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HETEROCYCLIC N-DITHIOCARBOXYLIC ACIDS

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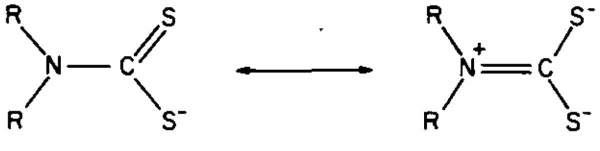
Abstract — A survey is given of the methods of preparation and of the physical and chemical properties of heterocyclic dithiocarbamic acids in which the NCS_2H nitrogen atom forms part of a heteroaromatic ring.

I. INTRODUCTION

Addition of carbon disulphide to a strongly nucleophilic anion yields the anion of a dithiocarboxylic acid. Dithiocarbamates (1), an important class of chelating agents, can be prepared from secondary amines, a base and carbon disulphide.[1] Much of their stability is attributed to the strong ground state contribution of the zwitterionic form 1b.



1a 1b

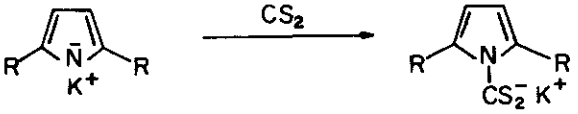
The salts of N-dithiocarboxylic acids of many heteroaromatic azoles (pyrroles, di- and triazoles and their benzo derivatives) are well characterised compounds. However, the corresponding free acids are unknown, presumably owing to their instability.

This review, which covers the literature up to mid-1985, includes 60 references, and covers the synthesis and properties of the dithiocarbamates of pyrroles, indoles, carbazoles, imidazoles, benzimidazoles, triazoles, benzotriazoles and pyrazoles.

II. SYNTHESIS OF DITHIOCARBAMATES

The pyrrole N-dithiocarbamate anion is an interesting ligand for several reasons. An early report by Duffy and coworkers [2] indicated that such dithiocarbamates would be difficult to prepare, partly because of the low basicity of the amine hydrogen. The first report by Kellner and coworkers [3] of the synthesis of the above dithiocarbamate speculated that a rearrangement might occur to yield the 2-substituted pyrrole anion. Additionally, the pyrrole N-dithiocarbamate ligand does not favour the normal resonance structures ascribed to dithiocarbamates in which a positive charge is localised on the nitrogen atom. Thus, a potentially new set of properties of the metal complexes might arise.

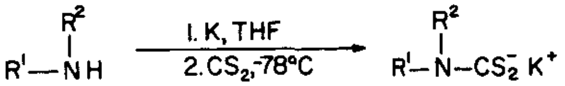
In 1938, Oddo and Alberti[4] prepared the potassium pyrrole-1-dithiocarboxylates 2 (R=H or CH_3) directly from CS_2 and the potassium derivatives of the corresponding pyrrole, using toluene as solvent. These salts are extremely hygroscopic and air-sensitive. Recently, an improved synthesis of the potassium pyrrole N-dithiocarboxylate 2 (R=H) was carried out by Bereman and Nalewajek[5] by treating potassium pyrrolide in dry THF with CS_2 at -78 °C.[4,5]



2a R=H
2b R=Me

El A'mma and Drago[6] prepared sodium pyrrole-1-dithiocarboxylate as an approximately 1M solution by reacting NaH in dimethyl sulphoxide with pyrrole and CS_2.[6]

It had been generally accepted that dithiocarbamates derived from indole, indoline, carbazole and imidazole could not be prepared; some have been treated theoretically.[7] The failure of these amines to form dithiocarbamates has often been ascribed to the inability of the usual synthetic routes to activate the amine proton sufficiently.[1] However,in 1978 Bereman and Nalewajek reported[8] the preparation of the dithiocarbamates of indole, indoline, carbazole and imidazole 3. The general method consists of treating a solution of the parent amine in dry THF with potassium metal. After 24 h, the mixture is cooled to -78 ^0C and CS_2 added. The dithiocarbamate is then *precipitated in as the potassium salt by the addition of degassed hexane.*



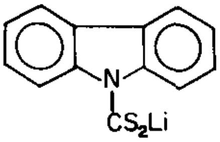
$$R^1R^2N{-}H \xrightarrow[2.\ CS_2,\ -78^\circ C]{1.\ K,\ THF} R^1R^2N{-}CS_2^-\ K^+$$

3a R^1R^2 = indole
3b R^1R^2 = carbazole
3c R^1R^2 = imidazole

Potassium Dithiocarbamates of Indole, Carbazole and Imidazole:[8]

Derivative	Yield(%)	m.p.(^oC)	Sensitivity to Air
Indole	90	58-61	Very hygroscopic, extremely air-sensitive
Indoline	90	240(decomp)	Relatively air-stable
Carbazole	80	120(decomp)	Very hygroscopic, extremely air-sensitive
Imidazole	90	158-161	Relatively air-stable

Lithium carbazole-9-dithiocarboxylate 4 was prepared by treating carbazole with phenyllithium in ether followed by addition of CS_2.[9,10] Islamova[11] found that the reaction of carbazole with CS_2 proceeds only in alkaline media and that a metal carbazole N-dithiocarboxylate salt was formed. With di-, tetra-, and hexa-hydrocarbazole, it is reported[11] that the reaction occurred in the absence of alkali to give the hydrogenated carbazole N-dithiocarboxylate salt and a mole of hydrogenated carbazole.



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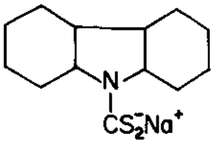

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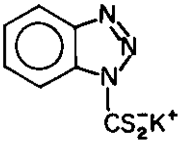

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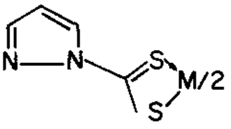
Dodecahydrocarbazole N-dithiocarboxylate 5 was prepared from dodecahydrocarbazole by reaction with CS_2 in an alkaline medium.[12] In addition, potassium benzotriazole-1-dithiocarbamate 6 was prepared by the reaction of benzotriazole with KOH and CS_2.[13]

Trofimenko[14] thought it of interest to prepare pyrazole N-dithiocarboxylates, since it appeared likely that chelates of structure 8 rather than 7 would be formed with divalent transition metal ions, owing to the favourable geometry involved.[15-17] Addition of CS_2 to a suspension of a potassium pyrazolide in benzene or THF results in the exothermic formation of potassium pyrazole N-dithiocarboxylates 9 which are moderately stable to storage in a sealed vessel.[14] Sodium pyrazole N-dithiocarboxylates were prepared analogously, from sodium pyrazolide and CS_2. Sodium pyrazole-1-dithiocarboxylate is less stable to storage than the corresponding potassium salt.[14]



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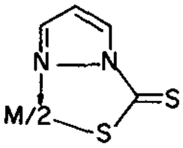

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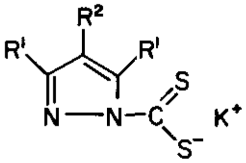

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III. PROPERTIES OF DITHIOCARBAMATES

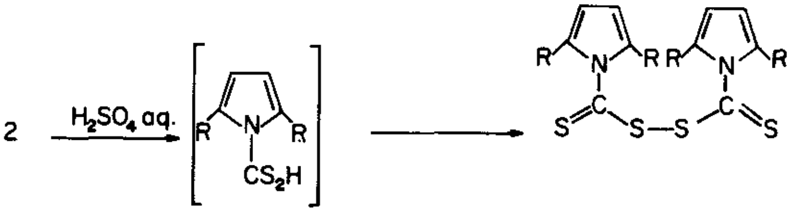
A. Physical Properties

The alkali metal N-dithiocarbamates of pyrroles, indoles, carbazoles, imidazoles, triazoles, benzotriazoles and pyrazoles are usually coloured, air-sensitive solids. The dithiocarbamate salts of pyrrole, indole and carbazole are highly hygroscopic and extremely air-sensitive, while the imidazole-1-dithiocarboxylate salts are relatively air-stable.[8] Potassium pyrazole-1-dithiocarboxylate is moderately stable to storage in a sealed vessel, in which it develops a pressure of CS_2, but sodium pyrazole-1-dithiocarboxylate is less stable to storage. All of the above dithiocarbamate salts are soluble in water and in ethanol, giving alkaline solutions.

B. Chemical Properties

i. Action of Acids and Alkalis

Treatment of a cold aqueous solution of potassium pyrrole-1-dithiocarboxylate 2 (R=H or CH_3) with dilute H_2SO_4 immediately produces a light yellow oil, doubtless the respective free pyrrole-1-dithiocarboxylic acid 10 (R= H or CH_3), which undergoes rapid oxidation to the corresponding disulphide 11.[4] The pyrrole N-thiocarbonyl disulphide 11 (R=H) was also obtained from the oxidation of pyrrole derivative 2 with 10% H_2O_2.[4]



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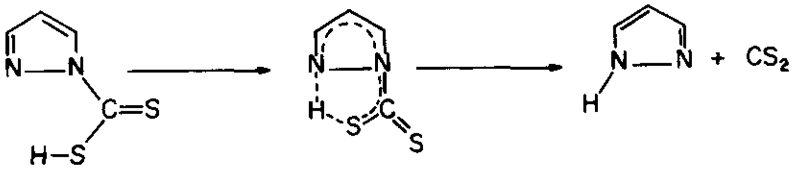
Solutions of alkali metal pyrazole-1-dithiocarboxylates are less stable than the solid salts, particularly when acidified.[14] For these compounds, decomposition by acid is even faster than that of alkyl dithiocarbamates because a direct intramolecular route (Scheme 1) allows proton transfer from sulphur to nitrogen, thereby leading to reformation of pyrazole and CS_2. Such a cyclic transition state probably operates in most, if not all, reactions of these pyrazole derivatives which involve bond making or bond breaking at the 1-position.[14]



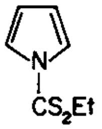
Scheme I

ii. Formation of Esters

The structure of the dithiocarbamates is supported by the great facility with which they form esters when treated with diverse alkyl halides. Such esters are usually formed in good yields and form well-characterised derivatives.

1) Pyrrole N-Dithiocarboxylate Esters

Potassium pyrrole-1-dithiocarboxylate 2a reacts readily with excess ethyl iodide in absolute ethanol to yield ethyl pyrrole-1-dithiocarboxylate 12,[4] with phenyldiazonium chloride to give (among other products) the corresponding phenyl pyrrole-1-dithiocarboxylate 13[4] (R= H or CH_3 prepared), and with benzyl chloride to yield benzyl pyrrole-1-dithiocarboxylate 14.[18,19]



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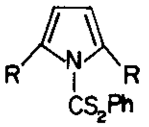

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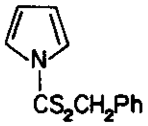

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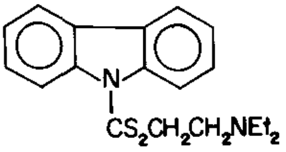
2) Carbazole N-Dithiocarboxylate Esters

These esters have been prepared by direct alkylation of metal dithiocarboxylates of carbazole. Thus, the diethylaminoethyl ester 15 of carbazole-9-dithiocarboxylic acid, which is useful as a spasmolytic, was prepared by heating lithium carbazole-9-dithiocarboxylate 4 under reflux with diethylaminoethyl chloride in a xylene.[9] The hydrochloride and methiodide salts of carbazole 15 have also been prepared.[9,10]



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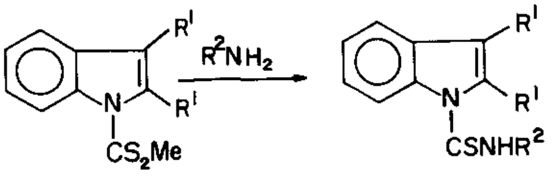

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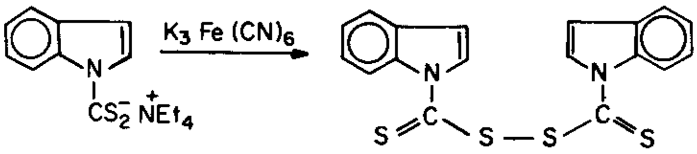
R¹= H or Me

3) Indole N-Dithiocarboxylate Esters

Methyl indole-1-dithiocarboxylate derivatives 16 have been synthesised by the reaction of NaH and CS_2 with indoles, followed by treatment with dimethyl sulphate.[20] Substitution of the methylthio group has been carried out with various amines, thereby affording the thioamide derivatives 17.[20] Oxidation of the dithiocarbamate 18 with potassium ferricyanide yielded the disulphide 19.[21]



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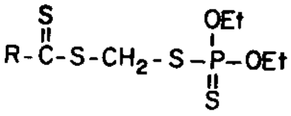


$R-\overset{\overset{S}{\|}}{C}-S-CH_2-S-\underset{\underset{S}{\|}}{\overset{OEt}{P}}-OEt$

20

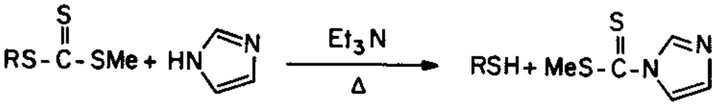
R= N-indolyl or N-imidazolyl

Dithiophosphoric esters 20 of substituted dithiocarbamates were prepared by reacting *O,O*-diethyl-*S*-chloromethyldithiophosphate with an ammonium salt of dithiocarbamic acid.[22] They have been used effectively as insecticides and acaricides against *Musca domestica*, *Sitophilus granarius*, *Mamestra brassicae*, *Aphis fabae* and *Tetranychus urticae*.[22]

4) Imidazole N-Dithiocarboxylate Esters

Imidazole- and benzimidazole-thioesters have also been obtained by substitution or cyclisation methods. Heating imidazole with heterocyclic methyl trithiocarbamates 21 (R=benzimidazol-2-yl or benzthiazol-2-yl) in the presence of triethylamine afforded methyl imidazole-1-dithiocarboxylate 22.[23]

In this reaction the heterocyclic thiols were displaced in preference to methanethiol on account of the low pK of the former thiols; hence the formation of ester 22 rather than the formation of the doubly heterocyclic ester.



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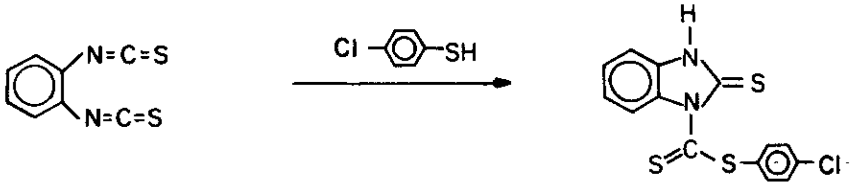
22

o-Tolylene diisocyanate 23 underwent cyclisation when treated with *p*-chlorothiophenol to give the thioester 24.[24]



23

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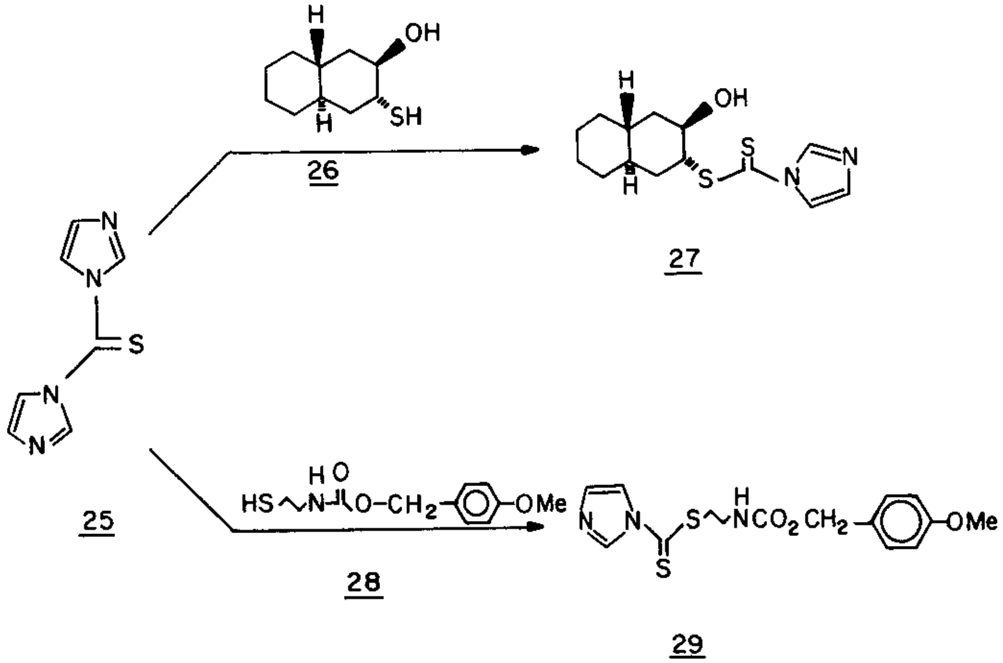
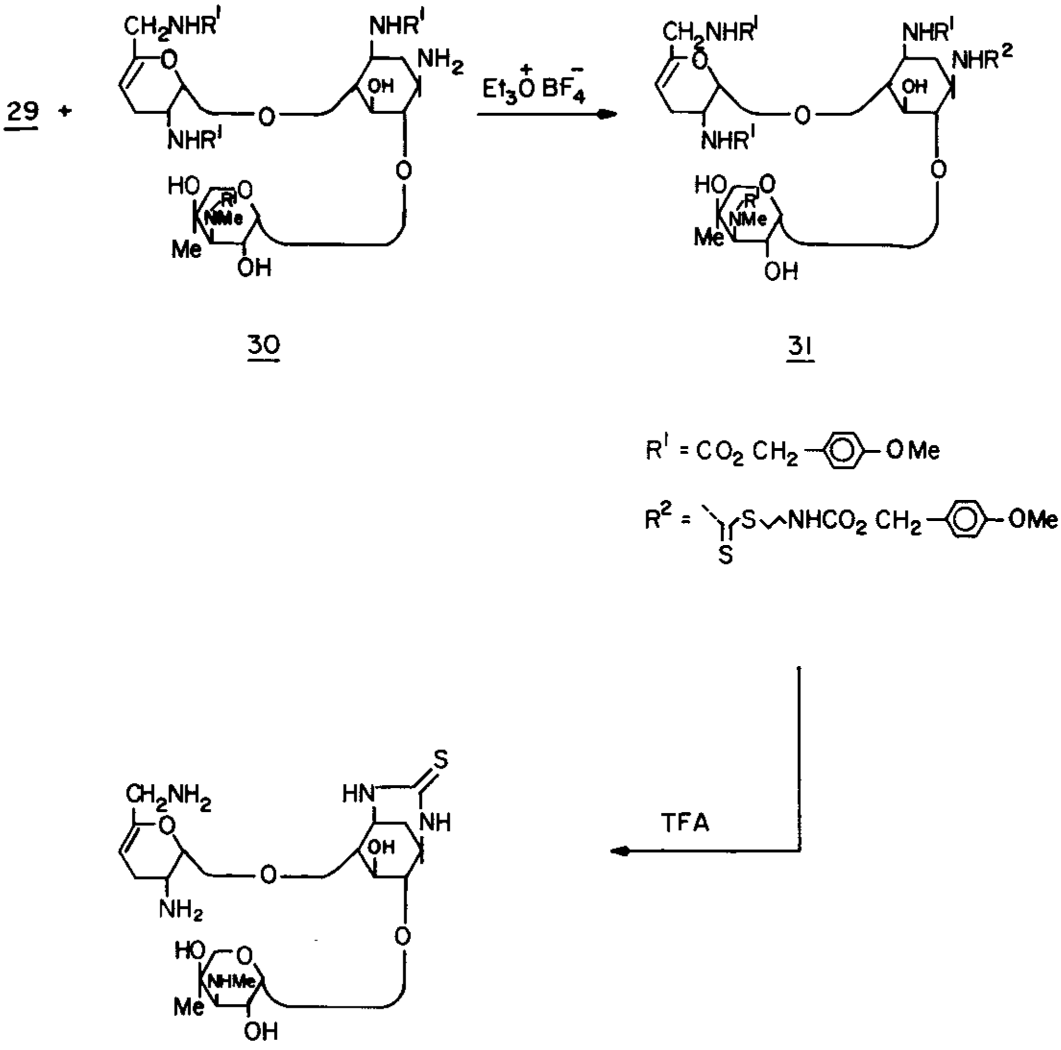
Forster and Owen[25] found that a cyclic thiolthioncarbonate could not be obtained by the reaction of 3-(alpha-mercapto)-*trans*-decalin-2-beta-ol 26 with *N,N'*-thiocarbonyldi-imidazole.[23] The only identified product was the imidazolyl derivative 27.[25] In contrast, reaction of 1,1'-thiocarbonyldi-imidazole 25 with the thiol 28 afforded 1-[2-(4-methoxybenzyloxycarboxylamino)-ethanethiocarbonyl]imidazole 29.[26]



After treatment of ester 29 with triethyloxonium tetrafluoroborate, the adduct was condensed with the 3,2',6',3''-tetrakis-*N*-(4-methoxybenzyloxycarbonyl)sisomicin 30 to give the protected thiocarbonyl sisomicin derivative 31 in 73% yield. Deprotection of heterocycle 31 with trifluoroacetic acid afforded 1-*N*:3-*N*-thiocarbonylsisomicin 32 as the only isolable product.

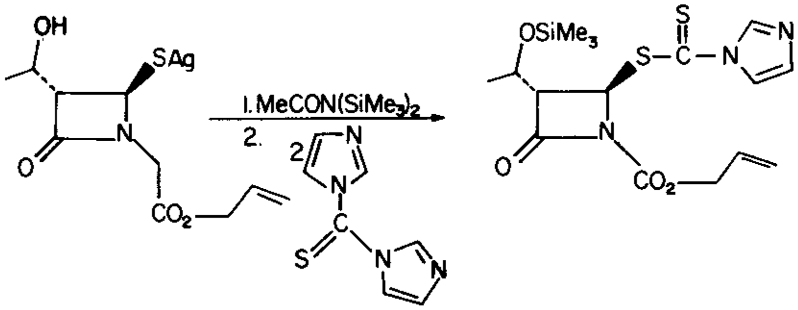
Treatment of the silver salt 33 with bis(trimethylsilyl)acetamide in methylene chloride gave the trimethylsilylether,[27] which without isolation was treated with two equivalents of thiocarbonyldi-imidazole, thereby affording the dithiocarbamate 34.


29 +
CH2NHR1
NHR1
NH2
OH
O
HO
R1
NMe
Me
OH
Et3O+ BF4−
NHR2
R1 = CO2 CH2—⟨⟩—OMe
R2 = S—S⌃NHCO2 CH2—⟨⟩—OMe
TFA
S
HN
NH
CH2NH2
NH2
NHMe

30

31

32

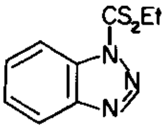

OH
SAg
O
N
CO2
1. MeCON(SiMe3)2
2.
2
N
S
C
OSiMe3
S—C—N

33

34

5) Triazole and Benzotriazole N-Dithiocarboxylate Esters

Esters of benzotriazole-1-dithiocarbamates were prepared by the usual method of reacting benzotriazole-1-dithiocarbamate salts with the appropriate alkyl or dialkyl halides. Thus, the reaction of potassium benzotriazole-1-dithiocarboxylate 6 with ethyl iodide gave the corresponding thioester 35 in 26% yield.[28] Reaction of the benzotriazole derivative 35 with dichloromethane and with dichloroethane gave the respective bis(benzotriazolyldithiocarbamates) 36 and 37 .[13]



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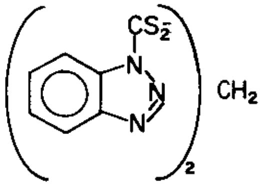

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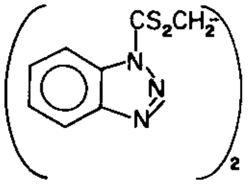

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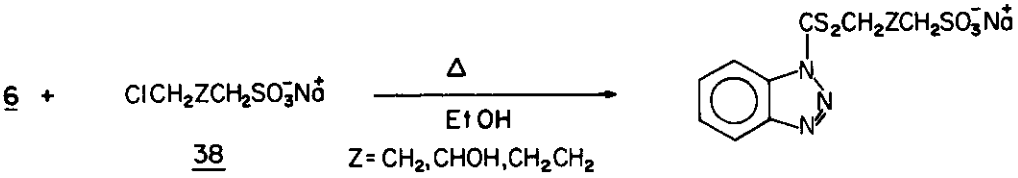
Reaction of potassium benzotriazole-1-dithiocarbamate 6 with propane- or butane-sultones 38 in refluxing ethanol gave the corresponding esters 39.[29]



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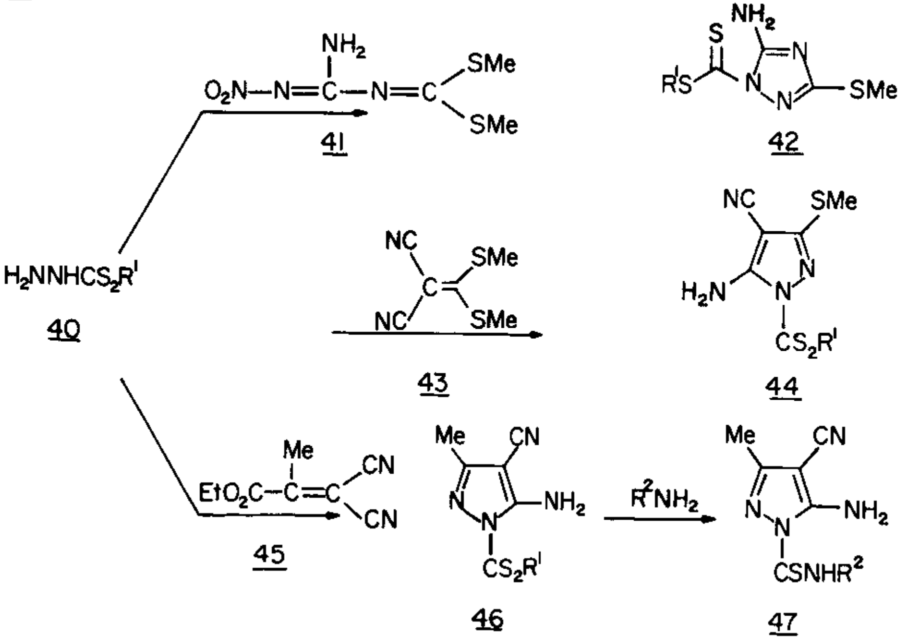
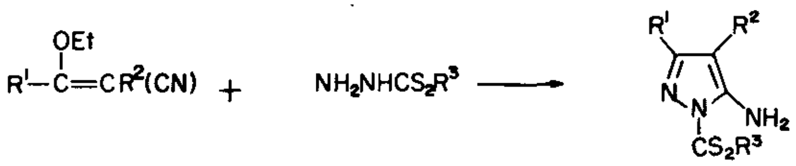
According to Russian workers[30] aryl beta-(triazole-1-dithiocarboxylate)ethanesulphonates can be prepared by the reaction of triazole-1-dithiocarboxylic acid with aryl ethanesulphonates. 1,2,4-Triazole-1-dithiocarboxylate esters 42 were obtained by the cyclisation of the hydrazine derivatives 40 with the thioacetals 41.[31]



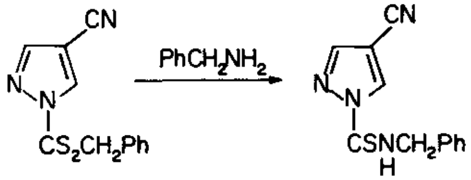


48 40 49

6) Pyrazole N-Dithiocarboxylate Esters

Pyrazole N-dithiocarboxyl esters have been prepared by both cyclisation and alkylation methods:

a) Cyclisation. Cyclisation of the thioacetal 43 with the hydrazine derivative 40 gave various pyrazole-1-dithiocarboxylate esters 44.[32] Reaction of the hydrazine derivative 40 with the unsaturated esters 45 yielded the pyrazole-1-dithiocarboxylate esters 46, which readily react with various primary amines to give the thioamides 47.[33] The reaction of hydrazine esters 40 with ethoxyacrylonitriles 48 gave the corresponding pyrazole-1-dithiocarboxylate esters 49.[34]



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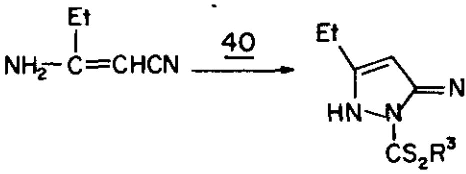
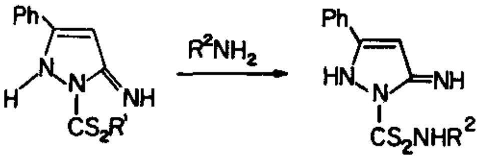
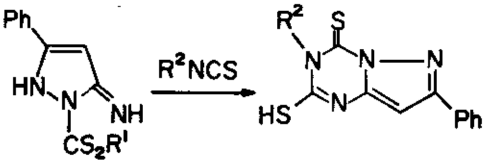


52 53

Treatment of pyrazole-1-dithiocarboxylate esters with primary or secondary amines has been shown to give thioamides such as 51.[35] Pyrazoline-1-dithiocarboxylate esters 53 were prepared by the condensation of the hydrazine derivatives 40 with unsaturated nitriles such as 52.[36,37] Treatment of methyl 3-imino-5-phenylpyrazoline-1-dithiocarbamates with primary amines gave the corresponding thioamides 55.[38] The reaction of the iminopyrazolines 54 with R^2NCS or H_2NCN yielded the pyrazolotriazinethiones 56.[39]



54a R^1=Me 55



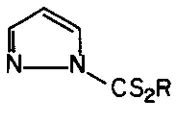
54 56

b) Alkylation.

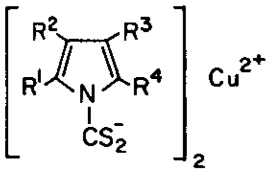
Alkylation of pyrazole-1-dithiocarboxylate salts with diverse alkyl halides gave the corresponding thioesters 57.[14]

iii. Formation of Metal Complexes

Dithiocarbamate anionic ligands can easily be chelated with metal ions to give complexes:



57 a $R = Me$
b $R = CH_2CH = CH_2$
c $R = n\text{-}Bu$



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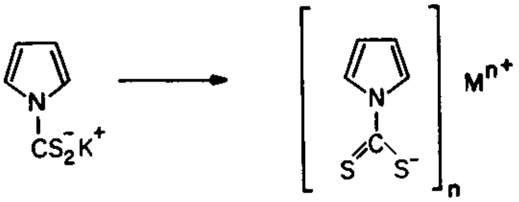
$R^1 = R^2 = R^3 = R^4 = H$
$R^1 = R^2 = R^3 = H, R^4 = Me$
$R^1 = R^3 = H, R^2 = R^4 = Me$
$R^1 = R^3 = CO_2Et, R^2 = R^4 = Me$

1) Pyrrole N-Dithiocarboxylate Complexes

Copper complexes of pyrrole-1-dithiocarboxylates 58 were prepared by dissolving the appropriate pyrrole in dioxane followed by the addition of CS_2 and NaOH; to this mixture a saturated aqueous solution of copper(II) acetate was added, to form the desired complexes.[40]

Since the first reports by Cambi and co-workers over 40 years ago[41,42] of the unusual properties of iron dithiocarbamate complexes, these ligands have generated much interest.[1,43-45] Of particular interest are the resonance structures of the dianion of cyclopentadienedithiocarboxylic acid in relation to the electronic structure of coordinated metals.[46-51] These studies show that the driving force towards forming an aromatic five-membered ring creates a dominant pi-accepting character at the sulphur atom and produces some unusual properties at the coordinated metal centre. Hitherto, the interesting properties of N-dithiocarbamate complexes have been ascribed to a major contribution of a resonance structure 1b in which a positive charge is localised on the nitrogen atom, with an effectively dianionic electronic structure.[43] By careful choice of the N-substituent, a dithiocarbamate ligand can be constructed in which canonical form 1b does not contribute to the overall electronic structure of the ligand system, so that potentially new and interesting metal complexes might result.

59a 59b



2a 60

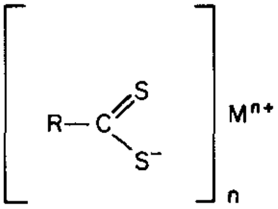
M = Cr, Fe, Co,
Cu, Zn, Cd, Pd,
Pt and $PtCl_2$;
n = 2 or 3

Bereman and Nalewajek[5] investigated this possibility by formally substituting a nitrogen atom in dianion 59, resulting in the pyrrole-1-dithiocarboxylate anion 2a, the structure carrying a positive charge localised on nitrogen is anti-aromatic, and hence not a relevant canonical form. Accordingly, the above authors[5] studied the complexes 60 prepared by the reaction of potassium pyrrole N-dithiocarboxylate 2a with different metal salts.

The tris(N,N-diorgano dithiocarbamateo)iron(III) complexes, $[Fe(S_2C\text{-}NR_2)_3]$, have been studied extensively[52-57] because of the considerable interest in the electronic properties of complexes derived from sulphur ligands. The spectral and magnetic properties of a large number of these complexes are very dependent on the nitrogen substituent of the dithiocarbamate[2,58] and on temperature.[57,58] These properties have been attributed on the one hand to the *R-N-R bond* angle,[58] and on the other to the inductive effects of the R substituent.[2] One of the main problems lies in ascertaining the degree of the inductive effect which a substitutent exerts. Most investigators have employed the basicity of the parent amine as a criterion of electron donation towards the CS_2 group. El A'mma and Drago[6] report the preparation of iron(III) dithiocarbamate 60 with unusual redox properties, derived from the pyrrole N-dithiocarbamate ligand 2a. The preparation of the analogous complexes 60 of Cr(III) and Zn(II) have also been reported.[6]

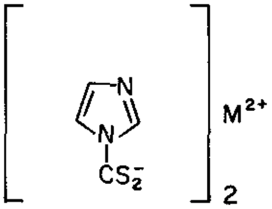
2) Indole, Carbazole and Imidazole N-Dithiocarboxylate Complexes

Indole, carbazole and imidazole, like pyrrole, yielded the desired metal complexes when their potassium or sodium dithiocarbamates were reacted with the appropriate metal salts. Accordingly, complexes of indole and carbazole dithiocarbamates 61 were prepared by adding the appropriate metal bromide to a solution of the corresponding dithiocarbamate in dry acetonitrile.[8] Complexes of imidazole-1-dithiocarboxylate 62 were prepared by adding an alcoholic solution of potassium imidazole-1-dithiocarboxylate to an aqueous solution of the appropriate metal chloride.[8]



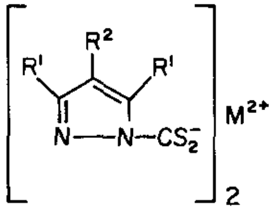
61

M = Fe, Ni, Cu, Zn and Cd;
n = 2 or 3
R = N-indolyl or N-carbazolyl



62

M = Ni, Cu, Zn and Cd



63

M = Fe, Co, Ni, Cu and Zn

($R^1 = R^2 = H$; $R^1 = Me$, $R^2 = H$; $R^1 = H$, $R^2 = Cl, Br$; $R^1 = Me$, $R^2 = Br$)

3) Pyrazole N-Dithiocarboxylate Complexes

Pyrazole-1-dithiocarboxylate complexes 63 have been prepared[14] by mixing an aqueous solution of the appropriate metal salt with an aqueous solution of a potassium pyrazole-1-dithiocarboxylate.

IV. USES OF DITHIOCARBAMATES

a) Purification of $NaNO_3$. Very pure $NaNO_3$, suitable for optical fibre fabrication[59] has been obtained by using dithiocarbamate ligands to remove impurities by complexation. Impurities such as Fe, Mn and Co ions form insoluble stable complexes with ammonium pyrryldithiocarbamate and can be readily separated from $NaNO_3$ by extraction with methyl isobutyl ketone.[59]

b) Radiometric Titration. The successive radiometric titration of a mixture of metal cations such as Tl^{3+}-In^{3+}, Tl^{3+}-Zn^{2+}, and Cd^{2+}-Zn^{2+} was possible by using sodium 3-methyl-5-phenylpyrazole-1-dithiocarboxylate.[35 60]

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