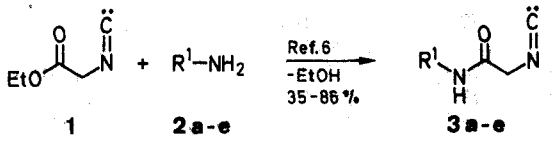
As the starting isocyanoacetamides we chose *N*-alkylisocyanoacetamides **3a–e** which were easily prepared by treating ethyl isocyanoacetate (**1**) with primary amines **2a–e**.



2, 3	R^1	2, 3	R^1
a	n-C_3H_7	d	furfuryl
b	i-C_3H_7	e	c-C_5H_9
c	$PhCH_2$		

Table 1. *N*-Alkylisocyanoacetamides 3 Prepared

Product	Reaction Time (h)	Yield[a] (%)	mp (°C) (solvent)	Molecular Formula[b] or Lit. mp (°C)	IR (KBr) ν (cm^{-1})
3a	24	35	49–50 (petroleum ether 30–50 °C)	$C_6H_{10}N_2O$ (126.2)	3300, 2160, 1660
3b	24	86	74–75 (i-Pr_2O)	68–71[6]	3300, 2160, 1670
3c	26	60	124–125 (EtOH)	122–124[6]	3300, 2150, 1660
3d	28	60	76–77 (EtOH)	$C_8H_8N_2O_2$ (164.1)	3250, 2160, 1670
3e	25	62	82–83 (CCl_4)	$C_8H_{12}N_2O$ (152.2)	3290, 2160, 1670

[a] Yield of pure isolated product.
[b] Satisfactory microanalyses: C ±0.25, H ±0.30, N ±0.26.

A Novel Synthetic Route to Imidazole Derivatives: Synthesis of Mesoionic 3-Alkyl-2-arylthio-1,3-diazolium-4-olates

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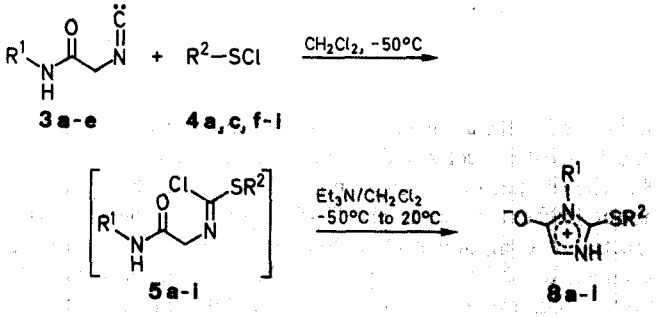
The reaction between *N*-alkylisocyanoacetamides **3a–e** and arylsulfenyl chlorides **4a, c, f–i** affords arylcarbonimidochloridothioates **5a–i** which on treatment with triethylamine undergo ring-closure to give 3-alkyl-2-arylthio-1,3-diazolium-4-olates **8a–i**.

Continuing our studies on the synthesis of heterocyclic compounds by means of isocyanides and arylsulfenyl chlorides or chlorosulfanes[2–5] we investigated the reaction of some arylcarbonimidochloridothioates (obtained from isocyanoacetamides and arylsulfenyl chlorides) with triethylamine.



4, 5, 8	R^1 in 5 and 8	R^2 in 4, 5, and 8
a	n-C_3H_7	2-$O_2NC_6H_4$
b	i-C_3H_7	2-$O_2NC_6H_4$
c	benzyl	4-ClC_6H_4
d	furfuryl	4-ClC_6H_4
e	c-C_5H_9	4-ClC_6H_4
f	c-C_5H_9	4-$CH_3C_6H_4$
g	i-C_3H_7	4-$O_2NC_6H_4$
h	i-C_3H_7	2-O_2N-4-ClC_6H_3
i	i-C_3H_7	Ph

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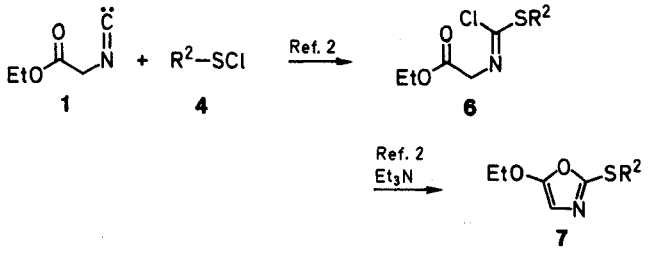
Table 2. 3-Alkyl-2-arylthio-1,3-diazolium-4-olates **8** Prepared

Product	Yield[a] (%)	mp[b] (°C)	Molecular Formula[c]	IR (KBr) ν(cm^{-1})	^{1}H-NMR (TMS)[d] δ, J(Hz)
8a	72	189–190	$C_{12}H_{13}N_3O_3S$ (279.3)	1690	7.19 (d, 1H, J = 0.3, H-5); 10.82 (br, 1H, NH)
8b	77	190–191	$C_{12}H_{13}N_3O_3S$ (279.3)	1693	7.14 (d, 1H, J = 0.3, H-5); 10.75 (br, 1H, NH)
8c	74	203–204	$C_{16}H_{13}ClN_2OS$ (316.8)	1685	7.07 (d, 1H, J = 0.3, H-5); 10.81 (br, 1H, NH)
8d	73	195–196	$C_{14}H_{11}ClN_2O_2S$ (306.7)	1680	7.23 (d, 1H, J = 0.3, H-5); 10.78 (br, 1H, NH)
8e	75	218–219	$C_{14}H_{15}ClN_2OS$ (294.8)	1675	7.07 (d, 1H, J = 0.3, H-5); 10.62 (br, 1H, NH)
8f	72	188–189	$C_{15}H_{18}N_2OS$ (274.4)	1675	7.01 (d, 1H, J = 0.3, H-5); 10.52 (br, 1H, NH)
8g	75	198–199	$C_{12}H_{13}N_3O_3S$ (279.3)	1688	6.84 (d, 1H, J = 0.3, H-5); 11.21 (br, 1H, NH)
8h	81	195–196	$C_{12}H_{12}ClN_3O_3S$ (313.8)	1690	6.92 (d, 1H, J = 0.3, H-5); 11.18 (br, 1H, NH)
8i	72	185–186	$C_{12}H_{14}N_2OS$ (234.3)	1680	6.89 (d, 1H, J = 0.3, H-5); 10.65 (br, 1H, NH)

[a] Yield of pure isolated product.
[b] From EtOH.
[c] Satisfactory microanalyses: C ±0.25, H ±0.30, N ±0.26.
[d] NMR solvents: **8a–f, i**: DMSO-d_6; **8g**: $CDCl_3$; **8h**: CD_2Cl_2.

The reaction between isocyanides **3** and arylsulfenyl chlorides **4** occurred easily, even at low temperatures, due to the high reactivity of sulfenyl chlorides towards isocyanides,[7] affording arylcarbonimidochloridothioates **5**. Compounds **5** are rather unstable and undergo quick decomposition on standing at room temperature. Evidence for the assigned structures **5** was provided by IR spectra of the crude reaction products: the strong absorption due to the N=C: group disappears. Treatment of compounds **5** with triethylamine in the reaction mixture of their preparation leads to cyclization to afford 3-alkyl-2-arylthio-1,3-diazolium-4-olates **8** in good yields.

The reaction **3** + **4** → **5** is substantially analogous to that between ethyl isocyanoacetate (**1**) and arylsulfenyl chlorides **4** to give carbonimidochloridothioates **6**.[2] However, in contrast to the unstable analogs **5**, compounds **6** are rather stable and can be isolated and characterized. Further, treatment of compounds **6** results in a different type of cyclization to afford *O,N*-heterocycles **7**.[2]



Evidence for the assigned structures **8** was provided by the IR and ^{1}H-NMR spectra and by an X-ray analysis of compound **8a**. The IR spectra of compounds **8** show strong absorptions at about 1690 cm^{-1} due to the C–O$^-$ group. In the ^{1}H-NMR spectra of compounds **8**, a doublet signal at $\delta \approx 7$ can be assigned to H-5 which appears to be coupled with the NH proton. On treatment with D_2O, the NH signal at $\delta \approx 11$ disappears and a singlet signal due to H-5 results. Tautomeric covalent structures do not seem reasonable. In fact, the presence of CH_2 and OH groups was never detected.

We have thus worked out a useful and simple method for the synthesis of the novel mesoionic 1,3-diazolium-4-olates **8** which are not easily obtainable by other routes and which represent interesting intermediates for further reactions.

Melting points (uncorrected) were determined on a Büchi 510 apparatus. IR spectra were recorded on a Perkin-Elmer 283 instrument, and ^{1}H-NMR spectra on a Varian VX 300.

Arylsulfenyl chlorides **4a**,[9] **4c**,[10] **4f**,[11] **4g**,[12] **4h**,[13] **4i**,[14] and isocyanoacetamides **3b**[6] and **3c**[6] were prepared following literature procedures.

***N*-Alkylisocyanoacetamides 3a, d, e; General Procedure:**
Cold 1-aminopropane (**2a**; 4.14 g, 70.2 mmol), 2-aminomethylfuran (**2d**; 6.80 g, 70.2 mmol), or aminocyclopentane (**2e**; 5.98 g, 70.2 mmol) is added dropwise to ethyl isocyanoacetate (**1**, 5.30 g, 4.68 mmol), maintaining the temperature at 20 °C. The reaction mixture is allowed to react at 5 °C overnight, and then the excess amine and ethanol are removed under reduced pressure (bath temperature 60 °C). The residue is then recrystallized from a suitable solvent (Table 1).

3-Alkyl-2-arylthio-1,3-diazolium-4-olates (Imidazolium-4-olates 8a–i); General Procedure:
A solution of the *N*-substituted isocyanoacetamide **3** (16 mmol) in CH_2Cl_2 (20 mL) is added slowly to a stirred solution of the sulfenyl chloride **4** (16 mmol) in CH_2Cl_2 (30 mL) at −50 °C, and stirring is continued at −50 °C for 30 min. Then, dry Et_3N (1.62 g, 16 mmol) is added dropwise and the mixture is stirred, without removing the cooling bath, until the temperature has reached 20 °C. It is then filtered, the filtrate is evaporated to dryness, and the residue is recrystallized from EtOH.

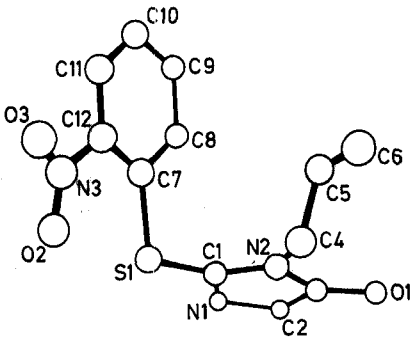


Figure. Molecular structure of **8a** according to X-ray analysis; $C_{12}H_{13}N_3O_3S$. System monoclinic, space group $P2_1/c$ (N14); a = 14.122(2), b = 11.605(2), c = 8.037(2) Å, β = 98.2(2)°, v = 1303.7 Å^3, Z = 4, Dc = 1.423 g cm^{-3}, μ = 2.0 cm^{-1}.
3360 Reflections were measured on a Philips PW 1100 diffractometer, 3156 unique (R int = 0.012), using Mo-Kα radiation (λ = 0.7107 Å) to 2θ = 50°, $\theta/2\theta$ scan mode. The solution was obtained by MULTAN 80 programm, and the structure was refined by the block-diagonal least-squares method, anisotropic for all non-hydrogen atoms. Hydrogen atoms were located on DF map and refined with "U" isotropic. The final conventional R factor for 1220 reflections with I 3σ(I) was 0.0618. No absorption correction applied. Refinement based on F with w = 1. Maximum shift to error = 0.8 for the coordinates Ull of 0(2).[8]

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