CXXXVI.—*The Action of Potassium Cyanide on Chloroaldehydes.*

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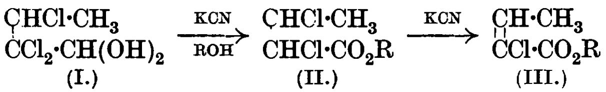
THE action of potassium cyanide on an aqueous, an alcoholic, or an ammoniacal solution of a chloroacetaldehyde or of ααβ-trichlorobutaldehyde follows in every case a similar course; heat is evolved, hydrogen cyanide is liberated, and potassium chloride is formed together with an acid, an ester, or an amide containing one halogen atom less than the parent aldehyde. The reaction may be represented thus:

$$:\mathrm{CCl{\cdot}CHO} \xrightarrow[\mathrm{H{\cdot}OH(OR)(NH_2)}]{\mathrm{KCN}} :\mathrm{CH{\cdot}CO{\cdot}OH(OR)(NH_2)} + \mathrm{KCl} + \mathrm{HCN}.$$

Wallach (*Ber.*, 1873, **6**, 114) found that in ethyl-alcoholic solution ethyl dichloroacetate was yielded by chloral and potassium cyanide. Ethyl monochloroacetate is similarly formed from dichloroacetaldehyde, and ethyl acetate from monochloroacetaldehyde.

The first product of the action of potassium cyanide on an alcoholic solution of butyl chloral hydrate (I) is an alkyl αβ-dichlorobutyrate (II) which loses hydrogen chloride so readily that, unless the reaction is carefully controlled, only an alkyl α-chlorocrotonate (III) is obtained (compare Wallach and Böhringer, *Annalen*, 1874, **173**, 301):

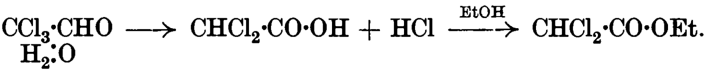


$$\begin{array}{c}CHCl{\cdot}CH_3\\ |\\ CCl_2{\cdot}CH(OH)_2\\ \text{(I.)}\end{array}\xrightarrow[\text{ROH}]{\text{KCN}}\begin{array}{c}CHCl{\cdot}CH_3\\ |\\ CHCl{\cdot}CO_2R\\ \text{(II.)}\end{array}\xrightarrow{\text{KCN}}\begin{array}{c}CH{\cdot}CH_3\\ \|\\ CCl{\cdot}CO_2R\\ \text{(III.)}\end{array}$$

α-Chlorocrotonic acid, $CH_3{\cdot}CH{:}CCl{\cdot}CO_2H$, or α-chlorocrotonamide, $CH_3{\cdot}CH{:}CCl{\cdot}CO{\cdot}NH_2$, is similarly formed by the action of potassium cyanide upon an aqueous or ammoniacal solution of butyl chloral hydrate, but in these cases the loss of hydrogen chloride from the intermediate αβ-dichlorobutyric acid or amide is too rapid to permit of its isolation.

Since potassium cyanide acts similarly upon all the aliphatic chloroaldehydes studied, it seems certain that the nature of the reaction is the same in every case.

No satisfactory explanation of it has, however, yet been put forward. Wallach (*Ber.*, 1877, **10**, 2124), after many years work on the reaction, adopted a suggestion made by Victor Meyer (*ibid.*, p. 1740) that the process was one of simultaneous oxidation and reduction of the chloral molecule catalysed by hydrogen cyanide, the dichloroacetic acid being subsequently esterified when the reaction was carried out in alcohol:



$$\begin{array}{c}CCl_3{\cdot}CHO\\ H_2{:}O\end{array}\longrightarrow CHCl_2{\cdot}CO{\cdot}OH + HCl \xrightarrow{\text{EtOH}} CHCl_2{\cdot}CO{\cdot}OEt.$$

This conclusion may be disregarded, since it is not chloral but chloral alcoholate that is concerned, and since the rate of esterification of dichloroacetic acid is comparatively slow.

Another explanation, put forward by Kötz (*J. pr. Chem.*, 1913, **88**, 531), assumes that the formation of chloral cyanohydrin is an essential part of the reaction. The strongest argument in favour of this assumption is the fact that reactions of the type under consideration are brought about only by alkaline cyanides.* Other

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* Mercury cyanide crystallises unchanged after heating for several hours with an alcoholic solution of chloral hydrate, no ethyl dichloroacetate being formed.

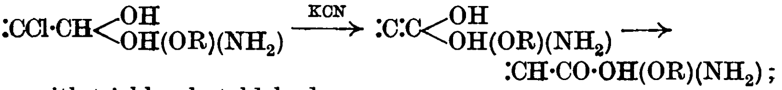
similarly weak alkaline reagents simply hydrolyse the chloral molecule to chloroform and a formate.

On the other hand, many facts seem to indicate that the formation of a cyanohydrin is not a necessary step in the reaction but a secondary reaction due to the liberation of hydrogen cyanide in the primary one. For example, the action of potassium cyanide upon an alcoholic solution of chloral alcoholate is as violent as, or even more violent than, its action upon a similar solution of chloral cyanohydrin, and all conditions which favour the formation of cyanohydrin in the reaction hinder rather than promote the formation of an alkyl dichloroacetate. Again, the action of potassium cyanide upon the chloroaldehyde-ammonias in presence of excess of ammonia follows a course closely resembling that between potassium cyanide and the alcoholates, although cyanohydrin formation under the conditions appears unlikely. For example, the action of potassium cyanide upon chloral-ammonia, dissolved in alcohol saturated with ammonia, yields dichloroacetamide thus :

$$\mathrm{CCl_3{\cdot}CH(OH){\cdot}NH_2 \xrightarrow[NH_3]{KCN} CHCl_2{\cdot}CO{\cdot}NH_2 + KCl + NH_4CN.}$$

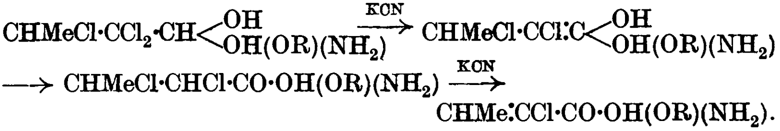
α-Chlorocrotonamide is similarly formed from butyl chloral-ammonia, the intermediate αβ-dichlorobutyramide, in presence of excess of ammonia, losing hydrogen chloride too rapidly to permit of its isolation.

In view of the unlikelihood of cyanohydrin formation in such cases, it seems more probable that the potassium cyanide first causes the elimination of hydrogen chloride from the aldehyde-hydrate, aldehyde-alcoholate, or aldehyde-ammonia, probably by the intermediate replacement of a chlorine atom by a cyanogen group, followed by a splitting off of the very slightly ionisable hydrogen cyanide, and leaves an unsaturated compound which by a familiar intramolecular rearrangement gives an acid, an ester, or an acid amide, thus :



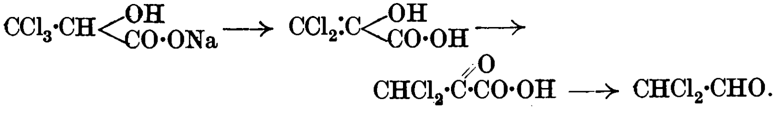
$$\mathrm{{:}CCl{\cdot}CH{<}\begin{matrix}OH\\OH(OR)(NH_2)\end{matrix} \xrightarrow{KCN} {:}C{:}C{<}\begin{matrix}OH\\OH(OR)(NH_2)\end{matrix} \longrightarrow {:}CH{\cdot}CO{\cdot}OH(OR)(NH_2)\,;}$$

or with trichlorobutaldehyde,



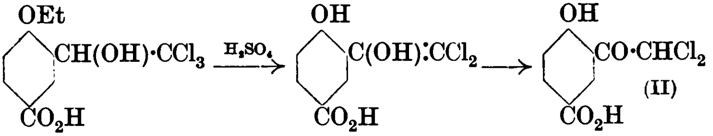
$$\mathrm{CHMeCl{\cdot}CCl_2{\cdot}CH{<}\begin{matrix}OH\\OH(OR)(NH_2)\end{matrix} \xrightarrow{KCN} CHMeCl{\cdot}CCl{:}C{<}\begin{matrix}OH\\OH(OR)(NH_2)\end{matrix}}$$
$$\mathrm{\longrightarrow CHMeCl{\cdot}CHCl{\cdot}CO{\cdot}OH(OR)(NH_2) \xrightarrow{KCN} CHMe{:}CCl{\cdot}CO{\cdot}OH(OR)(NH_2).}$$

There are certain analogous reactions which, although they involve a similar elimination of hydrogen chloride followed by intramolecular rearrangement, can take place in the absence of an alkaline cyanide. For example, when an aqueous solution of the sodium salt of a chlorolactic acid is boiled, carbon dioxide is evolved and sodium chloride is formed together with an aldehyde containing one chlorine atom less than the original acid (compare Reisse, *Annalen*, 1890, **257**, 331), the reaction without doubt taking the course



$$CCl_3\cdot CH{<}^{OH}_{CO\cdot ONa} \longrightarrow CCl_2{:}C{<}^{OH}_{CO\cdot OH} \longrightarrow$$
$$CHCl_2\cdot \overset{O}{C}\cdot CO\cdot OH \longrightarrow CHCl_2\cdot CHO.$$

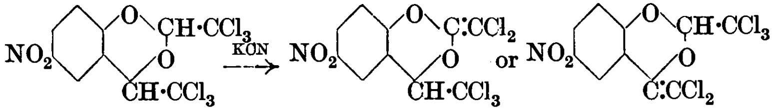
Again, ωω-dichloro-2-hydroxyacetophenone-5-carboxylic acid (II) is formed when 5-carboxy-2-ethoxy-1-βββ-trichloro-α-hydroxyethylbenzene (I) is heated for a short time with concentrated sulphuric acid (Chattaway and Calvet, J., 1927, 691):



(I.)

(II)

The facility with which potassium cyanide can promote the elimination of hydrogen chloride is shown by its action on 6-nitro-2 : 4-bis(trichloromethyl)-1 : 3-benzdioxin (III), whereby one molecule of hydrogen chloride is removed, giving 6-*nitro*-2(or 4)-*dichloromethylene*-4(or 2)-*trichloromethyl*-1 : 3-*benzdioxin* (IV):



(III.)

(IV.)

A similar elimination of hydrogen chloride from the second $>CH\cdot CCl_3$ group does not occur.

Other cases in which potassium cyanide fails to replace chlorine by cyanogen are well known. For example, potassium cyanide has little or no action upon monochloroacetal, $CH_2Cl\cdot CH(OEt)_2$ (compare Hesse, *Ber.*, 1897, **30**, 1441), αβββ-tetrachlorodiethyl ether, $CCl_3\cdot CHCl\cdot OEt$ (compare Busch, *Ber.*, 1878, **11**, 447), parachloral [2 : 4 : 6-tri(trichloromethyl)*cyclo*-1 : 3 : 5-trioxa-2 : 4 : 6-trimethylene] (Chattaway and Kellett, J., 1928, 2712), nor, as we have found, upon dichloroacetal, $CHCl_2\cdot CH(OEt)_2$, and 5-carboxy-2-methoxy-1-βββ-trichloro-α-hydroxyethylbenzene.

EXPERIMENTAL.

The Action of Potassium Cyanide on Chloral Alcoholates.—The action of potassium cyanide on solutions of chloral alcoholates in the corresponding alcohols is completed as rapidly as the reactants can be brought together, the time taken being apparently limited only by the violence of the reaction. The yields of the corresponding alkyl dichloroacetates are very large.

A solution of anhydrous chloral (1 mol.) in rather more than its own weight of the required alcohol was added as rapidly as possible to a suspension of finely powdered potassium cyanide (1·2 mols.) in the same alcohol, loss of alcohol by boiling being prevented by suitable cooling. After about 1 minute, water was added to dissolve the excess of potassium cyanide together with the potassium chloride formed. The ester, which then separated as a heavy lower layer, was washed repeatedly, first with a dilute solution of potassium hydroxide and then with water, freed from any traces of cyanohydrin by steam distillation, dried over calcium chloride, and fractionated. The following results were obtained :—Methyl dichloroacetate, b. p. 143° (yield, 84%); ethyl dichloroacetate, b. p. 157° (yield, 88%).

n-*Propyl dichloroacetate*, b. p. 176° (yield, 70%) (Found : Cl, 41·4. $C_5H_8O_2Cl_2$ requires Cl, 41·5%), and *allyl dichloroacetate*, b. p. 175·5° (yield, 64%) (Found : Cl, 42·0. $C_5H_6O_2Cl_2$ requires Cl, 42·0%), were similarly prepared, a solution of chloral hydrate in the required alcohol being used.

When potassium cyanide is allowed to act upon an alcoholic solution of chloral cyanohydrin, or when the reaction between potassium cyanide and chloral alcoholate is carried out under conditions which favour its formation (such, for example, as the slow addition of the cyanide to the solution of the chloral alcoholate at a fairly low temperature), the yield of alkyl dichloroacetate is greatly reduced. For example, when potassium cyanide (1 mol.) was added in small portions to a well-stirred solution of chloral ethyl alcoholate (1 mol.) in ethyl alcohol at such a rate that the temperature was kept at 25—30°, only a 43% yield of ethyl dichloroacetate was obtained, and much chloral cyanohydrin was isolated from the higher-boiling fractions of the product.

The action of potassium cyanide upon a solution of chloral cyanohydrin in ethyl alcohol, though very vigorous and accompanied by a considerable evolution of heat, was found not to commence immediately, was much less violent than when chloral alcoholate was used, and gave a smaller yield of ethyl dichloroacetate (61%).

The Action of Potassium Cyanide upon Dichloroacetaldehyde Ethyl Alcoholate : Formation of Ethyl Monochloroacetate.—64 G. of dichloroacetaldehyde ethyl alcoholate (1 mol.) were added as rapidly as practicable to 29 g. of finely powdered potassium cyanide (1 mol.)

suspended in 40 g. of ethyl alcohol at 20°. After 5 minutes, water was added to the red product, and the heavy lower layer which separated was washed with a dilute solution of potassium carbonate and with water, dried rapidly over calcium chloride, and fractionated, giving 19·9 g. of ethyl chloroacetate, b. p. 143·5—145° (yield, 38%). This was further identified by conversion into chloroacetamide, m. p. 117° (Found : Cl, 37·85. Calc. for C_2H_4ONCl : Cl, 38·0%).

The Action of Potassium Cyanide on Monochloroacetaldehyde.—(1) *In alcoholic solution.* 7 G. of powdered potassium cyanide (1 mol.) were added to a solution of 8 g. of monochloroacetaldehyde (1 mol.) in 30 c.c. of ethyl alcohol. A brisk reaction commenced at once, hydrogen cyanide was evolved and the temperature rose to the boiling point of the alcohol while the solution became deep red. After 5 minutes, water was added, and the oily liquid produced was washed several times with a strong solution of calcium chloride (50 g. in 50 c.c. of water) to remove alcohol, dried, and fractionated; ethyl acetate, identified by its smell and boiling point, 76—79°, was obtained, the yield being not more than 10% of the theoretical owing to loss in the process of isolation.

(2) *In aqueous solution.* 8·5 G. of potassium cyanide (1 mol.) were added to a solution of 10 g. of monochloroacetaldehyde in 50 c.c. of water. The temperature rose somewhat, but as there was no marked action the solution was boiled for 2 hours under reflux; it was then made strongly alkaline with potassium hydroxide and evaporated to dryness. The dry powdered mixture of potassium salts was distilled with concentrated sulphuric acid, acetic acid being obtained, b. p. 115—117° after several fractionations (yield, not more than 10%).

Owing to the great difficulty of preparing monochloroacetaldehyde larger quantities than the above could not be used.

The Action of Potassium Cyanide on Butyl Chloral Hydrate in Alcoholic Solution: Isolation of Ethyl αβ-Dichlorobutyrate, Ethyl α-Chlorocrotonate, and Butyl Chloral Cyanohydrin.—Unless the violence of the reaction is moderated when potassium cyanide is added to an alcoholic solution of butyl chloral hydrate, the only ester which is found in the product is ethyl α-chlorocrotonate (compare Wallach, *Annalen*, 1874, **173**, 301). When, however, the temperature is not allowed to rise during the reaction, ethyl αβ-dichlorobutyrate, which is the first product of the action, may be isolated.

11 G. of finely powdered potassium cyanide (1 mol.) were added in small portions to a mechanically stirred solution of 32·5 g. of butyl chloral hydrate (1 mol.) in 150 c.c. of ethyl alcohol at such a rate that the temperature did not rise above 15° (2 hours); the

solution became pale yellow and potassium chloride (11·9 g. Theoretical for 1 mol. KCl, 12·4 g.) separated. Strong brine was added to the filtrate until two layers formed and, after the whole had been made slightly acid with hydrochloric acid, the lower layer was separated, dried rapidly over calcium chloride, and distilled under reduced pressure (15 mm.) until a white solid which condensed in the receiver ceased to come over.

By repeated fractional distillation under reduced pressure, the liquid portion of the distillate was separated into ethyl α-chlorocrotonate (7 g.), b. p. 85°/35 mm. and 176°/760 mm. (Found: Cl, 23·9. Calc.: Cl, 23·9%), and ethyl αβ-dichlorobutyrate (4 g.), b. p. 97°/35 mm. and 180—200°/760 mm. with marked decomposition (compare Michael and Brown, *Amer. Chem. J.*, 1887, **9**, 274) (Found: Cl, 38·1. Calc.: Cl, 38·3%).

In the fractionation of the distillate, after distillation of the two esters a white solid residue of *butyl chloral cyanohydrin* was left. This crystallised from boiling water, in which it was moderately easily soluble, in colourless, shining, unctuous plates, m. p. 101—102°, and on prolonged boiling with concentrated hydrochloric acid was hydrolysed to ββγ-trichloro-α-hydroxyvaleric acid, m. p. 140·5° (compare Pinner and Klein, *Ber.*, 1878, **11**, 1488) (Found: Cl, 52·5; N, 7·1. $C_5H_6ONCl_3$ requires Cl, 52·5; N, 7·0%).

Ethyl αβ-dichlorobutyrate loses hydrogen chloride with great ease even at the ordinary temperature, giving ethyl α-chlorocrotonate. A specimen which had been kept for 2 days in a stoppered bottle gave Cl, 36·5%.

This elimination of hydrogen chloride is greatly accelerated by the presence of potassium cyanide as shown by the following experiment, which explains why ethyl αβ-dichlorobutyrate is not normally found among the products of the action of potassium cyanide upon an alcoholic solution of butyl chloral hydrate. To 5 g. of ethyl αβ-dichlorobutyrate (1 mol.), diluted with 20 c.c. of alcohol, were added 1·7 g. of powdered potassium cyanide (1 mol.). After 10 minutes, the reaction mixture was poured into water and the ester was washed with water, dried, and fractionated, 3 g. of ethyl α-chlorocrotonate, b. p. 176°, being obtained (yield, 75%).

In carrying out the reaction between potassium cyanide and butyl chloral hydrate it is not practicable to avoid the formation of cyanohydrin by adding the butyl chloral alcoholate to the cyanide, since the alkyl α-chlorocrotonate produced by the action of potassium cyanide on the alkyl αβ-dichlorobutyrate first formed, itself reacts with potassium cyanide to give viscous yellow products of indefinite composition (compare Claus, *Annalen*, 1878, **191**, 33).

For this reason it is essential to avoid an excess of potassium cyanide; by using, however, the correct amount of cyanide, a very satisfactory yield of any alkyl α-chlorocrotonate can be obtained provided that the temperature is not allowed to rise above 20°.

19 G. of finely powdered potassium cyanide (2 mols.) were added to a mechanically stirred solution of 29 g. of butyl chloral hydrate (1 mol.) in 150 c.c. of ethyl alcohol at such a rate that the temperature did not rise above 15° (3—4 hours). Hydrogen cyanide was evolved freely, especially towards the end of the reaction, and on filtration 21·5 g. of potassium chloride were obtained (theoretical for 2 mols. KCl, 21·7 g.). The filtrate was diluted with water, and the ethyl α-chlorocrotonate distilled in steam, dried over calcium chloride, and fractionated, 22 g., b. p. 176°, being obtained (yield, 90%) (Found : Cl, 23·9. Calc. : Cl, 23·9%).

Steam distillation and subsequent fractionation under reduced pressure are necessary to remove traces of cyanohydrin with which the alkyl α-chlorocrotonates, especially the higher-boiling ones, are contaminated. Several esters were prepared thus : Methyl α-chlorocrotonate, b. p. 161° (yield, 85%) (Found : Cl, 26·4. Calc. : Cl, 26·4%), *n*-propyl α-chlorocrotonate, b. p. 191° (yield, 67%) (Found : Cl, 22·0. Calc. : Cl, 21·8%), *n*-butyl α-chlorocrotonate, b. p. 205° (yield, 70%) (Found : Cl, 20·2. Calc. : Cl, 20·5%).

When potassium cyanide is added to an alcoholic solution of butyl chloral hydrate the hydrogen cyanide liberated reacts with the unchanged aldehyde, giving butyl chloral cyanohydrin, and by stopping the reaction when half the theoretical amount of cyanide has been added some 50% of the original aldehyde can be isolated as cyanohydrin. On account of its sparing solubility, this actually separates when the reaction is carried out in aqueous solution (*q.v.*).

Butyl chloral cyanohydrin will itself react with potassium cyanide in alcoholic solution, giving ultimately an alkyl α-chlorocrotonate. 9 G. of powdered potassium cyanide (2 mols.) were added in small portions to a mechanically stirred solution of 14 g. of butyl chloral cyanohydrin (1 mol.) in 100 c.c. of ethyl alcohol at such a rate that the temperature did not rise above 15° (2½ hours). 10·1 G. of potassium chloride (theoretical for 2 mols. of KCl, 10·3 g.) and ethyl α-chlorocrotonate, which was isolated and purified in the usual way (8·5 g., b. p. 176°; yield, 85%), were obtained.

The Action of Potassium Cyanide upon Butyl Chloral Hydrate in Aqueous Solution : Formation of α-Chlorocrotonic Acid and Butyl Chloral Cyanohydrin.—13·5 G. of potassium cyanide (2 mols.) were added to a solution of 19·5 g. of butyl chloral hydrate (1 mol.) in 500 c.c. of water at 40°. The temperature rose at once to 47° as the cyanide dissolved, and butyl chloral cyanohydrin separated as a heavy, colourless, oily liquid. After warming at 50° for a few minutes, the whole was cooled to 0° and the cyanohydrin extracted with chloroform (obtained, 4·1 g.; m. p. 101—102°). The remaining solution was made strongly acid with sulphuric acid, and the α-chlorocrotonic acid (6·2 g.) extracted with ether; it crystallised from low-boiling petroleum in long, slender, colourless needles, m. p. 98·5—99° (Found: Cl, 39·8. Calc.: Cl, 39·8%).

The Action of Potassium Cyanide on Chloral-ammonia: Formation of Dichloroacetamide.—13 G. of powdered potassium cyanide (1 mol.) were added to 33 g. of chloral-ammonia (1 mol.) suspended in 50 c.c. of aqueous ammonia (*d* 0·880) at 15°. A vigorous reaction started almost at once and the temperature rose rapidly to 70°; a clear solution was then obtained from which, on cooling, dichloroacetamide, m. p. 98·5—99·0°, separated (yield, 24 g.; 93%) (Found: Cl, 55·5. Calc.: Cl, 55·5%).

A similar vigorous reaction ensued when 50 c.c. of aqueous ammonia (*d* 0·880) were added to an intimate mixture of 13 g. of potassium cyanide (1 mol.) and 33·5 g. of chloral hydrate (1 mol.). The yield of dichloroacetamide was, however, only 50% of the theoretical, part of the chloral hydrate being converted into chloroform and formate by the ammonia.

The Action of Potassium Cyanide on Butyl Chloral-ammonia: Formation of α-Chlorocrotonamide.—19·5 G. of butyl chloral hydrate (1 mol.), when added to 50 c.c. of aqueous ammonia (*d* 0·880), immediately dissolved, giving a clear solution from which butyl chloral-ammonia (m. p. 62°) separated in a few seconds as a heavy colourless liquid. The whole was at once cooled in a freezing mixture and saturated with dry ammonia gas; it was then warmed to 10° and 14 g. of powdered potassium cyanide (1 mol.) were added. The temperature rose to 35° and a brisk reaction commenced which was completed by heating to 70°. On cooling, α-chlorocrotonamide (11·2 g.), m. p. 113·5°, separated (yield, 93%) (Found: Cl, 29·5; N, 11·7. Calc.: Cl, 29·7; N, 11·7%).

Potassium cyanide has little or no action upon dichloroacetal. 20 G. of dichloroacetal (1 mol.) were mixed with 7 g. of potassium cyanide (1 mol.). No action appeared to take place even after 24 hours, so the mixture was heated at 120° for 2 hours. The colour of the acetal darkened, but on filtration and fractionation 18 g. of dichloroacetal, b. p. 183°, were recovered unchanged.

2 G. of 5-carboxy-2-methoxy-1-βββ-trichloro-α-hydroxyethylbenzene were dissolved in 30 c.c. of alcohol and boiled with 1·2 g. of potassium cyanide (3 mols. + excess) for 2½ hours. No reaction appeared to take place and from the diluted acidified mixture the

original acid, m. p. 198° (from alcohol), separated unchanged as a granular precipitate.

The Action of Potassium Cyanide on Chloral Diacetate.—When potassium cyanide was added to chloral diacetate, $CCl_3{\cdot}CH(OAc)_2$, a violent action occurred and a black coked solid was formed from which nothing could be isolated.

15·5 G. of powdered potassium cyanide (1·5 mols.) were added in small portions to 40 g. of chloral diacetate (1 mol.) diluted with 60 g. of ethyl alcohol. A violent reaction ensued at each addition of the cyanide, hydrogen cyanide was evolved, and the temperature rose rapidly to the boiling point of the alcohol. After 5 minutes, water was added to the reaction product; the mixture of ethyl acetate and ethyl dichloroacetate produced was washed with water, dried, and fractionated, 20 g. of ethyl dichloroacetate being obtained (yield, 80%). A similar experiment in methyl-alcoholic solution gave 17·5 g. of methyl dichloroacetate (yield, 76%).

The Action of Potassium Cyanide on Butyl Chloral Hydrate in Benzene.—In 1874, Wallach found that a substance $C_7H_4O_3NCl_9$, m. p. 123°, was formed by the action of potassium cyanide under certain conditions upon a solution of chloral hydrate in benzene: to this substance a heterocyclic structure has been assigned by Crowther, McCombie, and Reade (J., 1914, **105**, 933). A similar *compound*, probably possessing the structure 6-keto-2 : 4 : 7-tri-(ααβ-trichloropropyl)*cyclo*-2 : 4 : 6 : 7-tetramethylene-1 : 3 : 5-dioxaimine,

$$O\begin{matrix}\diagup CH(CCl_2{\cdot}CHMeCl){\cdot}CO{\cdot}NH\diagdown\\ \diagdown CH(CCl_2{\cdot}CHMeCl)\text{———}O\diagup\end{matrix}CH{\cdot}CCl_2{\cdot}CHMeCl$$

is yielded by butyl chloral hydrate.

7·8 G. of powdered potassium cyanide (1·2 mols.) were added to a solution of 58 g. of butyl chloral hydrate (3 mols.) in 150 c.c. of benzene, and the mixture kept at the ordinary temperature with occasional shaking for 10 days. The solution darkened in colour but no visible reaction occurred, so the whole was filtered. The benzene was allowed to evaporate slowly from the filtrate. The viscous residue was dissolved in a little cold ligroin, in which it was very easily soluble; a bulky white solid slowly separated. This, after being washed with a little ligroin, crystallised from boiling light petroleum (b. p. 80—100°), in which it was moderately easily soluble, as a friable, colourless, microcrystalline powder, m. p. 99·5—100·5° (Found: C, 28·2; H, 2·9; N, 2·5; Cl, 57·7; *M*, cryoscopic in benzene, 548, 545. $C_{13}H_{16}O_3NCl_9$ requires C, 28·6; H, 2·8; N, 2·6; Cl, 57·7%; *M*, 553).

When solid butyl chloral hydrate (3 mols.) is added to a saturated aqueous solution of potassium cyanide (1 mol.) at 0°, the clear solution first formed soon deposits a colourless oily liquid which later solidifies. The product appears to be a mixture of the above substance with butyl chloral cyanohydrin, but a complete separation could not be effected.

The Action of Potassium Cyanide upon 6-*Nitro*-2 : 4-*bis*(*trichloromethyl*)-1 : 3-*benzdioxin : Formation of* 6-*Nitro*-2(or 4)-*trichloromethyl*-4(or 2)-*dichloromethylene*-1 : 3-*benzdioxin*.—6·5 G. of powdered potassium cyanide were added to a solution of 41 g. of 6-nitro-2 : 4-bis(trichloromethyl)-1 : 3-benzdioxin in 100 c.c. of ethyl alcohol. On heating, hydrogen cyanide was evolved. After refluxing on a water-bath for ½ hour to complete the reaction, the alcohol was distilled off in a current of steam; 6-*nitro*-2(or 4)-*trichloromethyl*-4(or 2)-*dichloromethylene*-1 : 3-*benzdioxin* was left suspended in the water as a crystalline residue. After being washed with water, it crystallised from boiling alcohol, in which it was easily soluble, in colourless, elongated, rhombic prisms, m. p. 136·5° (Found : Cl, 46·7. $C_{10}H_4O_4NCl_5$ requires Cl, 46·7%).

The substance does not readily form an addition compound with bromine.

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[*Received, February 23rd*, 1929.]