III. DISCUSSION

The cyanohydrins react readily with ammonia, ammonium carbonate or urea to give $\alpha$-amino nitriles, $\alpha$-ureidonitriles and hydantoins, which have been utilised for the synthesis of amino acids. However, the most important limitation of the reactions based on the cyanohydrins is the nonavailability of the corresponding aldehydes, which except in a few cases, are difficult to get as cheap and readily available starting materials. In view of this important limitation it was considered worthwhile to examine if $\alpha$-halonitriles could react to give the same products as cyanohydrins with ammonia, ammonium carbonate and urea.

\[ \begin{align*}
R - CH - CN + NH_3 & \rightarrow R - CH - CN \\
\text{Br} & \quad \text{NH}_2
\end{align*} \]

\[ \begin{align*}
R - CH - CN + (NH_4)_2CO_3 & \rightarrow R - CH - CO \\
\text{Br} & \quad \text{HN} \\
& \quad \text{NH} \quad \text{O}
\end{align*} \]
If $\alpha$-halonitriles could react in the above manner then the usefulness of these reactions would depend upon the availability of $\alpha$-halonitriles which, in view of the developments discussed earlier, can now be considered to be available more readily than the corresponding cyanohydrins.

For the purpose of present studies $\alpha$-bromo-$\alpha$-phenylacetonitrile which is an easily accessible $\alpha$-halonitrile, being readily prepared by the bromination of benzyl cyanide (Org. Syn. Col. III, 347 (1955), was selected for studies of its condensation reactions with ammonium carbonate and urea.

There was another advantage in selecting $\alpha$-bromo-$\alpha$-phenylacetonitrile for the study of condensation reactions with urea and ammonium carbonate and this was the fact that benzaldehyde cyanohydrin has been used for detailed studies of the condensation reactions of cyanohydrins with urea by Pinner and his associates and with ammonium carbonate by Bucherer and coworkers and therefore the use of $\alpha$-bromo-$\alpha$-phenylacetonitrile was expected to provide comparable data and products which were reported by other workers.
However, the most important consideration for selecting $\alpha$-bromo-$\alpha$-phenylacetonitrile for the purpose of the present studies was the fact that substitution reactions of $\alpha$-bromo-$\alpha$-phenylacetonitrile and $\alpha$-chloro-$\alpha$-phenylacetonitrile have already been studied, a brief account of which is given below.

Substitution Reactions of $\alpha$-Halobenzyl cyanides.

$\alpha$-Halo substituted benzyl cyanides are known to undergo nucleophilic replacement of the halogen by suitable nucleophilic replacement to give $\alpha$-substituted benzyl cyanide derivatives. A number of such reactions have been reported in the literature.

Barrow and Thorneycraft reported condensation of $p$-nitrosodimethylaniline with $\alpha$-chlorobenzyl cyanide to give the N-aryl ether of the corresponding oximino derivative.
Kretov and Abramov\textsuperscript{97} treated $\alpha$-bromoacetonitrile with mercury and obtained the organo-mercury compound which when treated with dil. HCl gave $\alpha\beta$-diphenylsuccinodinitrile.

$$
\begin{align*}
C_6H_5 - CH.CN + Hg &\rightarrow C_6H_5 - CH - CN + Hg_2Br_2 \\
&\quad \downarrow Hg-Br \\
&\quad \downarrow \text{dil. HCl} \\
C_6H_5 - CH - CN &\quad C_6H_5 - CH - CN
\end{align*}
$$

Thiourea reacts readily with $\alpha$-halo benzyl cyanides to give 2,4-diaminothiazoles. This reaction has been studied by Miller and his associates\textsuperscript{98}. Davies and coworkers\textsuperscript{99} further investigated this reaction in 1950 and showed that $\alpha$-bromo benzyl cyanide and $\alpha$-chloro benzyl cyanide react with thiourea to give 2,4-diamino-5-phenylthiazole.
Davies and his associates also used chloroacetonitrile, α-chloropropionitrile for the synthesis of the corresponding 2,4-diaminothiazoles. In the case of α-chloropropionitrile they, however, pointed out that due to the low reactivity of α-chloropropionitrile presence of sodium iodide was necessary. They failed to carry out condensation of α-bromo-isobutyronitrile with thiourea. Davies and his associates also failed to carry out condensation of chloroacetonitrile with urea which was found less reactive in this case than thiourea. This has also been pointed out by Anderson and coworkers. Davies and his associates also synthesised 2,4-diamino-1,3-selenazole by the condensation of α-substituted benzyl cyanides with selenourea.
Chase and Walker\textsuperscript{101} synthesised 2,4-diamino-5-phenyl-thiazole by the condensation of \(\angle\)-chloro-\(\chi\)-phenylacetonitrile with thiourea in acetone by allowing the reaction mixture to stand for three days at room temperature.

Davies and Maclaren\textsuperscript{102} studied reaction of \(\angle\)-bromo-\(\chi\)-phenylacetonitrile and ethyl Xanthamidate and obtained \(\angle\)-carbamylthiobenzyl cyanide when the reaction was carried out in benzene while in alcohol they obtained trans-\(\chi\beta\)-dicyanostilbene and ethyl xanthamidate was isomerised to ethylthiocarbamate.

\[
\text{Benzene} \quad \begin{array}{c} \text{EtOH} \\ \text{Br} \end{array} \rightarrow \begin{array}{c} \text{C}_6\text{H}_5-\text{CH-CN} + \text{H}_2\text{N-CS-OEt} \\ \text{EtOH} \end{array}
\]

\[
\text{C}_6\text{H}_5-\text{CH-CN} \quad \begin{array}{c} \text{EtOH} \\ \text{S-COCONH}_2 \end{array} \rightarrow \begin{array}{c} \text{C}_6\text{H}_5-\text{CH-CN} + \text{H}_2\text{N-CO-SEt} \\ \text{NO-C-C}_6\text{H}_5 \end{array}
\]

Coe and his associates\textsuperscript{90} treated \(\angle\)-bromo-\(\chi\)-phenylacetonitrile with ammonium thiocyanate when they obtained \(\angle\)-cyanobenzyl thiocyanate.

\[
\text{C}_6\text{H}_5-\text{CH-CN} + \text{NH}_4\text{SCN} \rightarrow \begin{array}{c} \text{C}_6\text{H}_5-\text{CH-CN} \\ \text{S-CN} \end{array} \quad \begin{array}{c} \text{Br} \\ \text{NH}_4\text{Br} \end{array}
\]
They also recorded that if potassium thiocyanate was used the dicyanostilbene was obtained.

Kretov and Panchenko\(^{103}\) treated $\alpha$-chloro-$\alpha$-phenylacetonitrile with $\text{Na}_2\text{S}$ in alcohol when they obtained bisphenylacetonitrile sulphide and phenylacetonitrile mercaptan along with some dicyanostilbene.

\[
\begin{align*}
\text{C}_6\text{H}_5-\text{CH-CN} + \text{Na}_2\text{S} \rightarrow & \quad \text{C}_6\text{H}_5-\text{CH-CN} \quad \text{C}_6\text{H}_5-\text{CH-CN} \\
& \quad \text{C}_6\text{H}_5-\text{CH-CN} + \text{C}_6\text{H}_5-\text{CH-CN} \\
& \quad \text{NC} - \text{C} - \text{C}_6\text{H}_5
\end{align*}
\]

They also recorded a similar reaction for $\alpha$-bromo-$\alpha$-phenylacetonitrile which gives higher yields of the mercaptan and the dicyanostilbene.

More recently, Vinograde and Vul'fson\(^{104}\) utilized bromoacetonitrile for the Reformatsky reaction with aldehydes as well as ketones.
Banfield in an attempt to further explore the nucleophilic character of the replacement of the halogens of α-halo benzyl cyanides, studied the action of a number of thiophenols with α-bromo-α-phenylacetonitrile and obtained the corresponding aryl-α-cyano benzyl sulphides and recorded that some dicyanostilbene was always produced in these reactions.

\[
\begin{align*}
C_6H_5 - CH - CN + C_6H_5 - SH & \rightarrow C_6H_5 - CH - CN + S-C_6H_5 \\
& + C_6H_5 - C - CN \parallel NC - C - C_6H_5
\end{align*}
\]

Banfield also noted that while neutral guanidine salts did not react with α-bromo-α-phenylacetonitrile, guanidine carbonate did react with the bromonitrile to give the dicyanostilbene. In view of the above facts he came to the conclusions that:

"the product of reaction of α-cyano benzyl bromide with nucleophile depends critically upon the nucleophilic reactivity on the one hand and the basicity of the reagent on the other."
From the above discussion it would appear that in the nucleophilic substitution reactions of α-bromo-α-phenylacetonitrile, the dicyanostilbene is frequently formed along with the main substitution products. The formation of dicyanostilbene has been explained by Coe and his associates in the following manner.

"Step (a) will proceed more readily the greater the stability of that is, the larger the dissociation constant of HX. The removal of proton in step (b) will also be facilitated by a more highly electronegative group X, as well as by the cyano- and the phenyl groups, which will weaken the carbon-hydrogen bond towards nucleophilic attack. Combination of the oppositely charged ions leads to the dibenzyl derivative, which may then lose HX to give the dicyanostilbene."
This mechanism assumes formation of the dicyanostilbene as a result of the abstraction of a proton from the reactive $\alpha$-position of the nitrile, the carbanion produced then competes with the nucleophile for carbonium ions formed from the bromo-nitrile in an $S_N^1$ type reaction. Thus it is apparent that the product of reaction of $\alpha$-bromo-$\alpha$-phenylacetonitrile with a nucleophile depends critically upon the nucleophilic reactivity on the one hand and the basicity of the reagent on the other.

Thus synthesis of $\alpha$-substituted phenylacetonitriles and their derivatives by nucleophilic replacement of the halogen of $\alpha$-chloro- or $\alpha$-bromophenylacetonitrile, in the presence of bases, is restricted by the formation of the dicyanostilbene through the above mentioned side reaction.

The conversion of $\alpha$-bromo-$\alpha$-phenylacetonitrile into the dicyanostilbene, when treated with bases, seems to be a general reaction of all $\alpha$-halo-$\alpha$-phenylacetonitriles and also for other negatively $\alpha$-substituted phenylacetonitriles. The yield of the dicyanostilbene from various negatively $\alpha$-substituted compounds depends on the dissociation constant of the acids. The higher the dissociation constant of the acid, the higher is the yield of the dicyanostilbene.
as indicated in the following table compiled by Coe and his associates.

**TABLE**

Yields of dicyanostilbene from various esters (A) and dissociation constants of HX in water.

<table>
<thead>
<tr>
<th>X</th>
<th>K</th>
<th>Yield (%)</th>
<th>X</th>
<th>K</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I (s)</td>
<td>50</td>
<td>Ph.SO₂</td>
<td>2x10⁻¹</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>Br (s)</td>
<td>&gt;35</td>
<td>NO₂</td>
<td>2</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Cl (s)</td>
<td>&gt;27</td>
<td>p-Me.C₆H₄.SO₃</td>
<td>1x10⁻¹</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>CNS (s)</td>
<td>60</td>
<td>B₂O</td>
<td>7x10⁻⁵</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>S.CO.NH₂</td>
<td>66</td>
<td>AcO</td>
<td>2x10⁻⁵</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

(s), Strong acid: the first three are in order of acid strength in acetic acid.

* Free acid unknown.

† The hypothetical acid is H-N=O which is unknown (and is not nitrous acid).


(Reproduced from:- J.C.S.,1957, 124).
From the above table it would appear that all negatively α-substituted phenylacetonitriles yield dicyanostilbene according to the strength of the negatively substituted group except in the case of benzoyloxy- and acetoxy-derivatives which did not produce dicyanostilbene but gave sodium salts of acids and benzoin as reported by Coe and his associates as well as by earlier workers \(^{105}\); Davis \(^{106}\), Greene and Robinson \(^{107}\). Coe and his associates have explained conversion of benzoyloxy- and acetoxy-derivative into benzoin by suggesting that the "nucleophilic reagents attack the acyl-oxygen bond instead of the C-X bond."

Formation of the carbanion, as suggested by Coe and his associates, can further be supported by the following facts.

Recent studies by Asami \(^{108}\) showed that phenylacetonitrile when treated with liquid ammonia-caustic alkali and the resulting product when treated with alkyl halides in liquid ammonia, gives alkyl substituted α-phenylacetonitriles. Similarly, studies by Smith \(^{109}\) showed that optically active α-chloro-α-phenylacetonitrile is very easily racemised catalytically by alcoholic alkali. This must involve formation of the anion which is rapidly equilibrated followed by rate- and product-determining steps.
A similar situation exists in the case of cyano-hydrins in which the hydrogen is similar in character to the \( \alpha \)-hydrogen of nitriles or esters. The dissociation of the \( \alpha \)-hydrogen gives an anion which attacks the carbonyl group of the second molecule of the benzaldehyde giving the bimolecular product benzoin.

\[
\begin{align*}
\text{C}_6\text{H}_5 - \text{CO} + \text{CN}^- & \rightleftharpoons (a) \text{C}_6\text{H}_5 - \text{CN}^- \rightleftharpoons (b) \text{C}_6\text{H}_5 - \text{C} - \text{CN}^- \\
\text{C}_6\text{H}_5 - \text{C} - \text{C} - \text{OH} + \text{CN}^- & \rightleftharpoons (d) \text{C}_6\text{H}_5 - \text{C} - \text{C} - \text{OH}
\end{align*}
\]

Keeping in view the above considerations, reactions of \( \alpha \)-bromo-\( \alpha \)-phenylacetonitrile with urea and ammonium carbonate can now be critically examined in order to determine
the course of reactions and to provide explanation for the formation of various products.

The present studies proved to be quite fruitful as far as elucidation of the course of reactions of \( \kappa \)-halonitriles with urea and ammonium carbonate are concerned and the products obtained were, in many cases, the expected ones as reported for cyanohydrins or amino nitriles by Pinner and his collaborator\(^{10,11}\) and later by Bucherer and his associates\(^{17,18}\). There were also formed products of side reactions and large quantities of resinous mass derived from the reaction products. The polymeric resins could not be further processed. Along with the resins there were, however, obtained the expected reaction products which were isolated and characterised.

The tendency of benzaldehyde and phenylacetaldehyde to undergo extensive resinification in the condensation reaction with ammonium carbonate has been recorded by Bucherer and his associates\(^{17,18}\). When benzaldehyde cyanohydrin was treated with KCN or HCN and ammonium carbonate in 50% alcohol only very little 5-phenylhydantoin was obtained, phenylacetaldehyde cyanohydrin gave still lesser yield of benzylhydantoin while formaldehyde and acetaldehyde
gave only dark resins. Pinner has also referred to the high sensitivity of benzaldehyde cyanohydrin in the condensation with urea by which, perhaps, he meant its tendency for resinification. On the other hand, most of the ketones particularly the less reactive ketones, their cyanohydrins and aminonitriles give excellent yields and in many cases almost quantitative yields of hydantoins were obtained in the Bucherer synthesis. These earlier studies indicate that the tendency for resinification is characteristic of the benzaldehyde, phenylacetaldehyde, formaldehyde and acetaldehyde in the condensation, reactions with ammonium carbonate and urea. In view of these considerations the tendency of \( \alpha \)-bromo-\( \alpha \)-phenylacetonitrile for resinification in its condensation reactions with urea and ammonium carbonate was not unusual. However, the tendency for resinification can be controlled, to a certain extent, by the reaction conditions so that reaction products could be obtained in sufficient quantities for characterisation. Therefore, in spite of extensive resinification and difficulties involved in the isolation of reaction products, which were obtained only in small quantities, the studies were continued and most of the products isolated were characterised in order to gain information regarding the reactions involved.
Another drawback in the studies under discussion was that under different conditions of reaction different products were obtained and therefore this led to considerable difficulties in the isolation and characterisation of the products. Nevertheless, different products obtained under different reaction conditions, really, turned out to be very helpful in providing a deeper understanding of the course of reactions.

Condensation of $\alpha$-Bromo- $\alpha$-phenylacetonitrile with Urea.

The following products were obtained by the condensation of $\alpha$-bromo- $\alpha$-phenylacetonitrile with urea.

(1) $\alpha$-Ureido- $\alpha$-phenylacetonitrile (II)
(2) $\alpha$-Ureido- $\alpha$-phenylacetamide (III)
(3) 5-phenylhydantoin (V)
(4) Diphenylhydantil (VI)
(5) Mandelic acid (VIII)
(6) trans-$\Phi$-dicyanostilbene (IX)
(7) Diphenylmaleic anhydride (XI)
(8) m.p. 236-238° (XIX)
(9) m.p. 135-137° (XVIII)
(10) m.p. 299-302° (XX)
For diagrammatic representation of the above reaction products please see table No. III.

Examination of the above products indicates that the condensation of \( \alpha \)-bromo-\( \alpha \)-phenylacetonitrile with urea is a complicated process which produces not only the products obtained by the condensation of benzaldehyde cyanohydrin with urea by Pinner but also certain products which were obtained later by Bucherer by the condensation of benzaldehyde cyanohydrin with ammonium carbonate. Moreover, some side reactions also take place, giving certain byproducts which were not obtained by the condensation of cyanohydrins with urea or ammonium carbonate.

Formation of \( \alpha \)-ureido-\( \alpha \)-phenylacetonitrile (II) was expected according to the reaction of benzaldehyde cyanohydrin with urea as carried out by Pinner.

\[
\begin{align*}
\text{C}_6\text{H}_5 & - \text{CH} - \text{CN} \quad \xrightarrow{\text{Br + NH}_2\text{CO-NH}_2} \quad \text{C}_6\text{H}_5 & - \text{CH} - \text{CN} \\
\text{Br} & + \text{NH}_2\text{CO-NH}_2 & \text{NH} & - \text{CO} - \text{NH}_2
\end{align*}
\]

However, in this reaction \( \alpha \)-ureido-\( \alpha \)-phenylacetamide (III) has also been obtained which must arise from II as a result of addition of water. III was isolated by
Bucherer from benzaldehyde cyanohydrin and ammonium carbonate and therefore this product is also according to the expectations.

\[
\begin{align*}
\text{C}_6\text{H}_5 - \text{CH} - \text{CN} & \quad \xrightarrow{\text{H}_2\text{O}} \quad \text{C}_6\text{H}_5 - \text{CH} - \text{CO} - \text{NH}_2 \\
\text{NH} - \text{CO} - \text{NH}_2
\end{align*}
\]

The reaction also provided 5-phenylhydantoin (V) which must arise from II or III as a result of cyclisation. The formation of 5-phenylhydantoin in this reaction was also expected since it represents major product of the Bucherer's condensation of benzaldehyde cyanohydrin with ammonium carbonate.

\[
\begin{align*}
\text{C}_6\text{H}_5 - \text{CH} - \text{CN} & \quad \xrightarrow{\text{H}_2\text{O}} \quad \text{C}_6\text{H}_5 - \text{CH} - \text{CO} - \text{NH}_2 \\
\text{NH} - \text{CO} - \text{NH}_2
\end{align*}
\]

\[
\begin{align*}
\text{C}_6\text{H}_5 - \text{CH} - \text{NH} & \quad \xrightarrow{\text{H}_2\text{O}} \quad \text{C}_6\text{H}_5 - \text{CH} - \text{C}=\text{O} \\
\text{NH} & \quad \xrightarrow{\text{NH}_3} \quad \text{NH} & \quad \xrightarrow{\text{NH}_3} \quad \text{NH}
\end{align*}
\]
Another interesting product of this reaction was diphenylhydantin (VI) which was obtained from the aqueous extract of the reaction mixture after refluxing with hydrochloric acid. VI was first reported by Gabriel who synthesised it by heating 5-bromo-5-phenylhydantoïn with 5-phenylhydantoïn.

Gabriel and later Kjaer also reported formation of diphenylhydantin by heating 5-phenylhydantoïn with alcoholic potassium hydroxide. However, these reactions do not explain formation of diphenylhydantin in the condensation reaction of α-bromo-α-phenylacetonitrile with urea. It appears that, in the first instance, a water soluble compound is formed which can be extracted from the reaction mixture. It does not crystallise from the aqueous solution and gives a viscous yellow solution. This may, perhaps, consist of ammonium salt of an acylic acid, which when
refluxed with hydrochloric acid may undergo cyclisation similar to those of the hydantoins. Therefore, the two hydantoin rings of the hydantil are formed as a result of refluxing with hydrochloric acid. In view of this the acyclic intermediate which is the actual product of the condensation reaction must bear two benzyl groups linked to the same nitrogen atom. Formation of this intermediate may be explained by the following sequence of reactions.

\[
\begin{align*}
C_6H_5 - \text{CHCN} & \quad \xrightarrow{H^+} \quad C_6H_5 - \text{OCN} \\
\text{Br} \quad \text{(I)} & \quad \xrightarrow{} \quad \text{Br} \quad \text{(XXI)}
\end{align*}
\]

\[
\begin{align*}
C_6H_5 - \text{OCN} + H_2N & \quad \xrightarrow{} \quad HN - \text{CBr}
\text{Br} \quad \text{CO} & \quad \xrightarrow{} \quad \text{CO} \quad \text{CN} \quad \text{(XXII)}
\end{align*}
\]

\[
\begin{align*}
HN - \text{CBr} & \quad + \quad HN - \text{CHCN} \\
\text{CO} \quad \text{CN} & \quad \xrightarrow{} \quad \text{CO} \quad \text{CN} \quad \text{NH}_2 \quad \text{HBr} \quad \text{(XXIII)}
\end{align*}
\]

(XXII) (II)
Formation of the bromobenzyl cyanide anion (XXI) has been suggested by Coe and his associates. They assumed that removal of the proton from α-bromo-α-phenylacetonitrile which is facilitated by the highly electronegative bromo as well as the cyano- and the phenyl- groups, which weaken carbon-hydrogen bond towards nucleophilic attack. Combination of this
negative ion (XXI) with urea would be expected to give α-bromo-α-phenyl-α-ureido-acetonitrile (XXII). This may condense with α-ureido-α-phenylacetonitrile (II) to give the intermediate (XXIII). The nitrile groups of this intermediate on hydrolysis would give a water soluble ammonium salt, which when refluxed with hydrochloric acid furnishes diphenylhydantoin (VI).

Isolation of mandelic acid by the hydrolysis of the resinous mass of the reaction mixture is not difficult to explain. This may arise by the hydrolysis of α-bromo-α-phenylacetonitrile or its derivatives which may be present in the resinous mass.

\[
\text{C}_6\text{H}_5 - \text{CH} - \text{CN} \quad \xrightarrow{\text{Br}} \quad \text{H}_2\text{O} \quad \xrightarrow{\text{HCl}} \quad \text{C}_6\text{H}_5 - \text{CH} - \text{COOH}
\]

Reimer in 1881 showed that α-bromo-α-phenylacetonitrile when heated at 160-180° is converted into dicyanostilbene and almost all the bromine is evolved as HBr.

\[
2 \text{C}_6\text{H}_5 - \text{CH} - \text{CN} \quad \xrightarrow{\text{Br}} \quad \text{C}_6\text{H}_5 - \text{CN} - \text{C}_6\text{H}_5 + 2\text{HBr}
\]
Coe and his associates have already established the mechanism of formation of the dicyanostilbene from \(\alpha\)-bromophenylacetonitrile. Banfield has shown that formation of the dicyanostilbene restricts yield of the nucleophilic substitution products. In view of this important side reaction conditions for the nucleophilic reactions have to be so chosen that formation of the dicyanostilbene and its derivatives is minimised. Alcoholic solution of \(\alpha\)-bromophenylacetonitrile with potassium hydroxide, ammonia or potassium cyanide are known to give upto 40% yield of the dicyanostilbene. However, under the conditions of the present studies there was not extensive formation of the dicyanostilbene.

The diphenylmaleic anhydride (XI) was obtained by the hydrolysis of the resinous mass with 20% sodium hydroxide solution. Therefore, this must, naturally, arise by the hydrolysis of the dicyanostilbene or its derivatives which may be present in the resinous mass.

In addition to the above products, the following three compounds were also obtained in very small quantities and could not be purified enough for the purpose of identification.
(i) Product m.p. 236-238° (XVIII) was obtained from the second reaction.

(ii) Product m.p. 135-137° (XIX) and product m.p. 299-302° (XX) were obtained from the third reaction.

In the reaction of \( \alpha \)-bromo-\( \alpha \)-phenylacetonitrile with urea, the resinous mass constitutes major product. In order to elucidate its composition the resinous mass was subjected to hydrolysis with conc. hydrochloric acid but only a small fraction of the material could be hydrolysed in spite of prolonged refluxing. Ethereal extract of the acid hydrolysate gave mandelic acid and therefore it may be assumed that \( \alpha \)-bromo-\( \alpha \)-phenylacetonitrile is in some way combine with the urea which when subjected to hydrolysis gives mandelic acid.

The resinous mass was also subjected to alkaline hydrolysis with 20% sodium hydroxide but even prolonged boiling led to very slow hydrolysis and to a very limited extent. Acidification of the hydrolysate gave diphenylmaleic anhydride and therefore it may be presumed that dicyanostilbene is also present in some polymeric form.
in the resinous mass, which when hydrolysed with 20% sodium hydroxide yields diphenylmaleic anhydride.

Thus it may be concluded that the resinous mass consists of polyamide structures derived from -bromo-phenylacetonitrile and dicyanostilbene.

Condensation of $\alpha$-bromo-$\alpha$-phenylacetonitrile with ammonium carbonate.

Condensation of $\alpha$-bromo-$\alpha$-phenylacetonitrile with ammonium carbonate was studied under four different conditions. The reaction proceeds quite smoothly, though with extensive resinification as in the case of urea. This reaction gives products in comparatively higher yields than in the case of urea and the number of products obtained is also fewer than with urea. Following are the main products obtained by the condensation of $\alpha$-bromo-$\alpha$-phenylacetonitrile with ammonium carbonate.

(1) $\alpha$-Ureido-$\alpha$-phenylacetamide (III)

(2) Compound XVII, m.p. 290-293°d. with approximate composition, $C_{24}H_{22}N_4O_5$.

(3) Mandelic acid (VIII)

(4) trans-$\alpha$-dicyanostilbene (IX)

(5) Diphenylmaleic anhydride (XI)
A diagram representation of the above products is given in table No. IV.

α-Ureido-α-phenylacetamide may be considered to be the main product of the condensation, which is obtained under all the four different conditions. This arises from α-Ureido-α-phenylacetonitrile (II) as already explained in the case of urea.

It is interesting to note that when ammonium carbonate is used α-ureido-α-phenylacetonitrile, the parent compound, is not obtained.

However, a new compound, XVII was obtained in this reaction which could not be found in the reactions with urea. This was obtained under reaction conditions 2 and 3, and to a smaller extent the condition 1. The compound melts with decomposition at 290-295°. It is highly insoluble in water, ether, benzene and chloroform but slightly soluble in alcohol and acetone and comparatively more soluble in hot acetic acid and nitrobenzene. However, the compound is readily soluble in sodium hydroxide but insoluble in sodium bicarbonate. When refluxed with conc. hydrochloric acid it was recovered unchange.Boiling with 20 % sodium hydroxide only slowly hydrolysed the
compound with the evolution of ammonia. In view of these physical and chemical characteristics it was extremely difficult to obtain the compound or its derivatives in a pure state and therefore it could not be assigned a definite formula. The analytical values of the compound XVII agree fairly with the molecular formula \( C_{18}H_{17}N_{3}O_{4} \) but they much more closely agree with the molecular formula \( C_{24}H_{22}N_{4}O_{5} \). However, in the absence of other data molecular formula could not be finalised and therefore, for the present, compound XVII has been assigned molecular formula \( C_{24}H_{22}N_{4}O_{5} \). Due to its high stability the compound could not be degraded into simpler products and therefore no structure can be assign to the compound, though from the Chemical Characteristics presence of hydantoin ring is indicated.

Mandelic acid (VIII) was obtained from the alcohol soluble fraction of the residue under the reaction condition 2, which must involve hydrolysis of \( \alpha \)-bromo-\( \alpha \)-phenylacetonitrile. This is in contrast with the reaction with urea where mandelic acid was not obtained directly in any of the reactions except through the acid hydrolysis of the resinous mass.
trans-\( \alpha \beta \)-Dicyanostilbene was obtained only in small quantities.

The resinous mass when subjected to hydrolysis with 20% sodium hydroxide followed by acidification yielded diphenylmaleic anhydride, which may have been formed by the hydrolysis of the dicyanostilbene or its derivatives which may be present in the resinous mass.

Though there is no experimental basis yet taking into consideration the unusually high reactivity of \( \alpha \)-bromo-\( \alpha \)-phenylacetonitrile and the variety of reaction products formed in addition to the expected reaction products it would not be out of place to suggest, purely on theoretical grounds, possibility of a carbene intermediate which has not yet been considered by anyone. Although Gloss and Gloss\(^{111} \) in 1960 reported formation of phenyl carbene from benzyl chloride and n-butyllithium which they demonstrated through a trapping experiment.

\[
\begin{align*}
\text{C}_6\text{H}_5 - \overset{\text{H}}{\text{C}} - \text{CN} & \quad \overset{-\text{HBr}}{\longrightarrow} \quad \text{C}_6\text{H}_5 - \overset{\text{CN}}{\text{C}} - \text{CN}
\end{align*}
\]
The three electron withdrawing groups attached to the carbon atom may help in the removal of the proton as well as the Br through $\alpha$-elimination. It is, however, open to question whether the very weak base urea is sufficient to pull out a proton from the substrate to initiate the reaction. There are, however, cases where carbenes are generated from suitably constituted substances even in the absence of a base. As an example Wanzlick, found that the product of reaction of dianilinoethane with chloral when heated in an inert solvent loses chloroform and gives a colourless crystalline solid regarded as a carbene. Its molecular weight suggests that the substance is in equilibrium with its dimer.
If formation of the carbene intermediate is presumed, it would help to explain the formation of a number of products. For example, the dicyanostilbene may arise simply by the dimerisation of the carbene intermediate.

\[
\begin{align*}
C_6H_5 - \cdot & \quad \text{CN} \\
+ & \quad \text{CN} - \cdot & \quad C_6H_5
\end{align*}
\]

Similarly, formation of the intermediate (XXIII) the proposed precursor of diphenylhydantil may be expected to be formed through the same carbene intermediate.

\[
\begin{align*}
\text{H}_2\text{N} - \cdot & \quad \text{C} - \quad \text{N} - \quad \text{CH} \\
\text{CO} + & \quad \text{CN} & \quad \text{CO} & \quad \text{CN} & \quad \text{CO} & \quad \text{CN} & \quad \text{CO} & \quad \text{CN} \\
\text{H}_2\text{N} & \quad \text{NH}_2 & \quad \text{H}_2\text{N} & \quad \text{NH}_2
\end{align*}
\]

(XXIII)
The extensive resinification may also be explained by the formation of the carbene intermediate, which would then readily react with urea, \((\text{NH}_4)_2\text{CO}_3\) or their derivatives to form large polymeric resinous products.