The Photohalogenation of Acrylonitrile

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The bulk photochlorination of acrylonitrile gave, in addition to 2,3-dichloropropionitrile, telomeric by-products of the structure I. The dimer, 2-chloro-4-(chloromethyl)glutaronitrile (III), comprises 80–90% of these. The treatment of III with aqueous disodium hydrogen phosphate gave an almost quantitative yield of the dehydrochlorinated derivative, 2-chloro-4-(methylene)glutaronitrile (IV). Treatment of IV with HCl gave the original dimer III. Polymerization of IV was readily achieved with styrene, acrylonitrile, butadiene, methyl methacrylate, and ethyl acrylate. The controlled acidic hydrolysis of IV yielded the cyclic imide VI. The structures of III, and its hydrogenated derivative V were verified by their infrared and nmr spectra. The use of a "zone reactor" led to the successful separation of the ionic and free-radical halogenation pathways. Yields of 95–99% of 2,3-dihalopropionitrile were achieved in the photochlorination and photobromination reactions. The optimum wavelength of light necessary for the most efficient reaction was determined. The range of 253–750 mμ was found to be the most practicable, with the greatest activity found in the lower end of the range.

The photochlorination of acrylonitrile has been a subject of some study[2–4] while the photobromination of acrylonitrile has been investigated to only a very limited extent.[5] The product of the bromination reaction is reported to be 2,3-dibromopropionitrile, presumably in good yield although specific yield figures and mention of other by-products were not given. The literature indicates that the photochlorination reaction is more complex. According to Lorette,[3] the major product of the reaction up to the point where hydrogen chloride is formed in appreciable quantities is 2,3-dichloropropionitrile. After the hydrogen chloride concentration exceeds some unspecified critical minimum, side reactions predominate in which 3-chloropropionitrile and 2,2,3-trichloropropionitrile are the principal products. It was suggested that hydrogen chloride is first formed during the free-radical photochlorination process but that, once formed, it will catalyze a concurrent ionic reaction pathway whereby most, but not all, of the 3-chloropropionitrile and 2,2,3-trichloropropionitrile by-products are formed. The following scheme (eq 1–9) has been proposed by Lorette[3] to

Free-radical mechanism

$$Cl_2 \xrightarrow{\text{ultraviolet}} 2Cl\cdot \qquad (1)$$

$$CH_2{=}CHCN + Cl\cdot \longrightarrow ClCH_2\dot{C}HCN \qquad (2)$$

$$ClCH_2\dot{C}HCN + Cl_2 \longrightarrow ClCH_2CHClCN + Cl\cdot \qquad (3)$$

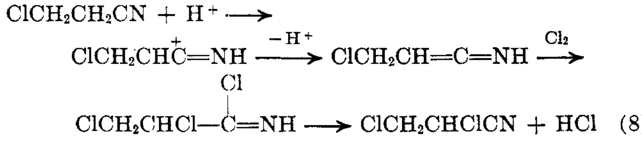
$$ClCH_2CHClCN + Cl\cdot \longrightarrow ClCH_2\dot{C}ClCN + HCl \qquad (4)$$

$$ClCH_2\dot{C}ClCN + Cl_2 \longrightarrow ClCH_2CCl_2CN + Cl\cdot \qquad (5)$$

$$ClCH_2\dot{C}HCN + HCl \longrightarrow ClCH_2CH_2CN + Cl\cdot \qquad (6)$$

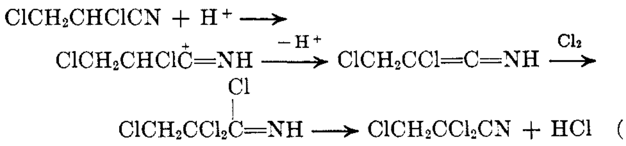
Ionic mechanism

$$HCl + CH_2{=}CHCN \longrightarrow ClCH_2CH_2CN \qquad (7)$$



$$ClCH_2CH_2CN + H^+ \longrightarrow ClCH_2CH\overset{+}{C}{=}NH \xrightarrow{-H^+} ClCH_2CH{=}C{=}NH \xrightarrow{Cl_2} ClCH_2CHCl{-}\underset{Cl}{\overset{|}{C}}{=}NH \longrightarrow ClCH_2CHClCN + HCl$$

(8)



$$ClCH_2CHClCN + H^+ \longrightarrow ClCH_2CHCl\overset{+}{C}{=}NH \xrightarrow{-H^+} ClCH_2CCl{=}C{=}NH \xrightarrow{Cl_2} ClCH_2CCl_2\underset{Cl}{\overset{|}{C}}{=}NH \longrightarrow ClCH_2CCl_2CN + HCl$$

(9)

account for his experimental results. Lorette reported that no products other than 3-chloropropionitrile, 2,3-dichloropropionitrile, and 2,2,3-trichloropropionitrile were formed during the bulk photochlorination of acrylonitrile. In a similar study Fugate and coworkers[4] reached the same conclusion regarding both the mechanism and products of the reaction. Sumner's[2] findings were consistent with this representation of the reaction, but he does mention a fourth reaction product—polymeric residues of undetermined structure.

An investigation has been made in our laboratories of both the photochlorination of acrylonitrile and the photobromination of acrylonitrile. The photobromination reaction has been found to be very uncomplicated as the previous literature implied; under normal conditions essentially only one product is produced, 2,3-dibromopropionitrile. Details of this reaction are given. In the photochlorination case, our results are in some variance in certain important respects with the published accounts of this reaction. Specifically, it has been found (1) that telomeric by-products are invariably formed during the bulk photochlorination of acrylonitrile; (2) that the wavelength of light required for most efficient reaction is different than that reported; and (3) that it is indeed possible to separate the free-radical chlorination process from the ionic pathway. When this is done, only two products are formed: 2,3-dichloropropionitrile and telomers of 2,3-dichloropropionitrile. The variables affecting the formation of these products have been elucidated.

Results and Discussion

The fact that telomeric by-products may be formed during the photohalogenation of acrylonitrile is not surprising. After the initial attack of a halogen atom on an acrylonitrile molecule, the resulting 3-halopropionitrile radical has two choices of reactants: halogen or acrylonitrile. Reaction with halogen gives 2,3-dihalopropionitrile while reaction with acrylonitrile gives dimer, etc. Obviously the preferred reaction of the 3-halopropionitrile radical is with halogen, especially in a bulk reaction system (*i.e.*, no solvent). Some re-

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[1] To whom correspondence should be addressed.

[2] J. K. Sumner, U. S. Patent 2,390,470 (Dec. 4, 1945).

[3] N. B. Lorette, *J. Org. Chem.*, **26**, 2324 (1961).

[4] W. O. Fugate, J. Ocampa, and G. G. Morrison, paper presented at American Institute of Chemical Engineers Meeting, New Orleans, La., March 1963.

[5] C. Moureu and R. L. Brown, *Bull. Soc. Chim. France*, **27**, 901 (1920).

action with acrylonitrile to give dimer, trimer, etc., definitely can and does occur. The proposed reaction scheme for the formation of telomeric by-products is given by eq 10–13 (where X = Cl or Br).

$$\mathrm{XCH_2\dot{C}HCN + CH_2{=}CHCN \longrightarrow XCH_2CHCNCH_2\dot{C}HCN} \quad (10)$$

$$\mathrm{XCH_2CHCNCH_2\dot{C}HCN + X_2 \longrightarrow \underset{\text{"dimer"}}{XCH_2CHCNCH_2CHXCN} + X\cdot} \quad (11)$$

$$\mathrm{XCH_2CHCNCH_2\dot{C}HCN + CH_2{=}CHCN \longrightarrow X(CH_2CHCN)_2CH_2\dot{C}HCN} \quad (12)$$

$$\mathrm{X(CH_2CHCN)_2CH_2\dot{C}HCN + X_2 \longrightarrow \underset{\text{"trimer"}}{X(CH_2CHCN)_2CH_2CHXCN} + X\cdot} \quad (13)$$

Appreciable quantities of telomeric by-products are formed during the bulk photochlorination of acrylonitrile. Negligible amounts are formed in a carbon tetrachloride solution reaction. Essentially no bromo telomers are formed in either the bulk or solution processes.

The quantity of chloro telomer formed during the bulk chlorination of acrylonitrile is dependent upon the relative concentration of chlorine (*i.e.*, chlorination rate) to acrylonitrile and on the temperature; low chlorine concentrations and high temperatures promote telomer formation. These results are plotted in Figures 1 and 2. Although it would appear that temperature is the more significant factor, it is believed the principal direct influence of temperature is on regulating the concentration of chlorine in the reaction mixture; lower temperatures allow higher concentrations of dissolved chlorine and therefore less telomer. Little or no chloro telomer is formed during a carbon tetrachloride solution photochlorination reaction because, it is believed, of the strong chain-transferring power of the solvent and the reduced relative quantity of acrylonitrile.

Bromination reactions also produce little or no telomer but probably for a different reason. Because of the boiling point of bromine (59° *vs.* −35° for chlorine) higher concentrations of the bromine are maintained in the reaction mixture. Additionally the product, 2,3-dibromopropionitrile, is very likely a superior chain-transferring medium (compared with the 2,3-dichloropropionitrile.)

The fact that previous workers did not recognize that telomeric by-products were formed during the bulk photochlorination of acrylonitrile is attributable both to the nature of the product mixtures and the methods of analysis. The reaction products are usually complex mixtures of limited thermal stability. Separation of these mixtures by fractional distillation is difficult and the chloro telomers above dimer are very difficult to distil. Both the infrared analytical technique of Lorette[3] and the gas chromatography method of Fugate and co-workers[4] have been found to be unsatisfactory for determining all of the possible acrylonitrile halogenated products. Lorette's infrared absorption method will not differentiate satisfactorily between 2,3-dichloropropionitrile and its telomers and the accuracy for the other products in low concentration is doubtful. Fugate and co-worker's gas chromatography technique will not elute, in recognizable form, telomeric by-products.

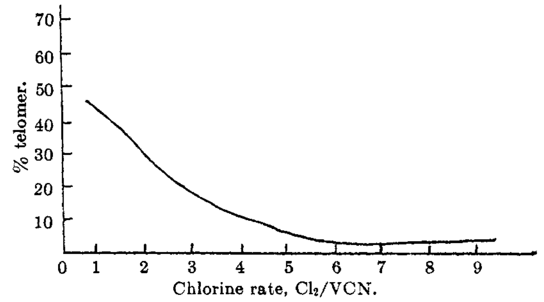


Figure 1.—Effect of chlorine rate on chlorotelomer formation; calibrated in drops/min of chlorine reflux *vs.* VCN addition, at 25°.

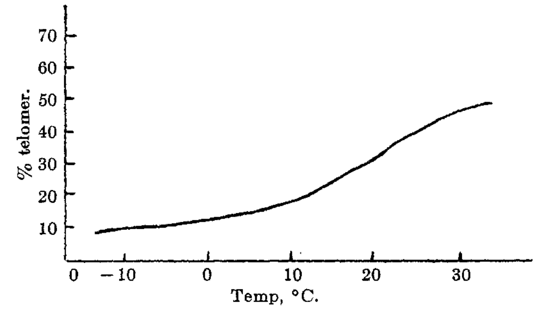
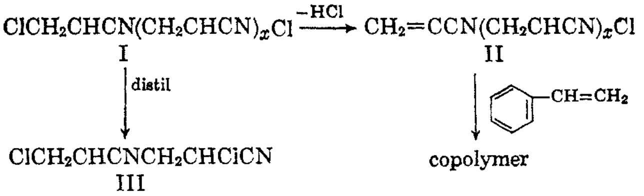


Figure 2.—Effect of temperature on chlorotelomer formation.

Successful analysis of all the reaction products has been accomplished by improved gas chromatography techniques. For the separation of the monomeric halogenated products, a 5-ft column packed with Chromosorb W containing 10% by weight of diisodecyl phthalate and 10% by weight of Carbowax 1500, operating at 130° and approximately 50 cc/min. of helium flow was used. To develop the telomeric products a special 0.25 × 9 in. stainless steel column packed with 15% Silicone 550 on C-22 was employed at a temperature of 160° and a helium flow rate of 50 cc/min.

The proposed general structure of the chloroacrylonitrile telomers (I) is given below. Confirmation of this structural assignment has been gained by analysis of the crude mixtures, conversion of the telomer mixture into its dehydrochlorinated form (II) with subsequent copolymerization of this derivative, and finally by separating and characterizing the pure dimer (III) which makes up over 85% of the telomer mixture. The further characterization and reactions of this dimer (III) will be discussed.



The quantity of dimer, 2-chloro-4-(chloromethyl)-glutaronitrile (III), isolated from the telomer mixtures has been found to be relatively constant (80–90%) regardless of the total amount of telomer formed during the acrylonitrile photochlorination reaction. From these yield figures, the fact that the original telomer mixtures are totally soluble in methanol, and the fact that the dehydrochlorinated form of the telomer mixtures (II) is completely copolymerizable with styrene, it is concluded that the telomer mixtures are composed essentially of dimer (III) and trimer (II, $x = 2$) in the approximate ratio of 9:1, respectively. Treatment of the dimer III with an aqueous solution of disodium hydrogen phosphate gave an almost quantitative yield of the dehydrochlorinated derivative, 2-chloro-4-(methylene)glutaronitrile (IV). The proposed structure of IV was verified by infrared, microanalysis, and nmr techniques. This derivative copolymerized readily with styrene, acrylonitrile, butadiene, methyl methacrylate, and ethyl acrylate giving further evidence as to the position of the double bond (facile copolymerization would occur only if the double bond were terminal). The results of these copolymerizations are summarized in Table I.

TABLE I

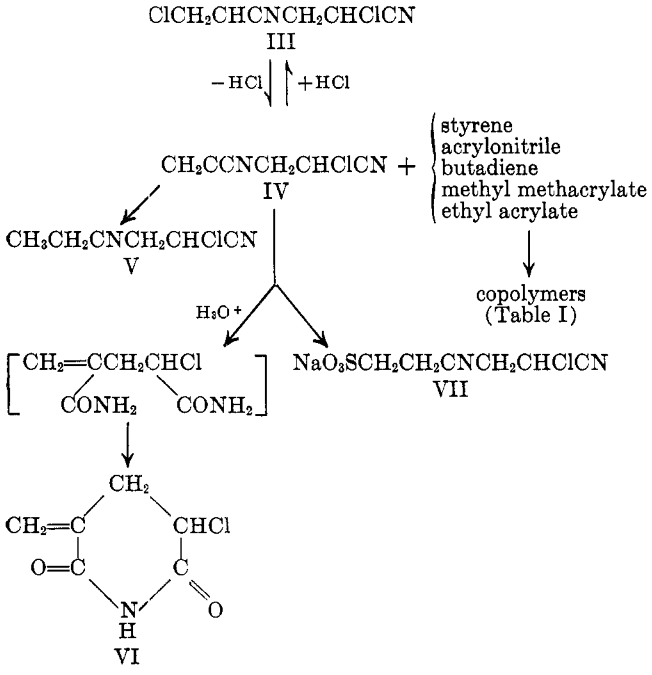
COPOLYMERIZATION OF 2-CHLORO-4-(METHYLENE)GLUTARONITRILE (IV)

Comonomer	Charge ratio IV:comonomer, wt %	Composition, wt % of IV	η_{inherent}[a]
Styrene	1:3	40	0.12
Acrylonitrile	1:9	37	..
Butadiene	1:9	55	1.2
Butadiene	1:3	24	...[b]
Methyl methacrylate	1:9	17.5	0.37
Ethyl acrylate	1:9	19	0.17

[a] 0.2 g of sample/100 ml of 2-butanone at 25°. [b] Product gelled.

The addition of hydrogen chloride to IV gave the starting material, III. The controlled reduction of IV gave 2-chloro-4-methylglutaronitrile (V). Comparison of the nmr spectrum of this compound with those of the original dimer, III, and its dehydrochlorinated form, IV, removes any doubt as to the correctness of these structural assignments. No other conceivable structures would be consistent with these data.

The structures of the telomeric derivatives with particular reference to the double bond have been verified by their infrared and nmr spectra. The alkaline hydrolysis of IV produced only polymeric residues of undetermined structure.



Compound IV was further characterized by converting it into the sodium bisulfite addition product VII.

The complicating factor of having an ionic, acid-catalyzed reaction mechanism operating concurrently with the free-radical photohalogenation process has been solved experimentally in two ways: (1) by means of a "zone reactor" in which the reaction is completed so rapidly that the acid is not given sufficient time to form; and (2) by the addition of a weakly basic acid-scavenging agent such as disodium hydrogen phosphate. The two methods are equally effective in inhibiting the ionic reaction mechanism while permitting the free-radical process to proceed unhampered.

As little as 0.1 mole of Na_2HPO_4/mole of acrylonitrile is sufficient to suppress hydrogen chloride formation during a bulk chlorination of acrylonitrile at 25°. Since the phosphate is heterogeneously dispersed, a finely divided form with good agitation gives best results. Hydrated or anhydrous forms have been used with equal effectiveness.

The bulk photochlorination of acrylonitrile in the absence of acid produces only two products—2,3-dichloropropionitrile and the telomers of 2,3-dichloropropionitrile. Under carefully controlled conditions not even traces of 3-chloropropionitrile and 2,2,3-trichloropropionitrile are detected. Whenever these by-products are obtained, their formation is directly attributable to acidic or ionic catalyst impurities. That these impurities are not formed in the course of a normal photochlorination is further demonstrated by the fact that all reaction ceases at the 100% acrylonitrile conversion point when the phosphate buffer is present. The carbon tetrachloride solution photochlorination of acrylonitrile in the presence of disodium hydrogen phosphate produces only 2,3-dichloropropionitrile.

The photobromination reaction gives almost exclusively 2,3-dibromopropionitrile whether or not an acid acceptor is present (provided the temperature of reaction does not exceed 50°). Occasional traces of α-bromoacrylonitrile are detected. It is believed that there is a lesser tendency to form by-products during the bromination reaction compared to the chlorination because of steric factors.

Experimental Section

Bulk Photochlorination of Acrylonitrile.—To a 500-ml three-neck flask equipped with magnetic stirrer, chlorine inlet tube, thermometer, and reflux condenser were added 106.0 g (2.00 moles) of acrylonitrile and 35.5 g (0.25 mole) of disodium hydrogen phosphate. The flask was immersed in a cold water bath (0–5°) and irradiated by a 200-w light bulb placed 6 in. away. Chlorine gas was charged to the solution at an average rate of 18 g/hr.

At the completion of the reaction (8 hr), 142.0 g of chlorine gas had been charged to the flask. Vapor phase chromatographic analysis of the reaction product gave the following results: 72.0% α,β-dichloropropionitrile, 7.8% acrylonitrile, and 20.2% 2-chloro-4-chloromethylglutaronitrile. No 2,2,3-trichloropropionitrile was found when disodium hydrogen phosphate was present.

Zone Photochlorination of Acrylonitrile.—Into a water-cooled column, 15 in. in length, 2-in. i.d., packed with 0.125-in. glass helices and equipped with a Dry Ice condenser and 2-l. receiver flask was charged, dropwise, 954 g (18 moles) of acrylonitrile.

During this addition the column was irradiated with three 200-w incandescent light bulbs and steady countercurrent flow of chlorine gas was maintained at the optimum rate by gas chromatographic analysis of the eluent. The product, obtained in 98–99% purity was α,β-dichloropropionitrile.

Solution Photochlorination of Acrylonitrile.—To a 2-l. three-neck flask equipped with a stirring motor, thermometer, chlorine inlet, and reflux condenser were charged 500 ml of carbon tetrachloride and 159 g (3 moles) of acrylonitrile. The flask was irradiated with a 200-w light bulb and chlorine was admitted at a rate of 72 g/hr. The reaction was maintained at 25° and was complete after 6 hr. The following products were found: 2% acrylonitrile, 2.2% 3-chloropropionitrile, and 95% α,β-dichloropropionitrile.

Bulk Photobromination of Acrylonitrile.—To a 1-l. three-neck flask equipped with magnetic stirrer, bromine addition funnel, thermometer, and reflux condenser was charged 318 g (6 moles) of acrylonitrile. The flask was irradiated with a 200-w incandescent light bulb and 960 g (6 moles) of bromine was added dropwise over a 2-hr period. The temperature was readily maintained at 25°. The product yield was 1277 g (99.9%) of orange liquid, α,β-dibromopropionitrile. When this reaction was maintained over 50°, higher boiling brominated materials, presumably telomers, were noted by gc analysis.

Zone Photobromination of Acrylonitrile.—To a water-cooled straight column (i.d. 0.5 in.), packed with glass helices and irradiated with two 150-w incandescent bulbs were added 106 g (2 moles) of acrylonitrile and 320 g (2 moles) of bromine. The dropwise addition was regulated by eluent analysis so as to obtain optimum rates of both reactants. The temperature was maintained at about 25°. The product collected at the bottom of the column contained (by gc) 3% acrylonitrile, 4% α-bromoacrylonitrile, 85% α,β-dibromoacrylonitrile, and approximately 8% unidentified higher boiling materials.

Solution Photobromination of Acrylonitrile.—To a 2-l. three-neck flask equipped with a stirrer, thermometer, dropping funnel, and reflux condenser were charged 500-ml of carbon tetrachloride and 159 g (3 moles) of acrylonitrile. The flask was irradiated with a 200-w incandescent light bulb and 480 g (3 moles) of bromine was added dropwise over a 2-hr period. The temperature was maintained at 25°. α,β-Dibromopropionitrile was prepared in 99% yield.

Effect of Radiation Wavelength on the Photohalogenation Reactions.—The effect of radiation wavelength on the photochlorination and photobromination of acrylonitrile was investigated by means of a continuous or "zone reaction." A fused quartz tube (20-mm i.d.) was used in order to achieve high transmission of ultraviolet as well as visible energy. Flow restriction and high contact area was provided by quartz fiber mat which absorbs a negligible amount of radiation. The light source was placed 6 in. from the tube, to allow interposition of the filter without thermal breakage. Acrylonitrile was metered to the reaction zone by a metering pump; chlorine or bromine was admitted according to demand (*i.e.*, proportional to reaction rate). Product was taken off every 15 min for analysis. The most effective wave length was found to be in the near-ultraviolet range. The range of 253–750 mμ proved to be the most efficient while the most active range was in the 250–300-mμ region.

Preparation of 2,3-Dichloropropionitrile Telomers.—To a 3-l. three-neck flask equipped with stirrer, gas inlet tube, thermometer, and reflux condenser were charged 636 g (12 moles) of acrylonitrile and 90.0 g (0.64 mole) of disodium hydrogen phosphate. The flask was immersed in a cold-water bath and irradiated with three 200-w light bulbs placed 6 in. away. Chlorine gas was charged to the solution at an average rate of 114 g/hr. The temperature was maintained between 44 and 46° during the addition.

Vapor phase chromatographic analysis of the crude reaction mixture indicated 1.3% acrylonitrile, a 40% mixture of mono-, di-, and trichloropropionitrile, and 48% of 2-chloro-4-chloromethylglutaronitrile.

The crude reaction mixture was distilled under reduced pressure to remove the low-boiling fractions. Dimer (III) was then isolated, bp 125–130° (0.2 mm), in 40% yield. Some dehydrochlorinated material was noted in the analysis of this fraction.

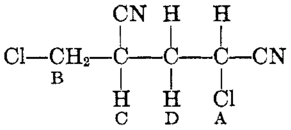
Isolation of 2-Chloro-4-(chloromethyl)glutaronitrile (III).—Distillation of the crude reaction mixture mentioned above at 125–130° (0.2 mm) yielded approximately 300 g of 2-chloro-4-chloromethylglutaronitrile containing approximately 2.5% of the dehydrohalogenated material 2-chloro-4-(methylene)glutaronitrile. The distillate was allowed to stand at room temperature for several days. Crystallization began after 48 hr and was essentially complete after 1 week. The white crystalline product was filtered, recrystallized from ether, and dried, mp 65–66°.

Anal. Calcd for $C_6H_6Cl_2N_2$: C, 40.70; H, 3.42; Cl, 40.06; N, 15.82. Found: C, 40.84; H, 3.39; Cl, 40.10; N, 16.05.

Table II represents the results found in the nmr spectrum of III. The peak at 3.2 is probably due to an olefin impurity with structure $CH_2{=}CR_1R_2$, where R_1 or R_2 = H. This follows from the fact that only geminal coupling (J = 2 cps) is observed. The spectrum of the major compound shows at least four different kinds of protons (A, B, C, and D). The intensities of these peaks are, respectively, 1:2:1:2, which indicates two kinds of methylene and two kinds of methine protons. It appears, therefore, that the structure is essentially

TABLE II

Peak	Approximate chemical shift, τ	Area	Relative area
A	3.2	...	Impurity
A	5.6	2.5	1.0 (1)
B	6.8	5.2	2.08 (2)
C	7.1	2.5	1.0 (1)
D	8.0	5.6	2.24 (2)


$$Cl{-}\underset{B}{CH_2}{-}\overset{CN}{\underset{\underset{C}{H}}{C}}{-}\overset{H}{\underset{\underset{D}{H}}{C}}{-}\overset{H}{\underset{\underset{A}{Cl}}{C}}{-}CN$$

The chemical shifts of the protons are in line with this assignment. Without going into great detail, the multiplicity of the peaks is also expected. For example, the methylene group protons D not only are coupled to the methine protons A and C, but also to each other since they are not equivalent (being pseudoasymmetric).[6]

2-Chloro-4-(methylene)glutaronitrile (IV).—To a 250-ml three-neck flask equipped with stirrer, condenser, thermometer, and heating mantle were charged 100 ml of water, 33.9 g (0.24 mole) of disodium hydrogen phosphate, and 38.2 g (0.23 mole) of 2-chloro-4-chloromethylglutaronitrile. The reaction mixture was heated to 100° and maintained at this temperature for 50 min. Distillation at reduced pressure yielded 27.6 g (90%) of 2-chloro-4-(methylene)glutaronitrile, bp 100° (0.5 mm). Gc analysis indicated one compound.

Anal. Calcd for $C_6H_5ClN_2$: C, 51.26; H, 3.59; Cl, 25.22; N, 19.93. Found: C, 51.42; H, 3.57; Cl, 25.35; N, 19.93.

Copolymers of 2-Chloro-4-(methylene)glutaronitrile (IV).—All copolymers were prepared by standard emulsion polymerization techniques using Sypon WD as emulsifying agent. The polymers were coagulated in methanol, dried under reduced pressure for 24 hr, and submitted for nitrile analysis (Table III).

TABLE III

NITRILE ANALYSES OF COPOLYMERS OF IV

Copolymer with	Nitrogen, %
Styrene	10.40
Acrylonitrile	19.55
Butadiene (1:9)	11.02
Butadiene (1:3)	4.99
Methyl methacrylate	4.13
Ethyl acrylate	5.00

Addition of HCl to 2-Chloro-4-(methylene)glutaronitrile (IV).—To 14 g (0.1 mole) of IV in a 100-ml round-bottom flask was added 0.5 g of pyridine. The solution was then immersed in a water bath and maintained at 25–30° while it was saturated with hydrogen chloride gas. Vapor phase chromatographic analysis of the reaction product showed it to be identical with III, 2-chloro-4-chloromethylglutaronitrile. The infrared spectrum of the reaction product was superimposable on that of III,

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[6] E. I. Snyder, *J. Am. Chem. Soc.*, **85**, 2624 (1963).

confirming its identity as 2-chloro-4-chloromethylglutaronitrile. The yield of this addition was quantitative.

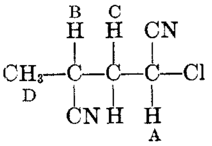
2-Chloro-4-methylglutaronitrile (V).—To a 500-ml Parr bottle was charged 14 g (0.1 mole) of IV dissolved in 100 ml of methanol. To this was added 1.0 g of 5% Pd–C and the bottle was attached to the Parr hydrogenator. The reaction proceeded rapidly at 40 psi and 50° and was essentially complete in 5 min. The reaction mixture was filtered to remove catalyst and distilled under reduced pressure to yield a clean colorless oil, bp 93–95° (0.5 mm).

Anal. Calcd: Cl, 24.61; N, 19.75. Found: Cl, 25.01; N, 20.72.

The nmr spectrum can be interpreted as shown in Table IV. From the chemical shift, D is a methyl group. From its splitting (J = 7 cps, doublet) it is attached to a carbon bearing only one hydrogen. For a very simple compound we would seek to find the proton split into a quartet by the methyl group. As a first approximation, this would appear to be given by the protons, B (an approximation only in that these protons are coupled to protons on another adjacent carbon, consequently, the multiplicity observed). From an examination of the neat spectrum, A is trying to be a triplet. It is probably safe to assume then that A is due to a proton adjacent to two other protons which are not equivalent. For these reasons, we feel the structure is (essentially) as shown below.

TABLE IV

Peak	Approximate chemical shift, τ	Area	Relative area
A	5.7	3.4	1.0 (1)
B	7.6	4	1.18 (1)
C	8.2	77.6	2.24 (2)
D	9.5	9.5	2.8 (3)

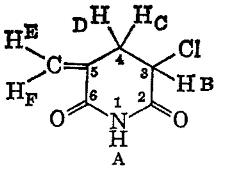


$$\mathrm{\underset{D}{CH_3}-\underset{\underset{CN}{|}}{\overset{\overset{\overset{B}{H}}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{\overset{C}{H}}{|}}{C}}-\underset{\underset{\underset{A}{H}}{|}}{\overset{\overset{CN}{|}}{C}}-Cl}$$

3-Chloro-5-(*exo*-methylene)glutarimide (VI).—To a 100-ml three-neck flask fitted with dropping funnel, drying tube, and magnetic stirrer was charged 25 g of concentrated sulfuric acid (85%). To this was added 14 g (0.1 mole) of IV over a 90-min period. The solution was stirred 4 hr and poured into 50 g of ice–water. The acidic solution was stripped to half its volume under reduced pressure; the precipitated solid was filtered and air dried. Recrystallization from methanol gave 5 g (30%) of light yellow powder, mp 141–142°.

Anal. Calcd for $C_6H_6ClNO_2$: C, 45.00; H, 3.87, Cl, 22.25; N, 8.78. Found: C, 44.91; H, 3.89; Cl, 22.24; N, 8.60.

The nmr spectrum of the structure



should give the area under the peaks due to H_B:(H_C + H_D):H_E = H_F as 1:2:1:1. The area found was as 1.1:2.0:0.9:1.1. H_A would be expected to be a singlet, which it is. Usually amino hydrogens give rise to broad peaks due to the effect of the nitrogen quadruple moment on the spin-lattice relaxation time. However, cases are known where the H in -CONH- groups gives rise to sharp singlets[7] as was observed here. Carbon 3 is asymmetric. Inspection of models show that H_B is slightly different (as far as magnetic environment is concerned) depending on which optical isomer, *d* or *l*, we inspect. Assuming that equal quantities of both are present, we would expect to see two very closely spaced triplets because of spin–spin coupling with H_C and H_D. Indeed, a gross triplet with signs of this extra complexity is noted in the spectrum. The spectrum of VI in CF_3CO_2D also shows a clear resonance at τ 5.24 as expected. H_C and H_D if equivalent would exist as a doublet due to spin–spin coupling with H_B. They are not equivalent though and each splits the other as well as being coupled to H_B. A complex peak attributed to this interaction is found at τ 5.78. H_E and H_F are not equivalent and hence should exist as small peaks which should each be split into doublets with small coupling constants. This was found at τ 3.98 and 3.33. Over-all, the predicted and observed nmr spectra are in excellent agreement.

Sodium Bisulfite Addition Product of 2-Chloro-4-(methylene)-glutaronitrile (VII).—To a 250-ml one-neck flask fitted with magnetic stirrer and heating mantle were charged 14 g (0.1 mole) of IV and 11.4 g (0.11 mole) of sodium bisulfite in 100 ml of water. The mixture was stirred and heated to its reflux temperature. Reflux was maintained for 3 hr. The solution was then cooled and the white, crystalline bisulfite addition product was separated by filtration. The bisulfite addition product was recrystallized from water and dried at reduced pressure to yield 24.0 g (97%), mp 235–236°, of white crystalline product.

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The Synthesis and Thermal Rearrangement of Substituted α,α-Diphenyl-N-benzhydrylnitrones

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The synthesis of several substituted α,α-diphenyl-N-benzhydrylnitrones is described. A comparison of synthetic methods involving either alkylation of benzophenone oxime anions with benzhydryl halides or the condensation of diaryl ketimines with N-benzhydrylhydroxylamine is presented. The nitrones were thermally isomerized to the corresponding oxime O-ethers.

A previous investigation of α,α-diphenyl-N-benzhydrylnitrone (Ia) revealed that this compound undergoes a nearly quantitative thermal rearrangement to benzophenone O-benzhydryloxime (IIa).[1] Limited evidence was presented in support of a concerted rearrangement involving a quasi-three-membered ring transition state. However, the evidence did not exclude the possibility of initial carbon–nitrogen bond breaking leading to a benzhydryl cation and an oxime anion followed by collapse to products. The present work was directed toward the preparation of a number of substituted α,α-diphenyl-N-benzhydrylnitrones (I) suitable for a detailed kinetic probe of this reaction. Authentic samples of the rearrangement products (II) were also required.

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[1] A. C. Cope and A. C. Haven, Jr., *J. Am. Chem. Soc.*, **72**, 4896 (1950).