\overset{Se}{\underset{Se-}{}}$ system when compared to the of $-C\overset{S}{\underset{S-}{}}$. The second absorption band (at 250 nm) which, in the case of thiadiazines is markedly and in the selenium analogs poorly pronounced.

The solvent effect upon λ_{max} has also been examined. The absorption band at 330 nm shows apparently pronounced negative solvatochromy (Fig. 2; Table 1). The extent of this phenomenon is given by the possibility of the formation of "N" and "Se" conjugation and thus different stability of the effective charges on the atoms of nitrogen and selenium [10].

In addition to the resonance signals of the substituents at the positions 3 and 5, the n.m.r. spectra of 3,5-disubstituted tetrahydro-1,3,5-selenodiazine-2-selenones show also

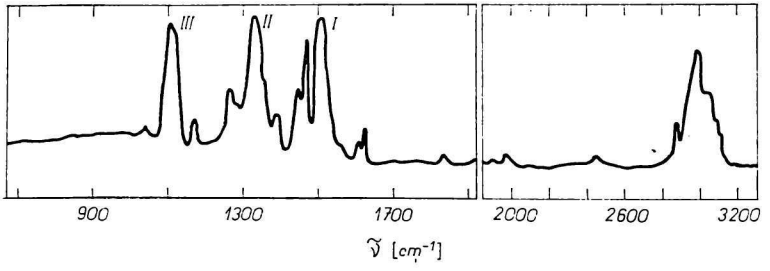


Fig. 1. Infrared spectra of 3,5-dibenzyltetrahydro-1,3,5-selenodiazine-2-selenone in chloroform.

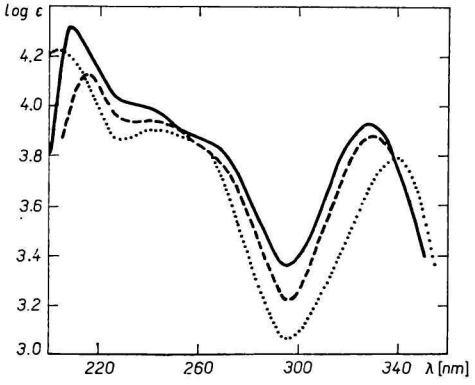


Fig. 2. Ultraviolet spectra of 3,5-dibenzyltetrahydro-1,3,5-selenodiazine-2-selenone.
———— methanol;
– – – – acetonitrile;
. . . . . *n*-heptane.

the signals of the skeletal methylene groups in the range of 5δ. On the basis of the study of analogous sulfur model compounds bearing different substituents in positions 3 and 5 [9] the individual signals were attributed to the corresponding methylene protons.

References

1. Barnard, D. and Woodbridge, D. T., *J. Chem. Soc.* ***1961***, 2922.
2. Grimm, H. G. and Metzger, H., *Ber.* ***69***, 1356 (1936).
3. Warner, J. S., *J. Org. Chem.* ***28***, 1642 (1963).
4. Ainley, A. D., Davies, W. H., Hudgeon, H., and Harland, J. C., *J. Chem. Soc.* ***1944***, 147.
5. Rieche, A., Martin, D., and Schade, W., *Arch. Pharm.* (Weinheim) ***293***, 957 (1960).
6. Rieche, A., Martin, D., and Schade, W., *Arch. Pharm.* (Weinheim) ***296***, 770 (1963).
7. Ives, D. J. G., Pittman, R. W., and Wardlaw, W., *J. Chem. Soc.* ***1947***, 1080.
8. Rao, C. N. R. and Venkataraghavan, R., *Spectrochim. Acta* ***18***, 541 (1962).
9. Bernát, J., *Thesis.* P. J. Šafárik University, Košice, 1973.
10. Kristian, P. and Bernát, J., *Collect. Czech. Chem. Commun.* ***34***, 2952 (1969).

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