solutions followed by codistillation with ethanol led to the aminodeoxyheptulosans IV.

Aminodeoxyheptulosan IVa.—A 200-mg. sample of nitroheptulosan IIIa (m.p. 173.5) was hydrogenated furnishing a crystalline product, $[\alpha]^{23}_{\mathrm{D}}$ $-46.7°$ (*c*, 0.5), which was revealed by paper chromatography to be not uniform. Besides the main spot of R_{gm} 1.03–1.04 there was a weaker spot of R_{gm} 1.20.[14] Recrystallization from the minimum amount of water and a tenfold excess of glacial acetic acid afforded 107 mg. of short prismatic columns which were chromatographically pure IVa; R_{gm} 1.03, $[\alpha]^{23}_{\mathrm{D}}$ $-54.7°$.

Anal. Calcd. for $C_7H_{14}O_5NCl$ (227.7): C, 36.93, H, 6.20; N, 6.15. Found: C, 37.03; H, 6.28; N, 5.94.

Aminodeoxyheptulosan IVb.—Nitrodeoxyheptulosan IIIb (130 mg.) upon hydrogenation yielded 110 mg. of elongated needlelike prisms with square, sometimes sloping, end faces. The product, IVb, was immediately chromatographically uniform (R_{gm} 1.30) and analytically pure; $[\alpha]^{23}_{\mathrm{D}}$ $+39.0°$, unchanged upon recrystallization from water–acetic acid.

Anal. Calcd. for $C_7H_{14}O_5NCl$ (227.7): C, 36.93; H, 6.20; N, 6.15; Cl, 15.57. Found: C, 37.12; H, 6.35; N, 6.00; Cl, 15.48.

In another run 280 mg. of IVa showing $[\alpha]^{23}_{\mathrm{D}}$ $+37.5$ was obtained from 315 mg. of IIIa.

Aminodeoxyheptulosan IVc.—Crystalline nitrodeoxyheptulosan IIIc (442 mg.) was hydrogenated to give 410 mg. of chromatographically uniform IVc (R_{gm} 1.00); $[\alpha]^{23}_{\mathrm{D}}$ $-124.0°$. Recrystallization from water–acetic acid gave fine needles (rapid crystallization) or rectangular prisms and platelets (slow crystallization in the air); $[\alpha]^{23}_{\mathrm{D}}$ $-126°$.

Anal. Calcd. for $C_7H_{14}O_5NCl$ (227.7): C, 36.93; H, 6.20; N, 6.15; Cl, 15.57. Found: C, 36.86; H, 6.23; N, 5.91; Cl, 15.71.

In another run 220 mg. of IVc showing $[\alpha]^{23}_{\mathrm{D}}$ $-123.5°$ was obtained from 221 mg. of IIIc.

Aminodeoxyheptulosan IVc was also obtained by the hydrogenation of levorotatory, sirupy nitrodeoxyheptulosan mixtures which originated in deionization of salt IIm (previously described). Thus, 3.76 g. of a sirup ($[\alpha]^{23}_{\mathrm{D}}$ $-90.5°$) was hydrogenated and furnished a slightly yellowish, partly crystalline product which on the chromatogram showed spots of equal strength corresponding to IVb and IVc, and an unidentified faint spot of R_{gm} 1.60. Recrystallization from water–glacial acetic acid afforded 705 mg. of colorless crystals of IVc containing but a trace of IVb; $[\alpha]^{23}_{\mathrm{D}}$ $-122.0°$. The mother liquor of the recrystallization gave another 160 mg. of crystals being mainly IVc ($[\alpha]^{23}_{\mathrm{D}}$ $-114°$), as well as various mixed fractions. Similarly, a nitrodeoxyheptulosan sirup (1.3 g.) stemming from the deionization of another fraction of the salts IIm was hydrogenated to a partly crystalline amine mixture ($[\alpha]_{\mathrm{D}}$ $-93°$) whose chromatographic pattern was the same as that just described. By recrystallization from water–glacial acetic acid, 390 mg. of rather pure IVc ($[\alpha]^{23}_{\mathrm{D}}$ $-121.5°$) was obtained. The mother liquor contained both IVc and IVb; 50 mg. of the former was deposited after 3 days. The infrared spectra of the preparations of IVc obtained *via* the sirupy nitrodeoxyheptulosan mixtures were identical with that of IVc from crystalline IIIc.

The Behavior of the *aci*-Nitro Salt IIb in Aqueous Solution.—Two 120-mg. samples of one preparation of the salt IIb were treated as follows.

Sample (a) was introduced into an ice-cold solution of 5.5 ml. 0.1*N* hydrochloric acid and 50 ml. of water. After 5 min., 5 ml. of Amberlite IR-120 (H^+) was added and the mixture was shaken for 10 min. in order to remove sodium ion. Upon filtration, the acid solution was immediately hydrogenated. Chromatographic inspection of the total residue of evaporation obtained after the hydrogenation indicated the presence of only *one* amine, namely IVb. It crystallized readily.

Sample (b) was dissolved in 30 ml. of carbon dioxide-free water at 23° and allowed to reach a constant specific rotation of $-92°$. After 18 hr. the solution was deionized with 5 ml. of Amberlite IR-120 (H^+), acidified with 5.5 ml. of 0.1 *N* hydrochloric acid and hydrogenated. Chromatography of the product revealed that it contained at least *two* amines, giving spots of about equal strength at R_{gm} 1.27 and R_{gm} 1.01.

Another sample of IIb was allowed to mutarotate in aqueous solution to the final $[\alpha]_{\mathrm{D}}$-value. By careful evaporation the solute was recovered. Its infrared spectrum was now clearly distinct from that of the starting salt IIb. It was also different from the spectrum of IIa, but it resembled closely those given by the non-uniform salts IIm.

Acknowledgment.—Preliminary experiments to this project were done in 1959 at the Max Planck Institute for Medical Research, Heidelberg, and subsequently at the National Institute of Arthritis and Metabolic Diseases, Bethesda, Md., where the author enjoyed great encouragement from and valuable discussions with Dr. N. K. Richtmyer, who also provided the sedoheptulosan, and Dr. H. G. Fletcher, Jr. A major part of the work was carried out in Ottawa with the skillful technical assistance of Mr. Frank Kienzle. Financial support by the Ontario Research Foundation is gratefully acknowledged.

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[14] The occurrence of that spot obviously is connected with the instability of IIIa and the difficulty of preparing it in entirely pure state (*cf.* ref. 12). It might be possible to obtain IVa in better yield and purity by directly hydrogenating an acidified solution of IIa, *i.e.*, without isolating the intermediate nitro compound, IIIa.

Direct Epoxidation of *o*-Chlorobenzylidenemalononitrile with Hypochlorite Ion

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Hypochlorite ion is a nucleophile toward the electronegatively substituted olefin, *o*-chlorobenzylidenemalononitrile. The product formed with stoichiometric amounts of the reactants is the epoxide (II).

The hydrogen peroxide epoxidation of olefins activated by electron-withdrawing groups such as carbonyl and nitrile is well known.[1-4] The active reagent species is the perhydroxyl anion, which is an extraordinarily powerful nucleophile, as noted by Edwards and Pearson.[5] It would appear that hypochlorite ion, another potent nucleophile,[5] has not found use in direct epoxidation,[6] with the possible exception of a single patent[9] on the epoxidation of acrolein and alkyl-sub-

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[1] C. A. Bunton and G. J. Minkoff, *J. Chem. Soc.*, 665 (1949).

[2] E. Weitz and A. Scheffer, *Ber.*, **54**, 2327 (1921); G. B. Payne, *J. Am. Chem. Soc.*, **81**, 4901 (1959); G. B. Payne, *J. Org. Chem.*, **24**, 2048 (1959); H. E. Zimmerman, L. Singer, and B. S. Thyagarajan, *J. Am. Chem. Soc.*, **81**, 108 (1959).

[3] G. B. Payne and P. H. Williams, *J. Org. Chem.*, **26**, 651 (1961).

[4] G. B. Payne, *ibid.*, **26**, 663 (1961).

[5] J. O. Edwards and R. G. Pearson, *J. Am. Chem. Soc.*, **84**, 16 (1962).

[6] In fact, mesityl oxide, which is epoxidized[1] by perhydroxyl ion at pH 11–13, reacts with hypochlorous acid at pH 4.5 to 10 to give the chlorohydrin,[7] and under very alkaline conditions to give 3,3-dimethylacrylic acid through a haloform reaction.[8]

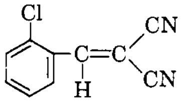
[7] J. Colonge and L. Cumet, *Bull. soc. chim. France*, [5] **14**, 838 (1947).

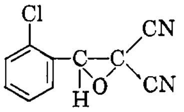
[8] L. I. Smith, W. W. Prichard, and L. J. Spillane, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 302.

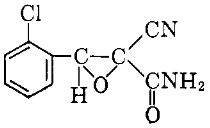
[9] G. W. Hearne, D. S. LaFrance, and H. de V. Finch, U. S. Patent 2,887,498 (1959).

stituted acroleins, in which instance the role of the anion was not made clear. Both hydrogen peroxide and hypochlorous acid are commonly employed as electrophilic reagents, but are ineffective in this capacity toward electronegatively substituted carbon-carbon double bonds. It now appears that *both* these electrophilic reagents (not uniquely hydrogen peroxide) can be converted to reagents which are nucleophilic toward olefins of suitable structure by the simple expedient of raising the pH from the usual acidic conditions in which these reagents are used. In a sense, the electronegative substituents provide an advantage, in that they make possible the conversion of olefin to epoxide in a single step instead of the two steps required for the chlorohydrin route.

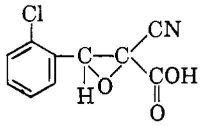
The present study concerned itself with the reaction of hypochlorite with *o*-chlorobenzylidenemalononitrile (I), a compound known[10] to react with nucleophilic reagents such as cyanide and bisulfite. By contrast, it was demonstrated early in the present work that I does not react with the electrophilic reagent chlorine (in carbon tetrachloride). Depending on reaction conditions, epoxidized *o*-chlorobenzylidenemalononitrile (II), the two isomers (III) resulting from hydrolysis of one or the other nitrile group of II to amide, and an acid or mixture of acids (IV) resulting from hydrolysis of the amide to carboxyl were obtained on treating I with hypochlorite. Possible mechanisms for the chlorine-mediated conversion of nitrile to amide to carboxyl have been presented in a previous publication,[11] and the present work offers additional evidence of the susceptibility of electronegatively substituted nitriles to nucleophilic attack by hypochlorite, as postulated there. Thus, when previously prepared compound II was kept at pH 8, it was recovered intact in the absence, but not in the presence, of hypochlorite.


I


II


III

a. (m.p. 138–140°)
b. (m.p. 189–190.5°)


IV

A few experiments were carried out on the kinetics of the hypochlorite epoxidation reaction (summarized in Table I). According to these experiments, the second order rate constant at 25° is approximately 2.2×10^4 M^{-1} sec.$^{-1}$ (assuming[12] $K_a = 4 \times 10^{-8}$). In the first experiment, a high concentration of sodium chloride was added, which, it may be calculated, should have converted about half the HOCl to Cl_2, at least a thousandfold more Cl_2 than could have been present in the sixth experiment; that this hardly affected the value of k_{obsd} leads one to dismiss any possible role for Cl_2 as a reactive species. For comparison purposes, a single experiment was carried out to determine the reactivity of I with perhydroxyl ion, whence the second-order rate constant of 4×10^5 M^{-1} (assuming[13] $K_a = 2.24 \times 10^{-12}$); and II was synthesized by the perhydroxyl method, some III being produced at the same time, to demonstrate the parallelism.

The kinetic experiments (on disappearance of the olefin bond of I) are of greatest significance in the choice among the possible reaction mechanisms below.

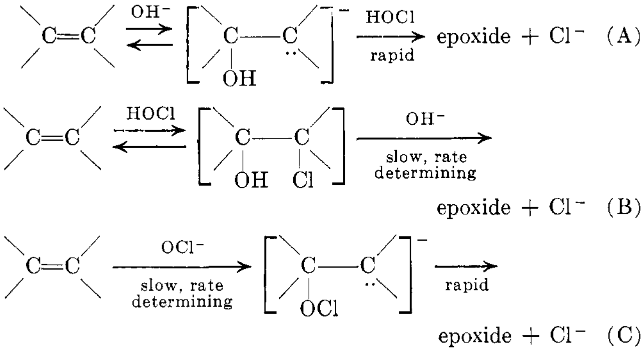


TABLE I

KINETICS OF EPOXIDATION OF *o*-CHLOROBENZYLIDENEMALONONITRILE WITH A LARGE EXCESS OF HYPOCHLOROUS ACID (IN WATER CONTAINING 1% ACETONITRILE) AT AMBIENT TEMPERATURE (APPROXIMATELY 25°)

pH	10^4 [HOCl]	Ionic strength	10^3 k_{obsd}, sec.$^{-1}$	k_2',[a] M^{-1} sec.$^{-1}$	10^8 K_a[b]	10^{-4} k_2, M^{-1} sec.$^{-1}$
3.24	6.98	1.0[c]	2.22	3.18	...	...
3.30	4.33	0.105	1.28	2.95	8.56	1.73
3.30	10.83	0.105	4.33	4.00	8.56	2.34
3.30	21.66	0.105	8.30	3.83	8.56	2.24
3.30	43.32	0.105	16.1	3.72	8.56	2.18
3.57	6.98	0.005	2.98	4.27	4.72	2.44
3.89	9.06	0.015	10.2	11.25	5.33	2.72
3.98	6.98	0.015	8.12	11.63	5.33	2.29
4.02	6.98	0.015	6.90	9.89	5.33	1.77

[a] $k_2' = k_{obsd}/[HOCl]$. [b] $\log K_a = \log K_{thermodynamic} + 1.02$ (ionic strength)$^{1/2}$. [c] 1 M in sodium chloride.

Mechanism A would imply linear rate dependence on hydroxyl ion concentration, as is indeed the case. This part of the reaction would have to be formulated as a reversible equilibrium lying far to the left because the disappearance rate of the double bond of *o*-chlorobenzylidenemalonitrile, in the absence of the nucleophile, is negligible within the pH range covered in Table I. This mechanism would also imply, however, independence of hypochlorous acid concentration at constant pH; this is controverted by the data for pH 3.30. Mechanism B would permit a concentration dependence on both hypochlorous acid and hydroxyl ion. This involves the unlikely elimination of hypochlorous acid in the reverse step of the equilibrium, which would have to be quite rapid in order for the equilibrium to lie substantially to the left, as it must to satisfy the concentration dependence requirements derived from a consideration of the steady state approximation.[14] Thus, mechanism C is left; it satisfies the experimental data, and is analogous to the well-studied perhydroxyl reaction.[1–5]

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[10] B. B. Corson and R. W. Stoughton, *J. Am. Chem. Soc.*, **50**, 2825 (1928).

[11] D. H. Rosenblatt and G. H. Broome, *J. Org. Chem.*, **26**, 2116 (1961).

[12] N. G. Lordi and J. Epstein, *J. Am. Chem. Soc.*, **80**, 509 (1958).

[13] W. C. Schumb, C. N. Satterfield, and R. L. Wentworth, "Hydrogen Peroxide," Reinhold Publishing Co., New York, N. Y., 1955, p. 393.

[14] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1961, p. 195.

The formation of II, III and IV is probably sequential. The mechanism for concurrent epoxidation of the olefinic linkage and hydrolysis of nitrile to amide, demonstrated in the reaction of α,β-unsaturated nitriles with hydrogen peroxide[3,4] can find no analogy where hypochlorite is the reagent. This is borne out by the failure to isolate III or IV when a stoichiometric amount of hypochlorite is used.

Hypochlorite ion, as shown above, is a weaker nucleophile towards *o*-chlorobenzylidenemalononitrile than perhydroxyl ion. Below pH 10, however, hypochlorous acid is more reactive than hydrogen peroxide because it is so much more highly ionized. By extension, it is evident that olefins sufficiently reactive toward hypochlorite could be epoxidized by this reagent under less alkaline conditions than those required for hydrogen peroxide; avoidance of alkaline conditions might be an important consideration. For less reactive olefins, however, perhydroxyl might be the only nucleophilic reagent, albeit only at very high pH. Another difference in the use of hypochlorite, as opposed to perhydroxyl, is peculiar to α,β-unsaturated nitriles. It lies in the fact that the dominant reaction of perhydroxyl ion with these compounds involves attack at the nitrile group first, followed by intramolecular epoxidation,[3,4] so that an epoxyamide is obtained in a single step, and often very little product of simple epoxidation. The epoxyamide can also be obtained with hypochlorite (*e.g.*, III), but most likely by a step subsequent to epoxidation.

Experimental

Failure of *o*-Chlorobenzylidenemalononitrile (I) to React in a Short Time, at Ambient Temperature, with Chlorine in Carbon Tetrachloride.—A carbon tetrachloride solution containing 0.05 *M* chlorine and 0.05 *M* *o*-chlorobenzylidenemalononitrile[10] was permitted to stand 10 min. A sample of the mixture was then diluted 3:2500 with the solvent and its absorption spectrum measured[15] in the vicinity of the 300 mμ maximum (absorptivity = 1.03). A blank solution, similar in all respects except for the absence of chlorine, exhibited a nearly identical spectrum.

Reaction of I (M.p. 96°) with Hypochlorite. A. In Stoichiometric Proportion.—Both partially neutralized chlorine water and hypochlorous acid[12] were used successfully in this preparation. An early preparation of the epoxide (II), using partially neutralized chlorine water, gave a product which, after repeated recrystallization from petroleum ether, sintered at 53.0–53.2° and melted at 53.2–53.5°, with the following analyses.

Anal. Calcd. for $C_{10}H_5ON_2Cl$: C, 58.69; H, 2.46; O, 7.84; N, 13.69. Found: C, 58.9; H, 2.6; O, 8.2; N, 13.5.

The following procedure incorporates a somewhat improved technique for isolation: Aqueous hypochlorous acid[12] (234 ml., 0.141 *M*) and 1 *N* sodium hydroxide (47 ml.) were added concurrently to a solution of 5.66 g. of I in 270 ml. of acetonitrile,[16] at such a rate that the solution was maintained in the vicinity of pH 7 with the help of a pH meter.[17] When reaction was complete, as evidenced by constancy of pH, a little sodium chloride was added and the mixture was extracted twice with ether (250 and 125 ml.). The combined ether extract was concentrated to remove all ether and steam distilled.[18] The oil collected in the distillate was recrystallized from petroleum ether (b.p. 30–60°) to give 2.2 g. of II, m.p. 51–52°.

B. With a Mole Ratio of Hypochlorite to I of 1.8:1.—Chlorine water was adjusted to pH 7 with sodium hydroxide to give a 0.121 *M* hypochlorite solution (by titration). When 225 ml. of this solution was added to a solution of 2.39 g. of I in 100 ml. of acetonitrile, the pH dropped quickly to about 3 and was adjusted to 7 with 14 ml. of 1 *N* sodium hydroxide. Solvent was removed on the rotating evaporator and the residue was washed well with ether, the ether containing mostly IIIa and the washed residue containing largely IIIb and sodium chloride. The crude IIIa (0.75 g.) left on evaporation of the ether washings was purified by fractional precipitation from benzene with petroleum ether, appearing as the more soluble fraction. Further recrystallizations of this crude IIIa from chloroform–carbon tetrachloride produced 0.08 g. of a mixture of slender needle-like and diamond-shaped transparent crystals, which became opaque on standing or heating, indicating that solvent was included; m.p. 138–140°.

Anal. Calcd. for $C_{10}H_7O_2N_2Cl$: C, 53.90; H, 3.17; O, 14.4. Found: C, 53.89; H, 3.2; O, 13.8.

The residue containing IIIb was washed with water and recrystallized several times from benzene to give 0.6 g. of pure IIIb, m.p. 189–190.5°.

Anal. Calcd. for $C_{10}H_7O_2N_2Cl$: C, 53.90; H, 3.17; O, 14.4. Found: C, 54.2; H, 3.2; O, 13.9.

The isomers IIIa and IIIb had very similar infrared spectra.

C. With a Mole Ratio of Hypochlorite to I of 4.3:1.—In this experiment, the attempt was made to permit I to react, in the neighborhood of pH 7, with as much hypochlorite as it would consume. Chlorine water, brought to pH 7, was therefore added periodically to a solution of 1.07 g. of I in 105 ml. of acetonitrile, with continual pH adjustment (no higher than pH 7.8) with 1 *N* sodium hydroxide, until the hypochlorite to olefin ratio had reached 4.3:1 (the total volume of added aqueous solutions being 330 ml.). After standing overnight, the mixture was evaporated to dryness at reduced pressure, and the residue taken up in a small volume of water and acidified with concentrated sulfuric acid to give a precipitate of IV, which was isolated and washed with cold water (0.458 g.). On recrystallization from chloroform–petroleum ether, the substance melted at 166.5–167° on a melting point block; the melting point is sometimes lower, evidently depending on conditions and age of the sample. The pK_a is about 2.4, close to that of cyanoacetic acid.[19]

Anal. Calcd. for $C_{10}H_6O_3NCl$: C, 53.7; H, 2.7; N, 6.3. Found: C, 53.5; H, 2.9; N, 6.3.

Preparation of II with Hydrogen Peroxide.—A mixture of 3 ml. of 30% hydrogen peroxide, 65 ml. of water and 1 ml. of 1 *M* potassium nitrate was found to be 0.524 *M* in peroxide by titration. A 20-ml. aliquot of this was added to a solution of 1.92 g. of I in 50 ml. of acetonitrile and the mixture was brought to pH 7.6 with 8 ml. of 0.03 *N* sodium hydroxide. After about 15 min., the mixture was concentrated in the rotating evaporator until a second phase appeared. Then ether and 2 *N* sodium chloride were added, and the mixture was shaken and separated. The ether layer was evaporated to an oil, which was extracted with several portions of hot petroleum ether (b.p. 30–60°); the petroleum ether extract, on chilling, deposited 0.79 g. of crude II; while the residue from extraction, 0.39 g., contained mostly impure IIIb, m.p 176–185°. On recrystallization of crude II from petroleum ether, nearly pure material, m.p. 49–50°, was obtained. Recrystallization of IIIb from benzene gave material of m.p. 190–191°; a small amount of IIIa was isolated from the mother liquors.

Kinetic Experiments.—Reaction mixtures for kinetic studies contained 0.1 *M* acetate buffer adjusted to pH with sodium hydroxide and 5×10^{-5} *M* I, introduced in acetonitrile (so that the reaction mixtures also contained 1% by volume of acetonitrile). The absorptivity (A) at 300 mμ was measured[15] as a function of time after introduction of the epoxidizing agent, and the half-lives, $t_{1/2}$, obtained from plots of log $(A - A_\infty)$ against time; $k_{\text{obsd}} = 0.693/t_{1/2}$; the apparent second-order rate constant $k_2' = k_{\text{obsd}}/[\text{oxidant}]$; the true second-order rate constant, $k_2 = ([H^+] + K_a)\, k_2'/K_a$. Data for hypochlorite are shown in Table 1. A single experiment conducted similarly with 1.1×10^{-3} *M* hydrogen peroxide in phosphate buffer gave $k_2' = 18.1\ M^{-1}\ \text{sec.}^{-1}$, or taking K_a as 2.24×10^{-12} for hydrogen peroxide,[13] $k_2 = 4.3 \times 10^5$.

Disappearance of II in the Presence of Hypochlorous Acid.—

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(15) Cells of 1-cm. light path, in a Beckman Model DU spectrophotometer modified for recording by Process and Instruments, Inc., were used.

(16) This solvent appeared to be relatively inert to the oxidizing reagent under conditions employed here.

(17) A Beckman Model G pH meter was used with glass and calomel electrodes.

(18) Glycidonitrile is similarly quite steam volatile.[3]

(19) I. Heilbron and H. M. Bunbury, "Dictionary of Organic Compounds," 3rd ed., Vol. 1, Oxford University Press, New York, N. Y., 1953, p. 624.

A mixture of 0.9 g. of II, 50 ml. of acetonitrile and 40 ml. of 0.17 *M* hypochlorous acid was adjusted to pH 8 with 7 ml. of 1 *N* sodium hydroxide. At the end of an hour the mixture was acidified to pH 4.7 and extracted with ether. About 32% of starting material was recovered after evaporating off the ether layer. When a similar amount of II was kept for an hour at pH 8 in a mixture of 50 ml. of acetonitrile plus 50 ml. of water, the starting material was almost completely recovered.

Interaction of 2-Chlorobenzothiazole with Aromatic Thiocarbamides. I. Formation of Guanylthiocarbamides and Sulfides

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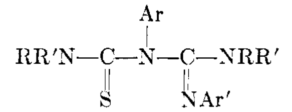
Interaction of 2-chlorobenzothiazole has been investigated with arylthiocarbamides. Hydrochlorides of the related substituted guanylthiocarbamides are obtained. 1,3-Diphenylthiocarbamide, however, gave bis(N,N'-diphenylguanyl) sulfide hydrochloride.

The interaction, mostly in alcoholic medium, of 2-chlorobenzothiazole with thiocarbamides has been investigated by Watt[1] and Scott and Watt.[2] Thiocarbamide and its monosubstituted derivatives were found to give mercaptobenzothiazole, benzothiazolyl sulfide and cyanamide corresponding to the thiocarbamide used, as the main products. Based on these facts a reaction mechanism which involved initial formation of S-2-benzothiazolylisothiouronium chloride as an intermediate stage was proposed, although this last could not be isolated in any of the cases studied. From disubstituted thiocarbamides even on prolonged action no products were obtained except in the case of N,N'-*o*-phenylenethiocarbamide (thiobenzimidazolone) where a gray solid believed to be an addition product was isolated. With trisubstituted thiocarbamides no reaction was observed.

In connection with our work[3] on 2-substituted benzothiazole derivatives the interaction of thiocarbamides and 2-chlorobenzothiazole was reinvestigated. In view of the extreme lability of the S-R link in isothiocarbamides where R was an acyl or an electronegative group in general, it was felt that the reaction conditions employed by the above workers were unconducive for the isolation of the addition or other more reactive products. In the present study, therefore, the reactions were carried out at the ordinary room temperature or at about 40–50° mostly without any solvent or with actone as solvent.

The reaction was investigated with (i) 1-phenyl-, (ii) 1-(*p*-tolyl)-, (iii) 1-(*o*-tolyl)-, (iv) 1-(2,6-dimethylphenyl)-, (v) 1-phenyl-3-methyl-, (vi) 1-phenyl-3-ethyl-, (vii) 1-(*p*-tolyl)-3-methyl-, (viii) 1-phenyl-3,3-dimethyl-, and (ix) 1,3-diphenylthiocarbamides.

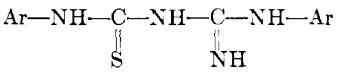
The products were colorless in all cases except the last one, *viz.*, (ix) where it had a lemon-yellow color. All were hydrochlorides, of unstable bases which could not be isolated in pure condition, except in the case of (v), (vi), (vii), and (viii) where they were found to be identical with the products obtained by the oxidation of the related thiocarbamides[4] with bromine in alcoholic medium and have been assigned structure Ia through Id, respectively.



$$RR'N{-}\underset{\underset{\displaystyle S}{\|}}{C}{-}\overset{\overset{\displaystyle Ar}{|}}{N}{-}\underset{\underset{\displaystyle NAr'}{\|}}{C}{-}NRR'$$

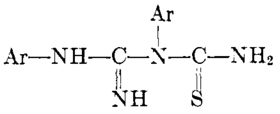
Ia from v, where $R = H$, $R' = CH_3$, $Ar = Ar' = C_6H_5$
Ib from vi, where $R = H$, $R' = C_2H_5$, $Ar = Ar' = C_6H_5$
Ic from vii, where $R = H$, $R' = CH_3$, $Ar = Ar' = CH_3C_6H_4$
Id from viii, where $R = R' = CH_3$, $Ar = Ar' = C_6H_5$

As judged from their decomposition products and other behavior there does not appear any doubt that the colorless products from other thiocarbamides also possessed similar structures. In the case of 1-phenyl- and 1-(*p*-tolyl)thiocarbamides, the products were found different from II, the 1-arylguanyl-3-arylthiocarbamides[5,6]



$$Ar{-}NH{-}\underset{\underset{\displaystyle S}{\|}}{C}{-}NH{-}\underset{\underset{\displaystyle NH}{\|}}{C}{-}NH{-}Ar$$

II

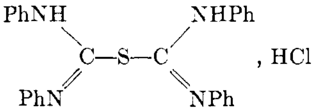


$$Ar{-}NH{-}\underset{\underset{\displaystyle NH}{\|}}{C}{-}\overset{\overset{\displaystyle Ar}{|}}{N}{-}\underset{\underset{\displaystyle S}{\|}}{C}{-}NH_2$$

III

where Ar = phenyl or *p*-(tolyl) group. That they were identical with III was confirmed by their almost quantitative and easy decomposition to diarylguanidine and thiocyanic acid, respectively.

The yellow product obtained from 1,3-diphenylthiocarbamide was proved by its identical behavior to be the hydrochloride (IV) corresponding to the hydrobromide of bis(N,N'-diphenylguanyl) sulfide described by Suresh.[7] The infrared absorption spectra of IV and of bis(N,N'-diphenylguanyl) sulfide hydrobromide prove unequivocally their identical sulfide structures.



IV

There is evidence suggesting that in the case of the above reactions the initial product is an S-(2-benzothiazolyl)isothiouronium chloride[8] as envisaged by Watt[1] and as shown by Suresh and D'Souza[9] in the case of reaction with *p*-toluenesulfonyl chloride and by

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[1] G. Watt, *J. Org. Chem.*, **4**, 436 (1939).

[2] W. Scott and G. Watt, *ibid.*, **2**, 148 (1937).

[3] C. P. Joshua, *J. Indian Chem. Soc.*, **37**, 621 (1960); **38**, 155, 979 (1961).

[4] P. K. Srivastava, unpublished work.

[5] S. N. Dixit, *J. Indian Chem. Soc.*, **37**, 153 (1960).

[6] K. S. Suresh, *J. Sci. Res. Banaras Hindu Univ.*, IX (**2**), 92 (1958–1959).

[7] K. S. Suresh, *J. Indian Chem. Soc.*, **37**, 483 (1960).

[8] R. H. Sahasrabudhey, C. P. Joshua, and S. N. Pandey, *Proc. Indian Sci. Congr.*, Part III, Abstracts, 102 (1961).

[9] K. S. Suresh and M. S. A. D'Souza, *J. Vikram Univ.*, 3 (**3**), 10 (1959).