sented by A, the peroxide by P and by ROOH, the nitrene by N:, and the radicals $C_6H_5SO_2NH\cdot$ or $C_6H_5SO_2NAr\cdot$ indiscriminately by $N\cdot$.

Assuming that ROI decomposes by an iodine-catalyzed polar mechanism and applying the steady-state approximation, the above mechanism gives an equation 6 of the required form.

$$k_{1P} = 4k_2[I_2]\left(\frac{k_1}{k_3}\right)^{1/2}\frac{[A]^{1/2}}{[P]} + \frac{2k_4k_2}{k_5}\left(\frac{k_1}{k_3}\right)^{1/2}[A]^{1/2} \qquad (6)$$

Experimental

Triphenylphosphine Method for the Azide.—A 5-ml. aliquot of the azide solution is added to 10 ml. of benzene in an azotometer equipped with a magnetic stirrer and a rotatable sidearm for adding a mixture of 5 ml. of triphenylphosphine reagent and 3 ml. of acetic acid. The triphenylphosphine reagent consists of 13.12 g. of triphenylphosphine in 50 ml. of chloroform. The gas buret is adjusted to zero, the sidearm is rotated so as to add the reagent, and the volume of nitrogen from the azide is read. Nitrogen is evolved quantitatively. A considerable excess of triphenylphosphine is used in order to destroy any unchanged peroxide.

$$(C_6H_5)_3P + C_6H_5SO_2N_3 \longrightarrow N_2 + (C_6H_5)_3\overset{+}{P}\text{—}\overset{-}{N}SO_2$$

$$(C_6H_5)_3P + (CH_3)_3COOH \longrightarrow (C_6H_5)_3PO + (CH_3)_3COH$$

Iodometry.—To a 10-ml. aliquot diluted with 25 ml. of isopropyl alcohol are added 5 ml. of acetic acid and 5 ml. of aqueous saturated potassium iodide solution, and the mixture is shaken and warmed for 20 min. at 60–70°. The solution is then diluted with water and titrated with 0.05 *N* thiosulfate.

For free iodine, the sample in isopropyl alcohol is titrated with thiosulfate without adding potassium iodide and acetic acid or warming.

Benzenesulfonylazide.—The method of preparation was essentially the same as that reported by Dermer and Edmison.[2a] Benzenesulfonyl chloride was allowed to react with sodium azide in an aqueous alcohol or aqueous acetone solution at about 0°. The product was taken up in ether, washed well with ice–water, and dried over sodium sulfate. If the solution was dried over calcium chloride, it became warm, bubbled, and turned pink or red. After the solvent was removed under reduced pressure at room temperature, the remaining oil was solidified by cooling in Dry Ice. It was then twice recrystallized from ether–petroleum ether (low boiling) and dried *in vacuo* at 30–40°. The azide melted at 13–14° and decomposed with bubbling at about 135°. The decomposition in chlorobenzene or xylene gave closely the theoretical amount of nitrogen.

***t*-Butyl Hydroperoxide.**—The commercial product was purified by fractional distillation through a short column, and the fraction, b.p. 38.5–39.5°/18 mm., was used for the rate measurements.

Chlorobenzene was dried over calcium chloride and distilled, b.p. 131–131.5°.

The Products of the Decomposition.—The product from the decomposition of 2.36 g. of the azide in chlorobenzene at 126° was chromatographed on alumina after evaporation of the solvent, giving 0.49 g. of oily crystals, 1.1 g. of needles, m.p. 123–128°, and 0.36 g. of plates, m.p. 114–120°. The first fraction melted at 116–120° after recrystallization from ether. The second melted at 127–129° after recrystallization from alcohol. The third fraction gave colorless plates, m.p. 119–121°. These products were identified by mixed melting points as the *m*-, *o*-, and *p*-chloroanilides of benzenesulfonic acid, respectively. The total yield was about 56% of the theoretical before purification.

In the presence of *t*-butyl hydroperoxide, the yield of these products was decreased. The low molecular weight material from 2.62 g. of azide and 1.16 g. of *t*-butyl hydroperoxide amounted to only 1.47 g. after chromatographic separation from tars, and the total yield of chloroanilides was less than 35%. *o*-Chloroanilide was the main product, and a small amount of unsubstituted benzenesulfonylamide was also obtained. There was a considerable amount of black material, insoluble in the usual organic solvents.

Reaction of Carbon Disulfide with Azide Ion[1]

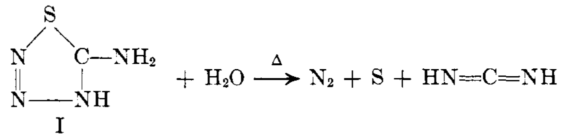
EUGENE LIEBER,[2a] EDWIN OFTEDAHL,[2b] AND C. N. R. RAO[2c]

Departments of Chemistry, Roosevelt University, and DePaul University, Chicago, Illinois

Received November 8, 1960

Carbon disulfide reacts with azide ion to form the 1,2,3,4-thiatriazolinethionate ion and not the acyclic azido·dithiocarbonate ion as previously reported. A series of salts of thiatriazoline have been prepared and none shows evidence for the presence of the azido group. Esters of thiatriazolinethione prepared by the reaction of the sodium salt with alkyl or acyl halides have been found to be either 5-(substituted) mercapto-1,2,3,4-thiatriazoles or 4-substituted 1,2,3,4-thiatriazoline-5-thiones. These structures have been assigned on the basis of degradative and spectroscopic evidence. The chemistry of the so-called azidodithiocarbonates has been reinterpreted in terms of the thiatriazole structure.

During the course of the investigations[3] on the 1,2,3,4-thiatriazole ring system, Lieber and co-workers were struck by the similarity in their chemistry with that reported for substances described in the literature[4] as azidodithiocarbonates. For example, 5-amino-1,2,3,4-thiatriazole (1)[5] and azidodithiocarbonic acid (II. R = H), respectively, decompose on warming[6] in water.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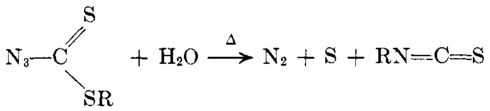
II[7]

Other similarities in the chemistry of the so-called II led to a preliminary re-examination[5] of the structure of the products obtained by the condensation of azide ion with carbon disulfide. The absence of the characteristic azido group frequencies in the infrared spectra

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[1] The authors gratefully acknowledge the support of this research by he U. S. Army Research Office.

[2] (a) To whom all correspondence should be addressed; (b) taken in part from M.S. thesis, DePaul University, 1960; (c) presently at the Indian Institute of Science, Bangalore, India.

[3] E. Lieber, J. Ramachandran, C. N. R. Rao, and C. N. Pillai, *Can. J. Chem.*, **37**, 563 (1959), which cites previous references in this series.

[4] L. F. Audrieth, *Chem. Rev.*, **15**, 169 (1934).

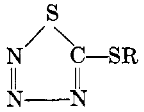
[5] E. Lieber, C. N. Pillai, J. Ramachandran, and R. D. Hites, *J. Org. Chem.*, **22**, 1750 (1957).

[6] Both structures I and II will slowly decompose in aqueous solution and room temperature.

[7] This is the structure corresponding to the descriptive name for this substance.

TABLE I

5-SUBSTITUTED MERCAPTO-1,2,3,4-THIATRIAZOLES

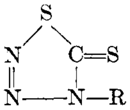


R	Organic halide	Yield, %	M.p., °C.[a] Found	M.p., °C.[a] Lit.	Formula	% S[b] Calcd.	% S[b] Found
CH_3[c,d,e,b]	CH_3Br	40	34–35	34	$C_2H_3N_3S_2$	48.15	47.76
$C_6H_5CH_2$[f,g,e]	$C_6H_5CH_2Cl$	70	66–67	66	$C_8H_7N_3S_2$	30.58	30.45
4-$(O_2N)C_6H_4CH_2$[h,f,i]	4-$(O_2N)C_6H_4CH_2Cl$	99	100–102		$C_8H_6N_4O_2S_2$	25.22	25.10
$C_6H_5COCH_2$[h,f,i]	$C_6H_5COCH_2Cl$	98	89		$C_9H_7N_3OS_2$	27.02	27.10
4-$ClC_6H_4COCH_2$[h,f,i]	4-$ClC_6H_4COCH_2Cl$	95	106–108		$C_9H_6ClN_3OS_2$	23.60	23.48
4-$(C_6H_5)C_6H_4COCH_2$[h,f,i]	4-$(C_6H_5)C_6H_4COCH_2Br$	98	98		$C_{15}H_{11}N_3OS_2$	20.46	20.50
CN[i,j,k]	CNBr	83	84–85[l]	80.5–81[l]	$C_2N_4S_2$	44.47	44.41

[a] With decomposition. [b] All compounds evolved one mole of nitrogen per mole on thermal degradation. [c] Crystallized from methyl alcohol. [d] Reaction time was six hours. [e] See ref. 4. [f] Crystallized from acetone and water. [g] Reaction time was twenty-four hours. [h] New compound. [i] The reaction was found to occur instantaneously. [j] Washed with water. [k] See ref. 2. [l] Decomposition takes place without melting forming a solid containing sulfur.

TABLE II

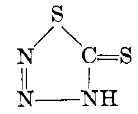
4-SUBSTITUTED THIATRIAZOLINETHIONES



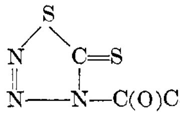
R	Organic halide	Yield, %	M.p., °C.[a] Found	M.p., °C.[a] Lit.	Formula	% S[b] Calcd.	% S[b] Found
C_6H_5CO[c,d,e]	C_6H_5COCl	98	92–93	92–94	$C_7H_5N_3OS_2$	28.72	28.70
$(C_6H_5)_2CH$[c,f,g]	$(C_6H_5)_2CHBr$	63	62–64	67	$C_{14}H_{11}N_3S_2$	22.47	22.10
$(C_6H_5)_3C$[c,d,e]	$(C_6H_5)_3CCl$	88	91–92	102–104	$C_{20}H_{15}N_3S_2$	17.74	17.78

[a] With decomposition. All compounds evolved one mole of nitrogen per mole on thermal degradation. [c] See ref. 4. [d] An instantaneous reaction was observed. [e] Crystallized from chloroform. [f] The reaction time was three hours. [g] Crystallized from ether.

of azidodithiocarbonic acid[8] (II. R = H) and benzoylazidodithiocarbonate (II. R = C_6H_5CO), suggested that they were derivatives of the 1,2,3,4-thiatriazole ring system, the structures represented as III and IV,

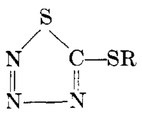


III

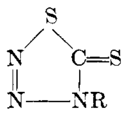


IV

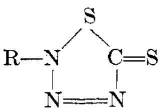
respectively. Structure III had been considered by Olivera-Mandala,[9,10] who rejected it in favor of II. On the basis of the older structure accepted for this reaction only one substitution product is possible[11] (II. R = alkyl or acyl). However, structure III can lead to three isomeric monosubstitution products[12] (V, VI, and VII). It was the objective of this investigation to prepare salts[13] and esters of the so-called azidodithiocarbonic acid and examine evidence for their structures in light of the fact that they are derivatives of the 1,2,3,4-thiatriazole ring system.



V



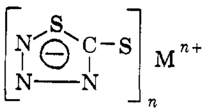
VI



VII

Results and Discussion

A series of ten esters (Tables I and II) as well as silver, lead, ammonium, guanidinium, anilinium, and benzylammonium salts of the so-called azidodithiocarbonic acid were prepared, all of which failed to show the characteristic asymmetric stretching frequency[14] of the azido group around 2140 cm.$^{-1}$, but showed characteristic frequencies of the 1,2,3,4-thiatriazole ring[3,15] in the regions 1610–1560 (w), 1320–1280 (v), 1240–1190 (v), and 1090–1000 (v) cm.$^{-1}$.[15b] The salts of thiatriazolinethione (III) are probable best represented by VIII, with the negative charge delocalized over the entire ring. These salts also show a band in the region



VIII (n = a small integer, M is a cation)

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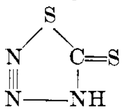
[8] G. B. L. Smith, F. Wilcoxon, and A. W. Browne, *J. Am. Chem. Soc.* **45**, 2604 (1923).

[9] E. Olivera-Mandala, *Gazz. chim. ital.*, **52**, II, 139 (1922).

[10] The structure was, however, represented by



with a triple bond between nitrogen atoms 2 and 3.

[11] L. F. Audrieth, J. R. Johnson, and A. W. Browne, *J. Am. Chem. Soc.*, **52**, 1928 (1930).

[12] The reaction involves the nucleophilic displacement of halogen from an alkyl or aryl halide by the anion of III.

[13] In a private communication Professor L. F. Audrieth expressed the opinion that the salts of II (R = H) in which the cations were heavy metals such as Ag^+ or Pb^{++} would exhibit the azido absorption frequencies in the infrared.

[14] E. Lieber, C. N. R. Rao, T. S. Chao, and C. W. W. Hoffman, *Anal. Chem.*, **29**, 916 (1957).

[15] (a) The discovery by infrared spectroscopy, that reactions which should theoretically lead to thiocarbamyl azides are, in reality, derivatives of the thiatriazole ring system, was made almost simultaneously by four investigators. See E. Lieber and F. Oftedahl, *J. Org. Chem.*, **24**, 1014 (1959). (b) See ref. 41a.

TABLE III

DEGRADATIVE STUDIES—IDENTIFICATION OF THIOCYANATES AND ISOTHIOCYANATES

Compound	M.p., °C.[a,b]	Synthetic m.p., °C. Found	Synthetic m.p., °C. Lit.	Infrared absorption assignments[c] Frequency, cm.$^{-1}$ —S—C≡N Degradative	—S—C≡N Synthetic	—N=C=S Degradative	—N=C=S Synthetic
NCSCN[d]	60	62	60/62	2174	2174		
$C_6H_5COCH_2SCN$[e]	73–74	74–75	74	2128	2146		
4-$ClC_6H_5COCH_2SCN$[f]	135–136	135–136	135.2	2169	2169		
4-$C_6H_5C_6H_4COCH_2SCN$[g]	138–140	138–141	...	2160	2164		
4-$NO_2C_6H_4CH_2SCN$[h]	85–86	85–86	85.5	2155	2155		
$(C_6H_5)_3CNCS$[i]	135–137	137–138	137			2083; 2020	2083; 2024
$(C_6H_5)_2CHNCS$[j]	Oil	Oil	61			2164; 2079	2183; 2150; 2088[k]
$(C_6H_5)_2CHSCN$[j]	...	Oil	59		2174; 2151; 2083[k]		

[a] This is the melting point of the product isolated from the thiatriazole degradation. [b] Mixture melting point with an authentic sample showed no depression. [c] In all cases the infrared absorption spectrum of the degradation product matched identically with that of the authentic sample. [d] See ref. 18. [e] See ref. 21. [f] See ref. 22. [g] New compound. *Anal.* Calcd. for $C_{15}H_{11}OSN$: S, 12.67. Found: S, 12.32. [h] See ref. 23. [i] See ref. 19. [j] See ref. 20. [k] This corresponds to a mixture of isothiocyanate and thiocyanate.

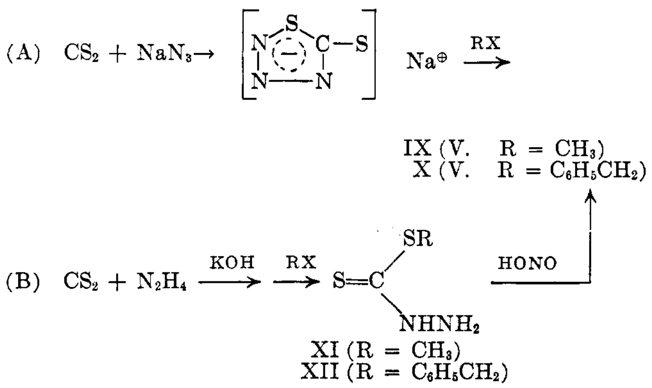


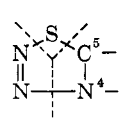
Chart I

Unequivocal Syntheses for Methyl and Benzyl Substitution Products of Thiatriazolinethione

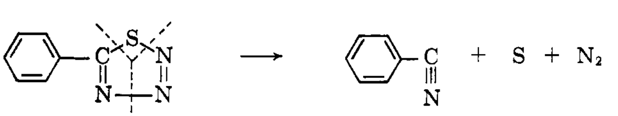
720–680 cm.$^{-1}$ probably due to the stretching of the exocyclic C—S band.

The question of deciding between the isomeric structures V, VI, or VII for the esters was established by unequivocal synthesis and by thermal degradation, using both methods wherever possible and making use of infrared spectroscopy. When the methyl (XI) and benzyl (XII) esters of dithiocarbazinic acid, respectively, were diazotized, the products isolated (IX and X) were shown to be identical to the carbon disulfide–sodium azide condensation (Chart I).

The structural interpretations based upon the degradation products obtained on pyrolyses of the substituted thiatriazolinethiones followed the assumption that the heterocyclic ring falls apart as follows:



the dotted lines representing heterolytic bond breaking. Abundant evidence for this mode of decomposition has been obtained. The mechanism for the thermal degradation of the thiatriazolinethiones is probably similar to that suggested for the 5-(substituted) aminothiatriazoles.[16] It may be noted that the degradation of the 5-(substituted) mercaptothiatriazoles (V) should yield organic thiocyanates while the 4-substituted derivatives (VI) should yield isothiocyanates. Thermal degradation of the 2-substituted derivatives (VIII) should yield isothiocyanates and azo compounds produced by the recombination of the radicals RN and CS. This assumption regarding the mode of thermal degradation of thiatriazoles (XIII) leads to benzonitrile, sulfur, and nitrogen:



XIII

Thermal degradation of the esters of thiatriazoles (Tables I and II) always gave rise to thiocyanates or isothiocyanates, thus indicating that these thiatriazole derivatives have structures V and VI with substituents in the 5- and 4-position. The isolation and identification of the organic thiocyanates or isothiocyanates produced in the degradation were based on the recognition of the *normal* or *isothiocyanate* group by infrared spectroscopy[17] and by comparison of the spectra and melting points with those of authentic specimens. Mixed melting points were also determined. The identifications of the degradative products were generally unequivocal (Table III). The structure assignments for the different thiatriazole derivatives are summarized in Tables I and II. It may be argued that the benzoyl, diphenylmethyl, and triphenylmethyl derivatives (Table II) may also be 5-(substituted) mercapto derivatives, since it is possible that the organic thiocyanates produced in the degradation might have isomerized into the corresponding isothiocyanates,[24–26] particularly in view of the fact that some of these thiocyanates have not been prepared.[27] It is felt that if such isomerization did occur, one would get mixtures of the thiocyanate and the isothiocyanate. Since only pure isothiocyanates were obtained as de-

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(16) Lieber and co-workers: (a) *J. Org. Chem.*, **22**, 1054 (1957); (b) *Can. J. Chem.*, **35**, 832 (1957); (c) *ibid.*, **37**, 101 (1959).

(17) E. Lieber, C. N. R. Rao, and J. Ramachandran, *Spectrochim. Acta*, **13**, 296 (1959).

(18) E. Soderback, *Ann.*, **419**, 217 (1919).

(19) K. Elbs, *Ber.*, **17**, 700 (1884).

(20) H. L. Wheeler, *Am. Chem. J.*, **26**, 345 (1901).

(21) W. Borsche, *Ber.*, **75**, 1312 (1942).

(22) W. L. Judefind and E. E. Reid, *J. Am. Chem. Soc.*, **42**, 1043 (1920).

(23) J. A. Lyman and E. E. Reid, *ibid.*, **39**, 701 (1917).

(24) A. Iliceto, A. Fava, U. Mazzucato, and O. Rossetto, *ibid.*, **83**, 2729 (1961).

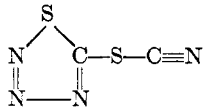
(25) C. N. R. Rao and S. N. Balasubrahmanyam, *Chem. Ind.* (London), 625 (1960).

(26) P. A. S. Smith and D. W. Emerson, *J. Am. Chem. Soc.*, **82**, 3076 (1960).

(27) E. Lieber and E. Oftedahl, *Chem. Ind.* (London), 1303 (1960).

gradation products, the thione structure VI for these thiatriazole derivatives seems correct. Further confirmation of the thione structure for the benzoyl, diphenylmethyl, and triphenylmethyl derivatives may be obtained by independent syntheses through the diazotization of the corresponding dithiocarbazinates (Chart I).[28] The thione structure (VI) for these derivatives was, however, substantiated by satisfactory assignments of group frequencies in the infrared spectra. Just like thiatriazolinethione (III), the three derivatives in Table II exhibited the "$\underset{|}{-\mathrm{N}}-\mathrm{C}{=}\mathrm{S}$ bands" in the regions 1490–1440, 1340–1320, and 1100–920 cm.$^{-1}$.[29] These derivatives showed only one band in the 700-cm.$^{-1}$ region which was clearly due to the C—H out-of-plane deformation of the monosubstituted benzene ring. The 5-mercapto derivatives (Table I), on the other hand, showed more than one band in the 720–680 cm.$^{-1}$ region, one of which is likely to be due to the exocyclic C—S stretching vibration.

Evidence for the structure of the cyano derivatives as 5-thiocyanothiatriazole, XIV, was unambiguous



XIV

both from degradative and spectroscopic data. The infrared spectrum of XIV showed a characteristic sharp nitrile frequency around 2185 cm.$^{-1}$. The absence of the N—C≡N unit was also confirmed by comparison with the spectrum of cyanamid. The degradation of XIV to N≡C—S—C≡N was easily established by isolation and comparison of spectra (Table III).

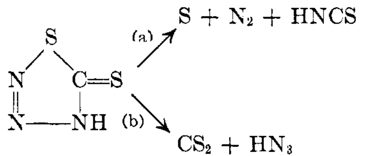
Thiatriazolinethione (III) is a strong acid. Its neutralization equivalent is readily determined by titration in aqueous solution. Smith, *et al.*,[30] studied the electrical conductivity of the so-called sodium and potassium azidodithiocarbonates, respectively, reported "azidodithiocarbonic acid" to be comparable to sulfuric acid in strength. The extensive delocalization offered by the thiatriazole anion (VIII) makes this observation understandable. Structure VIII also explains the proclivity of these salts to decompose into ionic thiocyanates.[31,32] In fact, the reaction between carbon disulfide and ionic azides can easily be pushed beyond the thiatriazoline stage so as to make it a preparative procedure for thiocyanate salts. Thus, Stolle[33] prepared sodium thiocyanate, in quantitative yield, by refluxing a mixture of sodium azide and carbon disulfide (in excess) in ethanol. Sulfur and nitrogen in quantities demanded by the equation

$$CS_2 + NaN_3 \longrightarrow NaSCN + N_2 + S$$

were also obtained. Audrieth, *et al.*,[34] prepared ammonium thiocyanate and tetramethylammonium thiocyanate by prolonged treatment (in refluxing ethanol) of ammonium azide and tetramethylammonium azide, respectively, with carbon disulfide. The ready formation of the thiocyanate ion can easily be interpreted as an internal oxidation–reduction of the thiatriazolinate ion.

The realization of the true structure of the carbon disulfide–azide ion condensation as VIII also reveals its possible mechanism of formation. Audrieth "assumed, on the basis that the condensation of covalently bonded azides fails, that the formation of the "azidodithiocarbonates" involved the transfer of an electron from the azide ion to "one of the sulfur atoms of the carbon disulfide." In view of the fact that the sulfur is in its lowest oxidation state this hypothesis appears untenable. It is suggested, in view of the isoelectronic relationship between carbon disulfide and azides, that the mechanism proposed by Lieber[35] for the condensation of azide ion with isothiocyanates is directly applicable to the condensation with carbon disulfide. There is reason to believe that, with suitable activation organic azides can be made to react with carbon disulfide. Thus, Borsche[21] isolated phenyl isothiocyanate from the reaction of carbon disulfide with phenylazide in the presence of aluminum chloride. Schonberg[36] obtained phenyliminodiphenylmethane by heating (110–140°) thiobenzophenone with phenyl azide. Both of these reactions are readily explicable on the basis that a thiatriazole is formed as an intermediate.

Previous work[8,37] on the properties of the carbon disulfide-azide ion condensation product has shown that III (azidodithiocarbonic acid) decomposes in aqueous solution by a monomolecular reaction but that the decomposition from the solid state is autocatalytic and is accelerated by one of its products of decomposition. The evidence indicates that the catalytic agent may be thiocyanic acid or one of its polymers. The present investigation would appear to favor the idea that the monomolecular reaction is simply the postulated internal oxidation–reduction leading to the formation of sulfur, nitrogen, and thiocyanic acid. In the solid state, however, two modes of decomposition can take place. It should be noted that route (b) (below)



III

$$HSCN + 3HN_3 \longrightarrow NH_4SCN + 4N_2$$

for the decomposition of thiatriazolinethione III represents its simple dearrangement to carbon disulfide and hydrazoic acid. This has been demonstrated by the alkaline degradation of thiatriazolinethione conducted in the present investigation.

While the present investigation has not been concerned with the so-called azidocarbon disulfide,[4,37–39] it was considered relevant to interpret the structures and properties described in the literature. The structures previously given[4] for azidocarbon disulfide are

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[28] Work along these lines is in progress at Roosevelt University.

[29] C. N. R. Rao and R. Venkataraghavan, *Spectrochim. Acta*, **18**, 541 (1962).

[30] G. B. L. Smith, F. P. Gross, G. H. Brandes, and A. W. Browne, *J. Am. Chem. Soc.*, **56**, 1116 (1934).

[31] A. W. Browne, L. F. Audrieth, and C. W. Mason, *ibid.*, **49**, 917 (1927).

[32] A. W. Browne and A. B. Hoel, *ibid.*, **44**, 2315 (1922).

[33] R. Stolle, *Ber.*, **55**, 1289 (1922).

[34] L. F. Audrieth, G. B. L. Smith, A. W. Browne, and C. W. Mason, *J. Am. Chem. Soc.*, **49**, 2129 (1927).

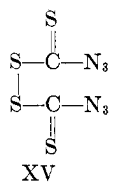
[35] E. Lieber and J. Ramachandran, *Can. J. Chem.*, **37**, 101 (1959).

[36] A. Schonberg, *J. Chem. Soc.*, 530 (1935).

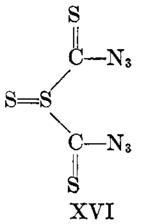
[37] F. Wilcoxon, A. E. McKinney, and A. W. Browne, *J. Am. Chem. Soc.* **47**, 1916 (1925).

[38] L. F. Audrieth, *ibid.*, **52**, 2794 (1930).

[39] A. W. Browne, A. B. Hoel, G. B. L. Smith, and F. H. Swezey, *ibid.*, **45**, 2541 (1923).

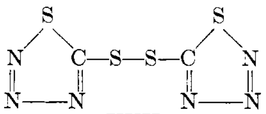


XV

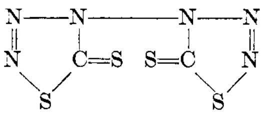


XVI

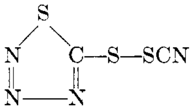
It is prepared[30] by the chemical or electrochemical oxidation of the free acid (*i.e.*, thiatriazolinethione, III). However, in terms of the thiatriazolinethione structure (V), the probable structures are XVII and XVIII. The substance is a white microcrystalline explosive solid[39] which decomposes fairly rapidly at room temperature. At higher temperature the decomposition proceeds with explosive violence. On this basis structure XVIII is appealing since it contains a chain of six nitrogen atoms. However, structure XVII explains the formation of thiocyanogen, $(SCN)_2$, on degradation.[39] Structure XVII can also explain the formation of 5-(thiocyanato)mercaptothiatriazole (XIX) as a decomposition product. The so-called azidocarbondisulfide is reported[39] to react with potassium hydroxide giving rise to the salts, $KSCSN_3$ and $KOSCSN_3$. In terms of the thiatriazole structure XVII these salts should be XX and XXI. Similarly, the structure of the so-called chlorine azidodithiocarbonate[40] should be XXII.



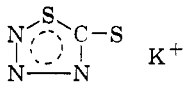
XVII



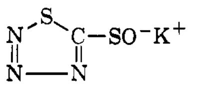
XVIII



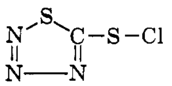
XIX



XX



XXI



XXII

Experimental[41]

Thiatriazolinethione (III).—To a 125-ml. Erlenmeyer flask, containing 50 ml. of water, was added 12 g. (0.18 mole) of sodium azide and 20 ml. of carbon disulfide. The mixture was magnetically stirred for 6–8 hr. at room temperature. The resulting solution containing the sodium salt of thiatriazolinethione was filtered, chilled in an ice bath and treated with cold concentrated hydrochloric acid. The whitish yellow, crystalline precipitate was filtered and washed with 100 ml. of ice-cold water. The product was allowed to remain on the Büchner funnel for about 0.5 hr. to remove any hydrazoic acid present. The thiatriazolinethione, so prepared, was usually used immediately for further work, or preserved in a desiccator protected from light, and kept at a temperature below 10°. In this manner, it may be kept for 24–48 hr. without appreciable decomposition.

Anal. Calcd.: neut. equiv., 119. Found: neut. equiv., 120.

Ring Substitution Reactions through Sodium Thiatriazolinethionate.—The following general procedure was developed: The free acid, thiatriazolinethione, was converted to the sodium salt by neutralizing with a 30% solution of sodium hydroxide to the phenolphthalein end point. To this was added 200 ml. of acetone and the appropriate organic halide. This solution was allowed to stand for a sufficient length of time to ensure completion of the reaction, after which it was diluted with water. At this point the crude product either precipitated as a crystalline solid or as an oil. If the product was crystalline, it was collected on a Büchner funnel, washed with water, and recrystallized from an appropriate solvent. If the product was an oil, it was separated from the reaction solution by means of a separatory funnel, washed with water, and converted to the crystalline state by storage at low temperature. After the oily product had been converted to the crystalline state, it was recrystallized from an appropriate solvent. All of the compounds prepared were preserved at a temperature below −10° for the studies described below. Tables I and II summarize the esters of thiatriazolinethione prepared.

Potassium Dithiocarbazinate.—A solution of 66 g. (1.18 moles) of potassium hydroxide and 65 ml. of 85% hydrazine hydrate (1.1 moles) in 200 ml. of ethanol was stirred and cooled in an ice bath while 63 ml. (1.04 moles) of carbon disulfide was added dropwise. A heavy yellow oil, containing the potassium dithiocarbazinate, separated during the course of this addition. The resulting mixture was chilled and two volumes of ether were added in order to cause the separation of more of the desired product. The oily layer was separated from the ether–alcohol layer. This oily layer, containing the product, was used in the subsequent steps, for the preparation of the organic esters of dithiocarbazic acid. The solid, potassium dithiocarbazinate, was also prepared by removing the water from the oily layer. This was done *in vacuo* over phosphorus pentoxide in a desiccator placed in the refrigerator.

Methyl Dithiocarbazinate (XI).—The entire oily layer, from the above reaction containing the potassium dithiocarbazinate, was dissolved in 300 ml. of water. The resulting solution was cooled in an ice bath and 150 g. (1.05 moles) of methyl bromide was added, in approximately 20-g. portions, over a period of 3 hr. The reaction mixture was stirred and cooled during the addition of the methyl bromide. The product precipitated during the course of the reaction. The reaction mixture was allowed to stand for several hours (at ice-bath temperature) after the addition of the methyl bromide was complete. The product was collected and recrystallized from ether–ligroin. The purified product, 75.6 g. (62%), melted at 80.5–82°.[42]

Anal. Calcd. for $C_2H_6N_2S_2$: S, 52.07. Found: S, 52.46.

Benzylidene Methyl Dithiocarbazinate, M.p. 156–157°.[43]

Benzyl Dithiocarbazinate (XII).—The preparation was similar to the methyl ester except that 64 g. (0.50 mole) of benzyl chloride was used to prevent disubstitution. The reaction mixture was stirred for 24 hr. at ice-bath temperature. The product was collected and recrystallized from benzene. The purified product, 36 g. (36%), melted at 124–125°.[43]

Anal. Calcd. for $C_8H_{10}N_2S_2$: S, 32.25. Found: S, 32.40.

Benzylidene Benzyl Dithiocarbazinate, M.p. 162–163°.[43]

Diazotization of Dithiocarbazinates. 5-Methylmercapto-1,2,3,4-thiatriazole (V. $R = CH_3$).—To an ice-bath solution of 23.5 g. (0.21 mole) of methyl dithiocarbazinate in 95 ml. of 2.2 *N* hydrochloric acid (0.21 mole), three 50-ml. portions of a sodium nitrite solution containing a total of 14.7 g. (0.21 mole) of sodium nitrite were added under stirring. After the 50-ml. portions were added, the product was collected and washed with 10 ml. of ice–water and was recrystallized from methyl alcohol and was found to melt at 33–34°. The index of refraction was determined immediately after melting and was found to be 1.602 at 35°.

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[40] W. H. Gardner and A. W. Browne, *J. Am. Chem. Soc.*, **49**, 2759 (1927).

[41] (a) Sulfur analysis were carried out by bomb peroxide fusion, followed by gravimetric barium sulfate. Nitrogen was determined by thermal decomposition collecting the gas in a Dumas azotometer. Metal analyses were standard procedures. Other analyses were carried out by Dr. C. Weiler and Dr. F. B. Strauss, Oxford, England. Melting points are uncorrected. (b) Infrared spectra were recorded using a Perkin–Elmer Model 21 spectrometer. Intensities are reported as w, weak and v, variable.

[42] L. F. Audrieth, E. S. Scott, and P. S. Kippur, *J. Org. Chem.*, **19**, 740 (1954).

[43] M. Busch, *J. prakt. Chem.*, **93**, 25 (1916).

Anal. Calcd. for $C_2H_3N_3S_2$: S, 48.15. Found: S, 47.80.

5-Benzylmercapto-1,2,3,4-triatriazole (V. R = $C_6H_5CH_2$).—The procedure was similar to that described above except that the sodium nitrite solution was added over a period of 1.5 hr. and the mixture stirred for an additional 4 hr. The product was recrystallized from acetone and water. The melting point of the purified product was found to be 65–67°.

Anal. Calcd. for $C_8H_7N_3S_2$: S, 30.58. Found: S, 30.10.

Salts of Thiatriazolinethione (VIII). (a) Metallic Salts.—The following general procedure was adopted. The heavy metal salts were prepared by the interaction of aqueous solutions containing freshly prepared thiatriazolinethione and aqueous solutions containing the appropriate metallic ion. After filtration and washing, a portion of the precipitate so obtained was set aside (in a vacuum desiccator over phosphorous pentoxide) for analysis and the remainder of the specimen preserved by suspending in white mineral oil and maintaining below −20°. These precautions were found to be essential due to the explosive instability of the heavy metallic salts. The mineral oil suspensions were utilized for the determination of the infrared absorption spectra at the earliest possible moment. In the same manner the analyses were carried out as early as possible after their preparation.

Silver thiatriazolinethionate (**VIII. M** = Ag^+; n = 1) was a white, slightly photosensitive solid. It was not recrystallized before analysis.

Anal. Calcd. for CN_3S_2Ag: Ag, 47.73. Found: Ag, 47.61.

Lead thiatriazolinethionate (**VIII. M** = Pb^{++}; $n = 2$) was obtained in the form of a light greenish yellow solid which was not purified further.

Anal. Calcd. for $C_2N_6S_4Pb$: 46.76. Found: Pb, 46.60.

(b) **Organic Nitrogen Salts. Ammonium Thiatriazolinethionate** (**VIII. M** = NH_4^+; n = 1). This compound was by prepared by neutralization of II[1] with ammonium hydroxide and isolated as a white crystalline solid by evaporation in a vacuum desiccator over phosphorus pentoxide at 5°, m.p. 110–115° dec.

Anal. Calcd. for $CH_4N_4S_2$: S, 47.09. Found: S, 46.78.

Guandininum Thiatriazolinethionate (**VIII. M** = $(NH_2)_3C^+$; n = 1).—This compound was prepared by adding thiatriazolinethione still moist, to an aqueous solution of guanidine carbonate until no further evolution gas was observed to take place. The turbid liquid was filtered, and the filtrate concentrated *in vacuo* over phosphorus pentoxide at 5°. After several days the crystalline material so obtained was recrystallized from water. The colorless crystals melted at 90–91° with decomposition.

Anal. Calcd. for $C_2H_6N_6S_2$: S, 35.99. Found: S, 36.05.

Anilinium Thiatriazolinethionate (**VIII. M** = $C_6H_5NH_3^+$; n = 1).—To a solution of benzene and aniline was added freshly prepared thiatriazolinethione, still moist. An oil separated, which was removed and shaken with dry benzene (to remove excess aniline). The oil so isolated was concentrated *in vacuo* over phosphorus pentoxide at 5°. After 2 hr. the solid yellow crystalline product was removed, washed with benzene, and allowed to dry, m.p. 70–72°.

Anal. Calcd. for $C_7H_8N_4S_2$: S, 30.21. Found: S, 30.27.

Benzylammonium Thiatriazolinethionate (**VIII. M** = $C_6H_5CH_2NH_3^+$; n = 1).—This compound was prepared by adding moist III to an ether solution of benzylamine. As aqueous lower layer appeared that was removed and washed several times with benzene. The aqueous layer so obtained was chilled and the product crystallized. This slightly yellow, crystalline product was removed from its aqueous suspension by filtration and washed several times with benzene. The decomposition point was found to be 99°.

Anal. Calcd. for $C_8H_{10}N_4S_2$: S, 28.34. Found: S, 28.18.

Degradative Studies. (a) **Reference Compounds.**—These were prepared by methods described in the literature and are summarized in Table III. The triphenylmethyl thiocyanate of Elbs[19] turned out to be triphenylmethyl isothiocyanate.[24,41,44] The procedure of Wheeler[42] for diphenylmethyl thiocyanate and diphenyl isothiocyanate gave mixtures[24] of these two compounds.

(b) **Pyrolysis of 5-(Thiocyano)-1,2,3,4-thiatriazole (V. R = CN).**—Approximately 5 g. of the substance was refluxed in carbon disulfide for 3 hr. After the reflux period, the carbon disulfide was distilled and the distillate allowed to evaporate to dryness at room temperature. A white crystalline product was obtained having a melting point of 60°. This was identified as sulfur dicyanide by mixture melting point with an authentic specimen[18] and by comparative infrared absorption spectroscopy.

(c) **General Procedure for Thermal Degradation.**—About 0.04 mole of the thiatriazole was refluxed in benzene for 2 hr. at which time a sufficient quantity of ligroin was added to cause precipitation of the degradation product on cooling. The products so obtained, after recrystallization (see Table III for melting point data), were examined by infrared absorption spectroscopy to determine whether the degradative product, so obtained, was a normal thiocyanate or an isothiocyanate. The data obtained are summarized in Table III.

(d) **Degradation in Basic Solution.**—1:2 mole ratio of III and sodium hydroxide, in 200 ml. of water, was gently warmed on a hot plate until the evolution of nitrogen gas had ceased. During the process of heating the solution turned from yellow to a bright orange-red color. Carbon disulfide was identified by the detection of sodium thithiocarbonate. The other degradation products identified were thiocyanate ion, azide ion, and sulfide ion.

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[44] A. Iliceto, A. Fava, and U. Mazzuccatv, *J. Org. Chem.*, **25**, 1445 (1960).

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ortho Substitution–Rearrangement and Other Reactions of the Benzyldimethylanilinium Ion by Sodium Amide in Liquid Ammonia[1]

GLENN C. JONES,[2] WILLIAM Q. BEARD, AND CHARLES R. HAUSER

Department of Chemistry, Duke University, Durham, North Carolina

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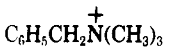
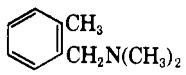
Whereas the benzyltrimethylammonium ion (I) undergoes exclusively the *ortho* substitution–rearrangement with sodium amide in liquid ammonia, the related benzyldimethylanilinium ion (III) exhibits, with this reagent, not only this type of rearrangement but also two other courses of reaction. One of the two latter courses of reaction involves a Stevens 1,2-shift, and the other self-condensation. The products formed from these two courses of reaction underwent β-elimination to give methylaniline and styrene, and dimethylaniline and stilbene, respectively. Also the self-condensation product underwent some rearrangement to produce apparently a dimeric amine. The *o*-xylyldimethylanilinium (XIV) ion exhibited similar reactions with sodium amide in liquid ammonia.

It has previously been shown[3] that the benzyltrimethylammonium ion I undergoes exclusively the *ortho* substitution–rearrangement with sodium amide in liquid ammonia to form tertiary amine II.



$C_6H_5CH_2\overset{+}{N}(CH_3)_3$

I



II

It has now been found that the related benzyldimethylanilinium ion (III) reacts with this reagent to give not only the *ortho* substitution–rearrangement

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[1] Supported in part by the National Science Foundation.

[2] Tennessee Eastman Fellow, 1959–1960.

[3] S. W. Kantor and C. R. Hauser, *J. Am. Chem. Soc.*, **73**, 4122 (1951).