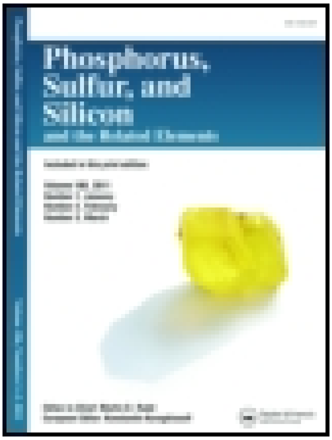

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SYNTHESIS AND CHARACTERIZATION OF MESOIONIC 1,3,4-TRIAZOLIUM-2-SELENOLATES

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SYNTHESIS AND CHARACTERIZATION OF MESOIONIC 1,3,4-TRIAZOLIUM-2-SELENOLATES

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A new improved synthesis of mesoionic 1,3,4-triazolium-2-selenolates is described and three new members of the series thus obtained. They were characterized by Elemental Analysis, I.R., ^{1}H and ^{13}C NMR and Mass Spectra. The data obtained have been discussed. The chemical shifts at C-2 in the negative region and at C-5 in the positive region were compared with data for corresponding mesoionic-2-thiolates. Our data were also compared with available data for some related classes of mesoionic compounds.

Keywords: mesoionic; selenolates; thiolates

1. INTRODUCTION

In the late 19th century, Büsch *et col.*[1,2] synthesized a series of compounds now classed as mesoionic but postulated at the time as bicyclic compounds. Later studies[3,4] established that the “endo-thiotriazolines” (1 or 2) were in fact the mesoionic 1,3,4-triazolium-2-thiolates (3).

A number of methods are described for the synthesis of mesoionic 3 *viz,* i) anhydro acylation of 1,4-disubstituted thiosemicarbazides[5] (4); ii) heating of 4-acyl-1,4-disubstituted thiosemicarbazides[6] (5); iii) reaction of

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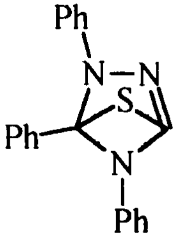
* Corresponding Author.



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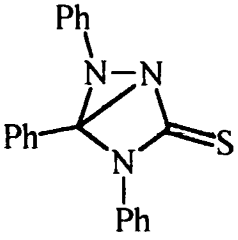

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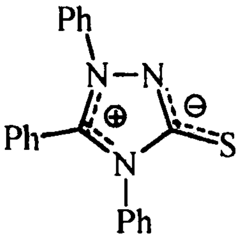
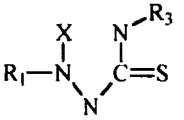
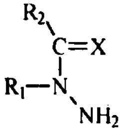


3

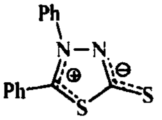
N-aminoamidines (6) with thiophosgene[6,7]; iv) reaction of N-aminoamidines or N-thioacylhydrazines[8] (7) with isothiocyanates or carbon disulfide-dicyclohexylcarbonylimide and v) reactions of mesoionic 1,3,4-thiadiazolium-5-thiolates (8) with primary amines[5,7].



(4) X = H; (5) X = COR$_2$



(6) X = NR3; (7) X = S



(8)

Recently Stefaniak *et al.* synthesized some mesoionic 1,3,4-triazolium-2-selenolates and carried out a multi-nuclear NMR study (^{1}H, ^{13}C, ^{15}N, ^{14}N and ^{77}Se)[9,10]

In the present work we describe a new and convenient procedure for the synthesis of the title compounds and give the preparation of three new derivatives (9), (10), (11).

The procedure required the synthesis of 1,4-diphenyl-selenosemicarbazides; from which the mesoionic compounds were obtained by reaction with the appropriate aroyl chlorides.

In a study of the ^{13}C NMR spectra of C-2 and C-5 in the three compounds we related the chemical shifts to the nature of the C-5 substituents In addition the data were compared with those of corresponding mesoionic thiolates (9′), (10′), (11′).

2. EXPERIMENTAL SECTION

Materials and Methods

Mass spectra were obtained on a Finnigan GCQ Mat type quadrupole-ion trap spectrometer. IR spectra were obtained on a Bruker IFS66 spectrometer with the sample in a KBr disc. ^1H and ^{13}C NMR spectra were obtained on a VARIAN UNITY PLUS 300 MHz spectrometer – the samples being dissolved in DMSO-d_6 with TMS as reference. Elemental Analysis was carried out on a Perkin Elmer Elemental Microanalyser. The melting points were determined on a Kofler hot-plate apparatus combined with a Carl-Zeiss microscope and are uncorrected.

Preparation of 1,4-diphenylselenosemicarbazide

A solution of phenyl isoselenocyanate (4.55 g; 25.0 mmole) in 30 mL of anhydrous toluene was added dropwise at 60° to a solution of phenylhydrazine (2.70 g, 25.0 mmole) in 50 ml of anhydrous toluene in a round-bottomed flask with mechanical stirring. A white precipitate formed after the addition of about half of the phenyl isoselenocyanate, however stirring was continued for 2 hours. After cooling, the suspension was filtered at reduced pressure. The crystals were washed sequentially with the minimum quantities of anhydrous toluene and anhydrous diethyl ether, then dried at reduced pressure. A 78% yield of crystalline product was obtained with M.p. 148–149°C (lit.[11] 149–152°C). In the mass spectrum the molecular ion was obtained: $M^+ = 290$ (29.48%).

General method of preparation of 1,4-diphenyl-5-aryl-1,3,4-triazolium-2-selenolates

1,4-diphenylselenosemicarbazide (1.0 g, 3.3 mmol) was suspended in 10 ml of dioxane with magnetic stirring. An equimolar quantity of benzoyl chloride (comp. 9); p-chloro-benzoyl chloride (comp. 10) or cinnamoyl chloride (comp. 11) was then added in small amounts. After 18 hours of stirring the solution was neutralized with triethylamine, leading to the formation of a crystalline precipitate. The solid was collected, washed with small portions of dioxane, diethyl ether and recrystallized from ethanol.

1,4,5-triphenyl-1,3,4-triazolium-2-selenolate (9)

Elemental analysis: calculated for $C_{20}H_{15}N_3Se$; C, 58.10; H, 3.87; N, 10.18 %; found: C, 58.00; H, 3.73; N, 10.19%; IR spectrum ν (cm^{-1}) 3049 (ν C_{Ar}-H), 1561 (ν NC-Se^-, selenolate), Mass spectrum m/z (%) 296 (100 $(M\text{-}SeH)^+$), ^1H NMR spectrum δ (ppm) 7.30 – 7.45 (m – 15H, aromatic); ^{13}C NMR spectrum δ (ppm) 160.8 (C-2), 149.9 (C-5) and M.p. 258 – 260°C.

1,4-diphenyl-5-p-chlorophenyl-1,3,4-triazolium-2-selenolate (10)

Elemental analysis: calculated for $C_{20}H_{14}ClN_3Se$; C, 53.90; H, 3.35; N, 9.39 %; found: C, 53.89; H, 3.37; N, 9.35%; IR spectrum ν (cm^{-1}) 3064 (νC_{Ar}-H), 1505 (νNC-Se^-, selenolate), Mass spectrum m/z (%) 330 (100 $(M\text{-}SeH)^+$) and 332 (37 $(M\text{-}SeH)^+$), ^1H NMR spectrum δ (ppm) 7.39 – 7.49 (m – 14H, aromatic); ^{13}C NMR spectrum δ (ppm) 160.8 (C-2), 149.9 (C-5) and M.p. 236 – 238°C.

(E) – 1,4-diphenyl-5-styryl-1,3,4-triazolium-2-selenolate (11)

Elemental analysis: calculated for $C_{22}H_{17}N_3Se$; C, 65.67; H, 4.20; N, 10.40 %; found: C, 65.68; H, 4.20; N, 10.38 %; IR spectrum ν (cm^{-1}) 3064 (ν C_{Ar}-H), 1637 (ν H-C=C-H), 1500 (ν NC-Se^-, selenolate), Mass spectrum m/z (%) 322 (100 $(M\text{-}SeH)^+$), ^1H NMR spectrum δ (ppm) 6.48 (d, 1H vinylic, J = 16.3 Hz); 6.52 (d, 1H vinylic, J = 16.3 Hz); 7.16 (d – 2H, aromatic); 7.28 (d – 2H, aromatic); 7.54 – 7.76 (m – 10H, aromatic) ^{13}C NMR spectrum δ (ppm) 162.9 (C-2), 147.0 (C-5) and M.p. 258 – 260°C.

3. RESULTS AND DISCUSSION

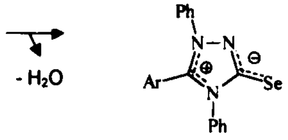
The synthesis of the title compounds involves three steps (Scheme 1). In the first step benzoisonitrile reacts with elemental selenium forming phenylisoselenocyanate (I). In the next step, this reacts with phenylhydrazine forming 1,4-diphenylselenosemicarbazide (II). In the third step this reacts with an aroyl chloride to give the title compounds by cyclodehydration.

These are presumed to be the thermodynamic products as in the corresponding triazolium-thiolate series (Scheme 1).

1^{a} step - $Ph\overset{+}{N}\equiv\overset{-}{C} + Se^{0} \rightarrow Ph\text{-}N{=}C{=}Se$ (I)

2^{a} step - Reaction of (I) with $Ph\text{-}NH\text{-}NH_2 \rightarrow Ph\text{-}NH\text{-}NH\text{-}C(Se)\text{-}NH\text{-}Ph$ (II)

3^{a} step - Reaction of (II) with Ar-COCl

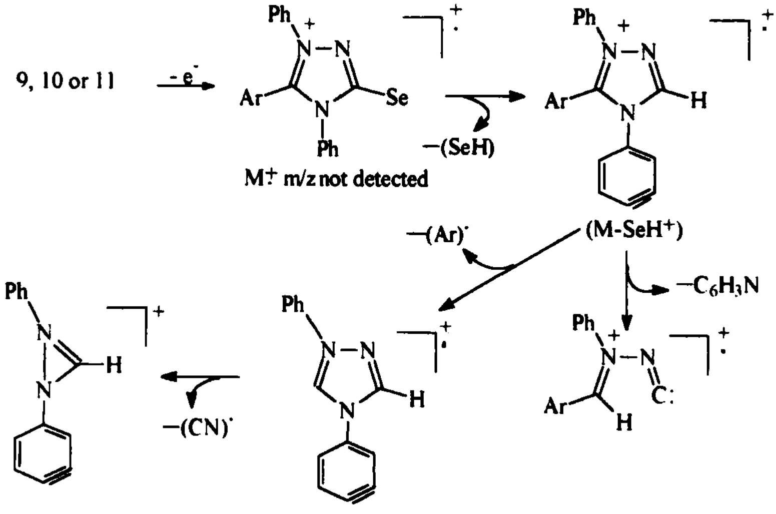


(9) Ar = Ph; (10) Ar = pCl-C_6H_4; (11) Ar = styryl

SCHEME 1

In the IR spectrum, the key peaks are at 3060 cm^{-1} (C_{Ar}-H str.) and 1500 –1560 cm^{-1} (C-Se). For compound 10 there is a peak at 1092 cm^{-1} for C_{Ar}-Cl and for compound 11 at 1637 cm^{-1} for -CH=CH- str.

All the compounds show similar behaviour on electron impact – the base peaks corresponding to $[M\text{-}SeH]^{+}$. Scheme 2 show this and key subsequent fragmentations.



SCHEME 2

The ^{1}H NMR spectra show chemical shifts for the aromatic protons in the range 7.16 – 7.54 ppm. For compound 11 there are in addition doublets at 6.12 and 6.48 ppm attributed to the vinylic protons.

The ^{13}C NMR spectra were interpreted according to the comparative method used by Stefaniak *et al*[9,10], Bartels-Keith *et al.*[12] and by Miller and Montanari[13].

Comparing the 1,3,4-triazolium-2-selenolates (9, 10 and 11) and 2-thiolates (9′, 10′ and 11′) one observes high-field shifts 8.8 to 9.4 ppm at C-2. In contrast at C-5 there is a low-field shift of 2.8. to 1.6. Bartels-Keith *et al.*[12] made a similar observation with the 1,3,4,5-tetrazolium-2-selenolates (12) and 2-thiolates (12′). The chemical shift for the 2 carbon atom was 165.8 ppm for the selenolate and 175.5 ppm for the thiolate ($\Delta\delta = 7.7$ ppm).

The mildly greater difference in the triazolium series is presumably related to the differential effect of a ring-N and Ar-C at position 5: there should also be some differences in the levels of the LUMO as between the two series. Analogously, one may expect some difference in the HOMO, affecting the chemical shifts at C-2.

We have also compared 1,5-diphenyl-4-methyl-1,3,4-triazolium-2-selenolate (13) with 1-phenyl-4,5-dimethyl,1,3,4-triazolium-2-selenolate (14)[10]. This change had almost no effect on the C-5 chemical shift and but little effect on the C-2 chemical shift: $\Delta\delta$ values of 0.2 ppm an a 1.0 ppm respectively. Similar results were obtained when comparing the corresponding methyl-selenium salts (13′) (14′)[10].

In summary (a) the change of the 2-heteroatom, S by Se, results in a small up-field chemical shift at C-2 and small down-field shift at C-5; (b) a change of substituent at C-5, Ph by Me, mildly affects the chemical shifts at C-2. These differences appear to relate to changes in the field (electrostatic) effects across the ring *i.e.* between the positive and negative regions (see Scheme 3).

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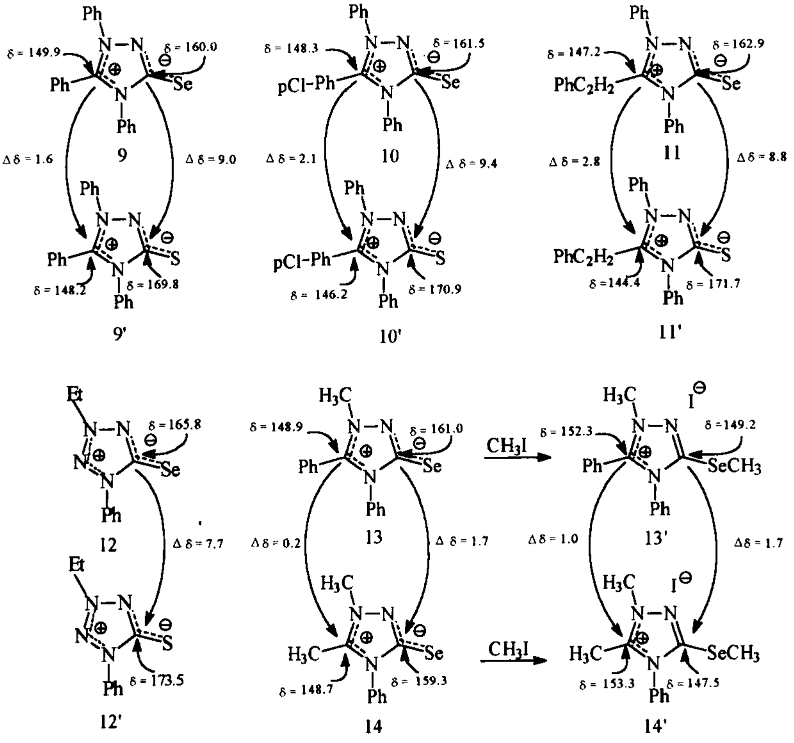

SCHEME 3

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