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Aerojet Solid Propulsion Company

2561:871
NAC

19 December 1988

Subject: CDRL A001, Progress Report
N00014-86-C-0164, Synthesis of Energetic Binders

To: Office of Naval Research
800 North Quincy Street
Arlington, VA 22217-5000

Attention: Dr. Richard S. Miller, Scientific Officer

The subject contract data item is submitted for your approval as Enclosure (1) in compliance with the requirements of CDRL A001.

Questions and/or comments should be directed to Nancy Conner, Data Manager, (916) 355-5297.

AEROJET SOLID PROPULSION COMPANY

T S Grace

T. S. Grace
Contract Manager
Technology & Development

Encl: (1) Seventh Quarterly Report (1 cy)
July to October

cc: Naval Research Laboratory/Director/Code 2627 (1 cy)
Defense Technical Information Center/S47031 (12 cys)
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Aerojet Solid Propulsion Company

15 December 1988

Office of Naval Research
800 North Quincy Street
Arlington, VA 22217

Attention: Dr. R. S. Miller (Code 1132P)

Subject: Seventh Quarterly Summary of Progress on
Contract "Synthesis of Energetic Binders"
Covering Period 1 July 1988 to 31 October 1988
Contract N00014-86-C-0164

Large scale synthesis of the cubane/oxetane monomer, CUBOX, was developed during the last reporting period. The key intermediate from commercially available cubane dicarboxylic acid is cubane monocarboxylic acid. Several routes to its synthesis were outlined in the Fifth Quarterly Summary. The original method supplied by Dr. Eaton was abandoned when scale-up gave poor yields. In this method, the n-hydroxypyridine-2-thion ester undergoes free radical decarboxylation in ter-butylmercaptan. Also the odor (natural gas) of ter-butylmercaptan could not be contained and this was a concern in our laboratory. energetic binders. (Mgm)

The method in which the ter-butylperester of cubane undergoes free radical decaroxylation in refluxing cumene was utilized to give 8.5g of CUBOX in 26% overall yield. This method might be suitable for further scale-up except the purification of the final product was very difficult. The impurities generated in its synthesis required multiple distillations and column chromatography separations.

Dr. Baum of Fluorchem in Azusa utilized still another route we described to supply us with two lots (one 50g) of the desired cubane carboxylic acid. In this route the cubane monomethylester monoacid cubane is reacted with mercury(II) oxide and bromine in dibromomethane to give the bromocubane methylester. Free radical reduction with ter-butyltin hydride gives the cubane monocarboxylic acid. Dr. Baum is also working on a more fundamental route that appears even more promising.

A preliminary lot (4.18g) of the CUBOX monomer was polymerized using DCC-$AgSbF_6$. Samples were sent to China Lake and Professor Fred Hawthorne for physical characterization. A sample of the monomer and polymer were sent to Dr. Philip Eaton as was requested at the Chestertown meeting. He has confirmed the structure of both materials.

At the Chestertown meeting a nitrile substitute cubane-oxetane monomer was proposed as a potentially useful compound and we have put priority on its preparation. We have a promising route to its synthesis and have begun work. First, the previously prepared cubane monoacid chloride monomethyl ester is reacted with ammonia in THF to give the monoamide monomethyl ester. This reaction has proved successful and the material has been characterized. The structure was confirmed by x-ray crystallography. Following reduction of the

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ester with $LiBH_4$, the amide is transformed to the nitrile with either phosphorous oxychloride or triphenylphosphine in carbon tetrachloride. The resulting chloromethyl cubanenitrile should couple with the sodium salt of hydromethyl-3-methyloxetane to give the desired monomer.

During this reporting period we have also begun the large scale synthesis of the carborane-oxetane monomer, CARBOX. From 100g of 1-methyl-2-propanol carborane we have made and isolated over 40g of pure, solid monomer. This material is ready for polymerization and formulating into propellant for burn rate measurements. A further purified sample of CARBOX was sent to Dr. R. Nissan of the Naval Weapons Center for extensive NMR analysis and to Dr. R. Gilardi of the Naval Research Lab for x-ray single-crystal diffraction analysis.

These large scale reactions of CARBOX enabled us to study this two-step synthesis of CARBOX in greater detail. First, the bromination of 1-methyl-2-propanol-carborane with 47% hydrobromic acid gave 1-methyl-2--bromopropylcarborane in better than 80% yield. Isolation of the crude product upon scale-up gave some problems and needs improvement. Second, the coupling reaction of 1-methyl-2-bromopropyl-carborane with the sodium salt of 3-hydroxymethyl-3-methyl-oxetane gave a 45-50% crude yield. Parameters that we found important were these: amount of sodium hydride used, rate of addition of Na-HMMO, temperature, and work-up procedure. Third, we found that the G.C. method for analyzing the crude product had a precision of ± 15%; therefore, two parameters from our previous data need re-examining. On is the choice of solvent. DMF and HMPA/THF may give nearly equal yields, but DMF is still the solvent of choice because of its low toxicity and cost. The second is the choice of leaving group on the carborane. The differences in yield between using the tosyl or bromo group is now unclear. Preparation of the tosyl derivative has shown to be easier to scale up and may be the leaving group of choice.

An alternate route to carborane-oxetane monomers via reaction of decaborane with an alkyn-oxetane was pursued during this reporting period. Previously we prepared a sample of 3-propynyloxymethyl-3-methyloxetane, and sent it to Professor Hawthorne at UCLA for reaction with decaborane. This reaction did not give the desired product, and it was thought that the oxygen and triple bond were too close together for the reaction to succeed. Therefore, two other alkyn-oxetanes were prepared, 3-(3-pentynyloxymethyl)-3-methyloxetane and 3-(4-pentynyloxymethyl)-3-methyloxetane. Reaction with decaborane again gave no product but a polymeric material. It is now believed that decaborane is a strong enough Lewis acid to catalyze the polymerization of oxetane. Further work on this route has been suspended.

Participating personnel: L. S. Newton, H. W. Cheung.

Respectfully submitted,

G. E. Manser, Scientist
Chemical Research and Development

cc: Phillip Miller, Consultant
LSN:amb:2131:1212-L