

lowing communication). The inhibition of conjugation and steric strain in 2,4,6-trimethylbenzoyl thiocyanate combined with the electron-donating abilities of the methyl groups probably favor a unimolecular rearrangement *via* the 2,4,6-trimethylbenzoylium ion.

The isomerization of aroyl thiocyanates to aroyl isothiocyanates seems to be catalyzed by bases. This effect undoubtedly explains why only a minor amount of benzoyl thiocyanate could be detected in the reaction between *S*-benzoyl dithiocarbamate and silver(I) oxide in the presence of anhydrous magnesium sulfate. According to the IR spectra benzoyl isothiocyanate was the main product.

Experimental. Melting points are not reported, since all the substances decomposed on heating. The IR spectra were recorded in chloroform solution (about 10 %) using a Perkin-Elmer Model 337 Grating Infrared Spectrophotometer (accuracy ± 5 cm^{-1} above 2000 cm^{-1} and ± 2 cm^{-1} below 1300 cm^{-1}).

5-Aroylthio-1,2,3,4-thiatriazoles. To a solution of sodium 1,2,3,4-thiatriazole-5-thiolate (about 18 mmol, freshly prepared from carbon disulfide and sodium azide⁶) in water (6 ml) was added dropwise with stirring a solution of aroyl chloride (15 mmol) in acetone (about 25 ml). Immediate precipitation occurred. If decomposition of the precipitate was noticed the reaction mixture was cooled in an ice bath. After the addition of aroyl chloride (20 min) the reaction mixture was stirred at room temperature for a further 10 min. The solid obtained on filtration was washed with water, acetone, and ether. Drying *in vacuo* (0.5–1 mmHg) over sulfuric acid in most cases afforded the analytically pure substance. The compounds could be recrystallized from chloroform.

Decomposition of 5-aryol-1,2,3,4-thiatriazoles. In most cases 10 % solutions or suspensions of the thiatriazoles in chloroform were made up. The decomposition proceeded at room temperature, but in order to shorten the time required the solutions were usually kept at about 40°C. Since the stabilities of the thiatriazoles are rather dependent on the nature of R, only rough estimates of the stability of the thiocyanates could be obtained by this procedure. Usually the decompositions of the thiatriazoles were completed after about 6–7 h at 40°C. Most of the thiocyanates were nearly completely isomerized by this time.

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1. Christophersen, C. and Holm, A. *Acta Chem. Scand.* **25** (1971). *In press.*
2. Goerdeler, J. *Quart. Rep. Sulfur Chem.* **5** (1970) 169.
3. Christophersen, C. *Acta Chem. Scand.* **25** (1971) 1162.
4. Audrieth, L. F., Johnson, J. R. and Browne, A. W. *J. Am. Chem. Soc.* **52** (1930) 1929.
5. Ruske, W. and Keilert, M. *Chem. Ber.* **94** (1961) 2695.
6. Lieber, E., Oftedahl, E. and Rao, C. N. R. *J. Org. Chem.* **28** (1963) 194.

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Acyl Thiocyanates

II. Aralkanoyl, Alkanoyl and 2-Alkenoyl Thiocyanates

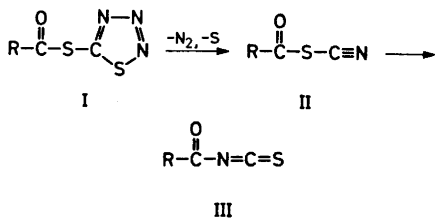
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Aroyl thiocyanates are known to exist, at least in solution.^{1,2} Thiocyanates of certain carbonic acid derivatives have been known for some time.³ Apparently evidence for the existence of acyl thiocyanates that do not belong to the above mentioned classes has never been reported.

When 5-acylthio-1,2,3,4-thiatriazoles decompose in solution at room temperature nitrogen, sulfur, and acyl thiocyanates are formed. A pronounced tendency to isomerize to the corresponding acyl isothiocyanates in most cases prevents the isolation of the initially formed acyl thiocyanates.

In the cases b and e the thiatriazole derivatives were too unstable to allow satisfactory elemental analyses. The thiocyanates IIb, IIc, and IIe were found to be so unstable that identification of the



R-CO- = a: triphenylacetyl-
 b: trichloroacetyl-
 c: palmitoyl-
 d: 2,2-dimethylpropanoyl-
 e: 3,3-dimethylbutanoyl-
 f: 3-phenylpropenoyl-
 g: 2-butenoyl-
 h: 2-methylpropenoyl-

-(S)-C≡N stretching band was for IIc uncertain and for IIb and IIe not possible at all.

The derivatives If, Ig, and Ih were found to exhibit greater relative stability, as was also found for the thiocyanates IIc, IIg, and IIh. The observed stabilities lend further support to the idea proposed for the aroyl thiocyanates² that delocalization of the carbonyl group electrons stabilizes the thiocyanate structure against isomerization. An analogous hypothesis has been put forward to explain the greater stability of alkoxycarbonyl thiocyanates over (alkylthio)carbonyl thiocyanates.⁴

The thiatriazoles Ia and Id were relatively stable in chloroform solution. The stability of the thiocyanate IIc was second only to that of triphenylacetyl thiocyanate IIa, the latter being the most stable compound yet encountered in the series derived from carboxylic acids. It thus seems that steric influences may be a major factor in governing the stabilities of acyl thiocyanates.

However, whatever isomerization mechanisms operating, whether bimolecular or unimolecular, IIa and IIc could be expected to be rather stable. The bimolecular mechanism might be unfavourable owing to steric hindrance and the unimolecular mechanism is not favoured by the generation of a particularly stable acylium ion.

Assignments of the CN bands of II (in cm⁻¹)
 IIa 2165, IIc 2140, IIe 2166, IIg 2170, IIh 2170, IIi 2170.

In the light of the results reported above it was not unexpected that *S*-acetyl dithiocarbamate on treatment with silver(I) oxide in the presence of anhydrous magnesium sulfate yields only acetyl isothiocyanate according to IR spectroscopy.

A closer investigation of the isomerization reactions of acyl thiocyanates is at present being carried out in this laboratory. Further comments on the mechanism of this reaction are reserved for a full paper.

Experimental. For experimental details, see Ref. 2.

5-Acylthio-1,2,3,4-thiatriazoles. To a solution of sodium 1,2,3,4-thiatriazole-5-thiolate (about 18 mmol, freshly prepared from carbon disulfide and sodium azide⁵) in water (6 ml) and ether (10 ml) was added dropwise with stirring a solution of acyl chloride (15 mmol) in ether (30 ml) over a period of 15 min. The reaction mixture was maintained near 0°C by external cooling with ice. Stirring at 0°C for 1.5 h usually allowed the reaction to go to completion. The ethereal layer was then washed with water (50 ml), dried over anhydrous magnesium sulfate, and evaporated at reduced pressure, leaving the 5-acylthio-1,2,3,4-thiatriazole.

The compounds Ib, Ic, Id, Ie, Ig, and Ih were prepared by this procedure, except that in the cases g and h a total of 110 ml of ether was necessary to keep the thiatriazole dissolved.

5-Triphenylacetylthio- and 5-(3-phenylpropenylthio)-1,2,3,4-thiatriazole (Ia and If, respectively) were obtained by a procedure analogous to that used in the preparation of the aroyl derivatives.² Yields: Ia (85%), Ib (~100%), Ic (34%), Id (95%), If (99%), Ig (95%), and Ih (82%).

Analyses: All compounds except Ia were recrystallized several times from ether immediately before the analyses were performed.

Ia	Found: C 64.55, H 3.92, N 10.66, S 16.41.
Calc. for C ₂₁ H ₁₅ N ₃ OS ₂ :	C 64.78, H 3.88, N 10.79, S 16.44.
Ic	Found: C 59.42, H 9.00, N 10.86, S 16.64.
Calc. for C ₁₉ H ₃₅ N ₃ OS ₂ :	C 59.19, H 9.15, N 10.90, S 16.60.
Id	Found: C 35.42, H 4.51, N 20.92, S 31.21.
Calc. for C ₆ H ₉ N ₃ OS ₂ :	C 35.47, H 4.47, N 20.69, S 31.50.
If	Found: C 47.95, H 2.95, N 16.96, S 25.67.

Calc. for $C_{10}H_7N_3OS_2$:	C 48.20, H 2.83, N 16.86, S 25.69.
Ig Found:	C 31.78, H 2.71, N 22.56, S 34.48.
Calc. for $C_5H_5N_3OS_2$:	C 32.09, H 2.69, N 22.46, S 34.20.
Ih Found:	C 32.15, H 2.75, N 22.79, S 34.03.
Calc. for $C_5H_5N_3OS_2$:	C 32.09, H 2.69, N 22.46, S 34.20.

Triphenylacetyl isothiocyanate. A solution of triphenylacetyl chloride (0.01 mol) and potassium thiocyanate (0.01 mol) in acetone (30 ml) was stirred for 24 h at room temperature. Evaporation and extraction with benzene (25 ml) followed by evaporation of the resulting solution left 2.60 g (79 %) of solid material. Recrystallization from hexane and from ether gave the pure product, m.p. 115.5–116°C. (Found: C 76.55; H 4.73; N 4.08; S 9.75. Calc. for $C_{21}H_{15}NOS$: C 76.78; H 4.59; N 4.25; S 9.71).

Decomposition of 5-acylthio-1,2,3,4-thiaziazoles. Solutions in chloroform or carbon tetrachloride (about 10 %) were left at room temperature. The decomposition was followed by means of IR spectroscopy. The stability of the thiaziazoles is very much dependent on the nature of R. In some cases the decomposition was rather extensive in the compound as isolated (e.g. Ie), whereas in one case (Ia) the thiaziazole could be stored at room temperature for 5 days with only a little decomposition.

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1. Christophersen, C. and Holm, A. *Acta Chem. Scand.* **25** (1971) *In press.*
2. Christophersen, C. *Acta Chem. Scand.* **25** (1971) 1160.
3. Goerdeler, J. *Quart. Rep. Sulfur Chem.* **5** (1970) 169.
4. Spurlock, L. A. and Newallis, P. *J. Org. Chem.* **33** (1968) 2073.
5. Lieber, E., Oftedahl, E. and Rao, C. N. R. *J. Org. Chem.* **28** (1963) 194.

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The Crystal Structure of Dodecaammine-hexa- μ -hydroxo- tetracobalt(III) Chloride

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The polynuclear cobalt(III) complex cation $(Co_4(OH)_6(NH_3)_{12})^{4+}$ studied in this work was originally synthesized by Jørgensen.¹ It belongs to the group called "Werner's brown salts" the name of which derives from the ethylenediamine analogue, synthesized by Werner in 1907.² He showed by cleavage experiments that in the complex three out of the four Co atoms were each bonded to four NH_3 molecules, that the fourth Co atom was not connected to ammonia, and that the complex ion had no free hydroxo groups. He suggested that the structure for the complex ion should consist of four coplanar Co atoms with trigonal symmetry in which the central Co atom had six hydroxo ligands. The central cobalt atom should form double hydroxo bridges to the three other cobalt octahedrons by sharing edges. The complex would have no symmetry centre. This was confirmed in 1914,³ when Werner himself succeeded in resolving the complex into optically active forms, the first inorganic compound shown to be optically active. Further support, as given by Ballhausen and Jørgensen,⁷ is that the absorption spectrum of the complex agrees with that derived from the mononuclear links of the suggested structure.

Jørgensen in 1892⁴ synthesized salts of a chromium(III) complex with an analogous composition, and it was suggested by Pfeiffer⁵ that the structure of the two complexes were the same. A simple comparison by Schäffer⁶ of the visible spectra showed, fifty years later, that this could not be the case and later bridge cleaving experiments with the Cr compound gave *cis*-diammine and *cis*-tetraammine complexes. The structure of the complex was determined by Bang and Narasimhayya.^{8,9} It consists of four chromium atoms lying in a plane forming an elongated eight-membered ring alternating with four OH