[Contribution from the Research Division, Stamford Research Laboratories, American Cyanamid Company]

REACTIONS OF CYANOGEN CHLORIDE. II. AMINES FROM CYANOGEN CHLORIDE AND OLEFINS

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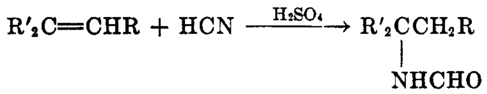
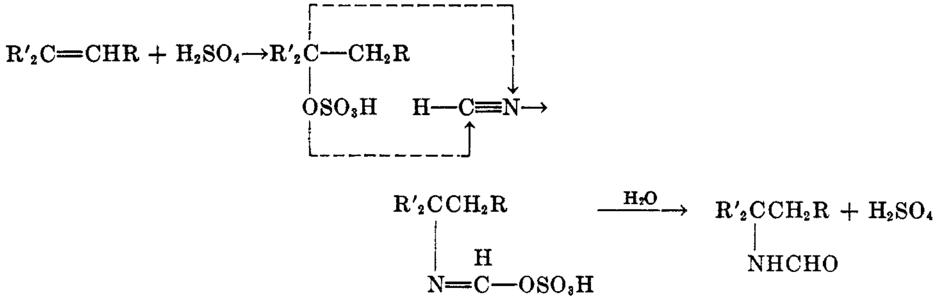
This paper reports on the reaction of cyanogen chloride with olefins in the presence of acidic catalysts. Hydrogen cyanide will add to certain olefinic double bonds in the presence of aluminum chloride and hydrogen chloride resulting in the formation of N-formyl substituted amines (1). This reaction is the basis for a process to convert olefins to the formyl derivatives of the corresponding amines using various acid catalysts with hydrogen cyanide (2). More recently the reaction of nitriles or HCN with certain types of olefins (or the alcohols from which these olefins were obtained *in situ*) in the presence of concentrated sulfuric acid (3–8) and other acidic catalysts (9), was established as a general reaction to give, in the case where HCN is used, the formyl derivative of the amine:



$$R'_2C{=}CHR + HCN \xrightarrow{H_2SO_4} \underset{NHCHO}{R'_2CCH_2R}$$

The mechanism proposed for this reaction was the addition of the elements of sulfuric acid to the olefin to give an alkyl hydrogen sulfate. This intermediate was postulated as adding to the hydrogen cyanide generated in the solution by the addition of acid to sodium cyanide already present. The latter intermediate was hydrolyzed by water to the N-formylamine. The mechanism was written (4) as follows:



$$R'_2C{=}CHR + H_2SO_4 \rightarrow \underset{OSO_3H}{R'_2C}{-}CH_2R \quad H{-}C{\equiv}N \rightarrow$$

$$\underset{N{=}\overset{H}{C}{-}OSO_3H}{R'_2CCH_2R} \xrightarrow{H_2O} \underset{NHCHO}{R'_2CCH_2R} + H_2SO_4$$

In every case the nitrogen atom was found to have become attached in accordance with Markownikoff's rule. Hydrolysis of the N-formyl group is required in order to obtain the free amine.

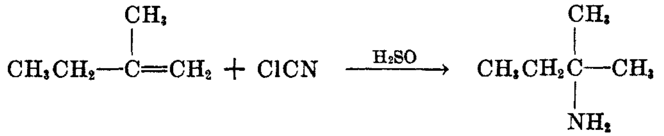
The olefin-sulfuric acid reaction has now been applied to cyanogen chloride. Cyanogen chloride was found to react with olefins containing internal or substituted terminal double bonds in the presence of sulfuric acid or other strong acid catalysts giving 20–30% yields of the corresponding amines, according to Markownikoff's rule. Thus the amine is obtained directly without requiring the

TABLE I

ACID-CATALYZED REACTION OF CYANOGEN CHLORIDE AND OLEFINS
Reaction Temperature 10–15°; Completed at 50°
Catalyst, 96% H_2SO_4

Run No.	ClCN, Moles	Catalyst, Moles	Olefin, 0.4 mole	Major Product	Yield, %	Boiling Point, °C.
3	0.4	0.4	Cyclohexene	Cyclohexylamine	14	132–135
23	.4	.5	Diisobutylene	N-*tert*-Octylamine	26.5	137–138
25	.5	.4	Butene-2	*sec*-Butylamine	22.7	62–63
28	.5	.4	2-Methylbutene-1	*tert*-Amylamine	32.8	77–78
16	.4	.4	Propylene polymer C = 9.8	Amine (primary)	27	162–167
13	.4	.4	Dodecene-1	Dodecanol-2	93	250
14	.4	.4	Octene-1	Octanol-2	91	177–178
6	.4	.4	Toluene	Starting material	91	110–111

subsequent hydrolysis step necessary when HCN is used. 2-Methylbutene-1 is an example.



$$CH_3CH_2-\overset{\displaystyle CH_3}{\overset{|}{C}}=CH_2 + ClCN \xrightarrow{H_2SO} CH_3CH_2\underset{\displaystyle NH_2}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_3$$

When early work demonstrated the course of the reaction, efforts of the investigation were for the most part devoted to raising the yields of amines obtained. The results of principal runs are listed in Table I. A brief preliminary investigation indicated that 96% sulfuric acid, later shown to be the most efficient catalyst for the reaction, causes cyanogen chloride to decompose, thus limiting ultimate yields.

The reaction seems to be applicable only to olefins of a limited structure. Aromatic double bonds did not react (Run 6). Unsubstituted terminal double bonds (octene-1, dodecene-1) did not form amines but instead added water to yield the corresponding 2-alcohols. Non-terminal double bonds react (butene-2, cyclohexene). Use of compounds containing non-terminal substituted double bonds (diisobutylene, propylene polymers) results in introduction of the nitrogen atom according to Markownikoff's rule. Terminal double bonds which contain a substituent in the 2-position (2-methylbutene-1) react to give a comparatively fair yield of N-*tert*-carbinamine.

Apparently the efficiency of the acid catalyst is a function of its strength so long as it is not too strong an oxidizing agent. As shown in Table II, 85% and 96% H_2SO_4 gave approximately the same yields of amine (Runs 3 and 7), but 100% H_2SO_4 (Run 9) was too strong an oxidizing agent and formed mainly tars, while 75% H_2SO_4 was too weak an acid (Run 10) to give a good yield of amine. Phosphoric acid (85%, Run 5) was too weak to cause any amine formation but difluorophosphoric (Run 24) gave a comparatively good yield of amine. Concentrated hydrochloric acid effected no reaction, while chlorosulfonic, fluorosulfonic,

TABLE II

EFFECT OF CATALYSTS

Run No.	Catalyst	Amine, % Yield
	Cyclohexene	
10	75% H_2SO_4	4.7
3	85% H_2SO_4	16.5
7	96% H_2SO_4	14.0
9	100% H_2SO_4	6.5
5	85% H_3PO_4	None
	Diisobutylene	
24	HF_2PO_2	19.1
26	35% HCl	None
20	$ClSO_3H$	2.2
21	FSO_3H	6.8
22	CH_3SO_3H	10.8
23	96% H_2SO_4	30.0

and methanesulfonic acids gave progressively larger yields of amine, in ascending order, although none was as satisfactory as 96% H_2SO_4.

Temperatures used were varied from a low of −10° to a high limited only by the refluxing of cyanogen chloride which boils at 13°. At atmospheric pressure the reaction could not be carried out much above 20°. While a lower reaction temperature was found to influence the yield only slightly, the products contained less polymeric matter and had less color. A lower temperature would be expected to decrease the tendency of the olefins to polymerize. Low temperatures appear to have as their chief disadvantage the slower rate of addition of acid, occasioned by difficulty in maintaining the low temperature in the reaction flask. When a temperature of −10° was used, a considerable amount of an insoluble white solid, apparently cyanuric chloride, was isolated. Probably the longer reaction time employed at the lower temperature caused cyanogen chloride to polymerize, rather than suffer the usual hydrolytic decomposition at the higher temperatures of 10–15°. The most favorable reaction temperature would appear to be in the 1–14° range.

The reaction time was governed by two factors: the length of time necessary to add the acid catalyst, and the cessation of the vigorous evolution of gas. Usually the acid could be added over a period of from 20 to 60 minutes. After an additional hour or two, the mixture was warmed to 50° where it was usually maintained for 30 minutes. Allowing the reaction mixture to stand at room temperature overnight did not raise the yield. Allowing it to stir at low temperatures for up to 9 hours raised the yield only slightly (compare Runs 21 and 23 in Table III).

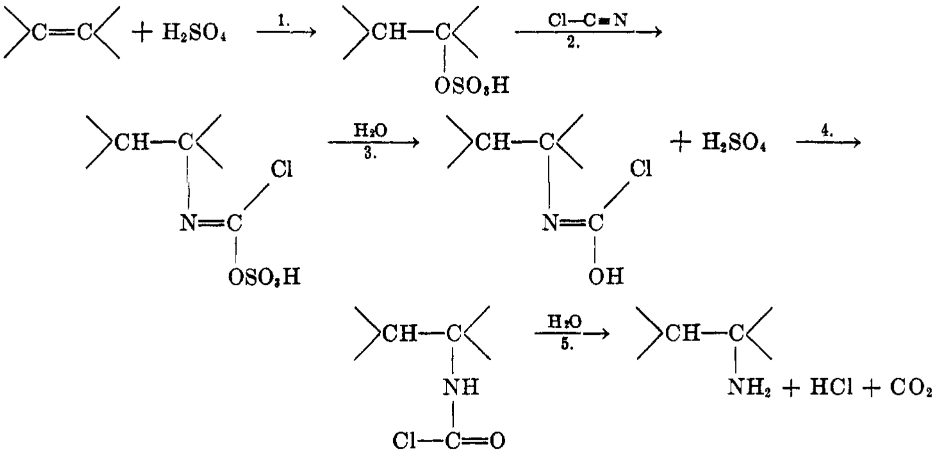
Only one solvent was tried, glacial acetic acid, and this only in two runs (11 and 12) (see Table III). This solvent was used successfully by Ritter (4) in his

TABLE III
MISCELLANEOUS VARIATIONS

Run No.	Olefin	Remarks	Products	
			Amine, %	Alcohol, %
1	Cyclohexene		30	—
3	Cyclohexene		14.0	
8	Cyclohexene	ClCN added to olefin-H_2SO_4	8.0	—
11	Cyclohexene	Solvent: 23 ml.	7	48
12	Cyclohexene	Glacial acetic acid	1.5	26
21	Diisobutylene	10 hrs. reaction time	30	—
23	Diisobutylene	1.5 hrs. reaction time	26.5	—

work on HCN. Its use did not increase the yield of amine, but only served to raise the conversion of the olefin to its corresponding alcohol.

At present no one mechanism for this reaction can answer all of the experimental facts completely. If the reaction proceeds in the same manner with cyanogen chloride as it does with hydrogen cyanide (and it does not appear unreasonable to assume it does), then, according to Ritter, using a sulfuric acid catalyst, the mechanism would be written thus:



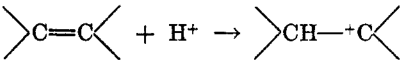
Our experimental results have brought this mechanism into question on several points. First, step 2 would require bond energy shifts seemingly out of proportion to the energy available under the reaction conditions utilized. Ritter's mechanism postulates the rupture of a carbon-oxygen bond and formation of another such bond as well as a carbon-nitrogen bond.

Secondly, and more important, if sulfation or the formation of an alkyl hydrogen sulfate were the first step, the addition of cyanogen chloride to an equimolar mixture of sulfuric acid and the olefin ought to have raised the final yield of amine by preforming an essential intermediate and decreasing the decomposition reaction of cyanogen chloride caused by free sulfuric acid. Moreover, an excess of cyanogen chloride ought to aid in obtaining a higher yield of amine.

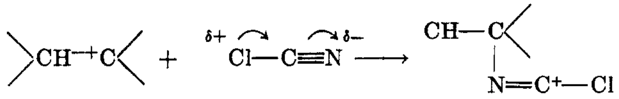
Actually, adding cyanogen chloride to the alkyl hydrogen sulfate lowered the yield by one-half (Run 8) while an 100% excess of cyanogen chloride (Run 12) did not materially increase the yield (Table III).

If, in place of the above mechanism, we seek another, the most logical postulation is a carbonium ion mechanism. Such an explanation, on closer examination, is only partially satisfactory. It may be represented thus:

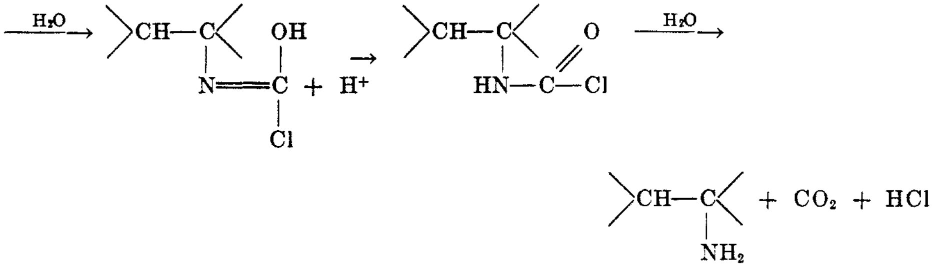
First proton addition:



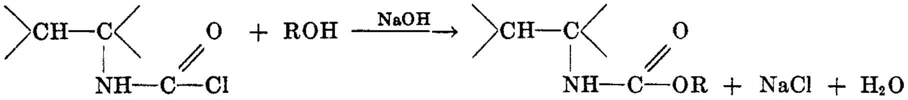
And then the addition of cyanogen chloride to the resulting carbonium ion:



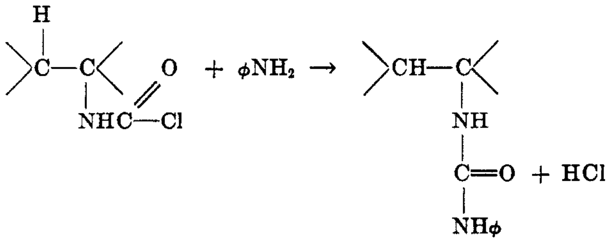
Followed by a 3-step hydrolysis:



One common intermediate in either reaction mechanism is the N-formyl chloride. Several attempts were made to show its existence in the reaction mixture. It had been hoped that this carbamyl chloride might react in a Schotten-Bauman type reaction to form a carbamate from the alcohol of the olefin which is formed by the sulfuric acid. Addition of base gave no detectable amount of carbamate expected according to the reaction:



Possibly the water formed from the neutralization of the sulfuric acid present caused hydrolysis of the carbamyl chloride before it could react. In another run excess aniline was added to the reaction mixture in an unsuccessful attempt to form a substituted urea which could be isolated from the reaction mixture:



The formation of large amounts of tars and aniline salts prevented any product isolation. The material balance was quite low in most cases where attempts were made to evaluate the recovery, especially where some reaction did occur. This is believed to be a result of the formation of considerable amounts of stable water-soluble sulfuric acid esters, which are known to be stable up to boiling temperatures in aqueous solutions (12).

EXPERIMENTAL

Description of apparatus. All runs were carried out in essentially the same set-up. This consisted of a 500-ml., three-necked flask. A 50-ml. Squibb-type separatory-funnel was fitted to one side arm and to the other was attached a Friedrich condenser through which a refrigerated methanol-water solution was circulated. The open end of the condenser was joined by rubber tubing to a $CaCl_2$ drying tube, and this successively to a 250-ml. suction flask used as a backup trap and then to a rubber tube extending almost to the bottom of another 250-ml. suction flask containing NaOH solution, and finally to a "U" tube containing dibutyl phthalate. The large neck of the flask was fitted with a rubber stopper through which were led a rubber sleeve-sealed two-paddle stirrer rotated by a variable-speed motor, a thermometer extending almost to the bottom of the flask, and a glass tube connected to a "Y" tube which in turn led to a source of nitrogen. The other lead from the "Y" had a connection to fit into the neck of the 50-ml. dropping-funnel in order that pressure might be equalized when liquid was added to the flask through the dropping-funnel while a gas was being evolved within the flask.

Procedure. The following typical procedure (Run 15) was used with the modifications herein described or listed in Table I. To a 0–5° mixture of 45 g. (0.4 mole) of diisobutylene and 24 g. (0.4 mole) of cyanogen chloride, 40 g. (0.4 mole) of 96% H_2SO_4 were very slowly added with vigorous stirring. Temperature was maintained between 10 and 15° until the evolution of gases had almost ceased (1–2 hours) and then was slowly raised to 50–55° and maintained there for 15–30 minutes, usually by the heat of reaction. In Run 8 the 50-ml. dropping-funnel was replaced with a short condenser and the required amount of cyanogen chloride was added as a liquid to a mixture of the olefin (cyclohexene in that case) and sulfuric acid.

The warm mixture was allowed to cool to 40° and then was cooled in ice to 15° taking care that the flow of nitrogen was increased to prevent sucking back. To the cool solution was added 30 ml. of distilled water, slowly at first, as more HCl was evolved. The aqueous mixture then was neutralized with 20% NaOH solution while cooling and stirring the whole until the solution was strongly basic. The organic layer was separated and the aqueous layer was extracted three times with 75-ml. portions of ether. The ether washings were added to the organic layer and the aqueous solution was discarded. The ether solution was washed once with 50 ml. of water and was extracted five times with 60-ml. portions of 5% HCl. The acid extracts were combined and made basic (with cooling and stirring) by the cautious addition of 20% NaOH. The amine was extracted from the basic solution with three 80-ml. portions of ether. These were combined, dried over potassium carbonate, and filtered. The ether was removed through a short column, and the amine was distilled at atmospheric pressure. Yield of N-*tert*-octylamine, b.p. 137–138°, was 16.4 g. or 22% based on the starting olefin used up. The ether solution from which the amine was extracted was dried over magnesium sulfate, and filtered. The ether was removed and the remainder was fractionally distilled. Yield, 14 g., or 31% of diisobutylene, b.p. 102–104°.

In those runs prior to Run 7, the reaction mixture was poured into water or into base. This is not thought to affect the yield, but adding the water was a matter of convenience.

In the runs where cyclohexene was used, the cyclohexylamine was isolated as the hydrochloride, obtained by passing dry hydrogen chloride into an anhydrous ether solution of the amine. This was necessary because of the small quantity of this amine obtained from the cyclohexene runs.

Cyclohexylamine was identified by its boiling point (134°) and by conversion to derivatives. The amine hydrochloride obtained melted at 201–203°. The reported (10) melting point for cyclohexylamine hydrochloride is 203–204°. By treating (11) a small amount of the free amine with benzoyl chloride and sodium hydroxide there was obtained, after recrystallization from ethanol, a substance melting at 147–149°. The reported (11) melting point for N-benzoylcyclohexylamine is 148–149°. A mixture melting point with an authentic sample showed no depression.

The N-*tert*-octylamine obtained boiled at 137–138°, which is the same as that reported by Ritter (4). The acetyl derivative melted at 98.5–99°, with no depression on mixing with an authentic sample.

The *sec*-butylamine distilled at 62–63°. It formed a benzamide melting at 75–76°, and a benzenesulfonamide melting at 70–70.5°, which are in agreement with accepted values (11).

The *tert*-amylamine boiled at 77–78° compared with 78–80° in the literature (13).

Anal. Calc'd for $C_5H_{13}N$: N, 16.17. Found: N, 16.34.

The amine mixture (b.p. 162–172°) obtained from propylene polymers was shown to contain a primary amino group by the Hinsberg method and was not further identified.

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SUMMARY

1. Cyanogen chloride has been found to react with the following olefins in the presence of an acidic catalyst to form the corresponding amine upon aqueous neutral hydrolysis: cyclohexene, butene-2, diisobutylene, propylene polymers, and 2-methylbutene-1. Yields of amine, formed in accordance with Markownikoff's rule, were in the 20–30% range.

2. Cyanogen chloride did not react with olefins containing an unsubstituted terminal double bond such as octene-1 or dodecene-1, nor with aromatic double bonds.

3. The following acids have been tested as catalysts for the reaction of olefins and cyanogen chloride: 75, 85, 96, and 100% sulfuric, 85% phosphoric, chlorosulfonic, fluorosulfonic, methanesulfonic, difluorophosphoric, and 35% hydrochloric. Sulfuric acid of 96% strength was best.

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