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THERMALLY STABLE POLYMERS.(U)

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Electrophilic trisubstituted ethylenes, $X \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} Y \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} Z$ in which X, Y, Z are electro- negative substituents, CN, COOCH ₃ , Cl, and F have been synthesized. They do not homopolymerize but readily undergo free radical copolymerization with electron-rich vinyl monomers such as styrene. The copolymers, obtained in reasonably high molecular weights, have glass transition temperatures in the 150-225°C. range, decomposed in the 225-275°F range, and were soluble in many organic solvents.		

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FINAL REPORT TO
U.S. ARMY RESEARCH OFFICE
"THERMALLY STABLE POLYMERS"

H. K. Hall, Jr.

Introduction

Demand by technology for materials retaining good properties under extreme conditions continues to grow. While conventional commercial polymers meet these requirements to some extent, the search for novel polymers and copolymers continues to be appropriate.

A particularly important group of such materials are those formed in place i.e. by addition polymerization. Here no small molecules are spilt out as in polycondensation, and shaped objects can be obtained directly from monomers. Such polymerizations can be either of the vinyl or ring opening types. We have been engaged in the synthesis and polymerization of trisubstituted ethylenes and bicyclobutane monomers (1).

Trisubstituted ethylenes had been neglected as polymerizable monomers perhaps because it was thought that they are too sterically hindered to polymerize. In fact, this hindrance does prevent them from homopolymerizing; but they copolymerize readily with monosubstituted olefins, especially of opposite polarity. For example, tri-carbomethoxyethylene copolymerizes readily with styrene to give a high molecular weight alternating copolymer. The trisubstituted olefins preferably contain cyano, carbomethoxy, chloro, or other electron-attracting groups.

The copolymers prepared in this way are noncrystalline and have very high glass transition temperatures. This makes melt processing difficult. However, they are soluble in common organic solvents, and films can be cast.

The trisubstituted olefins also copolymerize with bicyclobutane monomers to yield new copolymers. However, the bicyclobutane monomers are not readily available.

Particular areas dealt with in this 3 year period are summarized below.

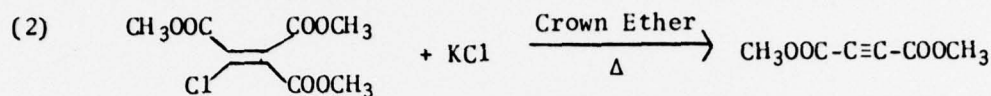
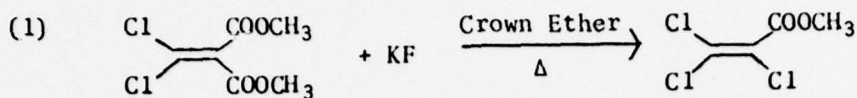
Electrophilic Olefins

A variety of trisubstituted ethylenes $\text{X}=\text{Y}_2$, in which X, Y, Z are electronegative substituents, CN, COOCH_3 , Cl, and F has been synthesized and examined as new vinyl monomers. They do not homopolymerize but undergo free radical copolymerization with electron-rich vinyl monomers such as styrene. If the trisubstituted ethylene is very electron-poor, and the styrene very electron-rich as in p-methoxystyrene, cationic homopolymerization of the latter occurs.

The copolymers were obtained in reasonably high molecular weights. Because of their crowded structures and plurality of polar groups, they had high glass transition temperatures ($150^\circ - 225^\circ\text{C}$). They decomposed in the range $225^\circ - 275^\circ$.

In the course of this work two novel reactions, chlorodecarbomethoxylation (1) and dechlorocarbomethoxylation (2) were found:

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These experiments had been aimed at olefins containing F and COOCH_3 groups. We made one such monomer, $\text{F} \begin{array}{c} \diagup \quad \text{COOCH}_3 \\ \diagdown \quad \text{COOCH}_3 \end{array}$.

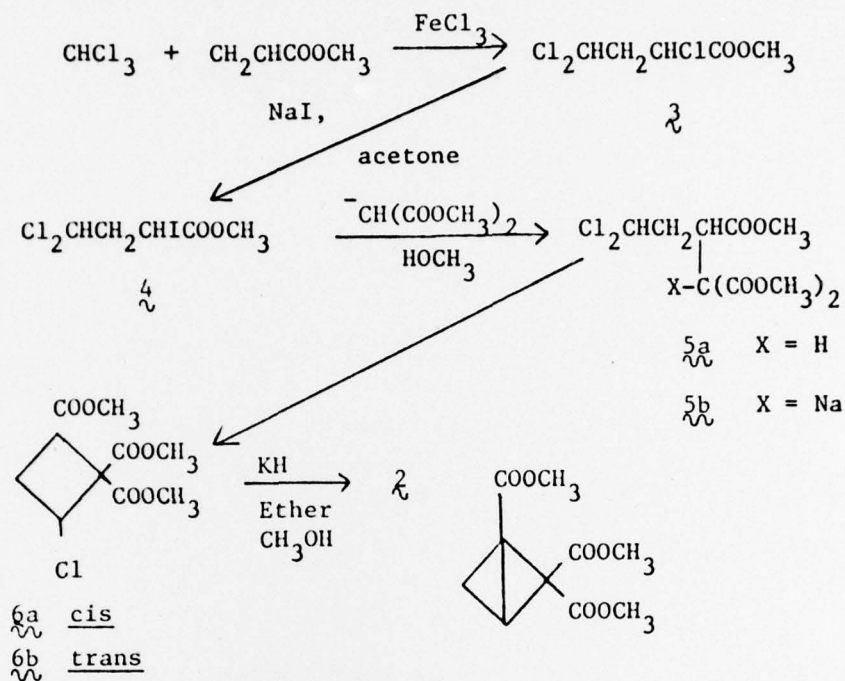
It was difficult to prepare, did not copolymerize well under radical conditions, and only dimerized under anionic conditions. No further work with these monomers is planned.

Bicyclobutanes

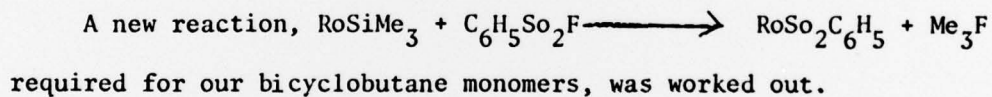
Trimethyl bicyclobutane-1,2,2-tricarboxylate 2 was synthesized by a facile five-step route, beginning with the ferric chloride-catalyzed addition of chloroform to methyl acrylate to give methyl 2,4,4-trichlorobutyrate 3. Replacement of the 2-chloro group by iodide was followed by displacement with dimethyl malonate anion to give trimethyl 4,4-dichlorobutane-1,1,2-tricarboxylate 5a. Thermolysis of the corresponding sodium derivative 5b gave trimethyl cis, trans-3-chlorocyclobutane-1,2,2-tricarboxylate 6. Closure of the bicyclobutane ring to yield 2 was accomplished by potassium hydride in ether, catalyzed by methanol.

Bicyclobutane 2 polymerized under free radical initiation with breakage only of the 1,3 bond. The homopolymers, obtained in moderate yields, were of low molecular weight, probably owing to steric, hindrance effects. Co-

polymerization occurred with vinyl monomers of varying polarity. The copolymers, obtained in moderate yields, had low molecular weights and consisted mostly of the vinyl comonomer units.



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Study has been given to organometallic chemistry of small ring compounds. It was hoped that basic knowledge will be gained in order to (1) find organometallic catalyst which will polymerize cyclopropanes and cyclobutane (2) find transition metal catalysts to cyclodimerize olefins to cyclobutanes, making them and bicyclobutanes cheap materials.

1,2-Dicyanocyclopropane and 1,1-dicyanocyclopropane formed metallocyclobutanes when treated with tris (triethylphosphins) platinum (0).

The latter reagent reacted with tricyanoethylene to give a metallo-cyclopropane. Polycyanocyclopropanes and -ethylenes react similarly.

Olefins and carbocycles containing substituents of opposite polarity ("push-pull") were studied. The olefins react similarly to the percyano derivatives. Thus bis (triphenylphosphino) (ethylene) platinum (0) with 2 ethoxy- 1,1-dicyanoethylene and with 2,2-diethoxy-1,1-dicyanoethylene gave crystalline metallocyclopropanes. However, with a "push-pull" cyclobutane, 1,2-dicyano-3-dimethylamino-4,4-dimethylcyclobutane, no reaction occurred.

Personnel

H. K. Hall, Jr. (principal investigator)
P. A. Ykman (post-doctoral associate)
W. Fischer (post-doctoral associate)
M. Lenarda (post-doctoral associate)

Cumulative Bibliography

Recent Relevant Publications (Based on U. S. Army Research Office Support)

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9. H. K. Hall, Jr. and W. Fischer, "Synthesis and Polymerization of Trimethyl Bicyclobutane-1,2,2-Tricarboxylate," *Helvetica Chimica Acta*, manuscript submitted.
10. Professor H. K. Hall, Jr., has had a research grant #DAHCO4-74-G-0143 which is continuing through September 30, 1977.