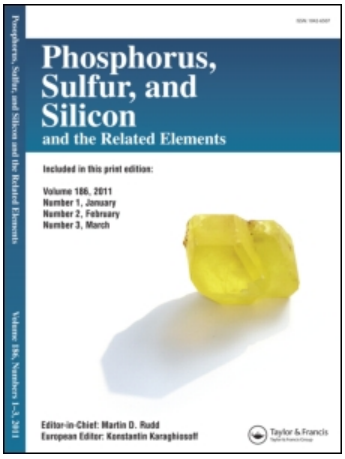


**Phosphorus, Sulfur, and Silicon and the Related Elements**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

# QUANTITATIVE STUDY OF THE NUCLEOPHILICITY OF THE THIOCARBONYL GROUP IN HETEROCYCLIC COMPOUNDS

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**To cite this Article** Arbelot, Michel , Gallo, Roger , Chanon, Michel and Metzger, Jacques(1976) 'QUANTITATIVE STUDY OF THE NUCLEOPHILICITY OF THE THIOCARBONYL GROUP IN HETEROCYCLIC COMPOUNDS', Phosphorus, Sulfur, and Silicon and the Related Elements, 1: 2, 271 — 279
**To link to this Article: DOI:** 10.1080/03086647608073332
**URL:** http://dx.doi.org/10.1080/03086647608073332

*Phosphorus and Sulfur*
1976, Vol. 1, pp. 271–279



# QUANTITATIVE STUDY OF THE NUCLEOPHILICITY OF THE THIOCARBONYL GROUP IN HETEROCYCLIC COMPOUNDS

by

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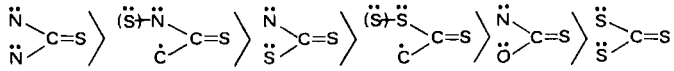
Received December 4, 1973

## ABSTRACT

When the kinetic constants of reactions between alkyl iodides and a number of heterocyclic thiocarbonyl derivatives are measured in solvent acetone, the reactivity extends over three orders of magnitude. The increasing nucleophiliticy is found in the series:



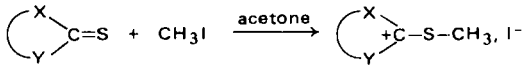
Bulkiness of the alkyl group in the alkylating agent has little influence when compared to the pyridine case. A correlation is found between the nucleophilic polarization energy calculated with HMO approximation and the measured constants.



## I. Introduction

In a study of the relationship between structure and nucleophilic reactivity of the thiocarbonyl group, the rate constants for S-methylation of various thiones were measured.

**Scheme I**



Earlier work in this field had been undertaken on the alkylation of thioureas[1-3] and $\Delta_4$-thiazoline-2-thiones.[4] The thiones in our study were chosen so that a general relationship between the nucleophilicity of the thiocarbonyl group and its electronic structure could be evaluated.

## II. Results

The rate constants for S-methylation of the selected thiones are shown in Table I.

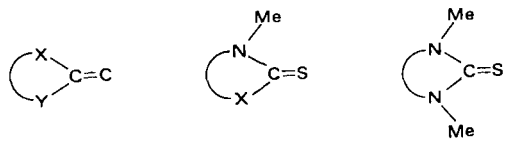
The enthalpies and entropies of activation were calculated directly from the experimental kinetic data by the Eyring equation[15] using a least-squares analysis.

The errors were calculated statistically[9] for a probability of 0.9.

## III. Discussion of Results

The reactivities of the compounds chosen ranged over three orders of magnitude, which seemed sufficiently wide for a useful evaluation of the relationship between the structure of the thiocarbonyl and its reactivity.

However, since the chosen thiones included compounds possessing the structures A, B and C, it was first necessary to confirm that the N–$CH_3$ group does not hinder the access of the electrophile to any appreciable extent.



(A) (B) (C)

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TABLE I

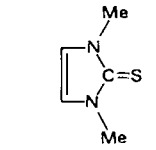
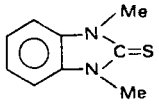
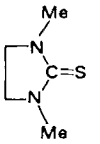
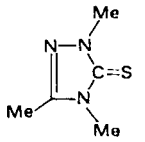
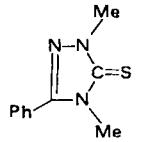
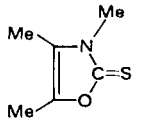
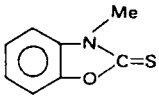
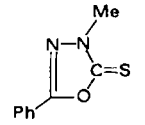
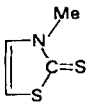
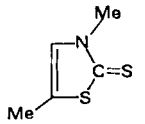
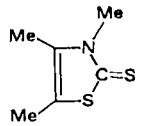
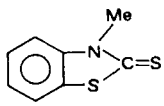
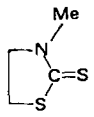
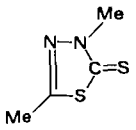
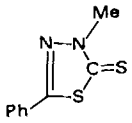
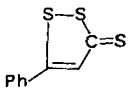
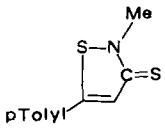
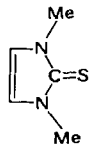
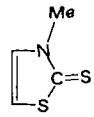
| Code | Thiones | Rate constants $k \times 10^6$ ($l mol^{-1} sec^{-1}$) 20°C | 25°C | 30°C | Enthalpies and entropies of activation x $mole^{-1}$ $\Delta H^{\neq}$ (kcal) | $\pm\Delta\Delta H^{\neq}$ | $-\Delta S^{\neq}$ (u.e.) | $\pm\Delta\Delta S^{\neq}$ |
|---|---|---|---|---|---|---|---|---|
| | Rate constants for the reaction of methyl iodide with thiones in acetone | | | | | | | |
| 1 |  | 2241 | 3198 | 4510 | 11.8 | 0.3 | 30.5 | 1.2 |
| 2 |  | 94.2 | 144.2 | 217.4 | 14.2 | 0.5 | 28.6 | 2 |
| 3 |  | 218.4 | 334.4 | 504.6 | 14.2 | 0.6 | 26.2 | 4 |
| 4 |  | 205.1 | 302.1 | 439.5 | 12.9 | 0.5 | 31.5 | 1.5 |
| 5 |  | 117.6 | 176.2 | 260.8 | 13.5 | 0.5 | 30.5 | 1.5 |
| 6 |  | 90.7 | 140.7 | 214.9 | 14.7 | 0.3 | 27.1 | 2 |
| 7 |  | 2.94 | 3.98 | 6.48 | 15.6 | 0.5 | 30.5 | 1.5 |
| 8 |  | 1.56 | 2.94 | 3.92 | 15.6 | 0.5 | 31.4 | 1.5 |
| 9 |  | 106.4 | 160.0 | 237.4 | 13.6 | 0.3 | 30.4 | 1 |
| 10 |  | 177.9 | 268.6 | 387.8 | 12.8 | 0.3 | 30.8 | 1.5 |
| 11 |  | 300.6 | 440.0 | 642.2 | 13.2 | 0.2 | 30.6 | 1 |
| 12 |  | 11.0 | 17.12 | 26.34 | 14.8 | 0.5 | 30.6 | 1.5 |

TABLE I—contd

| Code | Thiones | | Rate constants $k \times 10^6$ ($l mol^{-1} sec^{-1}$) 20°C | 25°C | 30°C | Enthalpies and entropies of activation x $mole^{-1}$ $\Delta H^*$ (kcal) | $\pm\Delta\Delta H^*$ | $-\Delta S^*$ (u.e.) | $\pm\Delta\Delta S^*$ |
|---|---|---|---|---|---|---|---|---|---|
| 13 |  | | 69.2 | 108.2 | 166.8 | 15.0 | 0.5 | 26.6 | 2.5 |
| 14 |  | | 11.8 | 17.12 | 26.05 | 14.5 | 0.5 | 31.6 | 2.5 |
| 15 |  | | 6.65 | 10.45 | 16.19 | 15.1 | 0.5 | 30.5 | 1.5 |
| 16 |  | (a) | 3.19 | 4.95 | 7.62 | 15.1 | 0.5 | 31.9 | 2 |
| 17 |  | | 18.0 | 28.4 | 44.3 | 15.3 | 0.4 | 27.9 | 1.5 |
| 18 |  | (a) | 436 | 665 | 976 | 13.6 | 0.5 | 27.2 | 1.5 |
| | Rate constants for the reaction of isopropyl iodide with thiones in acetone | | | | | | | | |
| 1 |  | | | 2.94 | | 15.9 | 0.5 | 30.5 | 1.5 |
| 9 |  | | | 0.228 | | 16.6 | 0.3 | 33.1 | 1.2 |

(a) Because of the low amount of compounds (a) prepared, the initial concentration of the solution was rather unprecise and therefore the errors in k and derived parameters are not quite as good as for the other compounds.

### *A. The Importance of Steric Effects*

It is very difficult to evaluate steric effects on reactivity independently of electronic effects. Whatever may be the importance of the differences in steric effects in the compounds studied, the order of nucleophilic reactivity would not be reversed since the most reactive centers are also the most sterically hindered.

Nevertheless, since the aim of the present study is to establish a quantitative relationship between the electronic structure of the thiocarbonyl group and its reactivity, it is necessary to evaluate the importance of this interaction.

There is almost no difference between the $pK_a$ of the 4-methyl, 2-methyl, 2-ethyl and 2-isopropyl pyridines (13). Thus we can consider that the inductive effects of these different alkyl groups are the same and that the differences in reactivity of these pyridines are due mainly to the differing degrees of steric interaction in the transition state.

Likewise the slight differences in reactivity of the 3-alkyl $\Delta_4$-thiazoline-2-thiones with methyl iodide in

**TABLE II**

**Rate Constants for the Reaction with Methyl Iodide in Acetone**

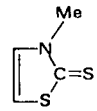
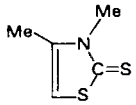
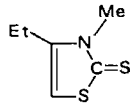
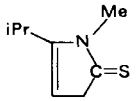
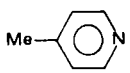
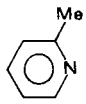
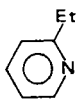
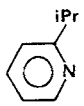
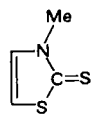
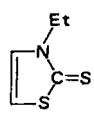
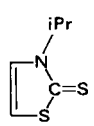
| Compounds | Rate constants at 30°C $k \times 10^6$ ($l$mol$^{-1}$ sec$^{-1}$) | Ref. |
|---|---|---|
|  | 237.8 | |
|  | 396 | 10 |
|  | 385.4 | 10 |
|  | 365.8 | 10 |

**TABLE III**

**Rate Constants for the Reaction with Methyl Iodide at 25°C**

| Compounds | Rate constants $k \times 10^6$($l$mol$^{-1}$ sec$^{-1}$) | Solvent | Ref. |
|---|---|---|---|
|  | 760 | $NO_2Bz$ | 14 |
|  | 162 | $NO_2Bz$ | 14 |
|  | 74.4 | $NO_2Bz$ | 14 |
|  | 24.5 | $NO_2Bz$ | 14 |
|  | 160 | $(Me)_2CO$ | |
|  | 159.1 | $(Me)_2CO$ | 10 |
|  | 173.6 | $(Me)_2CO$ | 10 |

acetone (Table II) allow us to consider the inductive effects of methyl, ethyl and isopropyl groups as being essentially the same.

Having established this, we proceed to consider the reaction of methyl iodide at centers possessing differing degrees of steric hindrance in the two series: pyridines and $\Delta_4$-thiazoline-2-thiones (Table III).

It is clear that while steric hindrance increases in the order Me < Et < iPr for the pyridines, the differences are very slight in the case of the $\Delta_4$-thiazoline-2-thiones. In fact, the isopropyl group has a slightly activating effect due to steric decompression in the transition state by elongation of the C=S bond.[10]

Nevertheless it is possible that in the case of the $\Delta_4$-thiazoline-2-thiones, whatever the degree of steric hindrance to the approach of the electrophile, attack occurs only from the non-hindered side.

If this is the case, the ratio of the reactivities of N-methyl-thiazoline-2-thione (A) and NN′-dimethyl-imidazoline-2-thione (B) (*i.e.*, $R_2/R_1$) with methyl iodide and isopropyl iodide should be at least of the same size as the ratio of the reactivities for 4-methyl (C) and 2-methyl (D) pyridines (*i.e.*, $R_2'/R_1'$) in the same reaction (Table IV):

$$k_{A,MeI}/k_{B,MeI} = 0.05 = R_1 \quad k_{A,iPrI}/k_{B,iPrI} = 0.077 = R_2$$

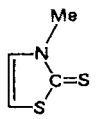
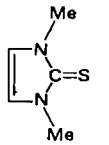
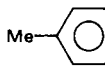
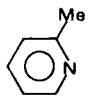
$$R_2/R_1 = 1.5$$

$$k_{C,MeI}/k_{D,MeI} = 4.7 = R_1' \quad k_{C,iPrI}/k_{D,iPrI} = 40 = R_2'$$

$$R_2'/R_1' = 8.5$$

**TABLE IV**

**Rate Constants for the Reaction with Methyl and Isopropyl Iodide in Acetone**

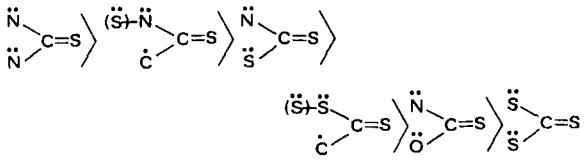
| Compounds | | Rate constants at 25°C $k \times 10^6$($l$mol$^{-1}$ sec$^{-1}$) $CH_3I$ | iPrI | Solvent | Ref. |
|---|---|---|---|---|---|
|  | (A) | 160 | 0.228 | $(CH_3)_2CO$ | |
|  | (B) | 3198 | 2.94 | $(CH_3)_2CO$ | |
|  | (C) | 760 | 1.99 | $NO_2Bz$ | 14 |
|  | (D) | 162 | 0.05 | $NO_2Bz$ | 14 |

This simple calculation demonstrates the weakness of the above hypothesis.

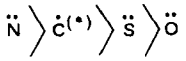
We can thus reasonably consider that for all the compounds studied the steric effects are of second order in comparison ot the variations in electronic effects.

*B. Qualitative Electronic Effects*

From the results, it is possible to give a qualitative relationship between reactivity and the nature of neighboring heteroatoms of the thiocarbonyl group. In general, the order of nucleophilicity is:



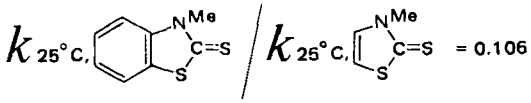
That is, the reactivity decreases as the atom to the thiocarbonyl group changes in order:



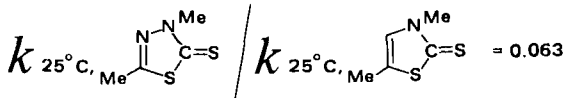
The same calssification is obtained by examining the $pK_a$ of several thiones in the same heterocyclic series (Table V).

On the other hand, for a given chemical environment of the thiocarbonyl group, certain qualitative relationships between the structure of the heterocycle and the nucleophilic character can be drawn.

Derivatives possessing a fused six-membered ring are much less reactive (10-20 times) than the corresponding unsaturated heterocyclic compounds.

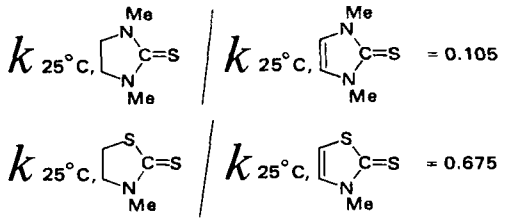


In the same way, substitution by a nitrogen in the 4-position of the heterocycle has a strongly deactivating effect (10-20 times.)

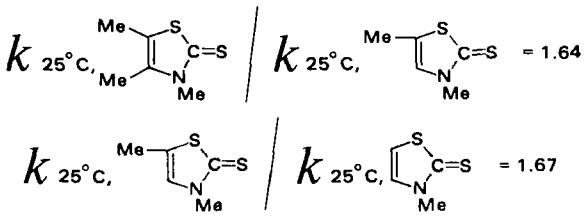


The 4,5-dihydro-derivatives are also less reactive than their unsaturated homologues but this effect is more variable than the previous two effects.

(*) One may note that the order of the C atom depends upon a sulfur atom in 4-position of the cycle.



An alkyl substituent in the position 4 or 5 of the heterocycle has an activating effect of about 1.5.



Finally, an aromatic substituent in the position 4 or 5 of the heterocycle has little, if any, effect.

*C. Comparison of Reactivity and Calculated π-Indices*

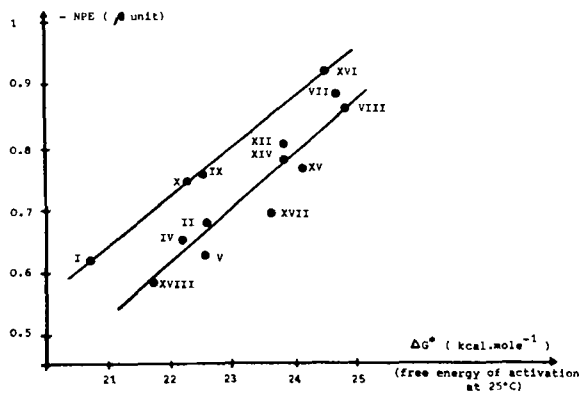
The nucleophilicity has been compared with various π-indices calculated using the ω*, π-LCAO method.[18] The parameters used are shown in Table VI (experimental section).

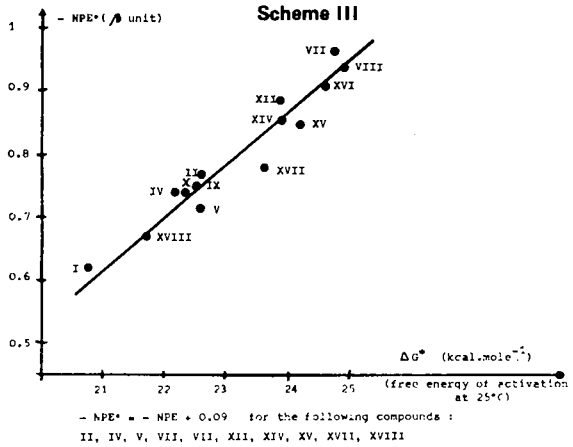
The correlations obtained with various static π-indices of the C=S bond, such as the π-electron density on the thiocarbonyl sulfur atom, are rather poor.

The best correlation was found using the nucleophilic polarization energy (npe) (Scheme V) which may be considered as dynamic indices characteristic of the π-system.

This correlation is shown in Scheme II. Here it can be seen that compounds with a hetero-atom in position

**Scheme II**






4 of the ring form a separate group. This is perhaps a result of a difference in solvation.[19]

The compounds can be regrouped to give a single correlation by adding a corrective factor, fixed empirically at $-0.09\beta$ unit, to npe of the above mentioned compounds (Scheme III).

Given this correction, the free energies of activation relate to the npe with a mean error of 0.3 kcal.

## IV. Conclusion

We have tried to lay the basis of a general study of the nucleophilicity of the thiocarbonyl group by drawing out several coherent lines of attack from what is essentially a new field of study.

We were able to collate a certain number of results relative to qualitative relationships between nucleophilicity and the chemical environment of the thiocarbonyl group. The correlation obtained between reactivity and the corrected energies of polarization of the $\pi$-bond can serve as an approximate previsional rule (a mean error of 0.3 kcal/mole in $\Delta G^*$).

At the present time we are developing an approach to this reactivity in terms of C.N.D.O. approximations[20] and seeking to localize the reactivity by means of the photoelectronic spectroscopy.[21]

## V. Experimental Section

### A. Kinetic study

(a) *Theory*

The technique used in the laboratory and the calculations carried out have already been described.[4,8,9,10] Briefly, the principle is as follows:

The reaction (Scheme I) gives rise to an ionic species; it is thus possible to follow the course of the reaction by conductimetry. The reaction is followed in the initial stages by measuring the variation in conductivity of the acetone solution.

The concentration of the salt at any moment is known by establishing an experimental relationship between the conductivity and this concentration.

Partly to avoid the eventual equilibria between thione and thiol,[7] and partly because the salt formed by the reaction with methyl iodide are not very stable in acetone at the temperatures used (Scheme 4), heterocycles of type I have been omitted from this study. The fluctuations observed make it impossible to measure the rate constants under normal conditions.[10]

**Scheme IV**

(b) *Calibration*

Numerous measurements show that the observed conductivity can be considered to be independent of the cation-type for a given temperature and concentration. Thus it was possible to establish a joint relation between the conductivity and the salt concentration.

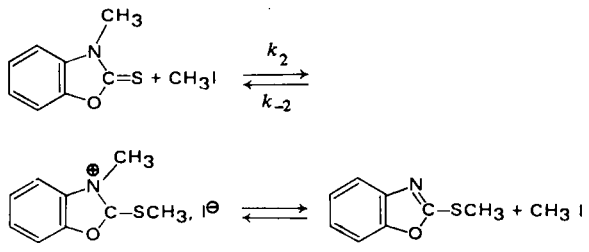
In addition to a considerable saving in time, such a relation allows the determination of rate constants of compounds whose salts are unstable.

(c) *Reaction Order*

Previous experiments[4] have established that reactions of this type are bimolecular and obey a first order rate law with respect to each of reagents. This has been confirmed for the series of compounds studied here.

(d) *Points of Note: Equilibrated Reactions and Secondary Reactions*

The preparation of salts of compounds in the series of oxazoline-2-thiones shows that the alkylation reaction is equilibrated. This phenomenon is particularly clear in the case of benzoxazoline-2-thione the salt of which, 2-methythio-benzoxazolium iodide cannot be isolated.[11] A study of the reaction by nmr suggests the following mechanism:



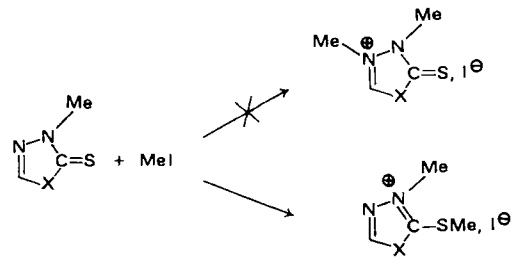
Nevertheless, when the measurements are taken at the beginning of the reaction, the deviation from normal behaviour is very slight and the rate constant $k_2$ can be calculated with sufficient precision.

In the case of dithiolane-2-thione, a very important deviation makes determination of the rate constant impossible under normal conditions.

This divergence from second order behaviour is due to a rapid condensation of the thione with the 2-methylthio-dithiolanium cation.[12]

For all the compounds studied by us, alkylation takes place

only on the thiocarbonyl sulfur. Methylation of the nitrogen in position 4 of the type 1,3,4-triazoline-2-thione, 1,3,4-oxadiazoline-2-thione and 1,3,4-thiadiazoline-2-thione was not detected by nmr.



This results agrees with the ratio of about 200/1 observed for the relative rates of S- and N-methylations in thiazoline-2-thione and thiazole series.[4]

### B. HMO calculations by $\omega^*$ technique[18]

**Scheme V**

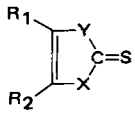
8 $\pi$-electrons distributed over 6 atoms. Calculated energy = $E_1$

6 $\pi$-electrons distributed over 5 atoms and 2 $\pi$-electrons localised on the sulfur. Calculated energy = $E_2$

$$E_2 - E_1 = \text{npe}$$

**TABLE V**

**p$K_a$ Values of Conjugate Acids of Some Thiocarbonyl Compounds:**



| $R_1$ | $R_2$ | X | Y | p$K_a$ | Ref. |
|---|---|---|---|---|---|
| Me | Me | NMe | NMe | −1.6 | 16 |
| H | Ph | NMe | NMe | −2.2 | 16 |
| Me | Me | S | NMe | −3.0 | 16 |
| H | Ph | S | NMe | −3.7 | 16 |
| H | H | S[a] | HC= | −3.96 | 17 |
| Me | Me | O | NMe | −4.3 | 16 |
| H | Ph | O | NMe | −4.8 | 16 |
| H | H | S | S | −5.25 | 17 |

[a] 1,2-Dithiol-3-thione.

### C. Preparation of compounds

For reasons already given above (Scheme IV), the hydrogen carried by the nitrogen $\alpha$ to the thiocarbonyl must be substituted by a methyl group. The preparations of compounds not substituted at nitrogen are generally described in the literature. The synthesis of N-methyl substituted derivatives is often delicate[5] and in the majority of cases direct synthesis is not possible.[6] The essential pathways for the synthesis of N-methyl thioamides type compounds is summarized in Scheme VI.

Only novel syntheses are reported here. The nmr shifts for most products are given.

**TABLE VI**

**Parameters for the Molecular Orbital Calculations**

| $\omega = 1$ | $\omega' = 1.2$ | $\omega'' = 0.85$ | $\omega^* = 0.6$ |
|---|---|---|---|
| Atom | $\delta_r^\circ$ | Bond | $\rho_{rs}^\circ$ |
| $\ddot{C}H_3$[(a)] | 2 | $\dot{C}$–$\dot{C}$ | 1 |
| $\dot{C}$ | 0 | $\dot{C}$–$\dot{N}$ | 1.1 |
| $\dot{S}$ | 0.5 | $\dot{C}$–$\dot{S}$ | 0.6 |
| $\dot{N}$ | 0.5 | $\dot{C}$–$\dot{N}$ | 0.8 |
| $\ddot{S}$ | 1 | $\dot{C}$–$\ddot{S}$ | 0.5 |
| $\ddot{N}$ | 1.5 | $\dot{C}$–$\ddot{O}$ | 0.7 |
| $\ddot{O}$ | 2 | $\dot{M}e$–$\dot{N}$ | 0.5 |
| | | $\dot{M}e$–$\dot{C}$ | 0.6 |
| | | $\dot{N}$–$\dot{N}$ | 0.7 |
| | | $\ddot{S}$–$\dot{N}$ | 1.1 |
| | | $\ddot{S}$–$\ddot{S}$ | 0.9 |

A.I.P.: $\delta_C^\circ = \gamma . \delta_X^\circ$

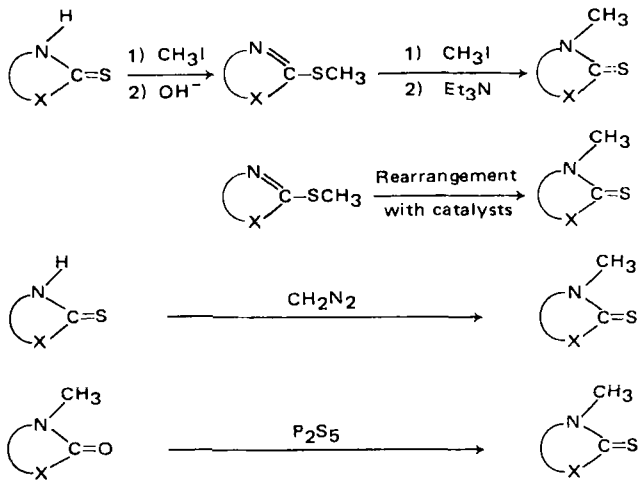
$\gamma = 0.1$ for $\dot{X}$ and $\ddot{X}$

Exception:

$\gamma = -0.3$ for $\ddot{X}$ = Me

[a] Methyl substituant is treated as an heteroatom bearing an electronic lone pair.

**Scheme VI**



*1,3-dimethylimidazoline-2-thione (1)*

1-Methylimidazoline-2-thione (Fluka A.G.) (0.1 mol) and methyliodide (0.1 mol) were left for 48 hr at room temperature. The mixture was then treated with potassium hydroxide solution (N/10, 100 ml) and extracted with chloroform. The chloroform was removed under vacuum and the resulting brown oil was distilled (bp 85°/18 mm). The colorless oil thus obtained was identified as 2-methylthio-1-methylimidazole (yield 75%).

7 g (0.055 mol) of this compound and 0.2 g (0.016 mol)

of iodine were sealed in an ampoule and heated to 120°C during 12 hr. The resulting solid was crushed, washed with an aqueous solution of potassium iodide and crystallized three times from benzene. The product was in the form of fine, pale, brown needles, mp 81°C (yield 40%) nmr (δ ppm, solv. $(CD_3)_2CO$: 3.60 (S, 6H); 6.95 (S, 2H).

*1,3-Dimethylbenzimidazoline-2-thione (2)*

Synthesis according to Fukati[22] yield 60%, mp 150°C (lit: 151°C,[22] 153–154°C[23]). (δ ppm; solv: $(CD_3)_2CO$: 3.04 (S, 6H); 3.55 (S, 4H).

*1,3-Dimethyl-imidazoline-2-thione (3)*

Synthesis according to Huenig.[24] Yield 78%, mp 110°C (lit. 110°C.[24] NMR (δ ppm; solv: $(CD_3)_2CO$): 3.40 (5, 6H); 3.55 (S, 4H).

*1,3,5-Trimethyl-1,3,4-triazoline-2-thione (4)*

Synthesis according to Kroger,[25] mp 104°C (lit. 105°C.[25] Nmr (δ ppm; solv: $CDCl_3$): 2.35 (S, 3H); 3.54 (5, 3H); 3.77 (S, 3H).

*1,3-Dimethyl-5-phenyl-1,3,4-triazoline-2-thione (5)*

Synthesis according to Sandstrom,[26] mp 136°C. Nmr (δ ppm; solv: $CDCl_3$): 3.67 (S, 3H); 3.88 (S, 3H); 7.60 (m, 5H).

*3,4,5-Trimethyl-$\Delta_4$-oxazoline-2-thione (6)*

Synthesis according to Kjellin.[16] Nmr (δ ppm; solv: $CDCl_3$): 2.11 (S, 3H); 2.19 (S, 3H); 3.47 (S, 3H).

*3-Methylbenzoxazoline-2-thione (7)*

10 g (0.06 mol) of benzoxazole-2-thiol (Fluka A.G.) were added to an ethereal solution of diazomethane. When the evolution of gas was finished the ether was evaporated and the resulting oil distilled (bp 55–60°C/0.05 mm). The distillate was a pale yellow oil (mp 9°C) which was identified as 2-methylthiobenzoxazole. 5 g (0.028 mol) and one drop of methyl iodide were sealed in an ampoule and heated to 90°C for one week. The resulting solid was purified by double crystallization from benzene. Yield 90%, mp 127°C (lit.: 132°C[29]). Nmr (δ ppm; solv: $(CD_3)_2CO$): 3.73 (S, 3H); 7.37 (S, 4H).

*5-Phenyl-3-methyl-1,3,4-oxadiazoline-2-thione (8)*

Synthesis according to Sandstrom,[26] mp 124°C. Nmr (δ ppm; solv: $CDCl_3$): 3.70 (S, 3H); 7.50 to 8.08 (m, 5H).

*3,4,5-Trimethyl-$\Delta_4$-thiazoline-2-thione (9)*

Synthesis according to Roussel.[34] Nmr (δ ppm; solv: $(CD_3)_2CO$): 2.10 (S, 3H); 2.17 (S, 3H); 3.53 (S, 3H).

*3,4-Methyl-$\Delta_4$-thiazoline-2-thione (10)*

Synthesis according to Roussel.[34] Nmr (δ ppm; solv: $(CD_3)_2CO$); 2.28 (d, 3H); 3.55 (S, 3H); 6.45 (q, 1H).

*3-Methyl-$\Delta_4$-thiazoline-2-thione (11)*

Synthesis according to Roussel,[28] mp 46°C. Nmr (δ ppm; solv: $(CD_3)_2CO$): 3.58 (S, 3H); 6.76 (d, 1H); 7.33 (d, 1H).

*3-Methylbenzothiazoline-2-thione (12)*

Synthesis according to Chambonnet,[30] mp 91°C. Nmr (δ ppm; solv: $(CD_3)_2CO$): 3.79 (S, 3H); 7.45 (m, 4H).

*3-Methylthiazolidine-2-thione (13)*

Synthesis according to Dewey,[31] mp 69°C. Nmr (δ ppm; solv: $(CD_3)_2CO$): 3.22 (S, 3H); 3.34 (t, 2H); 4.22 (t, 2H).

*3,5-Dimethylthiadiazoline-2-thione (14)*

Preparation according to Sandstrom,[26] mp 52–53°C.

*5-Phenyl-3-methyl-1,3,4-thiadiazoline-2-thione (15)*

Preparation according to Sandstrom,[26] mp 123–124°C. Nmr (δ ppm; solv: $CDCl_3$) 3.95 (s, 3H); 7.65 (m, 5H).

*1,3-Dithiole-2-thione (16)*

Preparation according to Mayer,[32] mp 48–49°C.

*5-Phenyl-1,2-dithiole-3-thione (17)*

Preparation according to Thuillier,[33] mp 126°C. Nmr (δ ppm; solv: $(CDCl_3)$): 7.20 (S, 1H); 7.5 (m, 5H).

*5-p-tolyl-2-Methylizothiazoline-3-thione (18)*

Preparation according to Le Coustumer.[27] Nmr (δ ppm; solv: $CCl_4$): 2.39 (S, 3H); 3.70 (S, 3H); 7.05 (S, 1H); 7.30 (S, 4H).

**Acknowledgements**

We thank Prof. J. Sandström for having supplied us with samples of products IV, V, VIII, XIV and XV and Prof. G. le Coustumer for a sample of compound XVIII.

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