nitrogen had ceased, the mixture was diluted to three times its volume and allowed to stand for one hour. The solid which formed was removed by filtration and recrystallized using charcoal from 95% ethanol (100 ml.); yield 2.4 g. (48%) of white needles, m. p. 189–190°.

2-Chloro-6-methylsulfinylbenzothiazole (XVI).—2-Amino-6-methylmercaptobenzothiazole (5 g., 0.03 mole) was dissolved by heating in 87% phosphoric acid (75 ml.). The solution was then cooled to 0° by means of an ice-bath. Cold concentrated nitric acid (25 ml.) was added with rapid stirring. A solution of sodium nitrite (2 g. in 5 ml. of water, 0.03 mole) was then added to the lower portion of the well-stirred acid medium. The deep red viscous diazonium mixture which formed was then poured in a small stream into concentrated hydrochloric acid (100 ml.) containing cuprous chloride (5.0 g., 0.03 mole). As soon as evolution of nitrogen ceased the mixture was stirred for an additional fifteen minutes and diluted to three times its volume. The diluted solution was extracted four times with benzene (100-ml. portions). The benzene was dried over anhydrous sodium sulfate and evaporated to dryness. The resulting orange solid was recrystallized, employing charcoal, from hot water (150 ml.); yield 2 g. (34%) of white fluffy crystals, m. p. 112–113°.

2-Chloro-6-methylmercaptobenzothiazole (XXI).—Identical conditions and amounts were employed as in the preparation of compound XVI with the exception that the diazotization was carried out at −20 instead of 0° using an acetone–Dry Ice-bath. The product was extracted with benzene and obtained in the solid form as before. The yellow material was transferred in two portions to a small fractionating column and distilled under reduced pressure. A yellow oil distilled over at 138–142° (3 mm.). This product was recrystallized, using charcoal, from hot petroleum ether; yield 1.5 g. (28%) of white crystals, m. p. 51–52°.

The condensations of amines with chloro compounds were carried out in a slightly over two mole excess of the amine so that the excess amine would form a salt with the hydrogen chloride eliminated. The method employed for isolation of the product was based on the fact that all the amines reacting were more soluble in water than the condensed products. The following preparations illustrate the procedure used.

2-(Benzylamino)-6-methylsulfonylbenzothiazole (XIV).—2-Chloro-6-methylsulfonylbenzothiazole (0.75 g., 0.003 mole) and benzylamine (0.86 g., 0.008 mole) reacted together in a 25-ml. round-bottomed flask equipped with a water condenser. Although some heat was evolved at once the mixture was heated at 150° for four hours in an oil-bath to complete the reaction. Upon cooling the reaction mixture solidified. The crystals which formed were washed thoroughly with dilute ammonium hydroxide and water to remove excess benzylamine. The solid that remained was recrystallized from ethyl acetate; yield 0.93 g. of fine white crystals, m. p. 220°.

2-(δ-Diethylaminobutylamino)-6-methylmercaptobenzothiazole Dihydrochloride (XXII).—2-Chloro-6-methylmercaptobenzothiazole (0.25 g., 0.001 mole) and δ-diethylaminobutylamine (0.43 g., 0.003 mole) reacted together on a steam-bath for twenty-two hours. The resulting liquid was mixed thoroughly with dilute ammonium hydroxide and extracted with three portions of diethyl ether (25 ml.). The combined solutions were washed three times with water (25 ml.), dried over anhydrous sodium sulfate and dry hydrogen chloride gas added until an oil separated. The oil was recrystallized, using charcoal, from methanol and anhydrous diethyl ether; yield 0.35 g. of a light brown solid.

Summary

1. 2-Amino-6-methylsulfonylbenzothiazole and 2-amino-6-methylmercaptobenzothiazole have been prepared from *p*-nitrochlorobenzene in good yields.

2. The above compounds were converted to the corresponding 2-chloro compounds producing in addition 2-chloro-6-methylsulfinylbenzothiazole.

3. All three chloro compounds were successfully condensed with benzylamine, piperidine, δ-diethylaminobutylamine and γ-diethylaminopropylamine.

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Some β-Amino-α-chloroacrylonitriles

BY JOHN G. ERICKSON

Except for a few β-aminoacrylonitriles prepared by Moureu and Lazennec,[1] no compounds of this class have been reported. The French workers prepared their compounds by the addition of various primary and secondary amines to several α,β-acetylenic nitriles.

Here we wish to report the preparation of a number of β-amino-α-chloroacrylonitriles (II) by the reaction of α,β-dichloroacrylonitrile (I) with ammonia and aliphatic and aromatic primary and secondary amines.

$$\mathrm{ClCH{=}\underset{\underset{\displaystyle Cl}{|}}{C}CN + RR'NH \longrightarrow RR'NCH{=}\underset{\underset{\displaystyle Cl}{|}}{C}CN + HCl}$$

I II

The reactions were carried out in alcohol or benzene solutions at or near room temperature. An acid acceptor, which was either a tertiary amine or an excess of the ammonia or amine being used in the reactions, was always present to neutralize the hydrogen chloride eliminated in the reactions.

The β-amino-α-chloroacrylonitriles are, in general, unstable. Although they may usually be distilled, even at high temperatures, without serious decomposition, those compounds which are liquids at room temperature slowly darken and decompose upon standing. The solid compounds appear to be relatively stable at room temperature. Of the liquid β-amino-α-chloroacrylonitriles, those derived from secondary amines are less stable than those derived from primary amines. The nature of the decomposition is not clear.

Attempts to confirm the structures of these compounds by conversion to known compounds failed, presumably because the chlorine in these

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[1] Moureu and Lazennec, *Compt. rend.*, **143**, 553 (1906).

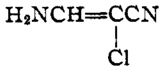
TABLE I

PREPARATION OF SEVERAL β-AMINO-α-CHLORACRYLONITRILES

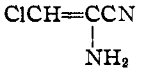
Moles of I	Moles of amine	Acid acceptor Formula	Acid acceptor Mole	$\mathrm{RR'NCH{=}\overset{Cl}{\overset{\vert}{C}}CN}$ Formula	R	R'	Yield, %	B. p. °C.	B. p. Mm.	M. p., °C.	Index of refr. °C.	Index of refr. n_D	Nitrogen, % Calcd.	Nitrogen, % Found
2.00[a]	4.33	Excess NH_3		$C_3H_3N_2Cl$	H	H	57	98	3.5	40–43			27.32	27.01
0.40[b]	0.85	Excess amine		$C_7H_{11}N_2Cl$	H	*n*-C_4H_9	92	82	0.5–1.0		25	1.5236	17.66	17.04
.22[c]	.20	Pyridine	0.25	$C_{13}H_{23}N_2Cl$	H	*n*-$C_{10}H_{21}$	62	179–180	1		25	1.5018	11.55	11.37
.44[d]	.40	Pyridine	.50	$C_{15}H_{27}N_2Cl$	H	*n*-$C_{12}H_{25}$	41	175–185	1	37–40			10.35	10.18
.21[e]	.20	Pyridine	.25	$C_9H_6N_2Cl_2$	H	*p*-ClC_6H_4	12			139–140			13.15	12.74
.45[f]	.40	$(C_2H_5)_3N$	.50	$C_{11}H_{19}N_2Cl$	*n*-C_4H_9	*n*-C_4H_9	50	116–122	1		23.5	1.5068	13.05	12.49
.43[g]	.40	$(C_2H_5)_3N$	.43	$C_{10}H_9N_2Cl$	CH_3	Phenyl	14	127–130	1		23.5	1.6240	14.51	14.09

[a] Addition carried out over one hour in 320 g. of methanol at 30°. After two hours, part of the solvent was distilled off, benzene was added and the mixture was filtered. The filtrate was distilled. The product was crystallized from hexane. Calcd. for $C_3H_3N_2Cl$: Cl, 34.60. Found: Cl, 34.1. [b] Addition carried out over one hour in 200 cc. of benzene at 50–60°. After twenty-four hours, the mixture was filtered, washed with water and distilled. The product was redistilled. [c] Addition carried out rapidly in 50 cc. of methanol. After twenty hours, the mixture was poured into water and extracted with benzene. The benzene extract was distilled. Calcd. for $C_{13}H_{23}N_2Cl$: iodine number (cg. of I_2 per g.), 105. Found: 106. [d] Addition carried out over forty-five minutes in 100 cc. of ethanol at 30–35°. Product washed up as in preceding run and crystallized from ethyl acetate. [e] Addition carried out in 50 cc. of methanol. Little heat was evolved. After twenty hours, the mixture was poured into water. The product was filtered off and crystallized from cold methanol (hot methanol caused decomposition) to give a light orange solid. [f] Addition carried out over two hours in 100 cc. of methanol at 20–30°. Product worked up as in third and fourth runs. Calcd. for $C_{11}H_{19}N_2Cl$: Cl, 16.51; iodine number, 118; found: Cl, 16.05; iodine number, 114. [g] Addition carried out over fifteen minutes in 100 cc. of methanol at 35°. Product worked up as in third, fourth and sixth runs.

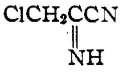
compounds is very tightly bound. However, the assigned structures of these compounds are substantiated by a study of the infrared absorption spectrum of β-amino-α-chloroacrylonitrile (II, R = R' = H) which shows, among others, absorption bands at 3500–3200 cm.$^{-1}$, 3070 and 1650 cm.$^{-1}$, and 2210 cm.$^{-1}$, attributable, respectively, to the structural features, —NH_2, H—C=C, and —CN. These features are all found in structure III.


$\mathrm{H_2NCH{=}\underset{\underset{Cl}{\vert}}{C}CN}$

III


$\mathrm{ClCH{=}\underset{\underset{NH_2}{\vert}}{C}CN}$

IV


$\mathrm{ClCH_2\underset{\underset{NH}{\Vert}}{C}CN}$

V

The isomeric structure, IV, resulting from replacement of the α-chlorine in I, although it possesses the structural features indicated by the infrared absorption spectrum, does not seem likely, since immediate rearrangement to the ketimine structure, V, would be expected. The existence of stable enamine forms, such as III, is also found in the closely related β-aminocrotonic esters. Replacement of the β-chlorine in I rather than the α-chlorine also seems the more likely since I may be regarded as a substituted vinylog of cyanogen chloride and since chlorine atoms alpha to nitrile groups appear to possess lowered activity, at least in certain reactions.[2]

Acknowledgment.—The author is indebted to Dr. R. C. Gore of the Physics Division of these Laboratories for the determination and interpretation of the infrared absorption spectrum of β-amino-α-chloroacrylonitrile.

Experimental

General Procedure.—Table I summarizes the results obtained. In each run, α,β-dichloroacrylonitrile (I) was added to a solution of amine and acid acceptor in some suitable solvent. The temperature of the reaction mixture was controlled by the use of a cooling bath. After standing at room temperature for a period of time after the addition, the reaction mixtures were worked up, usually being poured into water, extracted with benzene and distilled. Besides analyses for nitrogen, corroborative chlorine analyses and iodine number determinations were done in several cases.

Summary

β-Amino-α-chloroacrylonitrile and several of its N-substitution products have been prepared by the reaction of α,β-dichloroacrylonitrile with ammonia and various primary and secondary aliphatic and aromatic amines.

STAMFORD, CONNECTICUT RECEIVED MARCH 19, 1948

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(2) Mowry, *Chem. Revs.*, **42**, 197 (1948).