liming the appropriate amount of sulfur trioxide into pure D_2O. In separate experiments ethyl *o*-nitrobenzoate, ethyl *m*-nitrobenzoate and ethyl *p*-nitrobenzoate were exposed to this solvent at 85° for several hours. After recovery of the esters and hydrolysis, no deuterium could be detected in the acid; this fact showed that no exchange occurred. Ethyl benzoate was exposed to this solvent under similar conditions for 5 minutes. A small amount of ethyl benzoate could be recovered and the corresponding acid also had only a natural deuterium content. The second possibility was checked by hydrolyzing each of the esters under the conditions described before, except that pure D_2O was used. After isolation and purification of the acids they could be shown to have only natural deuterium contents.

Acknowledgment.—We wish to thank Dr. J. F. Neumer for his participation in the designing and building of the deuterium conversion apparatus, and Professor R. A. Clement for helpful discussions.

CHICAGO 37, ILL.

[CONTRIBUTION FROM THE STAMFORD LABORATORIES, RESEARCH DIVISION, AMERICAN CYANAMID CO.]

Polarographic Behavior of Unsymmetrical Polyhalogenated Compounds. Polychlorinated Propionitrile and Derivatives[1]

BY W. H. JURA AND R. J. GAUL

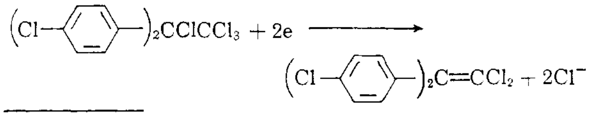
RECEIVED DECEMBER 16, 1957

The polarographic behavior of 2,2,3-trichloro- and 2,3-dichloropropionitriles and their derivatives was studied in order to determine the products formed in the reduction of unsymmetrical structures at the dropping mercury electrode. Reduction in all cases results in the formation of the double bond. Polarographic data, substantiated by cryoscopic and nuclear magnetic resonance measurements, are presented which represent the first published experimental evidence for the determination of the *cis* and *trans* isomers of 2,3-dichloroacrylonitrile. Each isomer is reduced to acrylonitrile *via* a different path. Polarograms of 2,2,3,3-tetrachloropropionitrile indicate that it is reduced to *trans*-2,3-dichloroacrylonitrile.

A search of the literature reveals that, while considerable work has been done on the polarographic behavior of halogenated organic compounds, no work has been reported on the behavior of compounds of the general types: $CHX{=}CXY$, CH_2XCHXY, CH_2XCX_2Y, CHX_2CX_2Y, where X = chlorine atom and Y = carboxyl, ester, amide or nitrile.

The closest approach to any of the above structures is found in the work of Elving, *et al.*,[2,3] who made a coulometric and polarographic study of the diastereoisomers of 2,2′-dibromosuccinic acid and their ethyl esters. Briefly, these studies showed that the reduction in all cases involved the elimination of both bromine atoms by a two-electron process to form an olefin. However, both bromine atoms in any of these compounds, excepting the acid at *p*H's where it contains one ionized and one un-ionized carboxyl group, are equivalent since both are alpha to a carboxyl or ester group. Stackelburg[4] also indicated that adjacent halogens could be removed electrolytically to form a stable double bond. Here again, only symmetrical structures were studied wherein the halogens must be considered equivalent.

During the preparation of this manuscript Rosenthal, *et al.*,[5] reported work on 1,1,1,2-tetrachloro-2,2-bis-(*p*-chlorophenyl)-ethane which led them to believe that the first cathodic wave is due to the reaction



Experimental

Apparatus.—All polarograms were obtained with a Leeds and Northrup Electrochemograph, type E, using damping position 1. The $m^{2/3}$, h, and other pertinent values for a given capillary are indicated in the tables. Heyrovsky cells were used throughout this work and polarograms were recorded against an external saturated calomel electrode (S.C.E.) *via* a KCl (aqueous)-KCl/agar/glass plug bridge. In those experiments where alkali metal ions would interfere, the "cell end" of the bridge was washed, dried and inserted into the unstirred solution in the cell just before the polarogram was recorded. A Beckman model G *p*H meter was used for all *p*H measurements. A Serfass conductivity bridge, model RC-M 15, was used to measure the cell resistance of all solutions examined which approached a value of 3000–3300 Ω in solutions containing 30% EtOH–0.05 *M* $(CH_3)_4NI$.

Controlled potential electrolyses were carried out with an automatic apparatus similar to that described by Lingane[6] and the total current passed was measured with a copper coulometer.

Polarographic Procedure.—In most cases, stock solutions of the compound being investigated were made up just before use in anhydrous ethyl alcohol in which all the compounds were stable. Aliquots of these solutions were diluted with predetermined amounts of electrolyte, ethyl alcohol and water. Airco prepurified nitrogen, equilibrated with a portion of the same solution as contained in the cell, was used to remove the oxygen prior to electrolysis. In cases where it was necessary to exceed polarizing voltages of ≃1.9 volts *vs.* S.C.E., deaeration was carried out prior to insertion of the KCl bridge from the S.C.E.

In the case of more volatile compounds, only approximate concentrations were used and the following procedure was adopted. After deaerating 10 ml. of solvent–electrolyte solution in the cell, 0.1 ml. (micro pipet) of a concentrated (~0.05 *M*) alcoholic solution of the compound in question was added. Nitrogen was passed through the cell for an additional 30 seconds to ensure mixing. After blanketing the solution with nitrogen, the "cell end" of the KCl bridge was inserted and the polarization was carried out.

All $E_{1/2}$ values have been corrected for iR drop and the distances stepped off along the current axis in the figures are equivalent to 1.00 μA. unless otherwise indicated. All potentials cited are "*vs.* S.C.E."

Syntheses.[7] **2,2,3-Trichloropropionitrile.**—2,2,3-Trichloropropionitrile was prepared by the procedure of Brintzinger, *et al.*,[8] with two modifications: the amount of pyri-

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[1] Presented at the Seventh Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, Pa., February 28, 1956.

[2] P. J. Elving, I. Rosenthal and A. J. Martin, THIS JOURNAL, **77**, 5218 (1955).

[3] P. J. Elving and I. Rosenthal, *ibid.*, **73**, 1880 (1951).

[4] M. V. Stackelburg and W. Stracke, *Z. Elektrochem.*, **53**, 118 (1949).

[5] I. Rosenthal, G. Frisone and R. J. LaCoste, *Anal. Chem.*, **29**, 1639 (1957); private communication.

[6] J. J. Lingane and S. L. Jones, *ibid.*, **22**, 1169 (1950).

[7] All melting points are corrected; boiling points are uncorrected.

[8] H. Brintzinger, K. Phannstiel and H. Koddebusch, *Angew. Chem.*, **A60**, 311 (1948).

TABLE I

COMPARISON OF $E_{1/2}$ AND I VALUES OF POLYCHLORINATED COMPOUNDS

Compound[e]	System	mM	$E_{1/2}$ W$_1$	$E_{1/2}$ W$_2$	$E_{1/2}$ W$_3$	I W$_1$	I W$_2$	I W$_3$
$(HOOCCHBr)_2$ "*meso*"	[a]	0.261				3.36[f]	3.25	
$CH_2XCX_2CONH_2$	[a]	.527	0.39	1.06		3.44[g]	4.00	
$CH_2{=}CXCONH_2$	[a]	.403	1.05			4.93[f]		
$CH_2{=}CXCONH_2$	[b]	.403	1.59			4.03[f]		
$CH_2XCX_2CONH_2$	[b]	.497	0.39	1.58		3.53[f]	3.61	
$(HOOCCHBr)_2$ "*meso*"	[c]	.261				2.52[h]		
$CH_2XCX_2CONH_2$	[c]	.511	0.59	1.69	1.91	3.12[h]	2.99	2.69
$CH_2{=}CXCONH_2$	[c]	.969	1.69	1.91		3.36[h]	3.16	
$CH_2{=}CHCONH_2$	[c]	.531	1.91			3.49[h]		
CH_2XCX_2CN	[c]	.303	Max.	1.52	1.96	2.58[h]	2.24	2.24
$CH_2{=}CXCN$	[c]	~ .5	1.52	1.95				
$CHX{=}CHCN$	[c]	~ .5	1.63	1.95				
$CH_2{=}CHCN$	[c]	~ .5	1.96					
$CH_2XCHXCN$	[c]	~ .5	0.88	1.95				
$CH_2XCHXCOOEt$	[c]	.291	1.07	1.82				
$CH_2{=}CHCOOEt$	[c]	~ .25	1.82					
$CH_2{=}CHCN$	[d]	~ .5	1.94					
$CH_2{=}CHCONH_2$	[d]	.531	1.91			3.42[h]		
$CH{\equiv}CCN$	[c]	~ .5	1.10	1.94				
$CH{\equiv}CCONH_2$	[c]	~ .5	1.60	1.90				
$CH{\equiv}CCOOCH_3$	[c]	~ .4	1.32	1.80		2.3[i]	2.2[i]	

[a] 10% EtOH-0.12 M HCl. [b] 10% EtOH-0.2 M NH_4OH-0.2 M NH_4Cl, *p*H 9.2. [c] 30% EtOH-0.05 M $(CH_3)_4NI$, *p*H ~7. [d] 30% EtOH-0.05 M $(CH_3)_4NOH$, *p*H ~14. [e] X = Cl. [f] $m^{2/3} = 1.226$; determined in 0.1 M KCl saturated air at 25 ± 0.1°, $h = 76.5$ cm., $t = 4.84$ sec., open circuit. [g] $m^{2/3} = 1.4115$; determined in 0.50 mM Tl^+-0.12 M HCl at −0.70 v., $h = 80$ cm., $t = 4.52$ sec., $T = 25 \pm 0.1°$. [h] $m^{2/3} = 1.084$, same as *f*, except $h = 63$ cm., $t = 5.75$ sec. [i] i_d (arbitrary units)/$t^{1/6}$.

dine catalyst was reduced to 1% by weight of the acrylonitrile employed, and the reaction temperature was kept at 65–75° throughout. In this way a 92% yield (based on chlorine added) of product, b.p. 154–155°, n^{25}_D 1.4655, was obtained.

2-Chloroacrylonitrile.—Crude 2-chloroacrylonitrile was obtained in a 67% yield *via* the procedure of Brintzinger, *et al.*[8] Fractional distillation, accompanied by considerable loss due to polymerization, afforded 46% of pure product, b.p. 82–88°. A heart cut had b.p. 88° and n^{25}_D 1.4270.

2,2,3-Trichloropropionamide.—2,2,3-Trichloropropionitrile (157.4 g., 1.0 mole) was added over a period of 21 minutes to a stirred solution of 1.1 moles of sulfuric acid monohydrate. The reaction temperature was held between 100–110° throughout the addition and for 30 minutes thereafter with cooling or heating as needed. The resulting viscous solution was poured onto a mixture of 500 g. of crushed ice and 190 ml. (1.5 moles) of concentrated ammonium hydroxide. The precipitated amide was collected by vacuum filtration and washed with 100 ml. of cold water. Further chilling of the filtrate afforded a second crop of amide for a total yield, after drying, of 124 g. (71%), m.p. 54.5–55.5° (reported[9] m.p. *ca.* 57°). An analytical sample, m.p. 56.5–57°, was obtained by recrystallization from hexane.

Anal. Calcd. for $C_3H_4NOCl_3$: C, 20.42; H, 2.28; N, 7.94; Cl, 60.29. Found: C, 20.73, 20.70; H, 2.68, 2.63; N, 8.06; Cl, 59.78, 59.74.

2-Chloroacrylamide.—2-Chloroacrylonitrile (29.5 g., 0.34 mole) was added gradually and with stirring to 45 g. (0.37 mole) of sulfuric acid monohydrate. The temperature was maintained at 90° during the addition (15 minutes) and for 30 minutes thereafter. The viscous solution was cooled to 40° and poured onto 100 g. of crushed ice. The precipitate, collected by suction filtration, redissolved on being washed with water. The original filtrate and the wash liquor were combined and, with chilling in ethanol–Dry Ice, neutralized with gaseous ammonia. The colorless platelets which separated were collected and dried in a desiccator for 12 hours to give 15 g. (42%) of crude product. Extraction of the crude product with acetone and then recrystallization from hexane gave the pure amide as colorless platelets, m.p. 91.5–93.5°.

***t*-Butyl 2,2,3-Trichloropropionate.**—According to the procedure for preparing *t*-butyl esters reported by McCloskey,[10] 87.2 g. (0.492 mole) of distilled, crystalline 2,2,3-trichloropropionic acid, 100 ml. of anhydrous ether and 5 ml. of concentrated sulfuric acid were placed in a 500-ml. pressure bottle. After freezing this mixture in acetone–Dry Ice, 38.6 g. of liquid isobutylene was added. The bottle was securely stoppered, shaken on a Parr shaker until a homogeneous solution resulted (15 minutes), then stored at room temperature for two days.

The contents from two such bottles were combined, each bottle was rinsed with 100 ml. of ether, and the entire solution was extracted with six 250-ml. portions of saturated sodium bicarbonate and two 250-ml. portions of water. After drying over sodium carbonate and filtration, slow evaporation of the ethereal solution afforded 106 g. (46%) of crude ester. Fractional distillation through a 35-cm. packed column gave 99.6 g. of colorless product, b.p. 60–64° (1.5 mm.). A center fraction had b.p. 62–64° (1.5 mm.), n^{25}_D 1.4503.

Anal. Calcd. for $C_7H_{11}O_2Cl_3$: C, 36.00; H, 4.75; Cl, 45.55. Found: C, 36.08; H, 4.88; Cl, 45.53.

2,2,3,-Trichloropropionic Acid.—2,2,3-Trichloropropionitrile (353 g., 2 moles) was hydrolyzed to the acid by the procedure described by Lichty[9] except that, after all the nitrile had been added, the mixture was held at 150° for only an additional 30 minutes. The yield of crude acid was 346 g. (98%).

Crude acid (376 g.) was treated twice with 250-ml. portions of benzene followed by vacuum concentration at 90° and 20 mm. The residue was distilled through a short Vigreux column to give colorless liquid, b.p. 90° (1.1 mm.), which rapidly crystallized. The crystalline acid was dried at 5 mm. over calcium chloride for three days to give 345 g. (92.5% recovery) of product which melted at 62–66°.

Ethyl 2,3-Dichloropropionate.—Ethyl acrylate (200 g., 2 moles) was chlorinated by the method of Burton.[11] The crude ester was washed with two 100-ml. portions of cold water, dried over anhydrous calcium chloride, filtered, and fractionally distilled to give 290.8 g. (82%) of pure ester, b.p. 81–83° (17–19 mm.), n^{25}_D 1.4454.

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(9) J. G. Lichty, U. S. Patent 2,400,463.

(10) A. L. McCloskey, *et al.*, *Org. Syntheses*, **34**, 26 (1954).

(11) C. D. Burton, U. S. Patent 2,647,923.

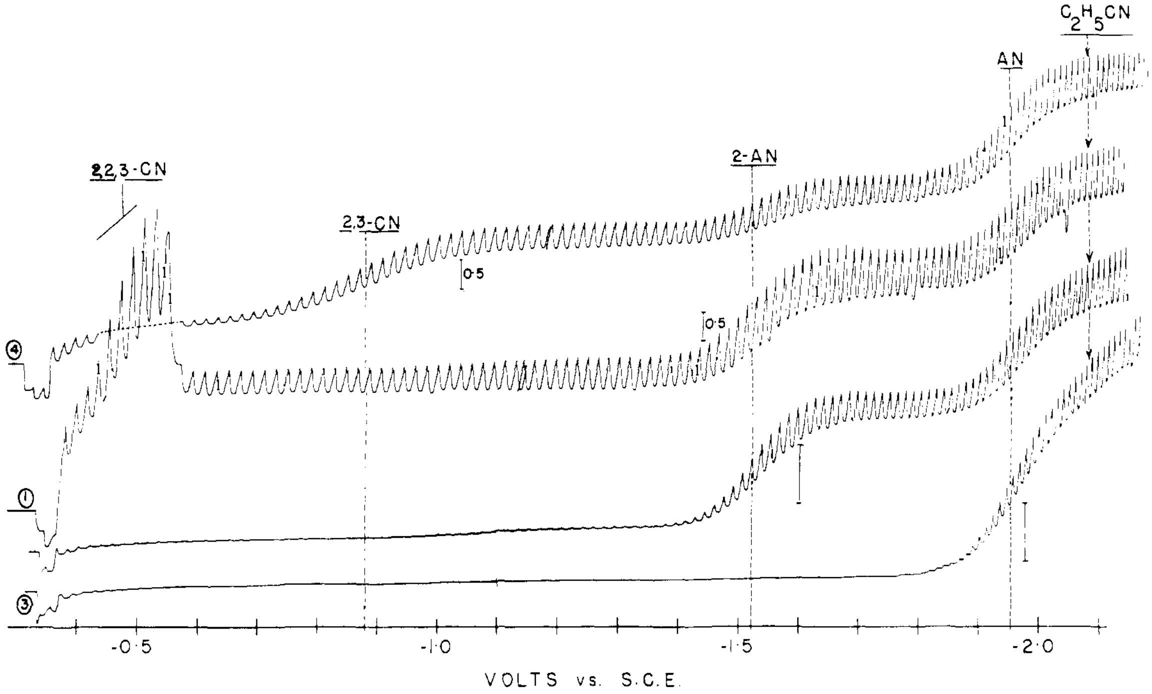

Fig. 1.—Polarograms of 2,2,3-trichloropropionitrile and 2,3-dichloropropionitrile and their reduction products in 30% EtOH–0.05 *M* $(CH_3)_4NI$: 1, 0.303 m*M* 2,2,3-trichloropropionitrile; 2, ~0.5 m*M* 2-chloroacrylonitrile; 3, ~0.6 m*M* acrylonitrile; and 4, ~0.3 m*M* 2,3-dichloropropionitrile.

Anal. Calcd. for $C_5H_8O_2Cl_2$: C, 35.11; H, 4.72; Cl, 41.46. Found: C, 34.79, 34.83; H, 5.19, 5.09; Cl, 41.33.

2,3-Dichloropropionitrile.—2,3-Dichloropropionitrile was obtained by the chlorination of 159 g. (3 moles) of acrylonitrile according to the procedure of Brintzinger, *et al.*[8] The crude product was washed with 300 ml. of 3 *N* hydrochloric acid and 300 ml. of water, then dried over anhydrous calcium chloride. After suction filtration, fractional distillation afforded 233 g. (63%) of nitrile, b.p. 75–79° (26–28 mm.). A center fraction had b.p. 78–79° (28 mm.), $n^{25}D$ 1.4636. At no time could we duplicate the yield claimed by Brintzinger, *et al.*,[8] nor obtain a product completely free of traces of 2,2,3-trichloropropionitrile, as determined polarographically.

Anal. Calcd. for $C_3H_3NCl_2$: C, 29.06; H, 2.44; N, 11.30; Cl, 57.20. Found: C, 28.53, 28.62; H, 2.71, 2.48; N, 11.01; Cl, 57.79, 57.42.

2,3-Dichloroacrylonitrile.—A modification of the procedure of Lichty,[12] wherein a mixture of 237.6 g. (1.5 moles) of 2,2,3-trichloropropionitrile and 64.5 g. (0.5 mole) of quinoline was heated under reflux for 18 hours, afforded, after vacuum treatment (90° and 20 mm.) of the dark viscous fluid, 116 g. (64%) of the desired product as a colorless, lachrymatory liquid. Highly purified material, b.p. 130–130.5°, $n^{25}D$ 1.4838, was obtained by precise fractionation through a Todd column filled with stainless, protruded packing.

Anal. Calcd. for C_3HNCl_2: C, 29.54; H, 0.83, Cl, 58.16. Found: C, 29.26; H, 1.13; Cl, 57.86.

3-Chloroacrylonitrile.—The compound, prepared essentially as described by Dutcher,[13] was obtained as a colorless, slightly lachrymatory liquid, b.p. 144–145°, $n^{25}D$ 1.4570.

2,2,3,3-Tetrachloropropionitrile.—The product, prepared by the chlorination of 3-chloroacrylonitrile, was obtained in 69% crude yield which, after two distillations, gave a 51% yield of pure 2,2,3,3-tetrachloropropionitrile as a colorless liquid, b.p. 62–65° (10 mm.) (reported[8] b.p. 92° (14 mm.), which solidified on chilling to colorless crystals which melt at about 26°.

Anal. Calcd. for C_3HNCl_4: C, 18.68; H, 0.52; Cl, 73.54. Found: C, 18.65; H, 0.83; Cl, 73.56.

Propiolamide and Propiolonitrile.[14]—Propiolamide was prepared in a 63% yield from methyl propiolate and ammonia and was dehydrated with phosphorus pentoxide to propiolonitrile, m.p. 5.8–6.2°, in 76% yield *via* the procedure of Moureu, *et al.*[15]

Miscellaneous Compounds.—Tetraalkylammonium compounds (Southwestern Analytical Chemicals, Austin, Texas); methyl propiolate (Farchan Research Laboratories, Cleveland, Ohio); 3-chloropropionitrile, *meso*-2,2′-dibromosuccinic acid, maleic acid (Eastman Organic Chemicals); 2,2-dichloropropionic acid (Dow's herbicide, Dalapon); reagent grade inorganic compounds used throughout.

Data and Discussion

2,2,3-Trichloropropionitrile, -Amide, -Ester, Acid.—In 0.05 *M* $(CH_3)_4NI$–30% EtOH, 0.303 m*M* 2,2,3-trichloropropionitrile (2,2,3-CN) gave three well developed waves which, after suitable correction for the change in $t^{1/6}$ with the change in the potential of the dropping mercury electrode (d.m.e.), were of equal height (Fig. 1, Table I). In the same medium 2-chloroacrylonitrile (2-AN) (~0.5 m*M*) gave two waves of equal height. The half-wave potentials ($E_{1/2}$) and slopes of these two waves corresponded to W_2 and W_3 of 2,2,3-CN. Finally, the identity of $W_3^{2,2,3-CN}$ and W_2^{2-AN} with the wave obtained for acrylonitrile (AN) confirmed the reduction of 2-AN to AN. The possibility that 2,2,3-CN was first reduced to 2,3-dichloropropionitrile (2,3-CN) was ruled out when it was shown (see discussion below) that 2,3-CN is reduced at a potential intermediate between the values obtained for $W_1^{2,2,3-CN}$ and W_1^{2-AN}. The successive electrode reactions may then be represented as (a).

Examination of polarograms obtained for 2,2,3-trichloropropionamide (2,2,3-$CONH_2$),2-chloro-

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[12] J. G. Lichty, U. S. Patent 2,328,984.

[13] H. A. Dutcher, U. S. Patent 2,419,488.

[14] We wish to thank Mr. N. M. Bikales of these laboratories for carrying out these preparations.

[15] C. Moureu and J. C. Bongrand, *Ann. chim.*, **14**, 17 (1920).

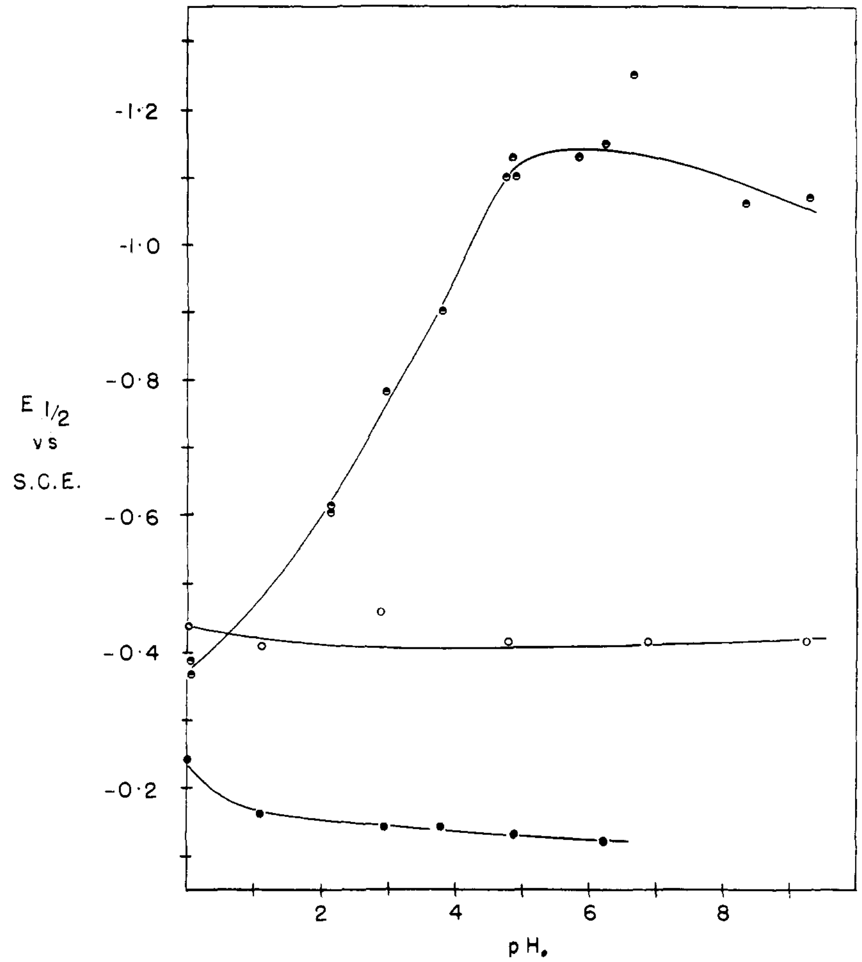

Fig. 2.—Showing the effect of pH upon the $E_{1/2}$ of 2,2,3-trichlorinated compounds: ◒, 2,2,3-trichloropropionic acid (top); ○, 2,2,3-trichloropropionamide (middle); ●, 2,2,3-trichloropropionitrile (bottom).

acrylamide (2-AMD), acrylamide (AMD), *t*-butyl 2,2,3-trichloropropionate (2,2,3-COO-*t*-Bu) and butyl acrylate indicated that the reduction sequence of the 2,2,3-trichlorinated amides and esters may be similarly represented.

$$\mathrm{CH_2ClCCl_2CN} \xrightarrow[W_1{}^{2,2,3\text{-CN}}]{2e} \mathrm{CH_2{=\!=}CClCN} \xrightarrow[\substack{W_2{}^{2,2,3\text{-CN}} \\ W_1{}^{2\text{-AN}}}]{2e,\ HOH}$$

$$\mathrm{CH_2{=\!=}CHCN} \xrightarrow[\substack{W_3{}^{2,2,3\text{-CN}} \\ W_2{}^{2\text{-AN}} \\ W^{\text{AN}}}]{2e,\ 2HOH} \mathrm{CH_3CH_2CN} \quad (a)$$

The variation of the heights of the waves of the above compounds with mercury height (*h*) and temperature (1.1 to 2.0%/°C.) were those expected for diffusion controlled processes.

The $E_{1/2}$'s of the first reduction step for 2,2,3-CN, -CONH$_2$ and -COO-*t*-Bu (Table II and III, Fig. 2) remain essentially constant and independent of pH. Ionic strength effects are reflected in some of the observations, but their magnitude does not alter the above conclusion. The pH-independence of this step is in agreement with the observations of Elving, *et al.*,[3] on *symmetrical* dihalogenated compounds and of Rosenthal, *et al.*,[5] in his study of the *unsymmetrical* compounds 1,1,1,2-tetrachloro-2,2-bis-(*p*-chlorophenyl)-ethane and 1,1,2-trichloro-2,2-bis-(*p*-chlorophenyl)-ethane and is to be expected for a system where hydrogen ions are not consumed in the potential-determining step of the electrode process.

TABLE II

EFFECT OF pH ON $E_{1/2}$ OF 2,2,3-TRICHLOROPROPIONITRILE AND *t*-BUTYL 2,2,3-TRICHLOROPROPIONATE

2,2,3-Trichloroproponitrile, 0.09 m*M*	pH	$-E_{1/2}$
1.2 *M* HCl, 0.1 *M* KCl, 10% EtOH	<0.1	0.24
0.12 *M* HCl, 0.1 *M* KCl, 10% EtOH	1.1	.16
0.25 *M* citric acid, 0.1 *M* Na_2HPO_4, 0.1 *M* KCl, 10% EtOH	2.9	.14
0.20 *M* citric acid, 0.2 *M* Na_2HPO_4, 0.1 *M* KCl, 10% EtOH	3.8	.14
0.15 *M* citric acid, 0.3 *M* Ha_2HPO_4, 0.1 *M* KCl, 10% EtOH	4.9	.13
0.10 *M* citric acid, 0.4 *M* Na_2HPO_4, 0.1 *M* KCl, 10% EtOH	6.2	.12
t-Butyl 2,2,3-trichloropropionate, 0.23 m*M*		
0.12 *M* $HClO_4$, 20% EtOH	0.8	0.12
0.12 *M* $HClO_4$, 20% EtOH, 0.5 *M* $NaNO_3$	0.8	.17
0.1 *M* AcOH, 0.1 *M* AcONa, 20% EtOH	4.8	.08
0.1 *M* AcOH, 0.1 *M* AcONa, 20% EtOH, 0.5 *M* $NaNO_3$	4.7	.15
0.1 *M* NH_4OH, 0.1 *M* NH_4Cl, 20% EtOH	9.2	.15
0.1 *M* NH_4OH, 0.1 *M* NH_4Cl, 20% EtOH, 0.5 *M* $NaNO_3$	9.3	.10

TABLE III[a,b]

$E_{1/2}$, I VALUES FOR 2,2,3-TRICHLOROPROPIONAMIDE AND 2,2,3-TRICHLOROPROPIONIC ACID AT VARIOUS *p*H'S

2,2,3-Trichloropropionamide, 0.527 m*M*	*p*H	$-E_{1/2}$	I
1.0 *M* HCl	<0.1	0.44, 1.0	3.48
0.1 *M* HCl	1.1	.41, 1.06	3.44
0.1 *M* $CH_2ClCOOH$, 0.1 M $CH_2ClCOONa$	2.9	.46, [d]	3.44
0.1 *M* AcOH, 0.1 *M* AcONa	4.8	.41, 1.39	3.43
0.2 *M* NH_4OH, 0.2 *M* NH_4Cl	9.2	.42, 1.60	3.41, 3.41
0.1 *M* $AcONH_4$	6.9	.42, [d]	3.41
2,2,3-Trichloropropionic acid, 0.50 m*M*			
1.0 *M* HCl	<0.1	.38	3.52
0.1 *M* HCl	1.1	.37	3.47
0.1 *M* HCl, 0.9 *M* KCl	1.0	.38	3.45
0.1 *M* $CH_2ClCOOH$, 0.1 *M* CH_2COONa, 0.1 *M* KCl	2.1	.62	3.25
0.1 *M* $CH_2ClCOOH$, 0.1 *M* CH_2COONa, 0.5 *M* KCl	2.1	.60	3.21
0.25 *M* citric acid, 0.1 *M* Na_2HPO_4, 0.1 *M* KCl	2.9[c]	.78	
0.20 *M* citric acid, 0.2 *M* Na_2HPO_4, 0.1 *M* KCl	3.8[c]	.90	
0.15 *M* citric acid, 0.3 *M* Na_2HPO_4, 0.1 *M* KCl	4.9[c]	1.10	
0.10 *M* citric acid, 0.4 *M* Na_2HPO_4, 0.1 *M* KCl	6.2[c]	1.15	
0.1 *M* AcOH, 0.1 *M* AcONa, 0.9 *M* KCl	4.7	1.10	3.18
0.1 *M* AcOH, 1.0 *M* AcONa	5.8	1.13	3.22
1.0 *M* NH_4Cl, 0.1 *M* NH_4OH	8.3	1.06	3.89
1.0 *M* NH_4Cl, 1.0 *M* NH_4OH	9.3	1.07	3.84

[a] All solutions contain 10% EtOH. [b] See footnote *f*, Table I. [c] Concentration of compound is 0.1013 m*M*. [d] Diffusion current and electrolyte discharge overlap.

Unlike 2,2,3-CN and 2,2,3-COO-*t*-Bu, a second, *p*H-dependent wave was observed for 2,2,3-$CONH_2$ over the *p*H range <0.1 to 9.2. Only in 0.2 *M* NH_4OH–0.2 *M* NH_4Cl was this wave well defined. In other solutions this wave merged with the discharge of the supporting electrolyte. The $E_{1/2}$ of the wave shifted toward more negative potentials with increasing *p*H and amounted to approximately 0.06 v./Δ*p*H. In addition, $W_2^{2,2,3-\mathrm{CONH_2}}$ is quite unique in that it represented the only *p*H-dependent carbon–halogen fission process observed in this study. The wave obtained for 2-chloroacrylamide (2-AMD) was identical in every respect with $W_2^{2,2,3-\mathrm{CONH_2}}$ and confirmed its origin. In 0.12 *M* HCl–10% EtOH slope values of 0.037 and 0.041 v. were obtained for $W_2^{2,2,3-\mathrm{CONH_2}}$ and $W_1^{2-\mathrm{AMD}}$, respectively. In 30% EtOH–0.05 *M* $(CH_3)_4NI$, however, $W_1^{2-\mathrm{AMD}}$ had a slope of 0.065 v. The height of $W_2^{2,2,3-\mathrm{CONH_2}}$ is consistently greater than $W_1^{2,2,3-\mathrm{CONH_2}}$ by some 18% in acidic solutions and to a much lesser degree in NH_4OH–NH_4Cl solutions. 2-AMD behaves similarly. The higher temperature coefficient (2.5%/°C.) and a slight decrease in the value of $i_d/h^{1/2}$ with increasing "*h*" may be due to the difficulty in measuring i_d of $W_2^{2,2,3-\mathrm{CONH_2}}$ because of its proximity to the background current.

The C–Cl fission which 2-AMD undergoes is strikingly similar to the *p*H-dependent C–F fission process reported for phenacyl fluoride by Elving, *et al.*,[16] and since it, *i. e.*, 2-AMD, can undergo similar polarization at the electrode surface the same mechanism may be involved. None of the other 2-halogen-2,3-unsaturated derivatives, however, exhibited similar polarographic activity.

2,2,3-Trichloropropionic acid (2,2,3-COOH) gave only one wave in buffered solutions (*p*H <0.1 to 9.3). A plot of $E_{1/2}$ *vs.* *p*H showed the usual S-shaped relationship which is so characteristic of ionizable compounds[17-23] and the same interpretations apply (Fig. 2, Table III). Comparison of the diffusion current constants indicated that the reduction of 2,2,3-COOH involved a total transfer of $2e^-$ and was confirmed by coulometric measurements under controlled potential conditions. Observations on other 2,2,3-trichloro compounds already cited and the subsequent separation, on standing, of an acidic, low molecular weight polymer from the solution electrolyzed at constant potential pointed to the formation of 2-chloroacrylic acid. Reduction to 2,2-dichloropropionic acid ($E_{1/2} \sim -0.8$ v.) was ruled out experimentally.

For all compounds i_d was proportional to concentration. In the case of 2,2,3-CN, 60% alcohol was necessary to keep the compound in solution.

In buffered solutions (Table II) $W_1^{2,2,3-\mathrm{COO}-t-\mathrm{Bu}}$ included a slight maximum, after which a normal limiting current was obtained. The "$E_{1/2}$" was taken as that potential on the rising portion of the wave which corresponded to the value *i*1/2. The maximum observed for $W_1^{2,2,3-\mathrm{CN}}$ (Fig. 1) is an exceptional case and is not usually observed.

Ethyl 2,3-Dichloropropionate and 2,3-Dichloropropionitrile.—In 0.05 *M* $(CH_3)_4NI$–30% EtOH, ethyl 2,3-dichloropropionate (2,3-COOEt) gave two irreversible waves of equal height. The second wave was identical with that obtained for ethyl acrylate and again indicated the formation of the double bond *via* the removal of the vicinal halogen atoms. $E_{1/2}$ for $W_1^{2,3-\mathrm{COOEt}}$ was found to be independent of *p*H. The temperature coefficient (1.5%/°C.) and the change in i_d with "*h*" indicates $W_1^{2,3-\mathrm{COOEt}}$ is diffusion controlled (0.05 *M* $(CH_3)_4NI$–0.11 *M* KCl–35% EtOH).

The reduction of 2,3-dichloropropionitrile (2,3-CN) was found to proceed similarly. The polarograms of 2,3-CN are somewhat complicated by the fact that small amounts of 2,2,3-CN, which could not be separated completely from 2,3-CN, was also present. W_1 and W_3 are associated with the reduction of 2,2,3-CN and W_2 represents the reduction of 2,3-CN to AN. W_4 thus represents the reduction of AN produced from both 2,3-CN and 2,2,3-CN. Thus, it was found that $W_1 + W_2 = W_2 + W_3 = W_4$. Failure to reduce 3-chloropropionitrile eliminated it as an alternate reduction product. Consideration of the published data on ethyl 2-chloroacetate[17] and the 2-bromo acids[22] also precluded reduction to 2-chloropropionitrile (or 2-chloro ester).

From our observations on *unsymmetrical* 2,3- and 2,2,3-polyhalogenated compounds, covering the broad class which includes the acid, amide, ester and nitrile functions, together with Rosenthal's

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(17) P. J. Elving and I. Rosenthal, *ibid.*, **74**, 6112 (1952).

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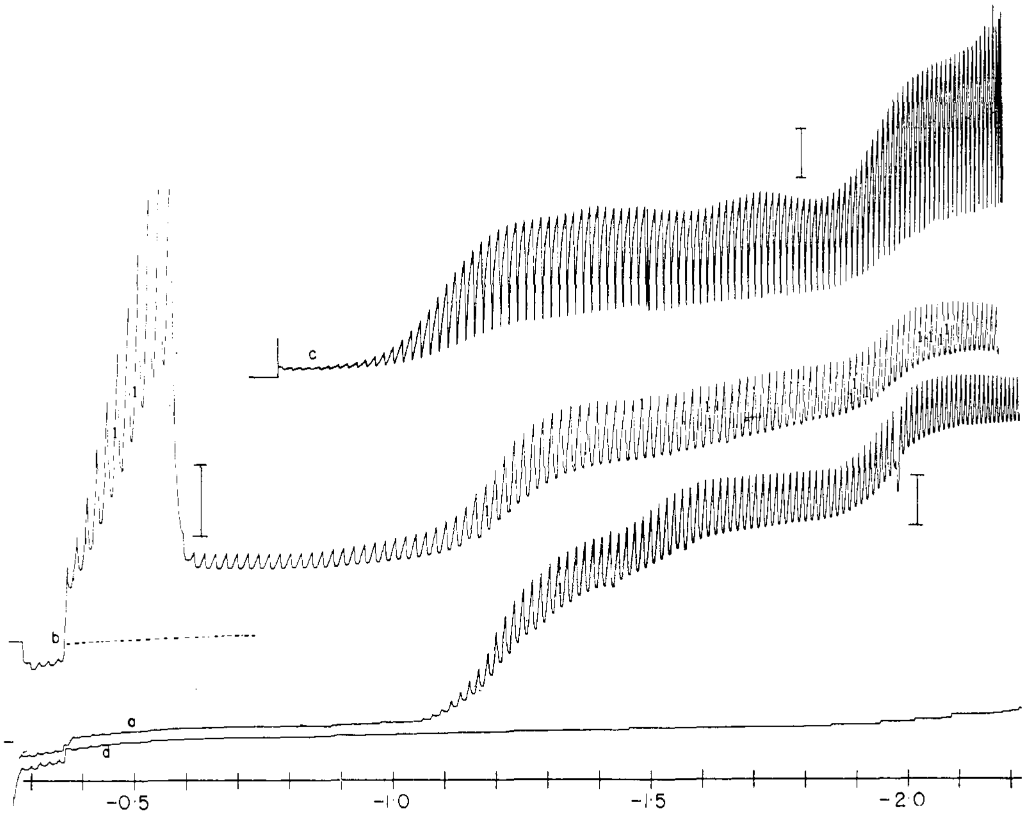

Fig. 3.—Polarograms of 2,3-dichloroacrylonitrile, 2,2,3,3-tetrachloropropionitrile and propiolonitrile in 30% EtOH–0.05 *M* $(CH_3)_4NI$: a, 0.4965 m*M* 2,3-dichloroacrylonitrile; b, 0.3058 m*M* 2,2,3,3-tetrachloropropionitrile; c, ~0.5 m*M* propiolonitrile; and d, blank.

observations on *unsymmetrical* polychlorodiphenylethanes, and finally the work of Elving[2] and Stackelberg[4] on *symmetrical* dihalogenated types, it is possible to conclude that the removal of vicinal halogens to form a double bond is indeed a very general type of electrolytic reduction. The mechanism proposed by Elving[3] for *symmetrical* structures appears to be applicable to the *unsymmetrical* types discussed. Thus, the data on saturated compounds derived from 2,2,3-trichloro- and 2,3-dichloropropionitrile allows us to conclude that reduction proceeds *via* scission of an α-carbon–halogen bond, formation of a carbanion and simultaneous *trans* elimination of a β-halogen with formation of a double bond.

2,3-Dichloroacrylonitrile.—It was of interest to learn what effect, if any, the presence of a 2,3-double bond might have on the removal of halogens located on both the 2- and 3-carbon positions.

A typical polarogram of "pure" 2,3-dichloroacrylonitrile (2,3-AN) is shown in Fig. 3. In 0.1 *M* AcOH–0.1 *M* AcONa–30% EtOH, only the first wave is observed. The slight shift in $E_{1/2}$ is due to ionic strength effects. It is significant that the three waves observed in Fig. 3 bear no simple multiple relationship to each other. The $E_{1/2}$ (−1.51 v.) of W_2 indicates that it is due to the reduction of 2-AN to AN. Since infrared spectra showed <1%, if any, 2-AN in the sample, it must have been produced at the surface of the d.m.e. The $E_{1/2}$ (−1.96 v.) of W_3 indicates that it is due to the reductive saturation of AN. The possibility that W_2 might be due to the reduction of 3-chloroacrylonitrile was eliminated experimentally ($E_{1/2}$ = −1.63 v., Table I). It is important to note that the AN wave (W_3) is greater than the 2-AN wave (W_2) and, since both 2-AN and AN are reduced by 2-electron processes, this indicates that 2-AN is not the only source of AN. The variation of i_d ($W_1 + W_2$) with "*h*" and a temperature coefficient of 2.19%/°C. indicate that both waves are diffusion controlled. When elemental analysis confirmed the high degree of "purity" of the sample it could only be concluded that the sample was a mixture of the *cis* and *trans* isomers[24] and that their reduction sequences differ. The following over-all electrode reactions are postulated to take place, with wave heights proportional to the number of electrons transferred.

$$\text{“one” isomer} - \text{2,3-AN} \xrightarrow{2e} \text{2-AN} \xrightarrow{2e} \text{AN} \xrightarrow{2e} CH_3CH_2CN \quad \text{(b)}$$

$$\text{“other” isomer} - \text{2,3-AN} \xrightarrow{4e} \text{AN} \xrightarrow{2e} CH_3CH_2CN \quad \text{(c)}$$

Considering the above reaction and the number and identity of the waves obtained, it follows that the first wave is a composite one representing the first reduction stage of both isomers. For any mixture of isomers it should be possible to cal-

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[24] *cis* and *trans* designations are assigned with respect to the adjacent halogens.

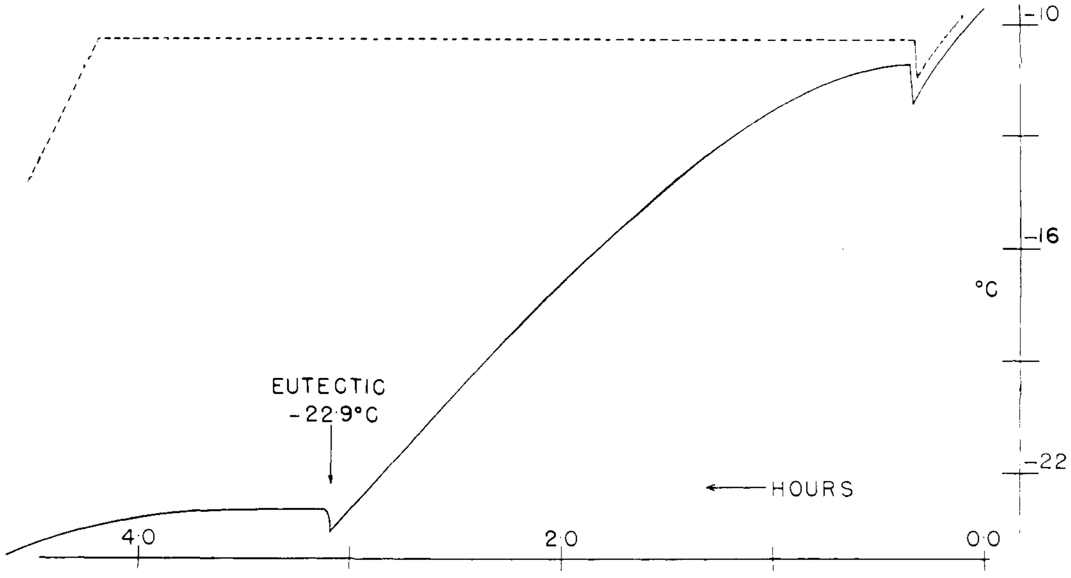


Fig. 4.—Cooling curve for "pure" 2,3-dichloroacrylonitrile.

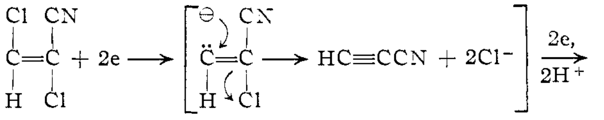
culate the height of the acrylonitrile wave (W_3) from the heights of W_1 and W_2, since both isomers are ultimately reduced to AN. Thus

$$W_3^{\mathrm{AN}\rightarrow \mathrm{CH_3CH_2CN}} = W_2^{2\text{-}\mathrm{AN}\rightarrow\mathrm{AN}} + {}^1/_2(W_1^{\mathrm{total}} - W_2^{2\text{-}\mathrm{AN}\rightarrow\mathrm{AN}}) \quad \text{(d)}$$

Using the above expression, theoretical values for W_3 of 1.25 and 2.24 μA. were calculated and compared with the observed values of 1.14 and 1.93 μA., respectively, for two samples. These values are in good agreement and fall within the limits of accuracy of such measurements.

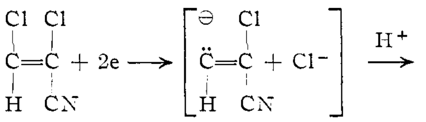
Cryoscopic examination according to the procedure of Witschonke[25] (Fig. 4) indicated that the sample is a two-component system containing 30–40% of a second component. This was the first evidence, by an independent technique, to support the polarographic interpretations.[26] Multiple fractional crystallization of "pure" 2,3-AN resulted in a material which on polarographic examination very nearly satisfied expression (b) and was estimated to contain ~94% of this "one" isomer (subsequently shown to be the *cis* isomer). Substantiated by n.m.r. spectra,[26] this further indicated that the sample was a mixture of the *cis* and *trans* isomers.

Reduction Mechanism.—Steric and electronic factors, and the experimental production of 2-chloroacrylonitrile from one of the isomers, indicate that the primary attack of the electrons in the reduction of 2,3-AN is on the β carbon–halogen bond. In the case of the *trans* isomer, the formation of the β-carbanion occurs with the simultaneous loss of the α-chlorine atom as chloride (*trans* elimination) and formation of propiolonitrile. The propiolonitrile is immediately reduced to acrylonitrile (see Experimental proof below). In the case of the *cis* isomer, the simultaneous loss of the chlorine atom is sterically prevented; consequently, the carbanion abstracts a proton from the solvent system to produce 2-chloroacrylonitrile. Thus, the reaction sequences may be written



$$\mathrm{Cl(H)C{=}C(Cl)CN} + 2e \longrightarrow \left[\mathrm{\overset{\ominus}{\ddot{C}}(H){=}C(Cl)CN} \longrightarrow \mathrm{HC{\equiv}CCN} + 2\mathrm{Cl^-}\right] \xrightarrow[2\mathrm{H^+}]{2e,}$$

$$\mathrm{CH_2{=}CHCN} \xrightarrow{2e,\ 2H^+} \mathrm{CH_3CH_2CN} \quad \text{(e)}$$



$$\mathrm{Cl(H)C{=}C(Cl)CN} + 2e \longrightarrow \left[\mathrm{\overset{\ominus}{\ddot{C}}(H){=}C(Cl)CN} + \mathrm{Cl^-}\right] \xrightarrow{\mathrm{H^+}}$$

$$\mathrm{H_2C{=}CClCN} \xrightarrow{2e,\ 2H^+} \mathrm{CH_2{=}CHCN} \text{ etc.} \quad \text{(f)}$$

A polarogram of ~0.5 m*M* propiolonitrile is shown in Fig. 3. It can be seen that it is reduced at less negative potentials than the *cis–trans* mixture and that it would be reduced at the electrode surface as quickly as it is formed from the reduction of *trans*-2,3-AN.[27] The second wave was identified by its $E_{1/2}$ as due to the reduction of AN. Irregularities in the i_d region are due to the tendency of the material to volatilize (b.p. 44°). In 0.1 *M* $HClO_4$–30% EtOH, $E_{1/2}$ of W_1 of propiolonitrile is −1.05 v. indicating reduction *via* a *p*H-independent process.

A polarogram of methyl propiolate permitted a closer examination of the waves produced. Two waves of equal height were obtained with $E_{1/2}$ values of −1.32 and −1.80 v. W_1 represents the reduction of the compound to methyl acrylate which subsequently gives W_2 ($E_{1/2}$ ethyl acrylate = −1.82 v. in the same medium). Both waves

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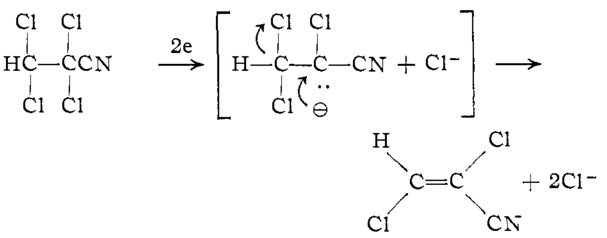
(26) Dr. J. E. Lancaster of these laboratories has obtained the nuclear magnetic resonance spectrum of "pure" 2,3-AN and observed two distinct proton peaks. The ratio of their areas corresponds to the ratio of isomers estimated polarographically; n.m.r. spectra of an enriched crystalline (see text below) phase which was estimated polarographically to contain ~94% of one isomer, showed a corresponding decrease in one of the proton peaks and again the ratio of peak areas indicated a material of ~95% purity.

(27) The authors are grateful to Dr. Stanley Wawzonek for having pointed out the possibility of the formation of propiolonitrile from one of the isomers. That both isomers would undergo the same initial attack appears to be most reasonable.

respond to changes in "h" as expected for diffusion-controlled processes. Similar results were obtained for propiolamide (Table I).

2,2,3,3-Tetrachloropropionitrile (2,2,3,3-CN).—This compound was of particular interest inasmuch as it was believed that it would be reduced exclusively to the *trans*-2,3-AN as



Reduction of *trans*-2,3-dichloroacrylonitrile should then proceed as above (e). One should, therefore, obtain a 2e wave at ~0.4 v., a 4e wave at −1.21 v. (*trans*-2,3-dichloroacrylonitrile → acrylonitrile), and a 2e wave at −1.95 v. (reductive saturation of acrylonitrile). This is precisely the polarogram obtained (Fig. 3). The wave heights observed (uncorrected for $t^{1/6}$ changes) were: $W_1 = 1.41\ \mu A.$, $W_2 = 2.04\ \mu A.$ and $W_3 = 0.92\ \mu A.$

Acknowledgment.—The authors wish to express their appreciation to members of the Stamford Laboratories staff and others for their helpful suggestions on various aspects of this investigation. We are particularly grateful to Mr. E. F. Williams for cryoscopic data, Dr. J. E. Lancaster for n.m.r. studies, and to the Infrared and Microanalytical Laboratories for their contributions.

STAMFORD, CONN.

[CONTRIBUTION FROM KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY]

The Reaction of Trimethoxyboroxine with Aromatic Grignard Reagents. A New Synthesis of Borinic Acids[1]

BY THOMAS P. POVLOCK AND WILLIAM T. LIPPINCOTT[2]

RECEIVED APRIL 23, 1958

A study of the reactions of trimethoxyboroxine with nine aromatic Grignard reagents is reported. Borinic acids, isolated as their aminoethyl esters, are obtained in yields of 21–63%. Low yields of boronic acids also are obtained. Studies of the effect of temperature, the ratio of reactants and the influence of some steric and electrical factors in the Grignard reagent on the yield of borinic acid are reported and discussed.

Arylborinic acids probably were first prepared in 1894 by Michaelis[3] who hydrolyzed diphenylchloroborane. Physical constants have been reported for only a few borinic acids.[4] Most of these have been prepared by the action of a Grignard reagent with an alkyl borate.[4c,d,e] However, Letsinger recently has revived interest in these compounds, and, in addition to developing an excellent method for the preparation of solid derivatives,[5] has prepared the first mixed borinic acid[6] and the first tricyclic borinic acid.[7] Lappert and co-workers[8a] recently have reported good yields of dibutylborinic anhydride from the reaction of a Grignard reagent with boron trifluoride. Considerably more information is available concerning boronic acids.[8b]

The reactions of trimethoxyboroxine with phenyl, *o*-, *m*- and *p*-tolyl, *p*-anisyl, *p*-biphenyl, *p*-chlorophenyl, mesityl and α-naphthyl Grignard reagents have been carried out in ether solution. The reaction proceeds at all temperatures between −60 and 35°. Products are principally borinic acids with low yields of boronic acids. The reaction may be represented by the equation

$$6\mathrm{ArMgBr} + (\mathrm{CH_3OBO})_3 \longrightarrow 3(\mathrm{Ar})_2\mathrm{B{-}O{-}MgBr} + 3\mathrm{CH_3OMgBr}$$

A study of the effect of temperature and ratio of reactants has been made with phenylmagnesium bromide. Maximum yields of borinic acids are obtained at 25° with a 9–1 mole ratio of Grignard reagent to boroxine. The yields obtained under these conditions range from 21 to 63% based on the boroxine and are, in most cases, approximately double those obtained by the reaction of a Grignard reagent with an alkyl borate.[4c,d,e] The borinic acids were isolated as their aminoethyl esters and identified by comparing the melting points, neutralization equivalents and elemental analyses of these esters with reported or calculated values. Boronic acids were identified by elemental analyses and by the melting points of their anhydrides.

Experimental

General Procedure.—Grignard reagents were prepared from the corresponding bromobenzenes by the method of Allen and Converse.[9] Trimethoxyboroxine, prepared from methyl borate and boric anhydride by the method of Goubeau and Keller,[10] was dissolved in ether and added to each Grignard reagent. The reaction of the boroxine with phenylmagnesium bromide illustrates the procedure followed.

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