CYANOFLUOROCARBON POLYMERS

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ABSTRACT

The purpose of this investigation is to synthesize cyanofluorocarbon polymers through the intermediate formation of cyanofluoromethylene \( FC(CN) \). Polymeric products were formed in reactions yielding cyanomethylenes \( XC(CN) \) under neutral or basic conditions. Where \( X = H, COOC_2H_5, Cl \) or \( F \), polymeric cyanomethylenes were isolated as dimers (olefine), trimers (cyclopropanes) or solid brown-black polymers. The brown-black polymers are believed to have conjugated structures of the "black orion" type, formed by cyclization of linear cyanomethylene polymers

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\begin{array}{c}
\text{C} \\
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\]

INTRODUCTION

The main aim of this research is to synthesize cyanofluorocarbon polymers

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\begin{array}{c}
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through the intermediate formation of cyanofluoromethylene \( FC(CN) \). Such polymers would be expected to be thermally stable because of the high dissociation energies\(^3\) of C-F bonds (106 Kcal) and C-CN bonds (103 Kcal), and because Fluorine atoms and Nitrile groups would have exceptional covering power for a carbon skeleton.

By analogy with the known diradical species propylene\(^5\), HC(=CH), the postulated divalent carbon intermediate FC(=CH) should probably be regarded as a methylene\(^5\) possessing diradical character (triplet state) rather than as a carbene (singlet state). Polymerization, including dimerization, of such cyanomethylenes would be expected under suitable conditions. Experiments were therefore directed toward forming cyanomethylenes \( XC(CN) \), where \( X = H, COOC_2H_5, Cl \) and \( F \), under conditions that would give rise to polymers. Three known methods for forming divalent carbon intermediates were used, based on dehalogenation, decarboxylation, and dehydrohalogenation experiments. For the formation of cyanofluorocarbon...
methylenec the methods are represented by the following equations:

1. Dehalogenation of dibromofluoroacetonitrile\(^2\).

\[
\begin{align*}
\text{Br} & \quad \text{F} \\
\text{Br} & \quad \text{CN} \quad \xrightarrow{\text{metal}} \quad [\text{FC(CN)}] \quad \xrightarrow{} \quad \text{polymer}
\end{align*}
\]

2. Decarboxylation of sodium cyanobromofluoroacetate\(^9\).

\[
\begin{align*}
\text{NaOOC} & \quad \text{CN} \quad \xrightarrow{\Delta} \quad [\text{FC(CN)}] \quad \xrightarrow{} \quad \text{polymer}
\end{align*}
\]

3. Dehydrohalogenation of chlorofluoroacetonitrile\(^4\).

\[
\begin{align*}
\text{H} & \quad \text{cl} \quad \text{F} \\
\text{Cl} & \quad \text{CN} \quad \xrightarrow{\text{base}} \quad [\text{FC(CN)}] \quad \xrightarrow{} \quad \text{polymer}
\end{align*}
\]

RESULTS AND DISCUSSION

1. Dehalogenation Reactions

(a) Reactions of cyanochloromethanes with copper (no solvent)

Refluxing of trichloroacetonitrile with finely divided copper yielded a mixture of products that were separated and characterized by elemental analysis and infrared spectroscopy. The products were cuprous chloride; a brown-black solid polymer, insuble and insoluble, with infrared spectrum bands at 3.0 \(\mu\) (broad), 4.5 \(\mu\) (sharp), and 6.2 \(\mu\) (broad); tetrachloroacetonitrile; dichlorofumaronitrile; and a yellow liquid \(\text{Cl}_2\text{ClCN}\) (bp 54.8°C/4.5 mm) with infrared spectrum bands at 4.96 \(\mu\), 4.50 \(\mu\), and 6.0-6.55 \(\mu\), believed to be \(\text{NO}_2\text{C-N=O-CN}\). 

\(\text{Cl} \quad \text{Cl} \quad \text{Cl}\)

The products from this reaction suggest the formation of the dichlorocyanomethyl radical and its ketenimine form as primary intermediates. Polymer formation could then occur as outlined below, or through the intermediate formation of cyanochloromethylene:

\[
\text{Cl}_2\text{C(CN)} + \text{Cl} \xrightarrow{\Delta} \text{Cl} \cdot \text{C} \quad \xrightarrow{-\text{OCl}} \quad \text{Cl}_2\text{C(CN)} \rightarrow \text{olefins} + \text{polymers}
\]

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To explain the color of the brown-black polymeric material and its infrared spectrum it is proposed that conjugated structures of the "black orion" type (B) are formed spontaneously from the linear polycyanochloromethylene (n) initially formed (A).
Further dechlorination could occur to give the doubly conjugated polymer C, which could undergo further cyclization to give the triply conjugated polymer D.

The infrared spectrum peak at 4.5 μ can be attributed to nitrile groups. The broad band at 6.2 μ can be attributed to >C=N- groups, while the broad band at 3.0 μ can be attributed to -NH₂ or -N-H groups, perhaps present as end groups. The infrared spectra of "black orion" structures of type B (with H replacing Cl and CN) possess broad bands in the regions 3.0 μ and 6.2 μ. Polymers closely resembling the brown-black solid in appearance and with very similar infrared spectra have been obtained by the polymerization of hydrocyanic acid, and have been assigned structures of the type B (with Cl replaced by NH₂), derived from the linear polymer

\[
\text{C} = \text{N} \quad \text{N} = \text{C} = \text{C} \quad \text{N} = \text{C} = \text{N} \\
\therefore \text{NH}_2 \\
\text{N} = \text{C} = \text{C} \quad \text{N} = \text{C} = \text{N} \\
\text{C} = \text{N} \quad \text{N} = \text{C} = \text{C} \quad \text{N} = \text{C} = \text{N}
\]

Reactions of dichloroacetanitrile and dibromoacetanitrile with copper have also yielded brown-black polymeric products at present being purified and characterized. Initial reactions of dibromofluoroacetanitrile with copper are being investigated. This cyanofluoromethylene precursor was synthesized by a five-step procedure starting with tribromoaetic acid:

\[
\begin{align*}
\text{Br}_3\text{COCH} & \xrightarrow{\text{PdCl}_2} \text{Br}_2\text{COCl} \\
\text{C}_\text{H}_3\text{OH} & \xrightarrow{80\%} \text{Br}_3\text{COOC}_\text{H}_2 \\
\text{Ag} & \xrightarrow{70\%} \\
\text{Br}_3\text{C} & \xrightarrow{95\%} \text{Br}_2\text{COCONH}_2 \\
\text{NH}_2 & \xrightarrow{90\%} \text{Br}_2\text{COOC}_\text{H}_2
\end{align*}
\]
In general, the above results suggest that reactions of polyhalocyanomethanes with copper yield conjugated polymers formed by the cyclization of linear cyanomethylene polymers.

(b) Reactions of cyanomethanes with zinc-copper couple (in polar solvents). Reaction of triiodoacetanilide or dibromacetanilide with zinc-copper couple\(^5\) in refluxing tetrahydrofuran yielded brown-black solid polymers, insoluble and infusible. The infrared spectra of the polymers resembled the spectra of the polymers obtained in the reactions with copper alone, with strong bands in the regions 3.0 \(\mu\), 4.5 \(\mu\) and 6.2 \(\mu\). Metal complexing with the polymers occurs.

(c) Reactions of ethyldibromocyanocacate with bases. Evidence for the formation of the cyanomethylene (NC\((\text{COOC}_2\text{H}_5)\)) was obtained by isolating the dimer (olefin) and trimer (cyclopropane derivative) from reactions of ethyldibromocyanocacetate with basic reagents:

\[
\begin{align*}
\text{Br}^+\text{COOC}_2\text{H}_5 & \quad \xrightarrow{\text{KP}} \quad \text{HC}_2\text{OOC} \quad \text{NC} \quad \text{COOC}_2\text{H}_5 \\
\text{Br}^-\text{COOC}_2\text{H}_5 & \quad \xrightarrow{\text{NaOH}} \quad \text{HC}_2\text{OOC} \quad \text{NC} \quad \text{COOC}_2\text{H}_5 \\
\text{Br}^-\text{COOC}_2\text{H}_5 & \quad \text{pentane} \quad \xrightarrow{\text{NaOH}} \quad \text{C}_2\text{H}_5\text{OCC} \quad \text{COOC}_2\text{H}_5 \\
\end{align*}
\]

2. Decarboxylation Reactions

Unsuccessful attempts were made to synthesize sodium cyano-
boronofluoracetate

\[
\begin{align*}
\text{Br}^+\text{COOC}_2\text{H}_5 & \quad \xrightarrow{\text{AgF}} \quad \text{Br}^-\text{COOC}_2\text{H}_5 \\
\text{NaOH} & \quad \xrightarrow{\text{NaOH}} \quad \text{Br}^-\text{COOC}_2\text{H}_5 \\
\end{align*}
\]

Attempts to convert ethyldibromocyanocacetate to ethylcyano-
boronofluoracetate by using silver fluoride or potassium fluoride under a variety of conditions were unsuccessful:

\[
\begin{align*}
\text{Br}^-\text{COOC}_2\text{H}_5 & \quad \xrightarrow{\text{KP}} \quad \text{Br}^-\text{COOC}_2\text{H}_5 \\
\text{AgF} & \quad \xrightarrow{\text{NaOH}} \quad \text{Br}^-\text{COOC}_2\text{H}_5 \\
\end{align*}
\]

Attempts were made to form cyanofluoromethylene indirectly by
decarboxylating sodium chlorodifluoracetate in the presence of excess sodium cyanide:

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$$\text{ClF}_{2}\text{CCOONa} \xrightarrow{\Delta} \text{[F}_2\text{C]} + \text{CO}_2 + \text{NaCl}$$

$$\text{[OP}_{2} \xrightarrow{\text{CN}^-} \text{[F}_2\text{O(CN)] \longrightarrow \text{F}^- + \text{[PC(CN)] \longrightarrow (\text{P} \text{CN})_n}}$$

Brown-black polymeric solids were obtained with infrared spectra bands at 3.0 µ, 4.5 µ, and 6.2 µ, suggesting that conjugated "black Orion" types of structures had been formed.

3. Dehydrohalogenation Reactions

Chloroformacacetanitrite was prepared from 2-chloro-1,1,2-trifluoroethyl ethyl ether by the method of Young and Farrant:

$$\text{ClH}$$

$$\text{H-O-C-C}_{2}\text{H}_5 \xrightarrow{60\%} \text{H-O-C-C}_{2}\text{H}_5 \xrightarrow{79\%} \text{H-O-C-NH}_2 \xrightarrow{79\%} \text{H}_2\text{O}$$

Reactions with potassium tert-butoxide in the presence of cyclohexene yielded mixed products, including chloroformacetamide, but no cyclopropane derivatives:

$$\text{Cl} \xrightarrow{\text{CN}} \text{KOC}_{2}\text{H}_{5} \xrightarrow{\text{KOH}} \text{[PC(CN)] \longrightarrow (\text{P} \text{CN})_n}$$

A control experiment with bromoformyielded dibromonorcarane (63%). With sodium methoxide (no solvent) at least twelve products were obtained (V.P.C.). Brown solids isolated from the alkoxide reactions are being characterized. Reactions of chlorofluoroacetanitrite with lithium butyl (in pentane at ~50°C) in the presence of cyclohexene yielded mixtures of products (V.P.C.) but not cyclopropane derivatives.

These unsuccessful attempts to trap cyanofluoromethylene with olefins suggest that the methylene intermediate reacts rapidly as a radical with neighboring molecules to give a variety of products including polymers.

CONCLUSIONS

Polymeric products are formed from reactions yielding cyano-methylene X(CN) under neutral or basic conditions. Where $X = H, \text{CO}_{2}\text{H}_2, \text{Cl}$ or $\text{F}$, polymeric cyanomethylene have been
isolated as dimers (olefins), trimers (cyclopropanes) or solid brown-black polymers. The brown-black polymers are believed to have conjugated structures of the "black orlon" type, formed by cyclization of linear cyanomethylene polymers \( \frac{X}{CN} \)^n.

Investigation of the synthesis, structure, and thermal stability of such polymers is in progress. Of special interest are the polymers derived from cyanofluoromethylene FC(CN).

REFERENCES