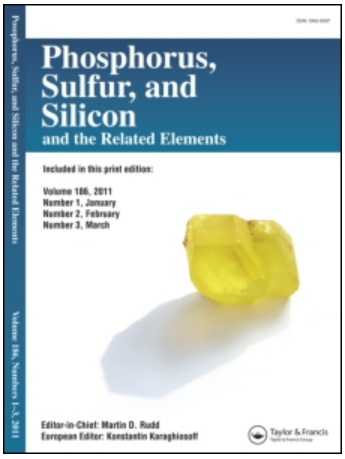

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BENZOTHIAZEPINONES, RELATED COMPOUNDS, AND THE SMILES REARRANGEMENT

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BENZOTHIAZEPINONES, RELATED COMPOUNDS, AND THE SMILES REARRANGEMENT

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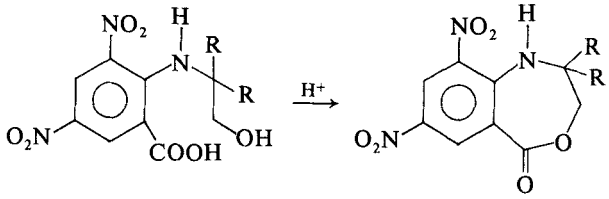
β-Hydroxyamine derivatives of negatively substituted aromatic acids cyclize readily in mild acid solution to benzoxazepinones. The corresponding β-thiolamine derivatives take more persuasion, the use of an effective dehydrating agent. Furthermore, the chemistry of such derivatives is complicated by Smiles rearrangements to β-amino aryl sulfides and/or oxidation to disulfides.

β-Hydroxyamine derivatives of negatively substituted aromatic acids cyclize to 4,1-benzoxazepinones under mildly acidic conditions[1,2] (Scheme 1). The corresponding 4,1-benzothiazepinones are not generated by acid catalysis but need an efficient dehydrating agent, dicyclohexylcarbodiimide. Compound (**3a**), obtained from (**1**) by a reaction with β-thiolethylamine (**2a**), was converted to (**4a**) with dicyclohexylcarbodiimide in pyridine (Scheme 2). Under the same conditions (**3b**) was converted into a mixture of (**4b**) and (**5b**), 4,1- and 1,4-benzothiazepinones, respectively, in a ratio of 1 : 1.4.

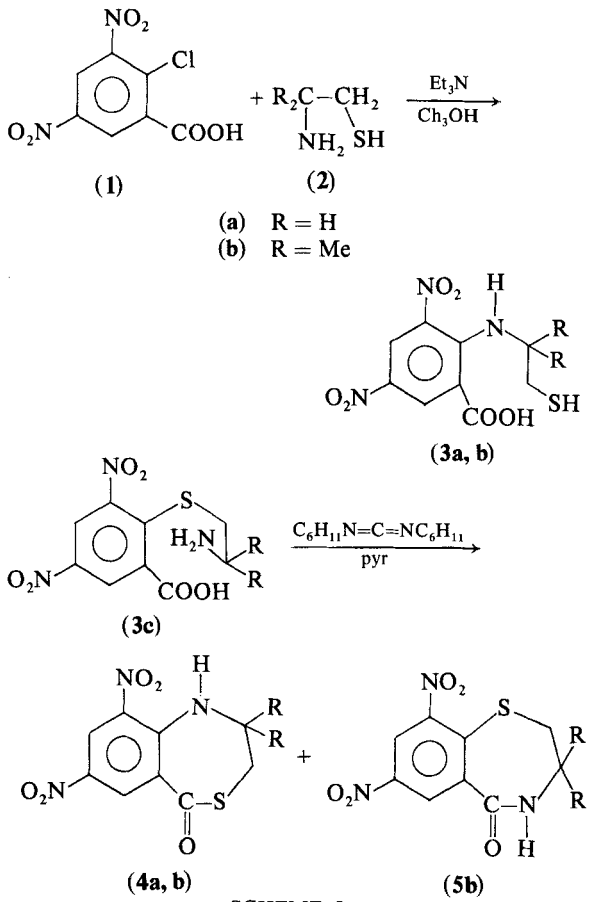


SCHEME 1

The result suggests that a Smiles rearrangement[3] must precede the cyclization to (**5b**). An alternative explanation is that (**3b**) and its isomer, β-amino-*tert*-butyl 2,4-dinitro-6-carboxyphenyl sulfide (**3c**) may have a common Meisenheimer intermediate (**6**) (Scheme 3).

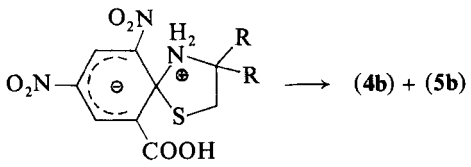
Bond breaking at the spiro S or N atom following by dehydration would then give (**4b**) and (**5b**) without a Smiles rearrangement. However, the Smiles rearrangement pathway is well established for negatively substituted aromatic compounds.

The definitive identification of the isomers (**4b**) and (**5b**) was made by ^{13}C nuclear magnetic resonance spectra. The carbonyl resonances in (**4b**)



SCHEME 2

(and **4a**) for the 4,1-benzothiazepiones were found at 196.3 and 194.4 ppm, respectively, while the carbonyl resonance in the 1,4-benzothiazepinone (**5b**) appeared at 163.8 ppm. The chemical shifts are



(6) → (4b) + (5b)

SCHEME 3

consistent for what might be expected of $-\overset{\overset{O}{\|}}{C}-NH-$[4] and $-\overset{\overset{O}{\|}}{C}-S$[5]– functions. The proton magnetic resonance, the infrared, and the ultraviolet spectra were consistent with the designated structures but not discriminating.

Replacement of the halogen by aminothiols (**2a**) and (**2b**) in various negatively substituted compounds related to (**1**) led to products characterized as β-mercaptoalkyl anilines (Table I), (**7d–g**). However, attempts to isolate the expected β-mercaptoalkyl anilines in other reactions resulted instead in oxidized products (**8i, j**). In one case both thiol (**7f**), and disulfide (**8f**), were isolated. In three examples, the disulfides (**8h, k, l**) and the Smiles rearranged products (**9h, k, l**) were isolated. The free NH_2 group in (**9h, k, l**) was identified by an acetyl derivative and in the definitive case (**9l**), both hydrogens in the amine nitrogen were displaced successively by an acetyl and a nitroso group. The molecular weights (Rast method) of compounds (**8h–l**) bear out the designation as disulfides.

Finally, in one example (**9c**), only the sulfide was isolated. An amine hydrochloride of (**9c**) was also obtained but acidic hydrolysis which might have given the thiol (**7c**) was not accomplished. In basic solution only the Smiles product (**9c**) was formed.

No attempt was made to oxidize compounds (**7**) to (**8**) other than by the use of base in the presence or absence of air. Since the disulfides, (**8**) were equally well formed in the absence of air, it is probable that they are formed by disproportionation involving one (or more) nitro group(s) in the aromatic ring. The yields of disulfides were in no case high enough to exclude that source of oxidation.

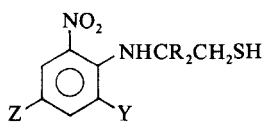
Attempts to replace the carbonyl oxygen by sulfur with phosphorus pentasulfide on (**4a**), (**4b**), and (**5b**) were unsuccessful.

DISCUSSION OF RESULTS

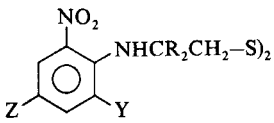
Nucleophilic displacement in aromatic compounds has been demonstrated to occur through Meisenheimer complexes in many cases (or a closely related transition state) and is generally accepted as the mechanism. In the case of displacements by β-aminoalcohols where both nitrogen and oxygen may act as the central nucleophilic atom, nitrogen appears always to win in displacing halogen or oxygen on negatively substituted aromatic compounds. In β-aminothiols, nitrogen and sulfur may be centers more nearly competitive as nucleophiles. Therefore, in the formation of (**9c**), the Meisenheimer complex may take the form (**10**) as precursor of product. In the examples where there are two negative *ortho* substituents (**7d–g**), two negative ortho and para substituents (**8h–l**), or three negative substituents (**3a, b**), the Meisenheimer complexes appear to have the structure (**11**).

The rules which govern subsequent oxidation of compounds (**7**) to disulfides (**8f, h–l**) and/or Smiles rearrangements to (**5b**), (**9h, k, l**) are not so clear. Three of the interlocking effects discussed by Truce for the Smiles rearrangement certainly involve in the

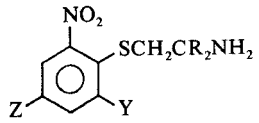
TABLE I



(7)

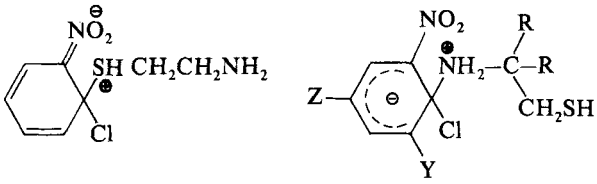


(8)



(9)

R = H		Y = H	
(c)	Y = Z = H	(h)	Z = CF_3, R = H
(d)	Y = Z = NO_2	(i)	Z = NO_2, R = Me
(e)	Y = CO_2Me, Z = H	(j)	Z = CO_2Me, R = Me
(f)	Y = CO_2Me, Z = NO_2	(k)	Z = CO_2Me, R = H
(g)	Y = NO_2, Z = H	(l)	Z = NO_2, R = H



(10) (11)

SCHEME 4

present examples the acidity of the NH group in (7), the nucleophilicity of the SH group, and "steric acceleration through regulation of rotational conformations" controlled by the NO_2, Y, and the R groups.

EXPERIMENTAL

Analytical and spectral data are given in Tables II and III, respectively.

N(β-Mercaptoethyl)-3,5-dinitroanthranilic acid (**3a**)

2-Chloro-3,5-dinitrobenzoic acid[1,6] (2.96 g, 12 mmol) and 2-aminoethanethiol hydrochloride (2.84 g, 25 mmol) were refluxed in 50 ml of absolute methanol as triethylamine (25 mmol) was added dropwise over 0.75 h. Refluxing was continued for 0.75 h and then 20 ml of 5% sodium hydroxide was added to the solution. Acidification with 30 ml of concentrated hydrochloric acid gave 3.25 g of yellow precipitate. Recrystallization of the dry product from chloroform–carbon tetrachloride gave 3.0 g, 88%, of pure *N*(β-mercaptoethyl)-3,5-dinitroanthranilic acid, mp 155–156°.

β-Aminoisobutyl 2,4-Dinitro-6-carboxyphenyl Sulfide (**3b**)

Triethylamine (0.1 ml, 0.7 mmole) was added to a solution of 2-amino-2-methyl-1-propanethiol hydrochloride[7] (0.1 g, 0.7 mmole) in 1.5 ml of absolute methanol, followed by addition of 2-chloro-3,5-dinitrobenzoic acid (0.17 g, 0.7 mmole). The mixture was refluxed for 10 min. A yellow precipitate formed after 5 min. After cooling in ice, the solid was removed and triturated with 8 ml of chloroform. Filtration gave 101 mg, 45% of β-aminoisobutyl 2,4-dinitro-6-carboxyphenyl sulfide. The analytical sample was prepared by two recrystallizations from absolute methanol, mp 245–246°.

7,9-Dinitro-1,2,3,5-tetrahydro-4,1-benzothiazepin-5-one (**4a**)

A solution of 11.5 g (0.040 mole) of *N*(β-mercaptoethyl)-3,5-dinitroanthranilic acid in 370 ml of dry pyridine was added in one portion to a solution of 8.25 g (0.040 mole) of dicyclohexylcarbodiimide. The mixture was heated to 105–110° (pot temperature) under nitrogen for one hour and then cooled to room temperature and filtered. The orange colored residue was washed with pyridine until it was nearly white leaving only dicyclohexylurea. Pyridine was removed from the filtrate and washings on a rotary evaporator at reduced pressure leaving an orange solid. The remaining dicyclohexylurea was extracted from the orange solid with 200 ml of boiling ethanol (95%). The residue was recrystallized from tetrahydrofuran to give 8.7 g, 81%, of yellow 7,9-dinitro-1,2,3,5-tetrahydro-4,1-benzothiazepin-5-one. Two more recrystallizations from tetrahydrofuran gave the analytical sample, mp 183.0–183.5°.

7,9-Dinitro-3,3-dimethyl-2,3,4,5-tetrahydro-1,4-benzothiazepin-5-one (**5b**) *and 7,9-Dinitro-2,2-dimethyl-1,2,3,5-tetrahydro-4,1-benzothiazepin-5-one* (**4b**)

A procedure similar to that described for compound (**4a**) was carried out on 5.88 g (18.6 mmole) of compound (**3b**) with an equivalent of dicyclohexylcarbodiimide (3.85 g) in a total of 176 ml of pyridine. Recrystallization of the residue from chloroform after the removal of pyridine gave 2.39 g, 43% of a yellow solid, mp 189–199°. An analytical sample of 7,9-dinitro-3,3-dimethyl-2,3,4,5-tetrahydro-1,4-benzothizaepin-5-one was obtained by two more recrystallizations from chloroform, mp 201–203°.

The chloroform filtrate from the above yellow solid was transferred to a column of 150 g of silica gel. Elution with ether and removal of the solvent gave 1.65 g 30%, of 7,9-dinitro-2,2-dimethyl-1,2,3,5-tetrahydro-4,1-benzothiazepin-5-one, mp 160–162°. One recrystallization from 95% ethanol and one from chloroform gave an analytical sample, mp 161–162.5°.

Negatively Substituted β-mercaptoaminobenzenes (**7d–g**)

In an analogous manner to the preparation of compound (**3b**), picryl chloride was used to synthesize compound (**7d**) in 48% yield, mp 169.5–170.5°, recrystallized from acetic acid.

Compound (**7e**) was made from 2.16 g (0.01 mole) of methyl 2-chloro-3-nitrobenzoate[1,8] in similar fashion. However, the reaction mixture was dissolved in 60 ml of water and the methyl *N*(β-mercaptoethyl)-3-nitroanthranilate was extracted with three 40-ml portions of methylene chloride. The dried methylene chloride extract was transferred to a silical gel column (150 g). Elution gave 2.14 g (84%) of an orange oil. Two distillations gave the analytical sample of (**7e**) bp 156° (0.25 mm).

Compound (**7f**) was prepared from methyl 2-chloro-3,5-dinitrobenzoate, which, contrary to early implications[9] can be obtained by direct esterification in 96% yield, mp 90.0–90.5°. Compound (**7f**) was synthesized in 77% yield, mp 101–102° after recrystallization from absolute methanol.

Compound (**7g**) was prepared analogously to (**7e**) in 49% yield. The orange *N*(β-mercaptoethyl)2,6-dinitroaniline was recrystallized from benzene–hexane to give the analytical sample, mp 75–76°.

Negatively Substituted Anilinoethyl Disulfides (**8f, h–l**)

(**8f**). Methyl *N*(β-mercaptoethyl)-3,5-dinitroanthranilate (**7f**), (0.60 g, 2 mmole), was stirred with 0.3 g (2 mmole) of potassium carbonate in 4.8 ml of dimethylformamide at room temperature for 8 h. The mixture was poured into 50 ml of water and the precipitate was collected and washed with water. After drying, the yellow product was dissolved in chloroform and transferred to a column of 40 g of silica gel. Elution with chloroform and removal of solvent followed by recrystallization from benzene gave 0.31 g, 52%, of 2-carbomethoxy-4,6-dinitrophenyl β-aminoethyl disulfide (**8f**), mp 142.5–143.5°. An analytical sample of the same melting point was obtained by two more recrystallizations from benzene.

(**8i**). Only the oxidized products (**8i**) and (**8j**) were obtained when the procedure applied to the preparation of (**3b**) and compounds (**7d–g**) was tried.

2,4-Dinitrochlorobenzene (1.14 g, 5.64 mmole) and 2-methyl-2-amino-1-propanethiol hydrochloride (1.6 g, 11.3 mmole) were refluxed in 16 ml of absolute methanol with a fivefold excess of triethylamine for 4 h. Solvent and excess triethyl amine were removed under vacuum. A solution of the residue in 50 ml of water was extracted with five 20-ml portions of ethyl acetate. Concentration of the dried extracts left a brown oil which was transferred to a column of 100 g of silica gel. Elution with methylene chloride gave 0.57 g, 37%, of bright yellow 2-methyl-2(2',4'-dinitroanilino)-propyl disulfide (**8i**). An analytical sample was prepared by two recrystallizations from absolute methanol, mp 123–124°.

(**8j**). 2-Methyl-2(2'-nitro-4'-carbomethoxyanilino)-propyl disulfide (**8j**), was obtained in a similar manner from methyl 4-chloro-3-nitrobenzoate in 45% yield, mp 124–126°.

(**8h**). Compounds (**8h**), (**8k**), and (**8l**) were obtained from the corresponding negatively substituted phenyl β-aminoethyl sulfides (see compound **9** below).

2-Nitro-4-trifluoromethylphenyl β-aminoethyl sulfide hydrochloride, (**9h**), (0.20 g, 6.9 mmole) was refluxed with excess triethylamine in absolute methanol for 4 h. Removal of solvent and excess base left a residue which was extracted three times with 10-ml portions of methylene chloride. Solvent was removed and the residue was transferred to a column of 20 g of silica gel with chloroform. Elution with chloroform gave 73 mg, 40%, of yellow 2-nitro-4-trifluoromethyl-phenyl aminoethyl disulfide. An analytical sample was obtained by two recrystallizations from ethyl acetate, mp 158–159°.

(**8k**). Compound (**8k**) was obtained in like manner from 2-nitro-4-carbomethoxyphenyl β-aminoethyl sulfide hydrochloride (**9k**) in 43% yield, mp 152.5–153.5°. The extracting and recrystallizing solvent was ethyl acetate.

(**8l**). Compound (**8l**) was obtained in like manner from 2,4-dinitrophenyl β-aminoethyl sulfide hydrochloride (**9l**) in 69% yield, mp 179–181°. The eluting solvent was acetonitrile.

Negatively Substituted Aryl β-Aminoethyl Sulfides

(**9c**), *o*-Chloronitrobenzene (7.88 g, 0.050 mole) was refluxed under nitrogen with 11.4 g (0.10 mole) of 2-aminoethanethiol hydrochloride in 175 ml of absolute methanol while 0.10 mole of sodium methoxide in methanol was added dropwise over 15 min. The mixture was refluxed for four hours and sodium chloride was removed by filtration. The filtrate upon concentration gave a brown oil which changed to a yellow solid. Recrystallization from methanol–ethyl acetate gave 3.2 g, 27% of yellow *o*-nitrophenyl β-aminoethyl sulfide hydrochloride. Two recrystallizations from the same solvent mixture gave the analytical sample, mp 211–213°. Attempts to rearrange the sulfide to a β-mercaptoethyl amine with strong base gave decomposition products. The hydrochloride was converted to the free sulfide with triethylamine as evidenced by the nmr spectrum but the sulfide could not be purified. The pure hydrochloride was obtained again by addition of concentrated hydrochloric acid.

(**9h**). Compound (**9h**) was prepared in similar fashion from 4-chloro-3-nitrobenzotrifluoride using triethylamine as base in 71% yield. The product was a pale yellow solid, mp 196–200° which was converted to an *N*-acetyl derivative without further purification. The *N*-acetyl derivative was recrystallized from benzene, mp 128–130°.

(**9k**). Compound (**9k**) was obtained by a similar procedure using methyl 4-chloro-3-nitrobenzoate and triethylamine as base in 71% yield, mp 190–195°. An acetyl derivative was prepared

TABLE II

Analysis of new compounds

Compound		Calcd				Found			
		C	H	N	S	C	H	N	S
(**3a**)	$C_9H_9N_3O_6S$	37.63	3.14	14.63		37.34	3.41	14.50	
(**3b**)	$C_{11}H_{13}N_3O_6S$	41.90	4.15	13.33	10.17	42.16	4.36	13.14	10.33
(**4a**)	$C_9H_7N_3O_5S$	40.14	2.62	15.61	11.91	40.20	2.75	15.32	11.84
(**4b**)	$C_{11}H_{11}N_3O_5S$	44.44	3.73	14.13	10.79	44.70	3.89	14.02	10.67
(**5b**)	$C_{11}H_{11}N_3O_5S$	44.44	3.73	14.13	10.79	44.14	3.70	13.96	10.80
(**7d**)	$C_8H_8N_4O_6S$	33.33	2.78	19.44		33.46	2.97	19.62	
(**7e**)	$C_{10}H_{12}N_2O_4S$	46.86	4.72	10.93		47.01	4.77	10.88	
(**7f**)	$C_{10}H_{11}N_3O_6S$	39.87	4.08	13.95		40.18	4.08	13.90	
(**7g**)	$C_8H_9N_3O_4S$	39.50	3.73	17.26		39.37	3.78	17.13	
(**8f**)	$C_{20}H_{20}N_6O_{12}S_2$	39.99	3.35	13.99	mol. wt. (Rast)	40.41	3.44	13.78	mol. wt. (Rast)
(**8h**)	$C_{18}H_{16}F_6N_4O_4S_2$	40.75	3.04	10.56	530	41.02	3.27	10.45	526
(**8i**)	$C_{20}H_{24}N_6O_8S_2$	44.43	4.48	15.55	541	44.22	4.41	15.59	478
(**8j**)	$C_{24}H_{30}N_4O_8S_2$	50.87	5.34	9.89	567	51.15	5.44	10.00	565
(**8k**)	$C_{20}H_{22}N_4O_8S_2$	47.05	4.34	10.98	511	47.18	4.45	10.69	501
(**8l**)	$C_{16}H_{16}N_6O_8S_2$	39.66	3.33	17.35	484	39.84	3.31	17.47	497
(**9c**)	$C_8H_{11}ClN_2O_2S.1/4H_2O$	40.17	4.85	11.71		40.28	4.80	11.58	
(**9h**)[a]	$C_{11}H_{11}F_3N_2O_3S$	42.85	3.59	9.09		42.72	3.75	8.86	
(**9k**)[a]	$C_{12}H_{14}N_2O_5S$	48.13	4.73	9.39		48.05	4.70	9.35	
(**9l**)[a]	$C_{10}H_{11}N_3O_5S$	42.08	3.92	14.72		41.88	3.88	14.74	
(**9l**)[b]	$C_{10}H_{10}N_4O_6S$	38.21	3.21	17.83		38.51	3.22	17.78	

[a] *N*-acetyl derivative.

[b] *N*-nitroso-*N*-acetyl derivatives.

TABLE III

Spectral data for new compounds

	ir		δ, nmr (DMSO-d_6)
	C=O (s)	NO_2 (s)	
(**3a**)	1700	1590, 1320	3.10 (m, 4), 7.30 (s, br, 2.7),[a] 8.82 (m, 2), 10.20 (s, br, 0.3)[a]
(**3b**)	1630sh	1570, 1330	1.36 (s, 6), 3.24 (s, 2), 7.66–9.00 (q, br, 5), 4.08 (m, 2)
(**4a**)	1610	1585, 1330	3.46 (m, 2)/8.40 (d, 1), 8.90 (d, 1), 9.18 (s, br, 1), ^{13}C (C=O), 194.4 ppm
(**4b**)	1630sh	1580, 1300	1.44 (s, 6), 3.34 (s, 2), 7.03 (s, 1), 8.46 (d, 1), 8.94 (d, 1), ^{13}C(C=O), 196.3 ppm
(**5b**)	1630	1530, 1340	1.34 (2, 6), 3.20 (s, 2), 8.66 (s, 1), 8.88 (m, 2), ^{13}C (C=O), 163.8 ppm
(**7d**)		1520, 1320	1.28 (t, 1), 3.34 (m, 4), 8.84 (s, br, 1), 8.86–9.16 (m, 2)
(**7e**)	1690	1510, 1355	1.52 (t, 1), 2.64–3.40 (m, 4), 3.94 (s, 3), 6.68 (t, 1), 8.10 (m, 2), 8.68 (s, br, 1)
(**7f**)	1700	1520, 1330	1.54 (t, 1), 3.10 (m, 4), 4.00 (s, 3), 8.90 (m, 2), 9.54 (s, br, 1)
(**7g**)		1530, 1330	1.50 (t, 1), 2.60–3.42 (m, 4), 6.84 (t, 1), 8.20 (d, 2), 8.51 (s, br, 1)
(**8f**)	1700	1540, 1330	3.20 (m, 4), 4.01 (s, 3), 8.90 (q, 2), 9.52 (m, 1)
(**8h**)		1540, 1330	2.99 (t, 2)[b], 3.64 (q, 2), 7.41 (d, 1), 7.69 (q, 1), 7.72–8.40 (m, br, 2)
(**8i**)		1510, 1340	1.62 (s, 6), 3.32 (s, 2), 7.21 (d, 1), 8.32 (m, 1), 8.88 (s, br, 1), 9.20 (d, 1)
(**8j**)	1720	1530, 1300	1.52 (s, 6), 3.24 (s, 2), 3.92 (s, 3), 7.16 (d, l), 8.10 (q, 1), 8.71 (s, 1), 8.90 (d, 1)
(**8k**)	1710, 1630	1540, 1300	3.07 (t, 2)[b], 3.75 (t, 2), 3.91 (s, 3), 6.89) (d, 1), 7.97 (q, 1), 8.31 (m, br, 1), 8.88 (d, 1)
(**8l**)		1580, 1350	2.86–3.17 (m, 2), 3.57–3.90 (m, 2), 7.24 (d, 1), 8.25 (q, 1), 8.60–9.00 (m, br, 2). Upon adding D_2O, the broad multiplet at 8.60–9.00 changed to 8.83 (d, 1) and a new singlet appeared at 3.57
(**9c**)	1670	1530, 1350	1.80 (s, 3), 3.34 (m, 4), 8.32 (m, br, 3), 8.5 (s, 1), ^{13}C (C=O), 169.6 ppm
(**9h**)		1570, 1300	3.00–3.80 (m), 8.00–9.00 (m)
N-($COCH_3$)	1670	1530, 1350	1.88 (s, 3), 3.34 (m, 4), 8.32 (m, br, 3), 8.5 (s, 1), ^{13}C (C=O), 169.6 ppm
(**9k**)	1710	1580, 1320	2.8–4.0 (m), 8.20–9.40 (m)
N($COCH_3$)	1720, 1670	1520, 1300	1.88 (s, 3), 3.38 (m, 4), 3.98 (s, 3), 7.66–8.40 (m, br, 3), 8.68 (d, 1)
(**9l**)		1560, 1340	3.0–4.0 (m, 4), 8.0–9.2 (m, 5)
N($COCH_3$)	1630	1520, 1350	1.84 (s, 3), 3.30 (m, 4), 7.91–8.60 (m, 3), 8.90 (d, 1), ^{13}C (C=O), 169.8 ppm
N-($COCH_3$) \ NO	1620	1520, 1530	2.71 (s, 3), 3.30 (t, 2), 4.21 (t, 2), 8.02 (d, 1), 8.52 (m, 1), 8.86 (d, 1)

[a] Carboxylic, amine, and thiol protons exchange.

[b] Acetone-d_6, Fourier transform.

for the analytical sample, a lemon-yellow solid, recrystallized from ethyl acetate, mp 142.0–142.5°.

(**9l**). Compound (**9l**) was obtained from 2,4-dinitrochlorobenzene with triethylamine as base in a similar manner in 57% yield, mp 204–205°. Both an acetyl derivative, mp 135–137° and its *N*-nitroso derivative, mp 118–120° were obtained for analysis, the latter prepared with liquid nitrosyl chloride at −77°C.

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