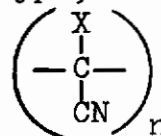


CYANOFLUOROCARBON POLYMERS

C. N. Matthews, R. M. Kliss and R. J. Wineman
Monsanto Research Corporation
Boston Laboratories, Everett, Mass.

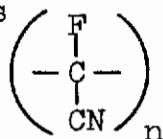
ABSTRACT

The purpose of this investigation is to synthesize cyanofluoro-carbon polymers through the intermediate formation of cyanofluoro-methylene FC(CN). Polymeric products were formed in reactions yielding cyanomethylenes XC(CN) under neutral or basic conditions. Where X = H, COOC₂H₅, Cl or F, polymeric cyanomethylenes were 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



INTRODUCTION

The main aim of this research is to synthesize cyanofluoro-carbon polymers

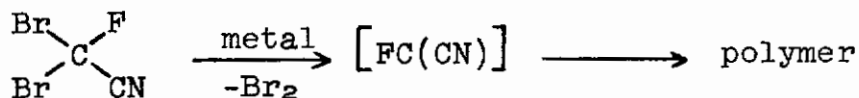


through the intermediate formation of cyanofluoromethylene FC(CN). Such polymers would be expected to be thermally stable because of the high dissociation energies² of C-F bonds (106 Kcals) and C-CN bonds (103 Kcals), and because fluorine atoms and nitrile groups would have exceptional covering power for a carbon skeleton.

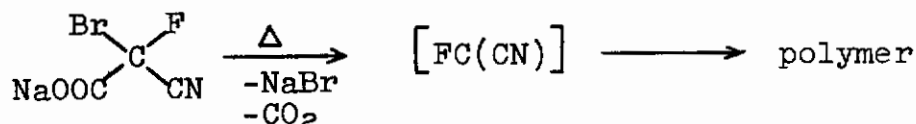
By analogy with the known diradical species propargylene⁵, HC(C≡CH), the postulated divalent carbon intermediate FC(C≡N) should probably be regarded as a methylene⁵ possessing diradical character (triplet state) rather than as a carbene (singlet state). Polymerization, including dimerization, of such cyanomethylenes would be expected under suitable conditions. Experiments were therefore directed toward forming cyanomethylenes XC(CN), where X = H, COOC₂H₅, 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 cyanofluoro-

methylene the methods are represented by the following equations:

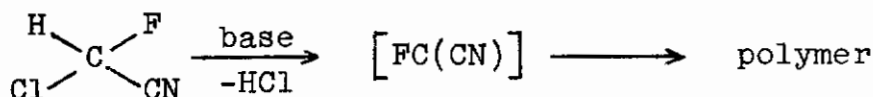
1. Dehalogenation of dibromofluoroacetonitrile².



2. Decarboxylation of sodium cyanobromofluoroacetate⁹



3. Dehydrohalogenation of chlorofluoroacetonitrile⁴



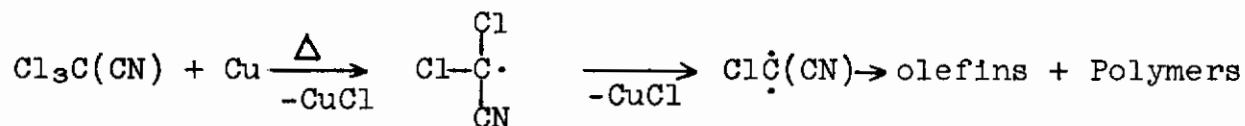
RESULTS AND DISCUSSION

1. Dehalogenation Reactions

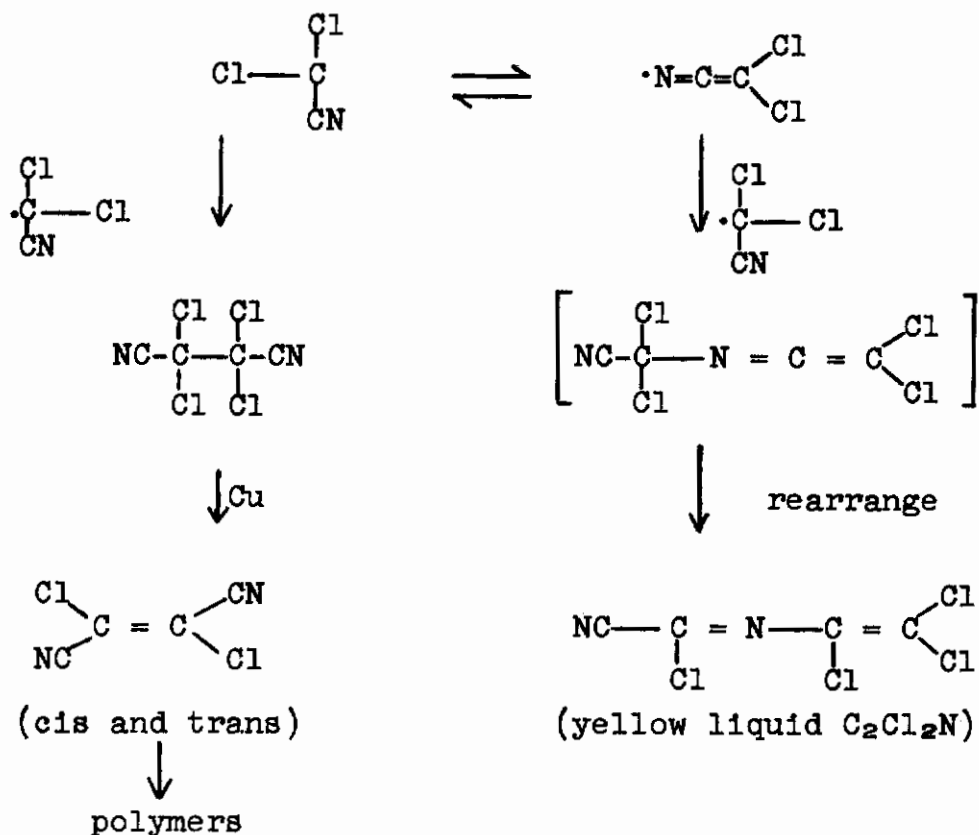
(a) Reactions of cyanohalomethanes with copper (no solvent)

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, infusible and insoluble, with infrared spectrum bands at 3.0 μ (broad), 4.5 μ (sharp), and 6.2 μ (broad); tetrachlorosuccinonitrile; dichloromaleonitrile; dichlorofumaronitrile; and a yellow liquid C₂Cl₂N (bp 54°C/4.5 mm) with infrared spectrum bands at 4.46 μ, 4.50 μ, and 6.0-6.55 μ, believed to be $\text{NC}=\underset{\text{Cl}}{\text{C}}=\text{N}-\underset{\text{Cl}}{\text{C}}=\underset{\text{Cl}}{\text{C}}$.

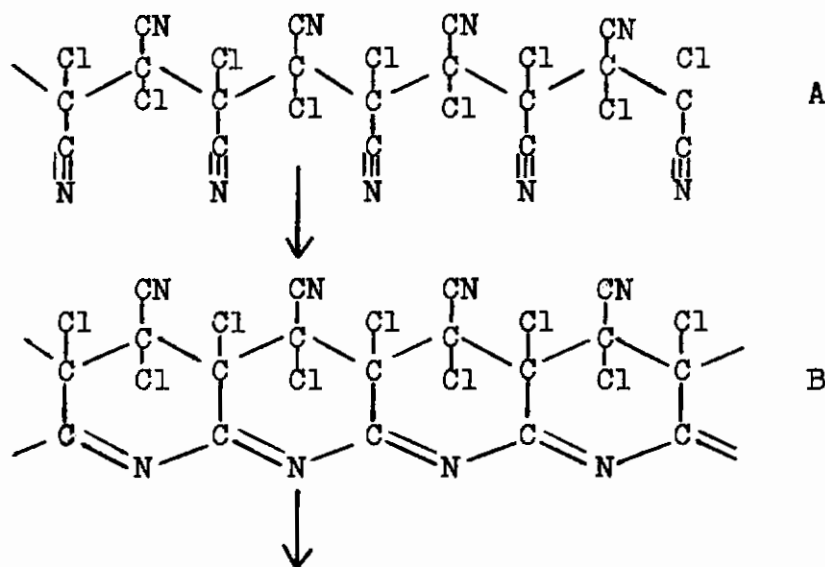
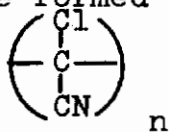
The products from this reaction suggest the formation of the dichlorocyanomethyl radical and its ketenimine form⁷ as primary intermediates. Polymer formation could then occur as outlined below, or through the intermediate formation of cyanochloromethylene:



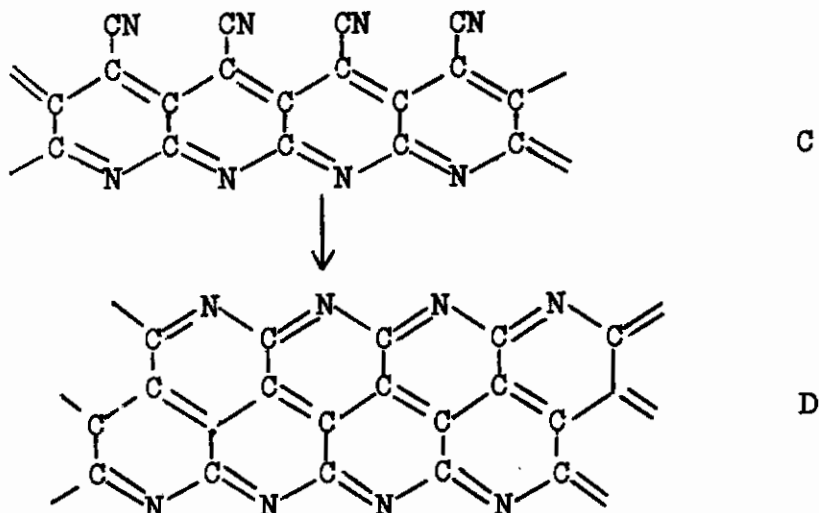
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To explain the color of the brown-black polymeric material and its infrared spectrum it is proposed that conjugated structures of the "black orlon" type (B) are formed spontaneously from the linear polycyanochloromethylene initially formed (A).

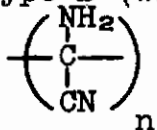


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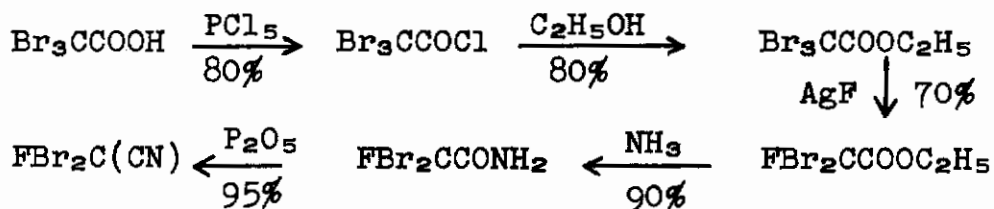


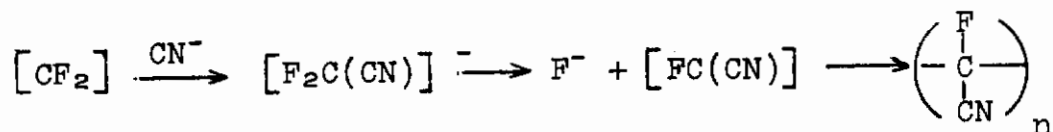
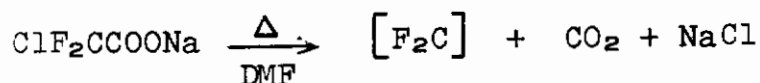
Further dechlorination could occur to give the doubly conjugated polymer C, which could undergo further cyclization to give the triply conjugated polymer D.

The infrared spectrum peak at 4.5μ can be attributed to nitrile groups. The broad band at 6.2μ can be attributed to $>C=N-$ groups, while the broad band at 3.0μ can be attributed to $-NH_2$ or $=N-H$ groups, perhaps present as end groups. The infrared spectra¹ of "black orlon" structures of type B (with H replacing Cl and CN) possess broad bands in the regions 3.0μ and 6.2μ . Polymers closely resembling the brown-black solid in appearance and with very similar infrared spectra⁸ have been obtained by the polymerization of hydrocyanic acid, and have been assigned structures of the type B (with Cl replaced by NH_2), derived from the linear polymer



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

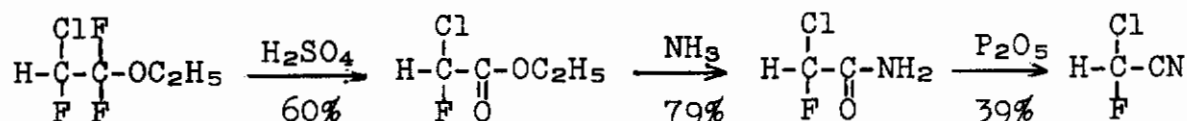




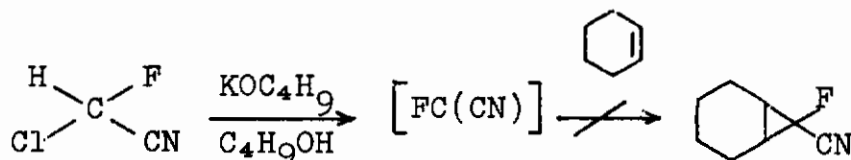
Brown-black polymeric solids were obtained with infrared spectra bands at 3.0 μ , 4.5 μ , and 6.2 μ , suggesting that conjugated "black orlon" types of structures had been formed.

3. Dehydrohalogenation Reactions

Chlorofluoroacetonitrile was prepared from 2-chloro-1,1,2-trifluoroethyl ethyl ether by the method of Young and Tarrant¹⁰:



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



A control experiment with bromoform⁴ yielded 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 chlorofluoroacetonitrile with lithium butyl (in pentane at -50°C) in the presence of cyclohexene yielded mixtures of products (V.P.C.) but not cyclopropane derivatives.

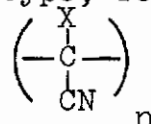
These unsuccessful attempts to trap cyanofluoromethylene with olefins suggest that the methylene intermediate reacts rapidly as a radical with neighboring molecules to give a variety of products including polymers.

CONCLUSIONS

Polymeric products are formed from reactions yielding cyanomethylenes $\text{XC}(\text{CN})$ under neutral or basic conditions. Where $\text{X} = \text{H}, \text{COOC}_2\text{H}_5, \text{Cl}$ or F , polymeric cyanomethylenes have been

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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



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).

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