Indian Journal of Chemistry
Vol. 45B, March 2006, pp. 758-761

Mass spectral analysis and X-ray structure of diethyl 2-[aryl(4-aryl-1,2,3-selenadiazol-5-yl)methyl]malonate

Sivaperuman Saravanan[a], Shanmugam Muthusubramanian*[a] & Kurt Polborn[b]

[a] Department of Organic Chemistry, Madurai Kamaraj University, Madurai 625 021, India

[b] Department of Chemistry, Ludwig-Maximilians University, Butenandt Street 5-13, D-81377 Munich, Germany

E-mail: muthumanian2001@yahoo.com

Received 5 May 2005; accepted (revised) 13 September 2005

The mass spectra of diethyl 2-[aryl(4-aryl-1,2,3-selenadiazol-5-yl)methyl]malonate have been studied by electron impact method using high resolution mass spectrometry. The X-ray structure of a representative compound is also investigated.

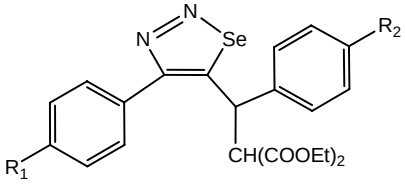
Keywords: Diethyl malonate; mass spectra; X-ray structure

IPC: Int.Cl.[7] C 07 D

Compounds containing 1,2,3-selenadiazole and 1,2,3-thiadiazole moieties are well known for their pharmacological properties like antifungal[1,2] and antibacterial[3,4] activities. Some of the 1,2,3-selenadiazole derivatives exhibit antimicrobial[5], antihaemostatic[6] and insecticidal[7] activities. Recently, we have reported the synthesis and characterization of 1,2,3-selenadiazoles[8] with additional functional groups, which can be further modified to give additional heterocyclic rings, starting from the diethyl malonate adducts of different chalcones.[9] This paper describes the mass spectral features of these compounds and the X-ray structure of a representative case.

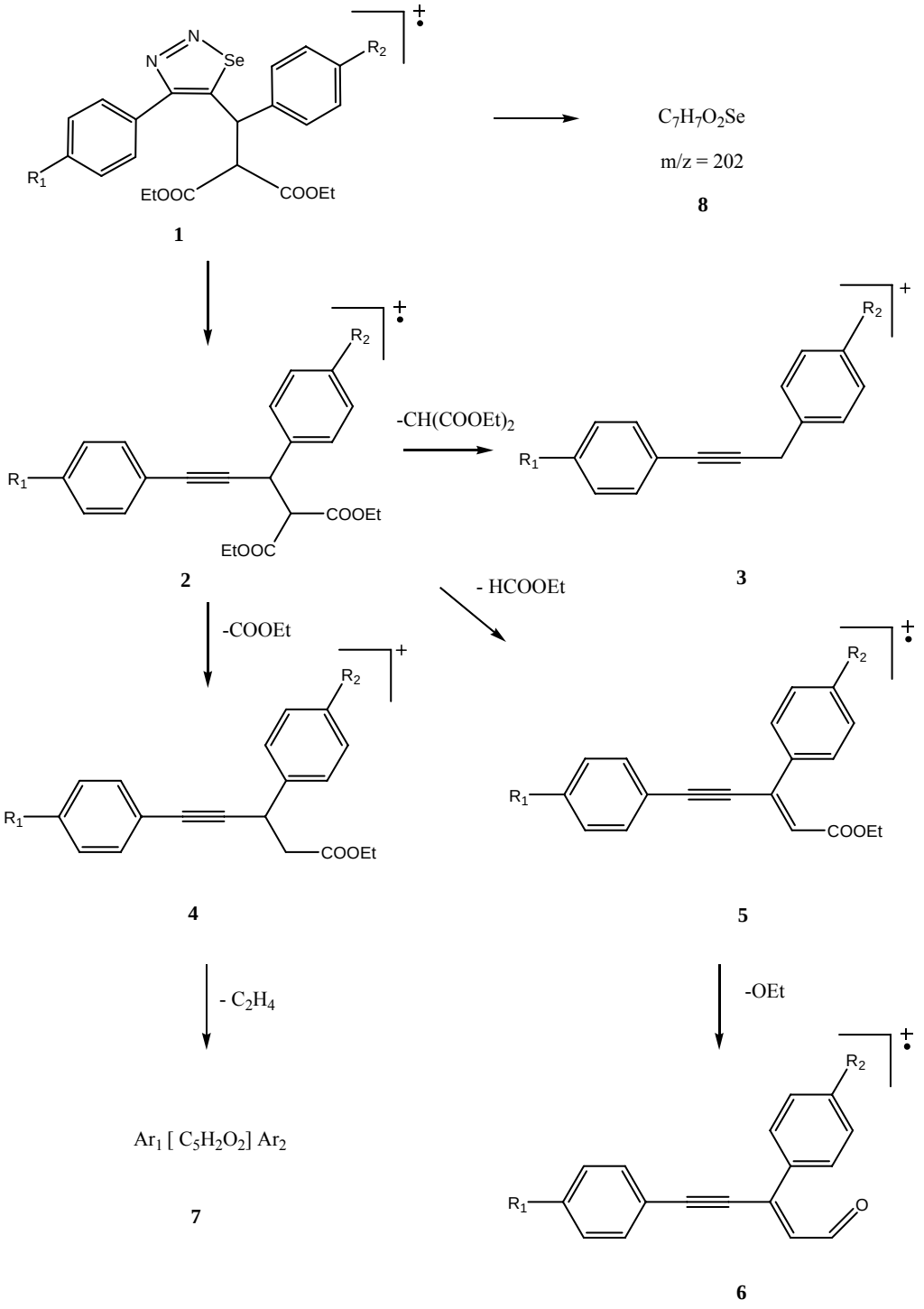
The mass spectra of the title compounds **1** (**Figure 1, Table I**) have been recorded by EI method. Though the M^+ peaks have been observed for ring fused selenadiazoles[10], the molecular ion peak is not observed in **1**. The first fragment that can be identified in these cases is that due to the alkyne unit **2** (**Scheme I**), obtained by the elimination of a nitrogen molecule and selenium atom. This fragment appears with poor intensity. It should be noted that for linear system, under thermal or photochemical conditions, selenadiazoles are well known to undergo elimination to give alkynes[11]. The most intense peak noticed in these cases is due to the species **3**. This is the base peak in many cases except for **1b** and **1e**. The relative stability of the radical $CH(COOEt)_2$ could be the reason for the radical ion **2** to loose this radical to give the positively charged species **3**. However in **1b** and **1e,** the species **2** rather prefers to loose HCOOEt to give the unsaturated radical cation **5**, which is the base peak. In addition, common peaks at m/z 202 and 189 appear in all the spectra. The other fragments formed are accounted in **Scheme I**.

The results of X-ray analysis of diethyl 2-[(4-methylphenyl)(4-phenyl-1, 2, 3-selenadiazol-5-yl)-methyl]malonate **1b**[12] are presented in **Table II**. The ORTEP diagram is shown in **Figure 2**. The two aryl rings, one in the heterocyclic ring and the other in the side chain, are almost parallel to each other. The



	R_1	R_2
a	H	H
b	H	CH_3
c	H	OCH_3
d	H	Cl
e	H	NO_2
f	Cl	H
g	Cl	CH_3
h	Cl	OCH_3
i	Cl	Cl

Figure 1



Scheme I

vicinal hydrogens are perfectly *anti* to each other in the solid state as noticed in solution.

Using Hyperchem 7.5, we have arrived at the minimized energy structure for the selenadiazole **1b** by semi empirical PM3 method. The single point energy of the selenadiazole **1b** is calculated as E = 5799.8434 with Grad 0.096 and the molecule converge in 403 cycles 874 points. The theoretically minimized structure is compared with that in solid state in **Table III (Figure 3)**. The torsional angle between the carbethoxy group and the aryl ring in the gauche geometry is calculated to be 71.12°, while the

Table I — Mass and IR spectral data of compounds **1a-i**

Compd	Mass fragment (% abundance)							IR (cm^{-1})			
	M^+	Alkyne 2	3	4	5	6	7	ν_{C-H}	$\nu_{C=O}$	ν_{C-O}	$\nu_{N=N}$
1a	457.38 (Not observed)	350.9 (1%)	191.1 (100%)	277.7 (32%)	276.3 (63%)	231 (33%)	249.1 (46%)	2974, 2927	1755	1279	1444
1b	471.41 (Not observed)	364.5 (8%)	205.2 (89%)	Not observed	290.8 (100%)	245.1 (37%)	263 (70%)	2981, 2927	1730	1251	1444
1c	487.41 (Not observed)	380.5 (8%)	221.1 (100%)	307.8 (38%)	306.5 (49%)	261.3 (20%)	279.2 (36%)	2978, 2929	1724	1252	1457
1d	491.83 (Not observed)	384.4 (2%)	225.0 (100%)	311.6 (39%)	310.3 (62%)	265.1 (17%)	283.1 (54%)	2977, 2927	1724	1251	1469
1e	502.38 (Not observed)	395.1 (14%)	235.9 (14%)	321.7 (56%)	320.6 (100%)	275.5 (36%)	293.4 (8%)	2981, 2929	1720	1253	1467
1f	491.83 (Not observed)	384.3 (2%)	225.0 (100%)	311.6 (38%)	310.3 (69%)	265.0 (22%)	283.1 (52%)	2983, 2933	1754	1277	1467
1g	505.85 (Not observed)	398.4 (4%)	239.0 (100%)	325.7 (42%)	324.4 (72%)	279.5 (24%)	297.2 (53%)	2981, 2922	1751	1276	1467
1h	521.85 (Not observed)	414.1 (4%)	255.1 (100%)	341.7 (42%)	340.4 (49%)	295.2 (18%)	313.2 (40%)	2978, 2929	1749	1271	1465
1i	526.27 (Not observed)	418.6 (2%)	259.0 (100%)	346.9 (41%)	345.7 (47%)	299.5 (8%)	317.1 (55%)	2981, 2927	1752	1278	1469

Table II — Crystal data and structural refinement for **1b**

Empirical formula	$C_{23}H_{24}N_2O_4Se$
Formula weight	471.40
Temperature	295(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 9.351(4) Å alpha = 102.75(3) deg
	b = 10.957(4) Å beta = 101.87(3) deg
	c = 12.427(5) Å gamma = 110.12(3) deg
Volume	1109.6(8) A^3
Z	2
Density (calculated)	1.411 Mg/m^3
Absorption coefficient	1.723 mm^-1
F(000)	484
Crystal size	0.53 × 0.40 × 0.10 mm
Theta range for data collection	2.48 to 23.98 deg
Index ranges	-10<=h<=10, -12<=k<=0, -13<=l<=14
Reflections collected	3686
Independent reflections	3477 [R(int) = 0.0299]
Absorption correction	Psi-scans
Max and min transmission	0.9942 and 0.4090
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3477 / 0 / 275
Goodness-of-fit on F^2	1.003
Final R indices [I>2sigma(I)]	R1 = 0.0578, wR2 = 0.1464
R indices (all data)	R1 = 0.0854, wR2 = 0.1732
Extinction coefficient	0.008(3)
Largest diff peak and hole	0.628 and -0.696 e.A^-3

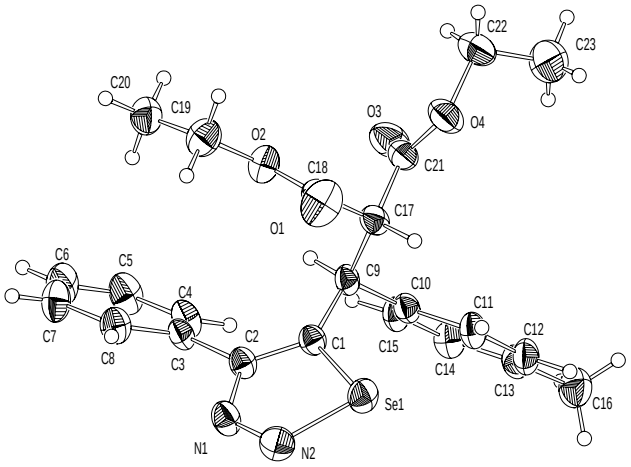
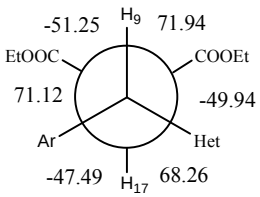


Figure 2 — ORTEP diagram of diethyl 2-[(4-methylphenyl) (4-phenyl-1,2,3-selenadiazol-5-yl)methyl]malonate **1b**

Table III — Selected dihedral angle [°] for **1b**

Entry	Selected atoms	Dihedral angle	
		By PM3 model	From X-ray
1	H9-C9-C17-H17	-169.86	-174.88
2	C10-C9-C17-H17	-47.49	-56.19
3	C10-C9-C17-C21	71.12	61.40
4	H9-C9-C17-C21	-51.25	-57.30
5	H9-C9-C17-C18	71.94	65.92
6	C1-C9-C17-C18	-49.94	-51.05
7	C1-C9-C17-H17	68.26	68.16
8	C1-C2-C3-C4	33.29	44.79
9	N1-C2-C3-C8	34.70	40.48

PM3



X-RAY

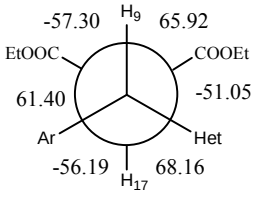


Figure 3 — Selected dihedral angle in **1b**

observed one in the solid state is relatively small, 61.40° (**Table III**, entry 3). The aryl ring is out of plane from the attached heterocyclic ring in the solid state than predicted by the PM3 calculation.

Experimental Section

The compounds **1a-i** were prepared according to a procedure[8] starting from diethyl malonate adduct of 3-aryl-1-aryl-2-propen-1-one **1a,** viscous liquid; **1b**: m.p. 73-74°C; **1c**: m.p. 82°C; **1d**: m.p. 98°C; **1e**: m.p. 136°C; **1f**: m.p. 104°C; **1g**: m.p. 91°C; **1h**: m.p. 128°C; **1i**: m.p. 102°C. GC/MS spectra were recorded on a Thermo Finnigan gas chromatograph (RTX-5 capillary column) with a Finnigan mass spectrometer operating on the electron impact mode (70 eV). IR spectra were recorded on a JASCO FT-IR instrument using KBr pellets.

The single crystal X-ray data were collected on a Nonius MACH3 kappa diffractometer with Mo K_α radiation (λ = 0.71073 A°). The structure was solved by direct methods from SHELXS-86 and refined by full matrix least squares on F^2 by SHELXL-93. All H atoms were placed in calculated positions with C-H = 0.93-0.98 A° and included in the refinement in a riding-model approximation, with U_{iso} values constrained to be 1.5 U_{eq} of the carrier atom for methyl hydrogen atoms and 1.2 U_{eq} for the remaining H atoms. Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 251421. Copies of the data can be obtained, free of charge, by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK (email: data_request@ccdc.cam.ac.uk; fax: +44 1223 336033).

Acknowledgement

The authors thank the UGC, New Delhi for assistance under the DRS program for the GC-MS facility. One of the authors (S S) is grateful to the CSIR, New Delhi for SRF.

References

1 Moawad E B, Yousif M Y & Metwally M A, *Pharmazie,* 44, **1989,** 820.
2 Kuroda K, Uchikurohane T, Tajima S & Tsubata K, *US Pat, US 6,166,054; Chem Abstr,* 134, **2001**, 38255.
3 El-Kashef H S, E-Bayoumy B & Aly T I, *Egypt J Pharm Sci,* 27, **1986,** 27.
4 Sasaki T, *Japan Pat,* 70, 27, 573; *Chem Abstr*, 74, **1971**, 3629.
5 El-Bahaie S, Assy M G & Hassanien M M, *Pharmazie,* 45, **1990,** 791.
6 Patil B M, Badami B V & Puranik G S, *Indian J Heterocycl Chem,* 3, **1994,** 193.
7 Padmavathi V, Sumathi R P & Padmaja A, *J Ecobiol,* 14, **2002,** 9.
8 Saravanan S & Muthusubramanian S, *Phosphorus Sulfur Silicon Relat Elem,* 179, **2004**, 2411.
9 Michael A & Ross J, *J Am Chem Soc,* 55, **1933**, 1632.
10 Reddy D B, Reddy A S & Padmavathi V, *Indian J Chem,* 37B, **1998,** 1194.
11 Arsenyan P, Oberte K, Pudova O & Lukevics E, *Chem Heterocycl Compd,* 38, **2002**, 1437.
12 Crystal data have been deposited to CCDC, number 251421.