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Fabricable Polymers with Excellent Heat, Oxidative and Hydrolytic Stability			
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H.K. Hall, Jr.			
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The study of extremely electrophilic imines was continued. Methyl dicyano-methanimine was synthesized and copolymerized with p-methoxy-styrene. The investigation of the polymerization of benzylidene cyanamide and pivalidene cyanamide was continued.			
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Author: H.K. Hall, Jr.

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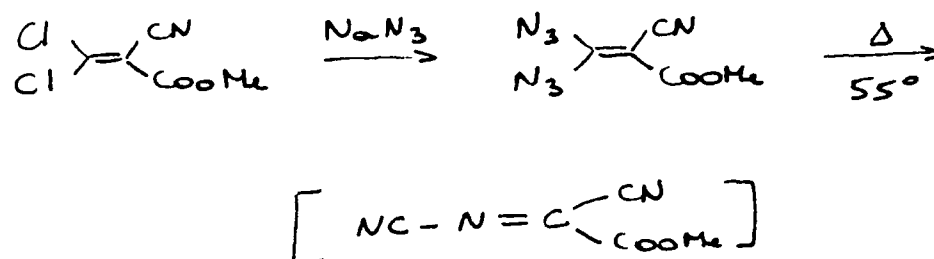
Tucson AZ 85721

Comment: This report had been submitted previously as a Progress Report. The moneys which were originally awarded to the late Dr. C.S. Marvel covered our research expenses for only this six-month period.

As agreed, the funds remaining from grant DAAG29-85-K-0110 were awarded to Dr. H. K. Hall, Jr. after the death of Dr. C. S. Marvel. These funds were used to continue the Principal Investigator's research on the "synthesis and Polymerization of Azaethylenes and Aza-1,3-Butadienes. New Reactive Monomers."

Results

The study of extremely electrophilic imines was continued. In contrast to C=C and C=O monomers, the C=N monomers are conspicuous by their absence in the literature. Tricyano-azaethylene had previously been synthesized and proved to extremely reactive. Therefore, methyl dicyano-methanimine carboxylate has been synthesized by the same method.

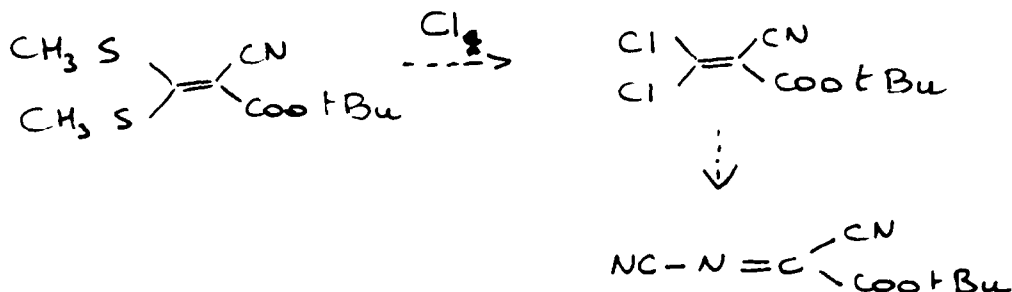


This monomer is more stable in solution and can be fully characterized. However, it cannot be isolated. Diels-Alder cycloadducts can be obtained with 2,3-dimethylbutadiene and cyclopentadiene. In the presence of p-methoxystyrene, spontaneous alternating copolymerization occurs, however this polymer was insoluble.

In order to improve stability and solubility, the t-butyl ester is now being synthesized.

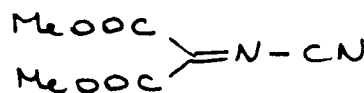
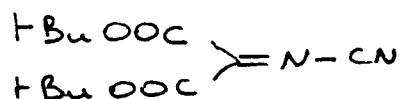


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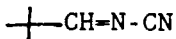
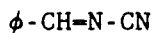


The chlorination step, in contrast to the methyl ester derivative, does not proceed in good yield and is currently being optimized.

We are also synthesizing the dibutyl and dimethyl N-cyanomethanimine dicarboxylate derivatives. These should be more stable, but hopefully still reactive enough to polymerize.



The investigation of the polymerization of benzylidene cyanamide and piralidene cyanamide was completed.



The former polymerizes in high yield both under anionic and free radical conditions, while the latter only polymerizes with anionic initiators.

Publications during this reporting period.

M. Ramezani, F.D. Saeva and H.K. Hall, Jr., "A New Azacyanocarbon, C₄N₄; Tricyanomethanimine," *Tetrah. Lett.* 29, 1235 (1988).

J.B. Kim and H.K. Hall, Jr., "Synthesis and Polymerization of 1-Carboethoxy-3-methyl-1-aza-1,3-butadiene," *Macromolecules* 21, 1547 (1988).

J.B. Kim, A.B. Padias, H.K. Hall, Jr. and F.D. Saeva. "Synthesis and Polymerization of Electron-Deficient Imines" (in preparation).

M. Ramezani, A.B. Padias and H.K. Hall, Jr., "Two Novel Electrophilic Imines" (in preparation).