[Contribution from the Rohm and Haas Company, Redstone Arsenal Research Division]

THE PREPARATION OF THE ISOMERIC CHLOROMETHACRYLONITRILES[1]

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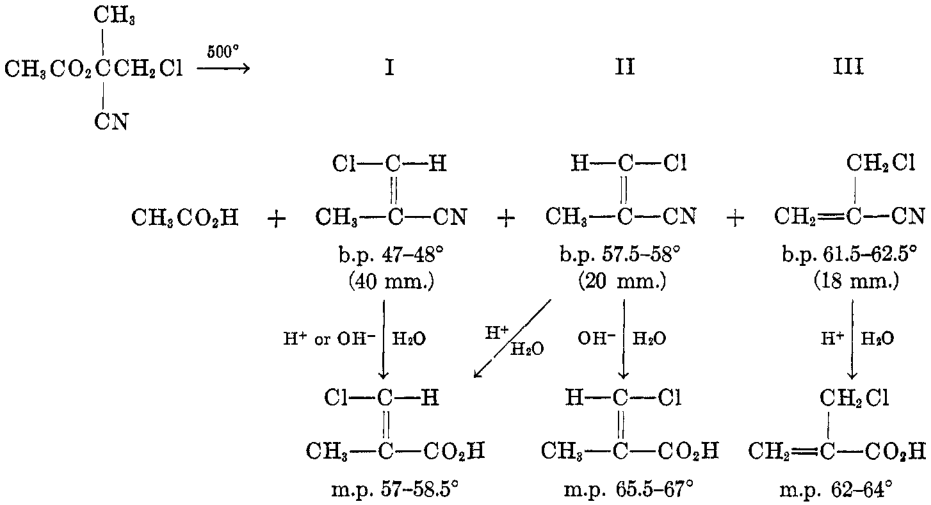
It has been found that pyrolysis of chloroacetone cyanohydrin acetate at 500° gives all three of the isomeric monochloromethacrylonitriles, that is, α-(chloromethyl)acrylonitrile (III) and *cis-* and *trans-β*-chloro-α-methylacrylonitrile (II and I, respectively). All of these isomers have been described previously, but with only tentative assignment of configuration to the β-chloro-α-methylacrylonitriles. Thus Berthet (1) reported that dehydration of chloroacetone cyanohydrin with phosphorus pentoxide gave α-(chloromethyl)acrylonitrile and a β-chloro-α-methylacrylonitrile of unknown configuration. Yields were not stated. Later Hurd and Rector (2) effected the dehydration with thionyl chloride and pyridine and obtained in low yield a different β-chloro-α-methylacrylonitrile along with considerable material which they were not able to separate. On the basis of the fact that the carboxylic acid obtained from their β-chloro-α-methylacrylonitrile by hydrolysis failed to react with boiling aqueous base to give methylacetylene, they concluded tentatively that it possessed the *trans* configuration. (In all the discussion which follows the terms *cis* and *trans* refer to the relative positions of the chlorine and the nitrile or carboxyl function.) Repetition of the work of Hurd and Rector in this laboratory has shown that both β-chloro-α-methylacrylonitriles are obtained, as well as some α,β-dichloroisobutyronitrile.



In a recent patent (3) the preparation of *cis-* and *trans-β*-chloro-α-methyl-

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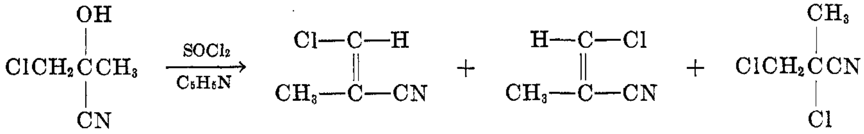
acrylonitrile has been described, although no evidence for the assignment of configuration was given. The physical constants cited for the *trans* nitrile agree reasonably well with those reported by Hurd and Rector (2), but comparison of the constants given for the "*cis*" nitrile with those reported by Berthet (1) makes it appear that the other material obtained was largely α-(chloromethyl)-acrylonitrile.

Pyrolysis of chloroacetone cyanohydrin acetate was effected by vaporizing it and carrying it in a slow stream of nitrogen through a glass-packed tube maintained at 500°. A contact time of approximately ten seconds gave a 74% conversion to acetic acid and an over-all yield of chloromethacrylonitriles of 87% (based on conversion). The acid was removed from the product by a bicarbonate wash, and the neutral residue was fractionated through a column stated to have an efficiency of 53 theoretical plates. The yields of pure products obtained were 23% of *trans*-β-chloro-α-methylacrylonitrile (I), 7% of *cis*-β-chloro-α-methylacrylonitrile (II), and 37% of α-(chloromethyl)acrylonitrile (III). Intermediate fractions accounted for the rest of the yield. Elimination of acetic acid in the pyrolysis thus was completely nonstereospecific, the yield of α-(chloromethyl)-acrylonitrile about equaling, when intermediate cuts were considered, the combined yield of β-chloro-α-methylacrylonitriles. Comparison of physical constants showed that the β-chloro-α-methylacrylonitrile reported by Hurd and Rector (2) was the one identified in this work as the *trans* isomer, and the one reported by Berthet (2) was the one identified as the *cis* isomer.

Assignment of structure and configuration to the three isomers was based on the accumulation of a number of pieces of evidence. Berthet's identification of α-(chloromethyl)acrylonitrile was confirmed, for the compound possessing the physical properties reported for this isomer reacted with silver trifluoroacetate in ether to give silver chloride in almost quantitative yield, whereas the other two isomers were inert to this reagent. Furthermore, the infrared spectrum of α-(chloromethyl)acrylonitrile was quite different from that of the other two isomers, and showed a broad C—H stretching band and no band in the methyl absorption region. The spectra of the other two isomers were very similar, and both showed bands attributable to the methyl group at about 1380 cm.$^{-1}$ and sharp bands at about 3060 cm.$^{-1}$ characteristic of a carbon bonded to a single hydrogen. All three of the nitriles were hydrolyzed by concentrated hydrochloric acid. α-(Chloromethyl)acrylonitrile gave the previously unreported α-(chloromethyl)acrylic acid in 44% yield. Both the β-chloro-α-methylacrylonitriles gave low yields of *trans*-β-chloro-α-methylacrylic acid, the acid reported by Hurd and Rector (2). Isomerization of the *cis* acid was avoided by carrying out the hydrolyses in a basic medium. When heated with 10% aqueous sodium hydroxide the *cis* nitrile gave *cis*-β-chloro-α-methylacrylic acid in 58% yield, and the *trans* nitrile gave the *trans* acid in 74% yield. The configurations of the acids could not be determined by the method suggested by Hurd and Rector, since neither of the acids reacted with boiling aqueous base. However, the *cis* configuration was assigned to the acid which was the more soluble in water, the more easily isomerized, and the stronger acid. Since in both the closely analogous pairs of isomers, the β-chloroacrylic acids (4) and the β-chloro-β-methylacrylic acids (5), the *cis* isomers were more soluble, more labile, and stronger acids, considerable confidence can be placed in the use of these criteria to establish the configurations of the β-chloro-α-methylacrylic acids and hence of the parent nitriles.

In an effort to ascertain the nature of the large amount of unidentified product reported by Hurd and Rector (2), the reaction of chloroacetone cyanohydrin with thionyl chloride and pyridine was re-examined. When the reaction was carried out exactly as described by the previous workers, an over-all yield of products of 63% was obtained. Fractionation through the 53 plate column gave a 14% yield of *trans*-β-chloro-α-methylacrylonitrile, as previously described, and the high-boiling residue was separated into two pure components, *cis*-β-chloro-α-methylacrylonitrile (27% yield) and α,β-dichloroisobutyronitrile (9% yield). Although α,β-dichloroisobutyronitrile has been mentioned as a reactant in several patents (3, 6, 7) its properties do not appear to have been recorded. To confirm the fact that the third product was indeed α,β-dichloroisobutyronitrile, this compound was synthesized independently by the addition of chlorine to methacrylonitrile. The product, obtained in 80% yield, was shown by physical constants and infrared spectrum to be identical to the material obtained from chloroacetone cyanohydrin.



$$\mathrm{ClCH_2\overset{\displaystyle OH}{\underset{\displaystyle CN}{C}}CH_3} \xrightarrow[C_5H_5N]{SOCl_2} \begin{matrix} \mathrm{Cl{-}C{-}H} \\ \| \\ \mathrm{CH_3{-}C{-}CN} \end{matrix} + \begin{matrix} \mathrm{H{-}C{-}Cl} \\ \| \\ \mathrm{CH_3{-}C{-}CN} \end{matrix} + \mathrm{ClCH_2\overset{\displaystyle CH_3}{\underset{\displaystyle Cl}{C}}CN}$$

EXPERIMENTAL[2, 3]

Chloroacetone cyanohydrin. To a solution of 62.4 g. (0.6 mole) of sodium bisulfite in 160 ml. of water was added dropwise 46.2 g. (0.5 mole) of chloroacetone. The temperature of the solution was kept below 35° by intermittent cooling. When all the chloroacetone had been added, the solution was cooled to 25° and 200 ml. of ether was added. Then a solution of 29.4 g. (0.6 mole) of sodium cyanide in 80 ml. of water was added dropwise at 25–30° with vigorous mechanical stirring. When all the cyanide solution had been added, the ether layer was separated immediately and the aqueous layer was extracted with two 100-ml. portions of ether. The combined ether solution was dried, and the ether removed under reduced pressure to yield 53.0 g. (89%) of oil. The crude oil was distilled under reduced pressure to give 43.8 g. (73%) of pure material, b.p. 73–74°/1.5 mm., n_D^{20} 1.4500 [lit. (2) b.p. 108–110°/20 mm., n_D^{20} 1.4520].

Chloroacetone cyanohydrin acetate. To 43.8 g. (0.367 mole) of chloroacetone cyanohydrin was added 1 ml. of concentrated sulfuric acid, and then 40.9 g. (0.40 mole) of acetic anhydride was added dropwise with vigorous stiring. The temperature was held at 60–70° by controlling the rate of addition of the anhydride. When all the anhydride had been added, the mixture was stirred for 30 minutes and then poured into 600 ml. of ice-water. The resulting mixture was neutralized with solid sodium bicarbonate and extracted with three 200-ml.

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[2] All melting points are corrected and all boiling points are uncorrected.

[3] We are indebted to Dr. Keith S. McCallum for assistance in interpreting the infrared spectra, and to Miss Annie Smelley for acid strength measurements and microanalyses.

portions of ether. The ether was removed under reduced pressure to give 56.7 g. (96%) of crude product. Distillation yielded 35.0 g. (59%) of chloroacetone cyanohydrin acetate, b.p. 57–59°/0.3 mm., n_D^{20} 1.4421, d_4^{20} 1.1861.

Anal. Calc'd for $C_6H_8ClNO_2$: C, 44.59; H, 4.99; N, 8.67; Cl, 21.94.

Found: C, 44.37; H, 5.12; N, 8.99; Cl, 21.57.

Pyrolysis of chloroacetone cyanohydrin acetate. A sample of chloroacetone cyanohydrin acetate amounting to 389.9 g. (2.41 moles) was passed at approximately 0.75 g./min. through a preheater held at 250° and a 2.8 x 30 cm. pyrolysis column held at 500°. The column was packed with short lengths of Pyrex glass tubing. Nitrogen at about 300 ml./min. was used as carrier. There was obtained 351.5 g. (325 ml.) of brown oil, which on titration was found to have an acid content of 5.48 meq./ml. (total acid 1.78 moles, 74% conversion). The product was poured into a liter of ice-water, and the resulting mixture was neutralized with solid sodium bicarbonate. Then the organic layer was separated, and the aqueous layer was extracted with four 200-ml. portions of ether. After drying, the ether was distilled off at atmospheric pressure to leave 250.8 g. of residue. This was fractionated at 10:1 reflux ratio through the Todd Fractionation Assembly, using the 1.2 x 90 cm. column packed with 4 mm. diameter Pyrex glass helices. Cuts were taken as follows:

No.	*b.p., °C.*	*mm.*	*Amount (g.)*
1	44–48.5	43	6.4
2	47–48	40	40.9
3	48–66	37	2.1
4	52.5–57	20	4.3
5	57.5–61	18	87.5
6	57–57.5	15.5	16.2
	Residue		44.8

Cuts 4 and 5 were combined and refractionated at 40:1 reflux ratio. Cuts were taken as follows:

No.	*b.p., °C.*	*mm.*	*Amount (g.)*
A	53.5–58.5	21	1.0
B	57.5–58	20	13.1
C	58–63	20	11.1
D	61.5–62.5	18	50.4
	Residue		4.5

Cut 2 (I) (Yield 23%), n_D^{20} 1.4597, d_4^{30} 1.0718, was the β-chloro-α-methylacrylonitrile reported by Hurd and Rector (2) (lit. b.p. 127–129°, n_D^{20} 1.4592). Cut B (II) (yield 7%), n_D^{20} 1.4575, n_D^{30} 1.4531, d_4^{30} 1.0796, was the β-chloro-α-methylacrylonitrile reported by Berthet (1) (lit. b.p. 58.8°/20 mm., n_D^{30} 1.4521, d_4^{30} 1.0769). Cuts 6 and D (III) (yield 37%), n_D^{20} 1.4618, n_D^{30} 1.4573, d_4^{30} 1.0941, were α-(chloromethyl)acrylonitrile, also reported by Berthet (1) (lit. b.p. 65.6°/20 mm., n_D^{30} 1.4574, d_4^{30} 1.0961).

α-(Chloromethyl)acrylic acid. A mixture of 8.0 g. (0.079 mole) of α-(chloromethyl)acrylonitrile (III) and 60 ml. of concentrated hydrochloric acid was stirred for an hour while being heated on a steam-bath. The acid solution was cooled and extracted with three 50-ml. portions of ether. The combined ether solution was then extracted with three 25-ml. portions of 5% sodium hydroxide solution, and the combined sodium hydroxide solution was backwashed with 50 ml. of ether. The basic solution then was cooled in ice and acidified with 5 *N* sulfuric acid, and the acid solution was extracted with three 50-ml. portions of ether. After drying, the ether was removed under reduced pressure to leave 4.2 g. (44%) of solid. This material oiled out in attempts to recrystallize it from water, but sublimation at 55–59°/0.02 mm. gave a product melting at 62–64°. Its infrared spectrum showed a carbonyl absorption band at 1697 cm.$^{-1}$ and an olefin band at 1629 cm.$^{-1}$.

Anal. Calc'd for $C_4H_5ClO_2$: C, 39.85; H, 4.18; Cl, 29.42; Neut. equiv., 120.5.
Found: C, 39.73; H, 4.05; Cl, 28.97; Neut. equiv., 120.4.

trans-β-Chloro-α-methylacrylic acid. To a solution of 4.0 g. (0.1 mole) of sodium hydroxide in 36 ml. of water was added 4.1 g. (0.04 mole) of *trans*-β-chloro-α-methylacrylonitrile. The mixture was heated to 90–100° and stirred at that temperature for 90 minutes. Ammonia was evolved vigorously. The solution obtained was then cooled to 25° and acidified with 5 *N* sulfuric acid. A solid separated and was filtered out, and the filtrate was extracted with three 50-ml. portions of ether. After drying, the solid amounted to 3.2 g., and another 0.3 g. was recovered from the ether, making the total yield 3.5 g. (73%). Recrystallization from 90 ml. of hot water gave 1.6 g., m.p. 57–58.5° [lit. (2) m.p. 58–58.5°]. The infrared spectrum of this acid showed the carbonyl band at 1680 cm.$^{-1}$ and the olefin band at 1607 cm.$^{-1}$.

cis-β-Chloro-α-methylacrylic acid. A 4.1-g. (0.04 mole) sample of cis-β-chloro-α-methylacrylonitrile was treated as described above. No solid separated when the basic solution was acidified, but 2.8 g. (58%) of gummy solid was recovered from the ether extract. Two crystallizations from petroleum ether (b.p. 34–47°) gave 0.7 g. of pure cis-β-chloro-α-methylacrylic acid, m.p. 65.5–67°. The infrared spectrum of this acid showed the carbonyl absorption at 1673 cm.$^{-1}$ and the olefin absorption at 1601 cm.$^{-1}$.

Anal. Calc'd for $C_4H_5ClO_2$: C, 39.85; H, 4.18; Cl, 29.42; Neut. equiv., 120.5.
Found: C, 39.94; H, 4.34; Cl, 28.95; Neut. equiv., 121.3.

Reaction of chloroacetone cyanohydrin with thionyl chloride and pyridine. The procedure of Hurd and Rector (2) was followed, using 120 g. (1.0 mole) of chloroacetone cyanohydrin, 158.2 g. (2.0 moles) of pyridine, and 238 g. (2.0 moles) of thionyl chloride. The crude product was fractionated through the Todd Fractionation Assembly, using the column previously described and a 20:1 reflux ratio. Cuts were taken as follows:

No.	*b.p., °C.*	*mm.*	*Amount (g.)*	n_D^{20}
1	48.5–49.5	42	2.3	
2	47.5–48.5	40	14.2	1.4602
3	38–56	20	2.3	
4	55.5–56.5	18	27.7	1.4577
5	56.5–60.5	16	10.1	
6	58–58.5	14	12.3	1.4523

Cut 2 (14%) was *trans*-β-chloro-α-methylacrylonitrile, and cut 4 (27%) was *cis*-β-chloro-α-methylacrylonitrile. Cut 6 (9%) analyzed correctly for a dichlorobutyronitrile. The infrared spectrum of this material showed a weak nitrile band at 2300 cm.$^{-1}$, and intense bands at 1433 and 1376 cm.$^{-1}$.

Anal. Calc'd for $C_4H_5Cl_2N$: C, 34.81; H, 3.65; N, 10.15; Cl, 51.39.
Found: C, 34.52; H, 3.83; N, 9.70; Cl, 51.24.

α,β-Dichloroisobutyronitrile. A few crystals of iodine were added to a solution of 67 g. (1.0 mole) of methacrylonitrile in 100 ml. of dry carbon tetrachloride, and the solution was illuminated by an ultraviolet lamp while chlorine was passed in slowly. Heat was evolved, and the reaction temperature was held at 20–30° by cooling and control of the chlorine rate. When the exothermic reaction had ceased, the gain in weight of the reactor was measured and found to be 71 g. (1.0 mole). The solvent was removed under reduced pressure to leave 138 g. (100%) of crude oil. Distillation gave 110.8 g. (80%) of α,β-dichloroisobutyronitrile, b.p. 61–62°/17 mm., n_D^{20} 1.4526. The infrared spectrum of this material was identical with that of cut 6 above.

Acid strength measurements. These were run in triplicate. Samples of the acids amounting to about 100 mg. each were dissolved in carbon dioxide free water, and the *p*H of the solutions was measured with a Beckman Model G *p*H Meter as small increments of 0.1 *N* sodium hydroxide solution were added. *p*K values were calculated from the data thus obtained by the method of Bennet, Brooks, and Glasstone (8). For *trans*-β-chloro-α-methylacrylic acid the *p*K values found were 4.06, 4.04, and 4.03; and for *cis*-β-chloro-α-methylacrylic acid the values were 3.05, 3.04, and 3.05.

SUMMARY

Pyrolysis of chloroacetone cyanohydrin acetate at 500° gave a 74% conversion to acetic acid and an 87% over-all yield of a mixture of α-(chloromethyl)acrylonitrile and the two isomeric β-chloro-α-methylacrylonitriles. Treatment of chloroacetone cyanohydrin with thionyl chloride and pyridine gave a 63% yield of a mixture of the two β-chloro-α-methylacrylonitriles and α,β-dichloroisobutyronitrile. Separation and characterization of these materials are described.

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