

Acyl Thiocyanates

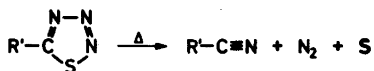
I. Aroyl Thiocyanates

CARSTEN CHRISTOPHERSEN

Chemical Laboratory II (General and Organic Chemistry), University of Copenhagen, The H. C. Ørsted Institute, DK-2100 Copenhagen, Denmark

Recently evidence has appeared for the existence of acyl thiocyanates derived from aromatic carboxylic acids.^{1,2} Although acyl thiocyanates of certain carbonic acid derivatives are known, none of the carboxylic acid series * have yet been isolated, owing to a pronounced tendency to isomerize to the corresponding isothiocyanates.^{1,2,4,5}

Generally, 5-substituted 1,2,3,4-thiazotriazoles decompose in solution to yield sulfur, nitrogen, and the corresponding cyano compound.

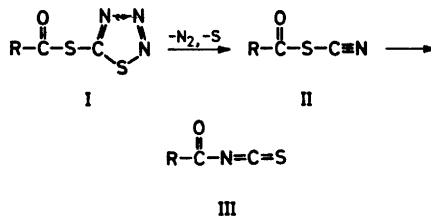


Browne and coworkers⁴ observed that the decomposition of 5-benzoylthio-1,2,3,4-thiazotriazole led to benzoyl isothiocyanate and assumed the latter product to be formed through the intermediacy of benzoyl thiocyanate. This assumption was later criticised,⁶ but a recent paper¹ strongly supports the view of the first authors. The present paper states some preliminary results of a further investigation of this decomposition.

Two examples of 5-aroyle-1,2,3,4-thiazotriazoles are reported in the literature, namely 5-benzoylthio- and 5-(4-bromobenzoylthio)-1,2,3,4-thiazotriazole.⁴ In Table I some further representatives are listed together with their elemental analyses. All compounds were found to decompose in solution at room temperature (ca. 24°C). The decompositions were followed by means of IR spectroscopy.

Soon after the evolution of nitrogen had started a sharp band was observed at $2172 \pm 5 \text{ cm}^{-1}$. After some time, depending

* For evidence of the existence of other acyl thiocyanates belonging to the carboxylic acid series, see a following paper.³



- R = a: phenyl-
b: 4-chlorophenyl-
c: 2,4-dichlorophenyl-
d: 3,4-dichlorophenyl-
e: 2-bromophenyl-
f: 4-nitrophenyl-
g: 4-methoxyphenyl-
h: 1-naphthoyl-

on the nature of R, this band reached a maximum intensity. On further aging of the solution the band in all cases decreased in intensity and finally disappeared. A parallel variation in intensity was also found for a carbonyl band situated, depending on the nature of R, between 1737 and 1775 cm^{-1} . During the decomposition the rise of a broad complex band around 1900 to 2000 cm^{-1} accompanied by a carbonyl absorption around 1700 cm^{-1} indicated the formation of aroyl isothiocyanate.

The carbonyl bands of I and III are given in Table 2 together with the $-(\text{S})-\text{C}\equiv\text{N}$ stretching band of II.

Although a discussion of the relative stability of the thiocyanates II must await a closer examination of the isomerization reaction, two major trends may be emphasized here. The stability of II f was found to be so low that the CN band could hardly be detected, a fact suggesting that electron withdrawal from the carbonyl group facilitates the isomerization. 5-(2,4,6-Trimethylbenzoylthio)-1,2,3,4-thiazotriazole decomposed too rapidly at room temperature to be isolated. IR spectroscopy of the decomposing thiazotriazole (in solution) revealed only bands from the isothiocyanate. The pronounced instability of 2,4,6-trimethylbenzoyl thiocyanate seems to reflect a special isomerization mechanism. The conjugation between the carbonyl carbon and the benzene ring most certainly is a factor which tends to stabilize aroyl thiocyanates in comparison with their aliphatic analogues (see the fol-

Table 1. 5-Aroylthio-1,2,3,4-thiaziazoles.

Compound	Formula	Analyses (C, H, N, S)	Yield %
Ia	$C_8H_5N_3OS_2$		~ 100
Ib	$C_8H_4ClN_3OS_2$	Calc.: 37.29; 1.56; 16.31; 24.89 Found: 37.29; 1.68; 16.52; 24.81	94
Ic	$C_8H_3Cl_2N_3OS_2$	Calc.: 32.89; 1.03; 14.38; 21.94 Found: 32.80; 1.07; 14.53; 22.07	87
Id	$C_8H_3Cl_2N_3OS_2$	Calc.: 32.89; 1.03; 14.38; 21.94 Found: 32.89; 1.10; 14.50; 21.83	94
Ie	$C_8H_4BrN_3OS_2$	Calc.: 31.79; 1.32; 13.91; 21.19 Found: 31.65; 1.41; 13.90; 20.95	93
If	$C_8H_4N_4O_3S_2$	Calc.: 35.83; 1.50; 20.90; 23.87 Found: 35.80; 1.61; 21.00; 23.90	38
Ig	$C_9H_7N_3O_2S_2$	Calc.: 42.69; 2.79; 16.60; 25.28 Found: 42.67; 2.87; 16.88; 25.08	90
Ih	$C_{12}H_7N_3OS_2$	Calc.: 52.75; 2.78; 15.38; 23.42 Found: 52.65; 2.70; 15.34; 23.42	98

Table 2. Assignments of IR absorption bands in cm^{-1} of I, II, and III.

Compound	II CN band	III C=O band	I C=O band
a	2171	1692	1687
b	2175	1692, 1711	1685
c	2172	1710	1670, 1682, 1710
d	2176	1695, 1715	1674
e	2169	1707, 1721	1692
f	(2174)	1716	1676
g	2172	1699	1692, 1670
h	2170	1696	1649, 1679, 1686

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-thiazotriazoles. To a solution of sodium 1,2,3,4-thiazotriazole-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-thiazotriazoles. In most cases 10 % solutions or suspensions of the thiazotriazoles 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 thiazotriazoles 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 thiazotriazoles were completed after about 6–7 h at 40°C. Most of the thiocyanates were nearly completely isomerized by this time.

Acknowledgement. The author is greatly indebted to Prof. M. Ettlinger for his kind interest in this work and for inspiring discussions.

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.

Received February 23, 1971.

Acyl Thiocyanates

II. Aralkanoyl, Alkanoyl and 2-Alkenoyl Thiocyanates

CARSTEN CHRISTOPHERSEN

Chemical Laboratory II (General and Organic Chemistry), University of Copenhagen, The H. C. Ørsted Institute, DK-2100 Copenhagen, Denmark

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-thiazotriazoles 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 thiazotriazole 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