

SYNTHESIS, CHARACTERIZATION AND MICROBIAL EVALUATION OF NEW UNSATURATED SELENIUM COMPOUNDS

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ABSTRACT

A new series of unsaturated selenide sulfides, selenonyl sulfides and selenonyl sulfones were synthesized from (E)-2-bromo-1,2-diphenyl-1-phenylselenyl ethylene and the structures of these compounds were confirmed by IR, ¹H NMR and MASS spectral analysis. The compounds were screened for antibacterial and antifungal activities.

KEY WORDS: (E)-2-bromo-1,2-diphenyl-1-phenylselenyl ethylene, (E)-2-bromo-1,2-diphenyl-1-phenylselenonylethylene, selenyl sulfides, selenonyl sulfides, selenonyl sulfones.

1. INTRODUCTION

Organo selenium compounds are important group of compounds due to their broad spectrum of biological and pharmacological activities such as bactericidal, fungicidal, antiparasitic, hypnotics, analgesic, tranquilizing, anti-inflammatory, antihistamine, anticancer properties (Daniel, 1973).

Biological studies carried out on vinyl sulfonyl compounds (Raaseh, 1961), mercapto halo ethylene sulfone derivatives (Bluestone and Bimber, 1964) and bis(organosulfonyl)ethylenes (Johnston, 1961; Gerjovich, 1961) revealed that they can be used as effective fungicides to protect seeds. Although some reports (Benati, 1963; Naidu and Peeran, 1975; Naidu, 1978; Ghose, 1982; Ghose, 1991) have appeared on the synthesis of cis and trans sulphide-sulfones and di sulfones, the data available on selenium analogues is scanty.

In the present investigation we have synthesized a new series of ethylenic selenide sulfides, selenonyl sulfides and selenonyl sulfones.

2. MATERIALS AND METHODS

Melting points were determined in open capillaries on Mel-Temp apparatus, Laboratory devices Cambridge, U.S.A and are uncorrected. IR spectra were recorded using KBr pellets on Perkin-Elmer SPECTRUM 100 FT-IR spectrophotometer. ¹H NMR spectra were recorded at 400 MHz on a BRUKER-400 spectrometer and their chemical shifts are reported in δ ppm with respect to TMS as an internal standard.

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Mass spectra were recorded on Micro Mass ESI-TOF Mass Spectrometer.

The addition of arenesulfonylhalides (Calo, 1969; Di, 1965; Calo, 1965) and areneselenylhalides (Chierici and Montanari, 1957) to acetylenes were reported to yield primarily the trans-addition products. During the present investigation a (E)-2-bromo-1,2-diphenyl-1-phenylselenyl ethylene was prepared by the trans addition of phenyl selenyl bromide to diphenyl acetylene. When (E)-2-bromo-1,2-diphenyl-1-phenylselenyl ethylene was treated with sodium salts of arene thiols, nucleophilic displacement of bromine took place with retention of configuration (Naidu and Peeran, 1975; Montanari, 1956; Modena and Todesco, 1959) and gave selenyl sulphides and these on oxidation with hydrogen peroxide gave corresponding selenonyl sulfones.

(E)-2-bromo-1,2-diphenyl-1-phenylselenyl ethylene on oxidation with hydrogen peroxide in acetic acid afforded (E)-2-bromo-1,2-diphenyl-1-phenylselenonylethylene. When (E)-2-bromo-1,2-diphenyl-1-phenyl selenonylethylene was treated with sodium salts of arene thiols, nucleophilic displacement of bromine occurred resulting in the formation of selenonyl sulfides and these on oxidation with hydrogen peroxide gave corresponding selenonyl sulfones which were obtained earlier and there was no depression in the melting points.

Preparation of (E)-2-bromo-1,2-diphenyl-1-phenylselenyl ethylene from diphenylacetylene

A solution of 10 g (0.056 moles) of diphenylacetylene in 250 ml of ethyl acetate was taken

in 500ml round bottom flask fitted with a reflux condenser protected with calcium chloride guard tube. To this solution 13.45g (0.057 moles) of phenylselenenylbromide was added at once and the mixture was refluxed until the colourless solution was obtained. The ethyl acetate solution was washed with water, sodium bicarbonate and again with water, dried over anhydrous Na_2SO_4 and ethyl acetate was evaporated to get a residue which was recrystallised several times from 95% ethanol to give 15g (65%) of (E)-2-bromo-1,2-diphenyl-1-phenylselenenyl ethylene m.p. 73-75°C.

General procedure for Nucleophilic Displacement

To a solution of NaOEt prepared from 0.23 g (0.01 mol) of Na and absolute EtOH (25 ml), arene thiol (0.01 mol) and alkyl bromide (0.01 mol) dissolved in absolute EtOH (85 ml) was added. The solution was refluxed for 8 hr, cooled and the product separated was filtered. Recrystallization of crude product from 95% EtOH gave colourless crystals. The yields varied in the range of 70-80%. Melting points, IR, ^1H NMR and MASS data were given in Table-I.

General procedure for oxidation

Into a solution of sulfide or selenide (0.3 g) in warm glacial AcOH (25 ml), 30 % of H_2O_2 (3 ml) was added and the solution was boiled gently for 1 hr. The mixture was allowed to stand for 1 hr and then poured over crushed ice. The product separated was filtered and recrystallized from 95 % EtOH to give colourless needles. The yields varied in the range of 71-85 %. Melting points, IR, ^1H NMR and MASS data were given in Table-I.

Antibacterial activity

The synthesized compounds were screened for their antibacterial activity against two gram positive bacteria, *Bacillus subtilis* & *Staphylococcus aureus* and two gram negative bacteria, *Escherichia coli* & *Salmonella typhi* using Ampicillin sodium as standard (Table-II).

Antifungal activity

The synthesized compounds were screened for their antifungal activity against *Candida albicans* & *Aspergillus niger* using Clotrimazole as standard (Table-III).

3.RESULTS AND DISCUSSION

The IR spectra of all the compounds showed a weak band (Nakanishi,1966) in the region of 1637-1638 cm^{-1} due to the C=C stretching frequency (Table-

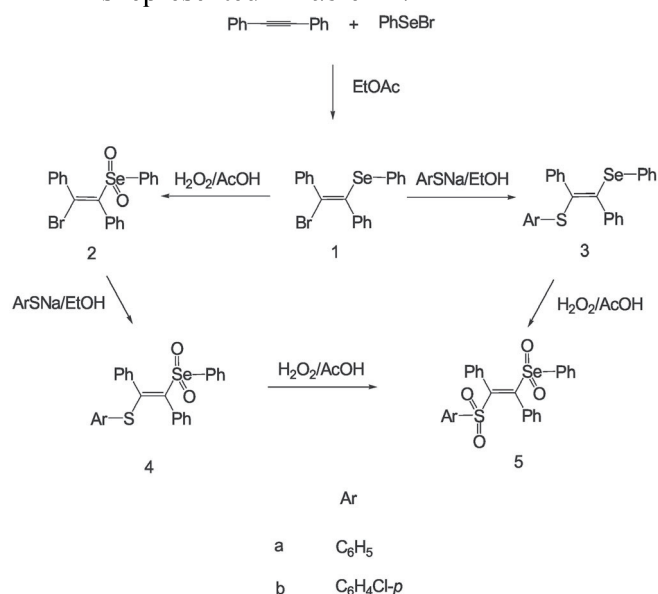
I). The compounds 3-5 showed a prominent band (Ham,1960) in the region of 1069-1094 cm^{-1} for S-aryl group and the sulfones 5 showed sharp asymmetric and symmetric stretching frequencies (Bavin,1960) in the region 1281-1302 cm^{-1} and 1144-1154 cm^{-1} respectively due to sulfone group. All the compounds showed a medium band (Barraclough,1969) in the region of 560-626 cm^{-1} for Se-C group and the selenones 2, 4, 5 showed sharp asymmetric and symmetric stretching frequencies (Paetzold and Bochmann,1968) in the region 882-889 cm^{-1} and 909-922 cm^{-1} respectively due to selenone group.

The NMR spectra of these compounds was observed in expected region. Aromatic protons appeared as multiplets at δ 6.8-8.0 ppm.

The mass spectra of all the compounds showed expected mass and the characterisation data is furnished in Table-I.

Most of the compounds displayed good inhibition of growth against gram positive and gram negative bacteria listed above. The compounds 3b, 4a, 4b showed good results against gram positive bacteria and 5a and 5b against gram negative bacteria. The remaining compounds have also showed moderate or weak antibacterial activity. The zone of inhibition in mm is represented in Table-II.

The compounds 3a, 3b, 4b, 5b exhibited a high antifungal activity. The remaining compounds have also shown moderate antifungal activity. The zone of inhibition in mm is represented in Table-III.



SCHEME-I

4. CONCLUSION

A new series of unsaturated selenides and selenones were prepared. The data suggests that the synthesized compounds with minor modification in the chemical structure may serve as a very promising basis for the development of effective antibacterial and antifungal agents.

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