Synthesis, Characterization and Crystallographic Studies of Three 2-Aryl-3-methyl-4-aryl-1,3-thiazolium-5-thiolates

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Abstract: Mesoionic 2,4-diphenyl-3-methyl-1,3-thiazolium-5-thiolate, 2-(4′-chlorophenyl)-3-methyl-4-phenyl-1,3-thiazolium-5-thiolate and 2-(4′-chlorophenyl)-3-methyl-4-(4′-isopropyl-phenyl)-1,3-thiazolium-5-thiolate were synthesized via *N*-methyl-*C*-arylglycines, involving a one-pot 1,3-dipolar cycloaddition/cycloreversion sequence. The two latter mesoionic compounds are new, as are some of the intermediates. Compounds were fully characterized, while X-ray diffraction studies of the three mesoionic compounds also confirmed their structures and our definition of mesoionic compounds. In particular they showed that the mesoionic ring system has two regions in which there is electron and charge delocalization separated by what are essentially single bonds. The data also suggested a tendency for the 2- and 4-aryl groups to lie in the plane of the mesoionic ring.

Key words: mesoionic, betaine, 1,3-thiazolium-5-thiolates, synthesis, crystallography

Earlier papers[1,2] have given firm support for our refined definition[3] of mesoionic compounds viz., 'Mesoionic compounds are planar five-membered heterocyclic betaines with at least one side-chain whose α-atom is also in the ring plane and with dipole moments of the order of 5D ($1D = 3.33564 \times 10^{-30}$ cm^{-1}). Electrons are delocalized over two regions separated by what are essentially single bonds. One region which includes the α-atom of the side-chain is associated with the HOMO and negative π-charge whereas the other is associated with the LUMO and positive π-charge'.

This is equivalent to indicating that mesoionic compounds are not aromatic although strongly stabilized by electron and charge delocalization. Figure 1 shows a convenient generic structure.

We have since amplified our comments and supporting data[4,5] in papers dealing with the non-aromatic character of mesoionic compounds and with their behavior as amphiphilic heterocyclic betaines. Their special character means they have a wide range of biological activity.[6] Furthermore, the special character of mesoionic compounds results in them showing great promise in the development of photonic devices based on their second and third-order non-linear optical properties.[3,7,8]

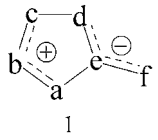

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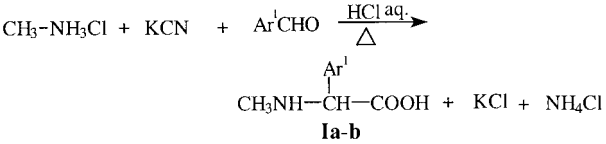
Figure 1

We have synthesized and made crystallographic studies of three mesoionic compounds belonging to the class of 1,3-thiazolium-5-thiolates, viz., 2,4-diphenyl-3-methyl-1,3-thiazolium-5-thiolate (**2**), 2-(4′-chlorophenyl)-3-methyl-4-phenyl-1,3-thiazolium-5-thiolate (**3**) and 2-(4′-chlorophenyl)-3-methyl-4-(4′-isopropyl-phenyl)-1,3-thiazolium-5-thiolate (**4**). We concluded that mesoionic 1,3-oxazolium-5-olates would be especially suitable as key intermediates in view of their ability to engage in 1,3-dipolar cycloaddition/cycloreversion reactions. We carried out the following four-step reaction sequence, in which the 3rd and 4th steps were carried out together in a one-pot reaction. We prepared the three 1,3-thiazolium-5-thiolates by this route, two (**3** and **4**) of which had not previously been reported in the literature (Scheme 1). Some of the intermediates in the reaction sequence are also novel (**I-b**, **II-b** and **II-c**). The sequence is outlined as follows:

The first step required the preparation of *N*-methyl-*C*-arylglycines [**I**; **Ia**: $Ar^1 = C_6H_5$, **Ib**: *p*-(*i*-Pr)C_6H_4] from selected aromatic aldehydes by a Strecker reaction with methylammonium chloride followed by hydrolysis (Equation 1).



Equation 1

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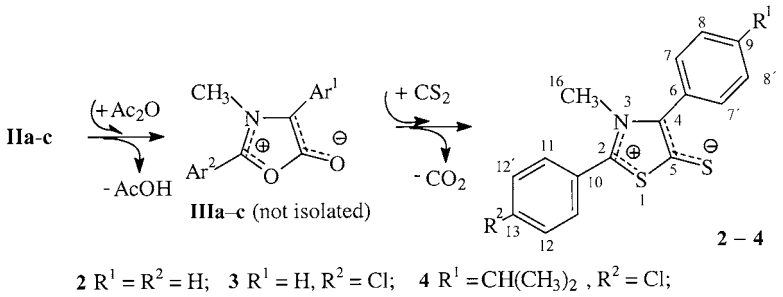
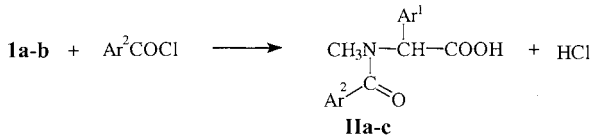


Scheme 1 Preparation of mesoionic 1,3–thiazolium-5-thiolates.

Intermediates **1a**,**b**, as shown in Equation 2, were subjected to aroylation to furnish **IIa–c** [**IIa**: $Ar^1 = Ar^2 = C_6H_5$; IIb: $Ar^1 = C_6H_5$, $Ar^2 = p$-Cl-C_6H_4; **IIc**: $Ar^1 = p$-(i-Pr)C_6H_4, $Ar^2 = p$-ClC_6H_4]



Equation 2

The final two steps involve the cyclodehydration of the intermediates **IIa–c** to 1,3-oxazolium-5-olates **IIIa–c** and their in situ 1,3-dipolar cycloaddition/cycloreversion reactions with CS_2 to form 1,3–thiazolium-5-thiolates **2**–**4**.

All the products gave satisfactory chemical analyses. The principal characteristic of the IR spectra is the C–H stretch of the 3-methyl group at 2920 cm^{-1}. The C16–N3 symmetric and asymmetric stretch frequencies at 1430 cm^{-1} and 1450 cm^{-1} are another important feature. The frequency of the thiolate bond stretch is less certain although Pretsch et al.[9] have suggested 1300 cm^{-1} for the exocyclic C–S^- stretch.

Specific to the 4-(4′-isopropylphenyl) compound are the doublet peaks at 1399 cm^{-1} and 1380 cm^{-1} (see ref.[10]).

Mass spectral data support the proposed structures. Scheme 2 shows the fragmentation pattern for 2,4-diphenyl-3-methyl-1,3-thiazolium-5-thiolate which serves well for all the compounds *mutatis mutandis*.

Both ^1H and ^{13}C NMR spectra are useful for the determination of structure, especially the chemical shifts of the aliphatic groups are diagnostic. In the intermediates **Ib**, **IIb**, and **IIc** the protons of the methyl group linked to N3 have chemical shifts at $\delta = 3.36$, 2.67, and 2.75 ppm, respectively. In the mesoionic compounds **2**, **3**, and **4**, there is a down-field shift to $\delta = 3.64$, 3.63, and 3.60 ppm, respectively as a result of the positive charge on N3. The hydrogen atoms of the attached benzene rings have chemical shifts between 7.33 and 7.66 ppm. Specifically for the 4-(4′-isopropylphenyl) compound, the isopropyl group is characterized by a doublet at 1.24 ppm representing the six hydrogen atoms and by a septet at 2.91 ppm for the tertiary hydrogen. The principal chemical shifts of the new intermediates and mesoionic compounds are shown in Tables 1 and 2.

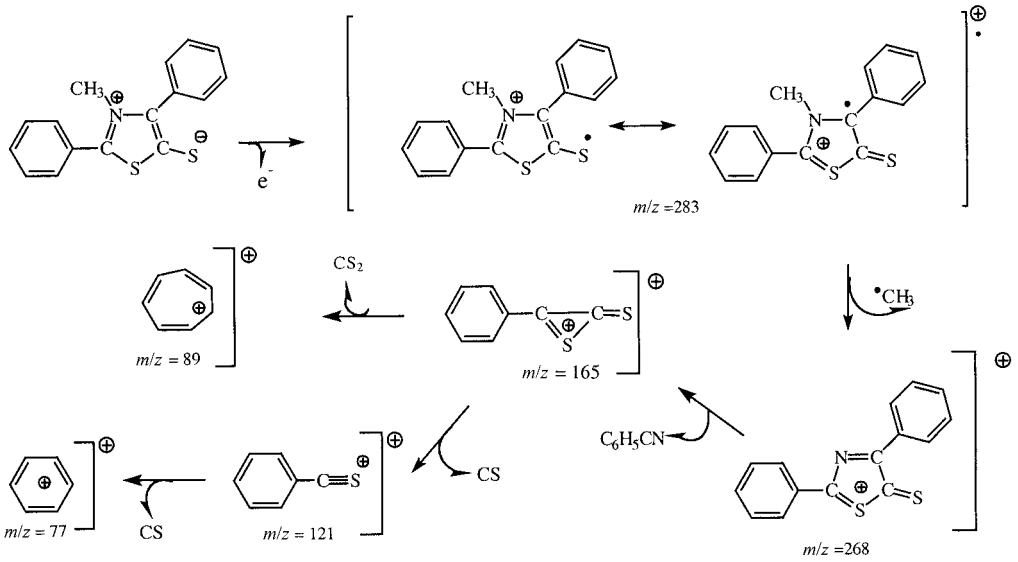
For the ^{13}C NMR spectra (compounds **2**–**4**) we refer to the chemical shifts of those carbon atoms which most help to elucidate the structures. The three peaks at ca 170, 150, and 140 ppm are attributed to C5, C2, and C4 respectively. The methyl group linked to N3 is characterized by a peak at 40 ppm.[11] The reason that C4 is at high field compared with C5; although both are in the negative region of

Table 1 Principal Chemical Shifts in the ^{13}C NMR Spectrum of the New Intermediate Compounds

Compd	CH_3N	N–*C*=O	COO^-	$(CH_3)_2CH$	$CH(CH_3)_2$	Ar–*C*H	C_{Ar}–Cl	C_{Ar}–*i*-Pr
Ib	33.4	–	169.2	23.9	31.1	63.2	136.1	150.5
IIb	35.1	171.8	173.7	–	–	61.8	–	–
IIc	34.9	171.9	174.9	23.8	33.7	60.8	135.2	149.5

Table 2 Principal Chemical Shifts in the ^{13}C NMR Spectrum of the Mesoionic Compounds

Compd	C2	C4	C5	C6	C9	C13	C14	C15–15′	C16
2	154.3	140.7	159.8	129.8	129.3	131.3	–	–	40.3
3	152.6	141.2	160.7	129.2	128.8	137.9	–	–	40.5
4	152.7	141.4	159.4	126.9	149.9	135.2	33.9	23.8	40.6



Scheme 2 Mass spectrum fragmentation pattern for 2,4-diphenyl-3-methyl-1,3-thiazolium-5-thiolate.

the mesoionic ring can be related to the significant partial double bond character of the carbon-thiolate bond (C5–S5).

Specifically for 4-(4′-isopropylphenyl) the isopropyl group is characterized by peaks at 33.6 ppm for C14 and 24.0 ppm for C15 and C15′.

Selected values of bond length, taken from the crystallographic data are shown in Table 3 and these are compared with selected standard values of single and double bonds,[12] shown in Table 4. The comparison is illustrated by formulas **IV** and **V** (Figure 2).

The molecular structures of the title compounds are shown in Figure 2 and the dihedral angles are shown in Table 5.

The crystallographic data confirm that there are two distinct regions separated by what are essentially single bonds; whereas in the regions, which include the HOMO and LUMO and comprise C4–C5–S5 and S1–C2–3 respectively all the bonds have orders between single and double bonds. The specific values in the HOMO and LUMO regions enable us to suggest that the bond orders of C2–N3 and C4–C5 may be a little greater than those of

Table 4 Standard Bond Lengths of Selected Single and Double Bonds

Bond	Length	Bond	Length
C–C	1.48	C=C	1.34
C–N	1.45	C=N	1.27
C–S	1.75	C=S	1.64
N–N	1.41	N=N	1.23

Table 3 Selected Bond Lengths for the Three 1,3-Thiazolium-5-thiolates

Compound	Bond	C4–C5	C4–N3	C2–N3	C2–S1	C5–S1	C5–S5
2		1.37	1.40	1.33	1.70	1.75	1.70
3		1.36	1.38	1.33	1.68	1.74	1.70
4		1.38	1.38	1.33	1.70	1.77	1.68
Average value		**1.37**	**1.39**	**1.33**	**1.69**	**1.75**	**1.69**

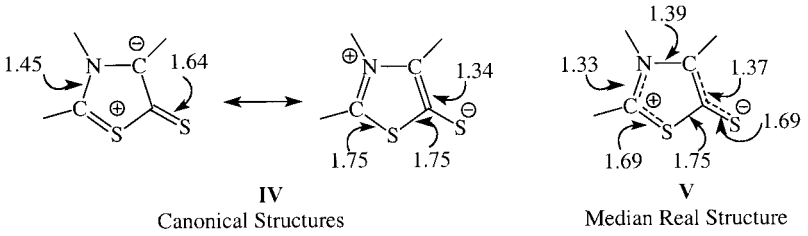


Figure 2 Comparison of canonical and real structures for a 1,3-thiazolium-5-thiolate.

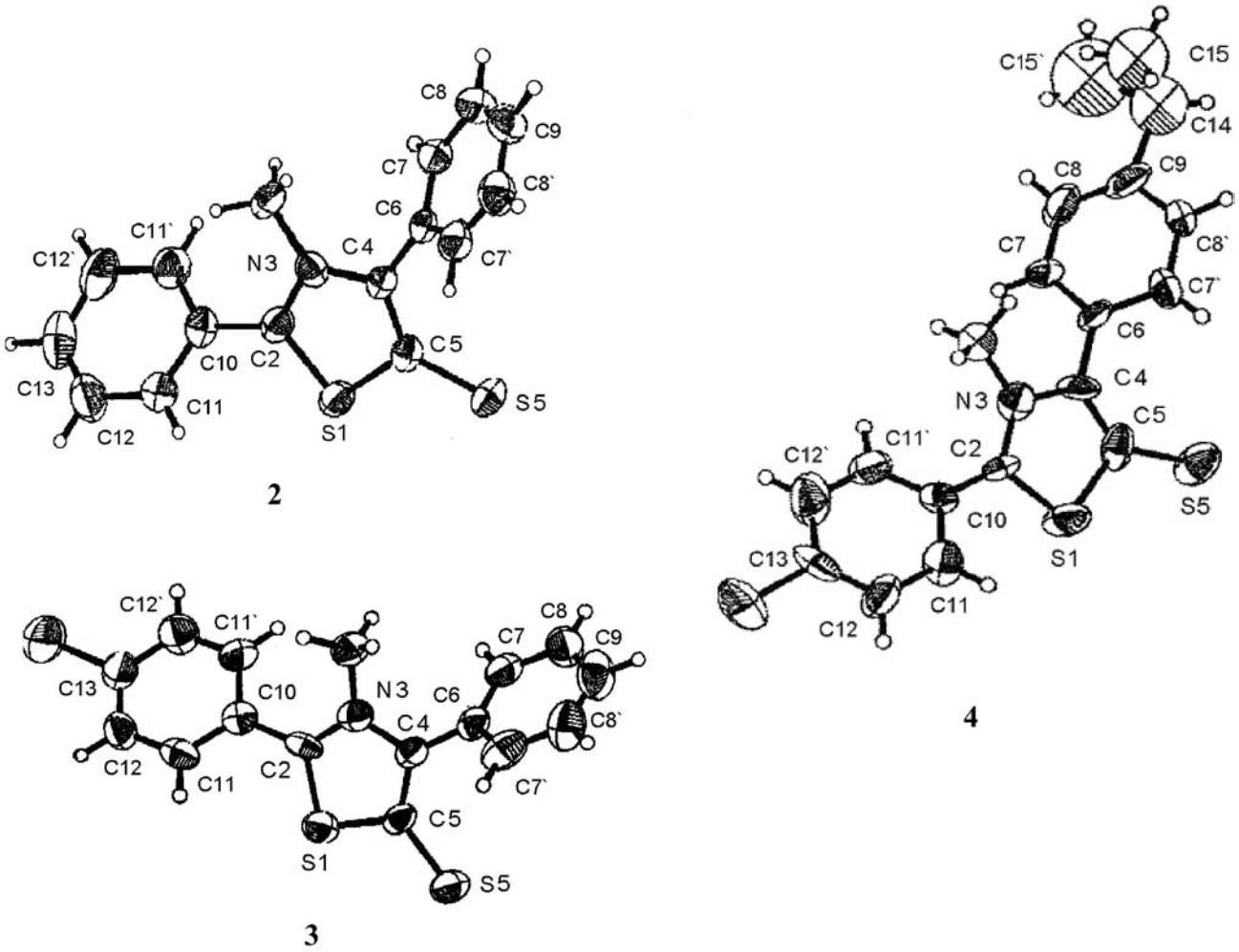


Figure 3 Molecular structures of the three mesoionic compounds.

Table 5 Dihedral Angles (°) Between Planes

Compound	Plane[a]	Plane	Dihedral Angle[b]
2	1	2	137.28 (0.09)
	2	3	126.90 (0.10)
	1	3	32.62 (0.17)
3	1	1	34.6 (0.60)
	2	3	51.9 (0.60)
	1	3	27 (0.10)
4	1	2	32.79 (0.63)
	2	3	48.12 (0.42)
	1	2	24.69 (0.90)

[a] Plane 1 – S1, C2, N3, C4, C5, S5, plane 2 – C10, C11, C11′, C12, C12′, C13, plane 3 – C6, C7, C7′, C8, C8′, C9.
[b] E.S.D's in parentheses.

C4–C5 and C5–S5. This implies that a substantial part of the overall positive charge may be associated with the N atom and a substantial part of the overall negative charge may be associated with S5. Nevertheless some negative charge should be associated with C4. These facts are relevant to the specific bond lengths S1–C5 and C4–N3. The value for S1–C5 is the same as the standard value for a C–S bond whereas that for C4–N3 is a little shorter than that a standard C–N bond. This mild bond shortening is attributed to the fractional positive and negative charges on N3 and C4. The crystallographic studies show further that in the title compounds even the attached benzene rings deviate little from the planarity of the mesoionic ring. This is not universal in mesoionic compounds however since there may be steric inhibition of such planarity in some cases.[13] The tendency to global planarity in the title compounds may also be in part related to the high values of the hyperpolarizabilities, which correlate with the non-linear optical properties. As a contribution to the discussion we have used the AM1 method implemented in the Hyperchem programme to calculate the optimal structure for one of these compounds, viz 2-(4′-chlorophenyl)-3-methyl-4-phenyl-1,3-thiazolium-5-thiolate and also for 2-(4′-chlorophenyl)-3-phenyl-1,3,4-triazolium-5-thiolate. For the former, the overall geometry is indeed close to planarity – as verified in the present study. In the latter, the aromatic rings are calculated to be perpendicular to each other. The curves representing the electrostatic potentials, shown in Figure 4, are closely related to their planarities.

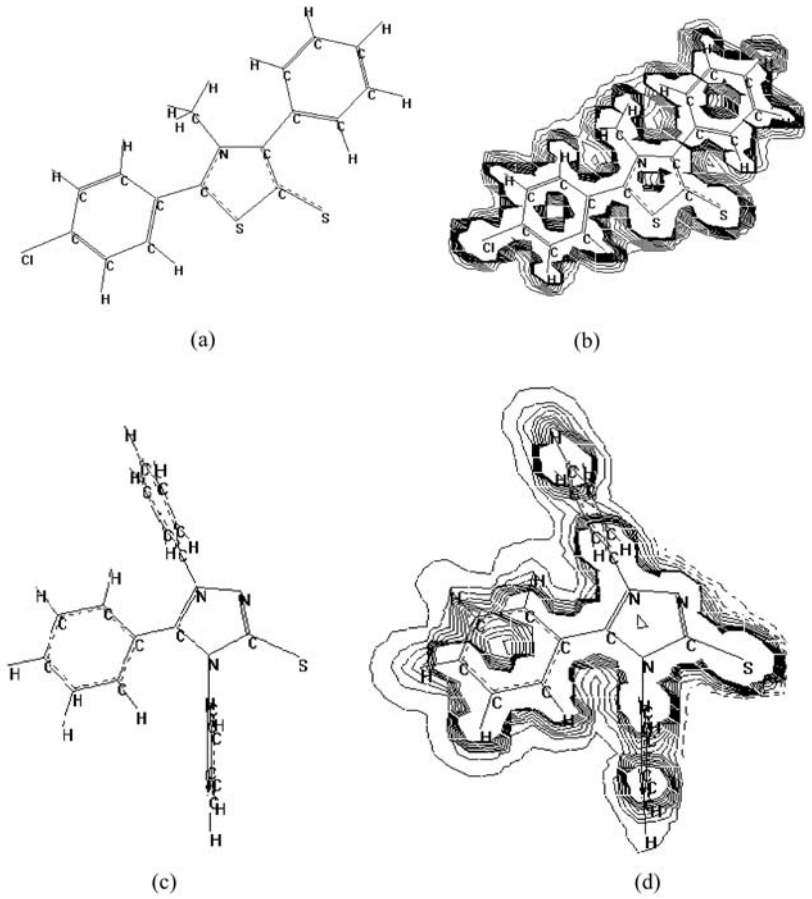


Figure 4 (a) Structure of mesoionic 2-(4′-chlorophenyl)-3-methyl-4-phenyl-1,3-thiazolium-5-thiolate, projected on the plane of the mesoionic ring; (b) Lines of force representing the electrostatic potential; (c) Structure of mesoionic 2-(4′-chlorophenyl)-3-phenyl-1,3,4-triazolium-5-thiolate, projected onto the plane of the mesoionic ring; (d) Lines of force representing the electrostatic potential. The geometry was optimized by the AM1 method, implemented in the *Hyperchem* programme.

Mass spectra were obtained on a Finnigan GCQ Mat type quadrupole-ion trap spectrometer. IR spectra were obtained on a Bruker IFS66 spectrometer. ^{1}H and ^{13}C NMR spectra were obtained on a Varian Unity Plus 300 MHz spectrometer 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.

N-methyl-*C*-arylglycines; General Procedure

KCN (12.50 g, 250 mmol) and methylammonium chloride (16.87 g, 250 mmol) were dissolved in distilled H_2O (100 mL). An equimolar quantity of the aromatic aldehyde in MeOH (100 mL) was added in portions with vigorous stirring and the reaction continued for 2 h. H_2O (250 mL) was added and the resulting mixture then added to toluene (250 mL). The toluene phase was separated then extracted with aq HCl (6 N, 3 × 100 mL). The combined acid extract was refluxed for 8 h giving the desired product in the form of white crystals on cooling. These were filtered off, washed with $CHCl_3$ and air-dried.

N-Methyl-*C*-phenylglycine (Ia)

Benzaldehyde (26.50 g, 250 mmol) was reacted according to the general procedure giving the title compound in 60% yield (25.30 g) as white crystals (Lit.[10] 45–61%); recrystallization from EtOH–H_2O (1:1); mp 232 °C (Lit.[14] 231–233 °C).

N-Methyl-C-4-isopropylphenylglycine (Ib)

4-Isopropyl-benzaldehyde (18.58 g, 125 mmol) was reacted according to the general procedure giving the title compound in 45% yield (19.35 g) as white crystals; recrystallization from EtOH–H_2O (1:1); mp 165 °C.

^{1}H NMR (DMSO-d_6): δ = 1.14 (d, 6 H, J = 6.9 Hz, CH_3), 2.63 (s, 3 H, CH_3N), 2.86 (septet, 1 H, J = 6.9 Hz ,CH), 4.96 (s, 1 H, CH), 7.29 (d, 2 H, J = 8.1 Hz, Ph), 7.42 (d, 2 H, J = 8.1 Hz, Ph), 9.67(d, 2 H, NH).

^{13}C NMR (DMSO-d_6): δ = 23.9, 31.1, 33.4, 63.2, 127.4, 128.4, 129.1, 150.5, 169.2.

Aroylation of *N*-Methyl-*C*-arylglycines; General Procedure

N-Methyl-*C*-arylglycine was dissolved in the minimum amount of aq NaOH (10%) with stirring which was continued for a further 2 h. An equimolar quantity of the required aroyl chloride was added dropwise and stirring continued for a further 2 h. During this time the crude product precipitated and the reaction mixture was then neutralized with aq HCl (10%). The white crystalline product was filtered off, washed with H_2O and air-dried. It was used in the final steps of the sequence without further purification.

N-Benzoyl-*N*-methyl-*C*-phenylglycine (IIa)

N-Methyl-*C*-phenylglycine (7.20 g, 23.80 mmol) and benzoyl chloride (3.39 g, 23.80 mmol) were reacted according to the general procedure giving the title compound in 50% yield (4.80 g) as white crystals (Lit.[15] 56%); mp 122 °C (Lit.[15] 122–124 °C).

_N_-(4-Chlorobenzoyl)-_N_-methyl-C-phenylglycine (IIb)
_N_-Methyl-_C_-phenylglycine (3.60 g, 21.95 mmol) and 4-chlorobenzoyl chloride (4.19 g, 21.95 mmol) were reacted according to the general procedure giving the title compound in 65% yield (4.54 g); mp 98 °C.

^{1}H NMR ($CDCl_3$): δ = 2.67 (s, 3 H, CH_3N), 6.33 (s, 1 H, CH), 7.24–7.37 (m, 9 H, Ph), 9.53 (1 H, NH).

^{13}C NMR (DMSO-d_6) δ = 35.1, 61.8, 128.5, 128.6, 128.7, 129.5, 131.4, 133.4, 133.6, 136.1 171.8, 173.7.

_N_-4-_N_-methyl-_C_-4-isopropylphenylglycine (IIc)
_N_-methyl-_C_-4-isopropylphenylglycine (7.00 g, 47.30 mmol) and 4-chlorobenzoyl chloride (8.27g 47.30 mmol) were reacted according to the general procedure giving the title compound in75% yield (10.16 g); white crystals; mp 146 °C.

^{1}H NMR ($CDCl_3$): δ = 1.26 (d, 6 H, _J_ = 6.0 Hz, CH_3,), 2.75(s, 3 H, CH_3N), 2.92 (septet. 1 H, _J_ = 6.0 Hz, CH), 6.39(s, 1 H, CH), 7.25–7.41 (m, 8 H, Ph).

^{13}C NMR ($CDCl_3$): δ = 23.8, 33.7, 34.9, 60.8, 127.0, 128.3, 128.7, 128.8, 129.4, 130.4, 133.6, 136.1, 149.5, 171.9, 174.0.

Preparation of Mesoionic 2,4-Diaryl-3-methyl-1,3-thiazolium-5-thiolates; General Procedure
The _N_-aroyl-_N_-methyl-_C_-arylglycine (16–20 mmol) was dissolved in Ac_2O (20 mL) and heated at 55 °C for 15 min with stirring. After cooling to ambient temperature, CS_2 (20 mL) was added and the reaction mixture allowed to stand for 48 h. MeOH–H_2O (1:1) was then added until the mixture became cloudy, after standing for a further 24 h the desired product formed as orange-red crystals, which were recrystallized from MeOH.

Mesoionic 2,4-Diphenyl-3-methyl-1,3-thiazolium-5-thiolate (2)
Yield: 51% (2.46 g) (Lit.[14] 55%); mp 183–184 °C (Lit.[14] 184 °C).

IR (KBr): 3025 (C_{Ar}–H), 2948 (C–H), 1482 (N–CH_3 asymmetric), 1424 (N–CH_3 symmetric), 1291 (C–S^-).

^{1}H NMR ($CDCl_3$): δ = 3.64 (s, 3 H, CH_3N), 7.33–7.52 (m, 10 H, Ph).

^{13}C NMR (DMSO-d_6): δ = 40.3, 126.6, 128.5, 128.9, 129.2, 129.3, 129.8, 131.0, 131.3, 140.7, 154.3 and 159.8.

MS: _m/z_ (%) = 283 (100.00), 268 (8.94), 179 (7.60), 165 (88.99), 121 (28.83), 89 (8.51), 77 (4.60).

Anal. Calcd for $C_{16}H_{13}NS_2$: C, 67.81, H, 4.62, N, 4.94. Found: C, 67.80, H, 4.42, N, 5.08.

Mesoionic 2-Phenyl-3-methyl-4(4′-chlorophenyl)-1,3-thiazolium-5-thiolate (3)
Yield: 51% yield (3.03 g); mp 158–159 °C.

IR (KBr): 3006 (C_{Ar}–H), 2916 (C–H), 1485 (N–CH_3 asymmetric), 1431 (N–CH_3 symmetric), 1285 (C–S^-), 1096 (C_{Ar}–Cl).

(100.00), 121 (25.21), 89 (7.78), 77 (3.31).

^{1}H NMR ($CDCl_3$): δ = 3.63 (s, 3 H, CH_3N), 7.41–7.51 (m, 9 H, Ph).

^{13}C NMR (DMSO-d_6): δ = 40.5, 125.2, 128.7, 129.2, 129.8, 130.8, 131.2, 137.9, 141.2, 152.6, 160.7.

MS: _m/z_ (%) = 319 (23.79), 317 (65.77), 304 (2.37), 302 (5.52), 179 (6.17), 165.

Anal. Calcd for $C_{16}H_{12}ClNS_2$: C, 60.46, H, 3.81, N, 4.41. Found: C, 60.28, H, 3.84, N, 4.04.

Mesoionic 2-(4-Chlorophenyl)-3-methyl–4-(4′-isopropylphenyl)-1,3-thiazolium-5-thiolate (4)
Yield: 46% (2.39 g); mp 177 °C.

IR (KBr): 3012 (C_{Ar}–H), 2959 [C–H, –$(CH_3)_2$], 2927 (C–H, C_{Ar}–CH), 2870 (C–H, N–CH_3), 1485 (N–CH_3 asymmetric), 1431 (N–CH_3 symmetric), 1399 and 1384 [C–$(CH_3)_2$], 1285 (C–S^-), 1085 (C_{Ar}–Cl).

^{1}H NMR ($CDCl_3$): δ = 1.24 (d, 6 H, _J_ = 6,3 Hz, CH_3), 2.91 (septet, 1 H, _J_ = 6.3 Hz, CH), 3.60 (s, 3 H, CH_3N), 7.25–7.55 (m, 8 H, Ph).

^{13}C NMR (DMSO-d_6): δ = 23.8, 33.9, 40.6, 125.3, 126.8, 126.9, 129.7, 130.8, 131.0, 137.8, 141.6, 149.9, 152.7, 159.4.

MS: _m/z_ (%) = 361 (10.16), 359 (23.61), 346 (5.85), 344 (15.37), 319 (19.53), 317 (48.69), 304 (4.20), 302 (10.47), 179 (6.71), 165 (100.00), 121 (26.68), 89 (8.16), 77 (3.90).

Anal. Calcd for $C_{19}H_{18}ClNS_2$: C, 63.40, H, 5.04, N, 3.89. Found: C, 63.44, H, 5.03, N, 3.80.

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