[CONTRIBUTION FROM THE WALKER LABORATORY OF THE RENSSELAER POLYTECHNIC INSTITUTE]

4-Chloro-3-methyl-3-butenonitrile and Related Compounds[1]

BY ARAM MOORADIAN[1a] AND JOHN B. CLOKE

Several years ago, Stehr[2] working in this Laboratory found that sodium cyanide will react with Eastman Kodak Co. practical 1,3-dichloroisobutane,[3] better named 1,3-dichloro-2-methylpropane, $ClCH_2CH(CH_3)CH_2Cl$ (I) to give γ-chloro-β-methylbutyronitrile $ClCH_2CH(CH_3)CH_2CN$ and a higher boiling product. He also found that cuprous cyanide will react with the so-called dichloroisobutane to give three unexpected nitriles, *viz.*, a liquid chloronitrile (A) different from the γ-chloro-β-methylbutyronitrile, a solid dicyanide (B) and a liquid dicyanide (C).

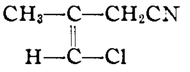
The work described in the present paper has led to the identification of the chloronitrile (A) as 4-chloro-3-methyl-3-butenonitrile, $ClCH{=}C(CH_3)CH_2CN$ (VI), exclusive of stereochemical considerations. It is now clear that this compound (VI) originated by the interaction of the cuprous chloride with 1,3-dichloro-2-methyl-1-propene, $ClCH{=}C(CH_3)CH_2Cl$, (V), an unsuspected impurity in the sharply boiling fraction of the "1,3-dichloroisobutane" which was used. These considerations led to the main synthetic work described in this paper.

1,3-Dichloro-2-methyl-1-propene (V).—Compound (V) was first described by Pogorshelski.[4] More recently, Rogers and Nelson[5] reported the preparation of a mixture consisting of 3-chloro-2-chloromethyl-1-propene, $H_2C{=}C(CH_2Cl)_2$ (XX),[6] and the *cis* and *trans* isomers of (V) by the pyrolysis of 1,2,3-trichloro-2-methylpropane (II). The same product (V) has also been prepared by the chlorination of isobutylene and methallyl chloride[7] and by the dehydration of 1,3-dichloro-2-methyl-2-propanol.[8]

In our synthesis of (V), (II) was dehydrohalogenated by the action of quinoline. The trichloro compound (II), in turn, was made by the action of chlorine and sulfuryl chloride on both 1,3-dichloro-2-methylpropane (I)[3] and methallyl chloride (III). The sulfuryl chloride methods were suggested by the related work of Kharasch and Brown.[9] In view of subsequent work by Gross,[10] it would appear that the portion of (V) used in our work was a mixture of geometrical isomers but relatively free from (XX).

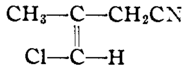
4-Chloro-3-methyl-3-butenonitrile.—The identification of the chloronitrile (A), prepared from the so-called "1,3-dichloroisobutane," as 4-chloro-3-methyl-3-butenonitrile (VI) was complicated by two special features. In the first place, the nitrile (A), although it boiled over a reasonably narrow range, gave analytical data at first which failed to correspond to any definite formula, and the same difficulty was encountered in the case of the derivatives. In order to obtain significant data, it was necessary to boil the nitrile with absolute alcohol for many hours. In the second place, the presence of the double bond was obscured at the beginning by the apparent failure of the product to react with bromine in a qualitative test. Later, however, the quantitative method of McIlhiney[11] revealed a 12.7 to 14.3% addition. The unsaturation was also supported by permanganate oxidation, which gave chloride, cyanide, carbonate and acetate ions.

The structure (VI-a) or (VI-b) for nitrile (A), suggested by the foregoing data and the fact that allylic halides react readily with cuprous cyanide, was largely confirmed by its synthesis from 1,3-dichloro-2-methyl-1-propene (V) and cuprous cyanide. However, it was also necessary to consider (VI-c) and (VI-d), possible rearrangement



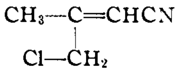
$$\begin{array}{c} CH_3{-}C{-}CH_2CN \\ \| \\ H{-}C{-}Cl \end{array}$$

(VI-a)



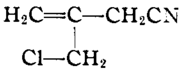
$$\begin{array}{c} CH_3{-}C{-}CH_2CN \\ \| \\ Cl{-}C{-}H \end{array}$$

(VI-b)



$$\begin{array}{c} CH_3{-}C{=}CHCN \\ | \\ Cl{-}CH_2 \end{array}$$

(VI-c)



$$\begin{array}{c} H_2C{=}C{-}CH_2CN \\ | \\ Cl{-}CH_2 \end{array}$$

(VI-d)

products, although (VI-d) might be formed from any (XX)[5,6] present in the dichloride (V). At one time, indeed, the α,β-structure (VI-c) appeared to be most likely since the reaction of the chloronitrile with sodium phenoxide gave a phenoxy derivative (XI) which gave a reasonably good yield of phenoxyacetone (XII) on ozonolysis, therefore indicating the structure (XI), namely, 4-phenoxy-3-methyl-2-butenonitrile. However, the wide boiling range of (XI) indicated a mixture of isomers, which may include *cis–trans* isomers.

---

[1] This paper is based upon the first part of a thesis presented by Aram Mooradian to the Rensselaer Polytechnic Institute in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1941.

[1a] Present address: Winthrop Chemical Co., Inc., Rensselaer, N. Y.

[2] E. Stehr, Bachelor's and Master's Theses, Rensselaer Polytechnic Institute, 1934–1935; Cloke, Stehr, Steadman and Westcott, THIS JOURNAL, **67**, 1587 (1945).

[3] 1,3-Dichloroisobutane has been discontinued by Eastman. Mr. Lee of E. K. C. has kindly informed us that the product was made by The Dow Chemical Company, Midland, Michigan.

[4] Pogorshelski, *J. Russ. Phys.-Chem. Soc.*, **36**, 1129–1184 (1904); *Chem. Zentr.*, **76**, I, 668 (1905).

[5] Rogers and Nelson, THIS JOURNAL, **58**, 1027 (1936).

[6] Mooradian and Cloke, *ibid.*, **67**, 942 (1945).

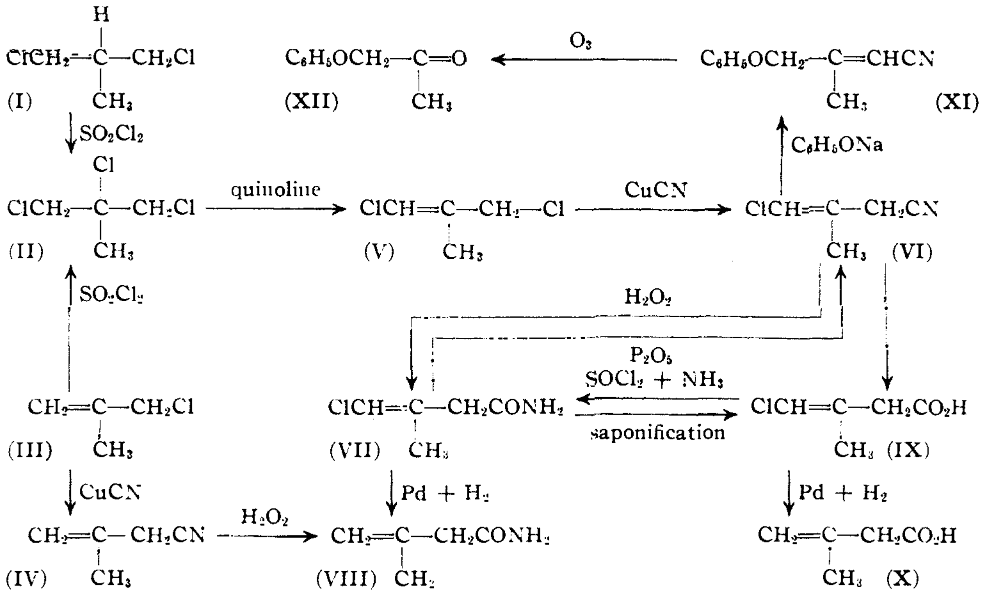
[7] Burgin, Engs, Groll and Hearne, *J. Ind. Eng. Chem.*, **31**, 1413 (1939); D'yakonov, *J. Gen. Chem. U. S. S. R.*, **10**, 402 (1940); Burgin, Hearne and Rust, *J. Ind. Eng. Chem.*, **33**, 385 (1941); Suter and Bordwell, THIS JOURNAL, **65**, 507 (1943).

[8] D'yakonov, ref. 7.

[9] Kharasch and Brown, THIS JOURNAL, **61**, 2142 (1939).

[10] P. L. Gross, B.S. Thesis, R. P. I., 1945.

[11] H. Meyer, "Lehrbuch der organisch-chemischen Methodik," Vol. I, p. 1126.



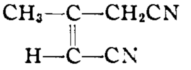
That the nitrile (VI) is primarily a β,γ-compound was indicated by a study of the related acid and amide. The 4-chloro-3-methyl-3-butenoic acid, $ClCH=C(CH_3)CH_2CO_2H$ (IX), was obtained from the nitrile (VI) by acidic saponification, preferably in an acetic acid–sulfuric acid solution; for the use of hydrochloric acid leads to the addition of some hydrohalogen acid. When the acid (IX) was reduced catalytically in the presence of palladium catalyst by the method applied by Braun[12] to chlorocrotonic acid, a liquid acid, $CH_2=C(CH_3)CH_2CO_2H$, 3-methyl-3-butenoic acid or isopropenylacetic acid (X)[12a] was obtained, whereas the isomeric α,β-acid, CH_3-$C(CH_3)=CHCO_2H$, which does not permit of *cis–trans* isomerism, melts at 70°.

The amide of 4-chloro-3-methyl-3-butenoic acid was prepared by three methods: first, directly from the chloronitrile (VI) by a modified Radziszewski method[13]; second, from the acid (IX) by the action of thionyl chloride and ammonia; and, third, by the pyrolysis of the ethyl imidoester hydrochloride (XIII) prepared from (VI)

$$\begin{aligned} &ClCH=C(CH_3)CH_2CN \longrightarrow \\ &\quad ClCH=C(CH_3)CH_2C(=NH_2Cl)OC_2H_5 \longrightarrow \\ &\qquad ClCH=C(CH_3)CH_2CONH_2 \end{aligned}$$

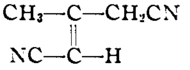
The Braun reduction[12] of the amide (VII), prepared directly from the nitrile by the modified Radziszewski method, gave the same isopropenylacetamide, $CH_2=C(CH_3)CH_2CONH_2$ (VIII), as that made directly from methallyl cyanide (IV) by the hydrogen peroxide method, therefore, indicating that the double bond was present in the β,γ-position. That no rearrangement had occurred in the formation of the chloroamide (VII) from the nitrile was indicated by the reconversion of the amide (VII) to the nitrile (VI) by the action of phosphorus pentoxide. The geometrical isomerism of (V), (VI), (VII), (IX), (XI) and (XIII) is now being studied.

The Dinitriles B and C.—As outlined in the introductory paragraph, technical 1,3-dichloroisobutane[3] when boiled with cuprous cyanide gave a solid (B) and a liquid (C) product in addition to chloronitrile (A). The solid (B), which corresponded to the formula $C_6H_6N_2$, absorbed 40% of the theoretical amount of bromine required for one ethylenic bond.[11] Various considerations pointed to two of the following formulas for products (B) and (C)



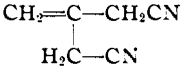
$$\begin{array}{c} CH_3-C-CH_2CN \\ \| \\ H-C-CN \end{array}$$

(XIV)



$$\begin{array}{c} CH_3-C-CH_2CN \\ \| \\ NC-C-H \end{array}$$

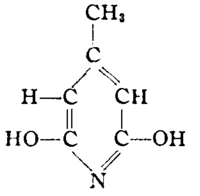
(XV)



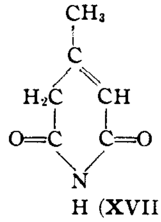
$$\begin{array}{c} CH_2=C-CH_2CN \\ | \\ H_2C-CN \end{array}$$

(XVI)

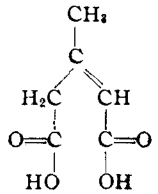
When heated with hydrochloric acid (B) gave 2,6-dihydroxy-4-methylpyridine (XVII) or the tautomer (XVIII), the β-methylglutaconic acid of m. p. 150° (the normal or *cis* acid) (XIX), and another acid of m. p. 112–115°, presumably the labile or *trans* isomer of (XIX). The identities of (XVII)–(XIX) were confirmed by mixed melting points with known samples prepared from diethyl α-cyano-β-methylglutaconate made



(XVII)



(XVIII)



(XIX)

---

(12) Braun, THIS JOURNAL, **52**, 3167 (1930).

(12a) Since this paper was submitted for publication, this acid has been described by Morton, Brown, Holden, Letsinger and Magat, *ibid.*, **67**, 2224 (1945). When cooled to 0°, they found the oil to give needles of m. p. approx. 20°.

(13) Murray and Cloke, *ibid.*, **58**, 2014 (1936).

by Rogerson and Thorpe[14] from cyanoacetic and acetoacetic esters. The somewhat impure liquid nitrile (C) gave the same hydrolysis products as (B) with hydrochloric acid. Although these data suggest that (B) may be *cis*-β-methylglutacononitrile (XIV) and (C) the *trans* isomer (XV), other experimental facts and theoretical considerations indicate that positive identification must await the outcome of further work now under way. Thus far, neither (B) nor (C) has been obtained from (V), (VI) or 3-chloro-2-chloromethyl-1-propene (XX).[6]

Experimental Part

1,2,3-Trichloro-2-methylpropane (II).—The 1,2,3-trichloro-2-methylpropane was prepared by a vapor phase and three liquid phase procedures.

Method 1.—By the use of the apparatus described by Perkin,[15] 1,3-dichloroisobutane (I)[3] was chlorin in the vapor phase. More than 200 g. of 1,2,3-trichloro-2-methylpropane (II) was prepared in this way together with some tetrahalogenated compound.

Method 2.—Following the peroxide catalyzed chlorination procedure of Kharasch and Brown,[9] 1905 g. (15 moles) of 1,3-dichloroisobutane[3] (b. p. 135–136.5°), 2025 g. (15 moles) of sulfuryl chloride and 3.6 g. of benzoyl peroxide were heated under a reflux condenser for about ten hours or until gas evolution ceased. The distillation of the mixture gave 1070 g. (73%) of the desired trichloride (II), of b. p. 160–164°, 227 g. of a material of b. p. 187–190°, 290 g. of b. p. 190–197° and 750 g. of unchanged dichloride.

Method 3.—Chlorine was passed into methallyl chloride until the theoretical amount had been absorbed, when the mixture was distilled giving a fair yield of II with a variety of other products.

Method 4.—To 362 g. (4 moles) of methallyl chloride, contained in a suitable reflux outfit, was added a 10-cc. portion of a total of 270 g. (2 moles) of sulfuryl chloride, Unless a visible reaction developed within a short time, the mixture was warmed carefully to initiate the reaction, at which time the remainder of the sulfuryl chloride was added gradually with very gentle heating. This procedure was followed in order to prevent the accumulation of reactants which may be followed by an uncontrollable reaction. Heating was continued until no more sulfur dioxide was evolved. The distillation of the mixture gave some unchanged methallyl chloride, a little material of b. p. 130–140°, and 278 g. of 1,2,3-trichloro-2-methylpropane of b. p. 159–165° (83%), as well as some higher boiling residue.

1,3-Dichloro-2-methyl-1-propene (V).—Equimolecular proportions of 1,2,3-trichloro-2-methylpropane (II) and quinoline were mixed in a Claisen–Vigreux flask, and heated for one and a half hours somewhat below the point where material would distil out of the reaction mixture. At the end of this period the temperature was raised and all material boiling below 140° was collected. The redistillation of the dried distillate gave 73–83% yields of (V) b. p. 131–132.5°. The product evolved hydrogen chloride on standing. In order to obtain an analytically pure product, dry air was passed through the liquid for one hour, when it was redistilled under diminished pressure.

Anal. Calcd. for $C_4H_6Cl_2$: Cl, 56.73. Found: Cl, 56.67, 56.71.

The compound was still liquid at −65°; $n^{20}\mathrm{D}$ 1.4744; d^{20}_{4} 1.1733; $MR\mathrm{D}$ calcd. 29.94; $MR\mathrm{D}$ found 29.90.

4-Chloro-3-methyl-3-butenonitrile (VI) from (V).—A suspension of 94 g. (1.05 moles) of cuprous cyanide in 125 g. (1 mole) of 1,3-dichloro-2-methyl-1-propene (V) was heated in a reflux apparatus from nine to ten hours, at which time a black tarry material had collected on the bottom of the flask. The distillation of the mixture gave 10 g. of unchanged dichloride (V) and 71.3 g. of the nitrile (VI) of b. p. 70–73° at 10 mm., a 67% yield based on the amount of (V) which had reacted.

In order to obtain a sample of (VI) having the correct halogen content, the foregoing product was boiled with an equal volume of absolute alcohol for seventy-two hours. The distillation of the alcohol-nitrile mixture gave a purer nitrile, which boiled as before at 70–73° under 10 mm. pressure; $n^{20}\mathrm{D}$ 1.4643; d^{20}_{4} 1.0856; $MR\mathrm{D}$ calcd. 29.46; $MR\mathrm{D}$ found 29.38.

Anal. Calcd. for C_5H_6NCl: Cl, 30.68. Found: Cl, 30.67, 30.79.

On standing, the chlorinated nitrile slowly deposits ammonium chloride.

4-Phenoxy-3-methyl-2-butenonitrile (XI).—A solution of sodium phenoxide was prepared by dissolving 5 g. of sodium in 100 cc. of absolute alcohol and then adding 22.6 g. (1.2 mole ratio) of phenol. To this was added, 23.1 g. (1 mole ratio) of the nitrile (VI), and the mixture was heated in a reflux apparatus for eighteen hours. At the end of this period the salt was collected on a filter, ether was added, and the ethereal extract washed with 5% sodium hydroxide in order to remove excess phenol. The distillation of the extract gave 26 g. (75%) of phenoxynitrile of b. p. 147–154 at 10 mm.; d^{20}_{4} 1.0498; $n^{20}\mathrm{D}$ 1.5348; $MR\mathrm{D}$ calcd. 50.51; $MR\mathrm{D}$ found, 51.35.

Anal. Calcd. for $C_{11}H_{11}ON$: N, 8.09. Found: N, 7.95, 8.04.

Ozonolysis of Phenoxynitrile.—The phenoxynitrile was dissolved in petroleum ether (b. p. 30–60°), treated with ozone[16] and decomposed with water. From the higher boiling fraction (200–220°), a semicarbazone of m. p. 167° was prepared. A mixed melting point with a sample of phenoxyacetone (m. p. 167°) showed the products to be identical.

4-Chloro-3-methyl-3-butenoic Acid (IX).—The acid was first obtained in 85–87% yields by heating 10 g. of the nitrile (VI) with 75 cc. of concentrated hydrochloric acid for two hours. The acid was extracted with ether and purified by vacuum sublimation, giving an acid of m. p. 35°.

Anal. Calcd. for $C_5H_7O_2Cl$: C, 44.60; H, 5.25; Cl, 26.36; neut. equiv., 134.52. Found: C, 44.25 (average of six runs); H, 6.09 (average of six runs); Cl, 26.81 (average of four determinations); neut. eq., 136.6 (av. of five).

The hydrolysis of the unsaturated derivatives, *e. g.*, (VI), by the use of hydrochloric acid appears to lead to the addition of some of the acid. Better analytical values were obtained on a sample of acid prepared by heating on a steam-bath for three hours a solution of 20 g. of the nitrile (VI) in a mixture of 100 cc. each of concentrated sulfuric acid, glacial acetic acid and water. The cooled mixture was diluted with water, extracted with ether and distilled giving 13 g. of acid (IX) of b. p. 113–114° at 10 mm. and m. p. 35° as above.

Anal. Calcd. for $C_5H_7O_2Cl$: Cl, 26.36. Found: Cl, 26.10, 26.18.

The acid (IX) was also prepared by the saponification of the corresponding amide (VII) which was obtained by the pyrolysis of the imido-ester hydrochloride (XIII).

The acid (IX) reacts with phenylhydrazine to give a solid derivative. In this procedure a mixture of 10 g. of (IX) and 20 cc. of freshly distilled phenylhydrazine was heated in an oil-bath to 160° at which point a vigorous reaction occurred. The product was extracted and recrystallized twice from hot water giving a compound of m. p. 147–148°.

4-Chloro-3-methyl-3-butenamide (VII).—A weight of 2.0 g. of (VI) was dissolved in 25 cc. of 10% hydrogen

---

[14] (a) Rogerson and Thorpe, *J. Chem. Soc.*, **87**, 1687 (1905); (b) Bland and Thorpe, *ibid.*, **101**, 865, 1557 (1912); (c) Kohler and Reid, THIS JOURNAL, **47**, 2803 (1925); (d) von Auwers and Ottens, *Ber.*, **57**, 441 (1924).

[15] W. H. Perkin, *J. Soc. Chem. Ind.*, **31**, 161 (1912).

[16] Sheehan and Carmody, *Ind. Eng. Chem.*, *Anal. Ed.*, **9**, 8 (1931).

peroxide and enough acetone to give a single phase, and then 4 cc. of 10% sodium hydroxide was added. The reaction mixture must be kept cool if good yields are to be obtained. After the mixture had stood overnight the acetone was allowed to evaporate and the crystals collected on a filter. Recrystallization from dilute alcohol gave a yield of 1.1 g. of amide (VII) of m. p. 158.5–159° cor.

Anal. Calcd. for C_5H_8NOCl: C, 44.95; H, 6.04; N, 10.47; Cl, 26.58. Found: C, 45.10, 45.15; H, 5.96, 6.11; N, 10.22, 10.29; Cl, 26.48, 26.64.

The same amide of m. p. 156–157° cor., was obtained by Steadman[2,17] by the pyrolysis of the imido ester hydrochloride (XIII). The amide was also prepared by the action of thionyl chloride and ammonia on the acid (IX).

The dehydration of 6 g. of the amide (VII) by the use of 4 g. of phosphorus pentoxide gave 4.4 g. of the nitrile (VI). The identity of (VI) was established by its reconversion to (VII).

Reduction of Chloro-acid (IX) to 3-Methyl-3-butenoic Acid (X).[12a]—The reduction was carried out by an extension of the same procedure applied by Braun[12] for the reduction of chlorocrotonic acid to crotonic acid.

The Catalyst.—A 6-g. portion of pure Norit was shaken in a hydrogen atmosphere with 100 cc. of water. After the Norit had been uniformly wetted, a suspension of 0.15 g. of very finely divided palladium chloride was added and the whole was shaken in the hydrogen atmosphere for four to five hours. The catalyst was then collected on a filter and washed with alcohol.

Reduction of Chloro-acid.—The reduction was carried out in a previously calibrated low pressure Adams hydrogenator at a gage pressure of 5–15 lb./sq. in. One-tenth mole of (IX) was dissolved in 0.2 mole of 1 *N* sodium hydroxide; 0.5 g. of the catalyst was suspended in this solution; the system was filled with hydrogen and the reaction flask shaken mechanically. When the pressure drop in the system corresponded to an absorption of 0.1 mole of hydrogen (within two hours), the Norit was collected on a filter and the filtrate was extracted with ether. There resulted a liquid acid b. p. 94–96° at 24 mm.; $d^{20}{}_4$ 0.9824; $n^{20}{}_D$ 1.4299; MR_D calcd. 26.36; MR_D found 26.32.

Anal. Calcd. for $C_5H_8O_2$: C, 59.99; H, 8.05. Found: C, 60.20; H, 7.90.

Reduction of Chloroamide.—A weight of 5.4 g. (0.04 mole) of (VII) was suspended in 40 cc. of 1 *N* sodium hydroxide. Enough dioxan was then added to give a clear solution. Palladium reduction of this material was carried out just as in the foregoing work. The catalyst was collected on a filter and the filtrate allowed to crystallize by evaporation at room temperature. Recrystallization of the product from benzene gave 3.8 g. of the amide of 3-methyl-3-butenoic acid (VIII), m. p. 119–120.

Anal. Calcd. for C_5H_9NO: N, 14.14. Found: N, 14.12, 14.21.

The identity of this amide was established by its preparation from 3-methyl-3-butenonitrile.[18] This nitrile was converted to the amide, m. p. 120°, by use of the same hydrogen peroxide hydrolysis applied to (VI). A mixed melting point determination gave 119–120°

4-Chloro-3-methyl-3-butenonitrile (A) from Eastman Kodak Co. 1,3-Dichloroisobutane.—Following the original procedure of Stehr,[2] 178 g. (2 moles) of dry cuprous cyanide was suspended in 1524 g. of Eastman practical 1,3-dichloroisobutane and the mixture was boiled for twenty four hours, at which time a black tarry material had collected in the bottom of the flask. The distillation of the liquid portion of the reaction mixture gave a first fraction consisting of unchanged dichloride, 60–70 g. of chlorinated nitrile of b. p. 70–73° at 10 mm. and 25–30 g. of a mixture of a solid (B) and liquid dicyanide (C), b. p. 130–145° at 10 mm. Several repetitions of the cyanide treatment on the recovered dichloride gave appreciable amounts of the three nitriles, but as the reacting impurity was used up, a longer period of heating was required in order to initiate the reaction. Furthermore, as would be expected, decreasing yields were obtained.

Ethyl Imido-4-chloro-3-methyl-3-butenoate Hydrochloride.—The imidoester was prepared by the method originally used by Steadman[17] from 17.4 g. of chloro-nitrile,[19] 7.3 g. of absolute alcohol, 50 cc. of anhydrous ether and dry hydrogen chloride. The imido ester, which was precipitated by the addition of 200 cc. of absolute ether, was recrystallized by dissolving it in warm, but not hot, anhydrous acetic acid and then adding enough anhydrous ether to precipitate the salt. The analysis of the product, after it had been dried for some time under diminished pressure, showed a high halogen content, just as in the case of other derivatives prepared from the nitrile (VI) by the use of hydrogen chloride.

Anal. Calcd. for $C_7H_{13}NOCl_2$: Cl, 35.85. Found: Cl, 37.62, 37.61.

The rate with which the imido ester salt reacts with water at 25° was determined by the general method of Stieglitz and Derby.[20] The reaction velocity constant, *k*, was calculated from the equation for a monomolecular reaction

$$k = \frac{2.303}{t_2 - t_1} \log \frac{V_1}{V_2}$$

where V_1 and V_2 represent the relative concentration of the imido ester hydrochloride at times t_1 and t_2. Table I presents a summary of the values for *k*, min.$^{-1}$ for two separate runs at 25° in 0.05 *M* aqueous solution. The average value, 0.00337 min.$^{-1}$, is of the same order of magnitude as that for ethyl imido-γ-chlorobutyrate hydrochloride, *viz.*, 0.0031 ±.[21]

TABLE I

k, MIN.$^{-1}$ FOR 0.05 *M* SOLUTION

Run 1	Run 2
0.00353	0.00347
.00318	.00335
.00356	.00348
.00326	.00333
.00317	.00336
Av. 0.00334	Av. 0.00340

Ethyl 4-Chloro-3-methyl-3-butenoate.—The imido ester hydrochloride was treated with cold water for several hours, the mixture extracted with ether and distilled, giving the ester of b. p. 71–72° at 8 mm.; $d^{20}{}_4$ 1.0792; $n^{20}{}_D$ 1.45237; MR_D calcd., 40.57; MR_D found, 41.18. As in the case of other compounds prepared from the chloronitrile by the use of hydrogen chloride, the analytical values for chlorine are high.

Anal. Calcd. for $C_7H_{11}O_2Cl$: Cl, 21.82. Found: Cl, 24.42, 24.49, 24.53.

Amide of 4-Chloro-3-methyl-3-butenoic Acid.—Following the Pinner reaction, the foregoing imido ester hydrochloride was heated at 110° for five to ten minutes to give ethyl chloride and the amide. Although the yield of amide is high and the melting point essentially correct, the excessively high halogen content of the imido ester salt is also exhibited by the amide obtained therefrom as described above.

The Dinitriles.—On standing, the higher boiling distillate (b. p. 130–145 at 10 mm.) obtained by the reaction of cuprous cyanide with Eastman 1,3-dichloroisobutane mixture deposited a crystalline product (B), leaving a liquid residue (C).

The Solid.—Redistillation of the solid (B) gave a product of b. p. 139° at 12 mm. and m. p. 52–52.5° (cor.); $d^{55}{}_4$ 0.9765; $n^{55}{}_D$ 1.4461; MR_D calcd. 28.92; MR_D found 28.90.

---

(17) T. R. Steadman, B.S. Thesis, R. P. I., 1937.

(18) M. Tamele, *et al.*, *Ind. Eng. Chem.*, **33**, 155 (1941).

(19) From the Eastman "1,3-dichloroisobutane."

(20) Stieglitz and Derby, *Am. Chem. J.*, **39**, 439 (1908); Cloke, Knowles and Anderson, THIS JOURNAL, **58**, 2547 (1936).

(21) Thompson, B. S. Thesis, R. P. I., 1930.

Anal. Calcd. for $C_6H_6N_2$: N, 26.41. Found: N, 26.10, 26.22.

Saponification of (B).—A mixture of 5 g. of the solid (B) and 35 cc. of concentrated hydrochloric acid was heated on a steam-bath for two hours and then evaporated on the steam-bath to dryness. Five to six extractions of the residue with ether removed 2.4 g. of an acidic material (D) leaving a residue (E).

The Acidic Product (D).—The crude acid (m. p. 97–116°) was recrystallized three or four times from benzene, giving *cis*-β-methylglutaconic acid of m. p. 150–151°. A mixed melting point with a sample of this acid prepared from diethyl α-cyano-β-methyl-glutaconate[14] gave no depression.

A product of m. p. 112–115° was also obtained from the acidic material (D). It is probable that this consisted in large part of *trans*-β-methyl-glutaconic acid.

The Residue (E).—When the chloride salt (E) was extracted with ammonium hydroxide, the filtered extract treated with acetic acid and cooled in a refrigerator, 2.6 g. of crystalline solid separated. Recrystallization of this from absolute alcohol gave 2,6-dihydroxy-4-methylpyridine, m. p. 192–193°. A mixed melting point with a synthetic sample[14] showed no depression.

The Liquid Residue (C).—The liquid nitrile remaining after the separation of the solid was cooled in an ether-Dry Ice-bath, but very little solid separated from the sirup. Several distillations led to the separation of more of the solid (B). Eventually a liquid product b. p. 130–132° at 12 mm. was obtained; d^{20}_4 1.0498; $n^{20}D$ 1.4726; *MR*D 29.61; d^{55}_4 0.9799; $n^{55}D$ 1.4590; *MR*D 29.48. However, the analytical results were inconclusive.

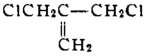
The saponification of the liquid nitrile gave the same *cis*-β-methylglutaconic acid and 2,6-dihydroxy-4-methylpyridine obtained from the solid (B).

The saponification of the dinitrile with sodium hydroxide gave a product of m. p. 208°.

Anal. Calcd. for $C_6H_8N_2O$: N, 22.59. Found: N, 22.63, 22.69.

Quantitative Behavior of Unsaturated Compounds with Bromine.—On account of the inconclusive nature of the qualitative bromine tests for unsaturation, the quantitative method of McIlhiney[10] was used on several of our compounds. In our study of the chloronitrile (VI), a weighed amount of the compound dissolved in carbon tetrachloride was transferred to an iodine flask and treated with a known excess of *M*/3 bromine solution in the same solvent. The flask was stoppered, shaken and set in a dark place for eighteen hours. Water was then poured around the stopper of the flask and the flask was cooled in order to create a decrease in internal pressure, when the stopper was slightly loosened so that water was sucked into the flask without permitting the escape of hydrogen bromide. The excess of bromine was then determined by titration with thiosulfate after the addition of potassium iodide solution. The amount of substitution was then ascertained by the addition of potassium iodate followed by a second thiosulfate titration. Table II summarizes the results.

TABLE II

Compound	Solvent	% Addition	% Substitution
$ClCH{=}C(CH_3)CH_2CN$	CCl_4	12.7 14.3	1.2 1.2
$ClCH{=}C(CH_3)CH_2Cl$	CCl_4	0 0	0 0
 $ClCH_2C(=CH_2){-}CH_2Cl$	CCl_4	2.6 2.9	0 0
$C_6H_5OCH_2C(CH_3){=}CH{-}CN$	CCl_4	83.4 80.4 80.5	38.6 38.8 37.2
Solid dinitrile (B)	$CHCl_3$	38.6 40.7	0.3 0.3
Liquid dinitrile (C)	$CHCl_3$	11.5 11.6	0.5 0.5

Summary

1. Eastman Kodak Co. practical "1,3-dichloroisobutane" reacts with cuprous cyanide to give 4-chloro-3-methyl-3-butenonitrile, which originates from 1,3-dichloro-2-methyl-1-propene, a 20–30% admixture in the Eastman product, now discontinued. A method is given for the preparation of the 1,3-dichloro-2-methyl-1-propene by the action of quinoline on 1,2,3-trichloro-2-methylpropane, whose synthesis from methallyl chloride and sulfuryl chloride is also described.

2. The structure of the 4-chloro-3-methyl-3-butenonitrile, exclusive of stereochemical considerations, has been deduced from a study of the corresponding acid and amide, whose formation from the nitrile and related imido ester salt is described.

3. The action of cuprous cyanide on the Eastman "1,3-dichloroisobutane" gives a solid and a liquid dinitrile, both of which on saponification with hydrochloric acid give *cis*-β-methylglutaconic acid and 2,6-dihydroxy-4-methylpyridine.

TROY, N. Y. RECEIVED[22] JANUARY 3, 1946

---

[22] Original manuscript received April 6, 1945.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Behavior of Nitro Alcohols toward Formic Acetic Anhydride

BY CHARLES D. HURD, STEVENS S. DRAKE AND OTIS FANCHER

The literature mentions only a few references to esterification of nitro alcohols. These esters are chiefly the acetates, propionates, butyrates and isobutyrates with no mention of formates. Pauwels[1] and Shaw[2] were the first to report in this field. They prepared 2-nitrobutyl acetate and 2-nitroisopentyl acetate by reaction of the corresponding nitro alcohols with acetic anhydride. Three 1-alkyl-2-nitroethyl acetates were synthesized, by Schmidt and Rutz,[3] alkyl representing methyl, ethyl and *n*-propyl. A few other acetates were added in 1940 by Vanderbilt and Hass and by Gloor.[4] The latest work on this subject was by Tindall[5] who reported the preparation of propionates, butyrates, and isobutyrates of twenty-five nitro alcohols. He found that the nitro primary alcohols could be esterified by interaction with the organic acid in the presence of a little sulfuric acid, whereas the nitro secondary alcohols required the use of the acid anhydride.

---

(1) Pauwels, *Rec. trav. chim.*, **17**, 27 (1898).

(2) Shaw, *ibid.*, **17**, 50 (1898).

(3) Schmidt and Rutz, *Ber.*, **61**, 2142 (1928).

(4) Vanderbilt and Hass, *Ind. Eng. Chem.*, **32**, 34 (1940); Gloor, U. S. Patent 2,185,297; *C. A.*, **34**, 2862 (1940).

(5) Tindall, *ibid.*, **33**, 65 (1941).