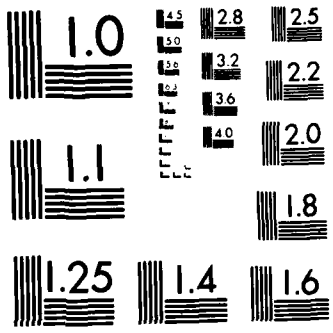
AD-A131 723 POTENTIAL ENERGETIC MATERIALS FORMED FROM COUPLING OF SUBSTITUTED HALO-S-.. (U) MICHIGAN TECHNOLOGICAL UNIV HOUGHTON DEPT OF CHEMISTRY AND CH.. G F REYNOLDS 1/1

UNCLASSIFIED 27 JUL 83 AFOSR-TR-83-0712 AFOSR-82-0191 F/G 19/1 NL



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REPORT DOCUMENTATION PAGE

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1. REPORT NUMBER: AFOSR-TR- 83-0712	2. GOVT ACCESSION NO.: AD A131723
3. RECIPIENT'S CATALOG NUMBER:	
4. TITLE (and Subtitle): POTENTIAL ENERGETIC MATERIALS FORMED FROM COUPLING OF SUBSTITUTED HALO-S-TRIAZINES	5. TYPE OF REPORT & PERIOD COVERED: Final Report 1 June 82 - 31 May 83
	6. PERFORMING ORG. REPORT NUMBER:
7. AUTHOR(s): Professor G. Fredric Reynolds	8. CONTRACT OR GRANT NUMBER(s): AFOSR-82-0191
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Michigan Technological University, Department of Chemistry and Chemical Engineering, Houghton, Michigan 49931	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: 2303/D9 61102F
11. CONTROLLING OFFICE NAME AND ADDRESS: Directorate of Chemical and Atmospheric Sciences, AFOSR, Bolling Air Force Base, DC 20332	12. REPORT DATE: July 27, 1983
	13. NUMBER OF PAGES: 10
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office):	15. SECURITY CLASS. (of this report): UNCLASSIFIED
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE:

16. DISTRIBUTION STATEMENT (of this Report)

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17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

s-triazines, heterocyclic chemistry, energetic materials

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The coupling of nucleophilic sites on substituted halo-s-triazines to electrophilic sites on other heterocyclic rings has been investigated. For example, by this type of reaction, 2,4-dichloro-6-dimethylmalonyl-s-triazine has been coupled to 2,4,6-trichloropyrimidine in good yield, and to 2,4,6-trichloro-s-triazine in very small yield. Attempts to form longer chains or rings by additional reaction in this manner with the coupled products has not as yet resulted in any significant yield of the desired product.

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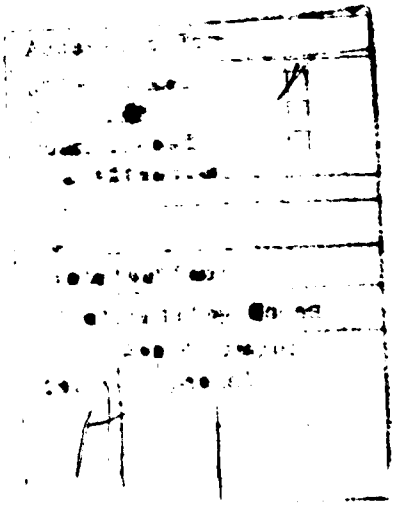
FOREWORD

The personnel working on this project in addition to Professor Reynolds were undergraduate student Rodney Briggs and graduate student Maria Huffman. Most of the work was carried out in the laboratories of the Department of Chemistry and Chemical Engineering, Michigan Technological University, Houghton, Michigan 49931.

Although the supporting grant AFOSR-82-0191 was for the twelve month period from 1 June 1982 to 31 May 1983, the research was suspended effective 1 January 1983 on which date Professor Reynolds was transferred to the Frank J. Seiler Research Laboratory, USAF Academy, Colorado Springs, Colorado 80840 under the USAF University Resident Research Professor program. Since that date Professor Reynolds has been working at FJSRL on the spectroscopic study of molten salt electrolytes as part of the electrochemistry task 2303-F2.



ABSTRACT

The following substituted s-triazines were prepared in good yield: 2,4-dichloro-6-dimethylmalonyl-s-triazine; 2,4-dichloro-6-ureido-s-triazine; 2,4-dichloro-6-(β-hydroxyethoxy)-s-triazine; and 2,4-dichloro-6-(4,6-dichloropyrimidin-2-yldimethylmalonyl)-s-triazine. Also prepared in good yield were: 2-chloro-4,6-bis(4,6-dichloropyrimidin-2-yldimethylmalonyl)-s-triazine; 2,4,6-tris(4,6-dichloropyrimidin-2-yldimethylmalonyl)-s-triazine; 2,4,6-tris(β-hydroxyethoxy)-s-triazine; and 2,4,6-triureido-s-triazine. The structures of these compounds were determined spectroscopically.

Attempts were made to isolate compounds analogous to those listed above in which an additional s-triazine ring had been attached. To date, these attempts have not resulted in any significant yields of the desired products.

DESCRIPTION OF THE RESEARCH

Substituted halo-s-triazines possess both electrophilic and nucleophilic sites, provided that the non-halogen substituent on the triazine ring contains an acidic proton. The carbon atom to which the acidic proton is attached acts as a site for electrophilic substitution which can couple to the nucleophilic site on another molecule, namely, the carbon atom on the ring attached to halogen. The aim of this research was to investigate conditions under which this coupling would occur, as well as to isolate pure compounds and study their structure by NMR, IR and mass spectroscopy.

The initial work showed that in the presence of excess base in dioxane solution, 2,4,6-trichloro-s-triazine reacts with sodiomalonic ester to give small yields of 2,2-bis(4,6-dichloro-s-triazin-2-yl)dimethyl malonate (figure 1, reaction 1). The product is verified by the mass spectrum showing the expected molecular weight of 428 assuming approximately equal distribution of chlorine of mass 35 and 37. Much work was done to find conditions under which the latter compound would form in good yield. Different reaction conditions and different solvents were tried including the use of diethoxydiethyl ether near the boiling point of 155^{o}, and the more polar solvents DMSO and DMF; and in addition, water-acetone solvent was tried near 0^{o} using sodium bicarbonate as a base. None of this work gave any appreciable amount of the desired 2,2-bis(4,6-dichloro-s-triazin-2-yl)dimethylmalonate, and as a result we have not proceeded to try and form cages containing four substituted triazine rings (figure 1, reaction 2).

The initial work also showed that whereas it was difficult to couple one s-triazine ring to another using sodiomalonic ester, it was facile to couple an s-triazine ring to a pyrimidine ring by first forming the sodiomalonate

derivative of chlorinated pyrimidine, and then reacting this with the desired molar ratio of 2,4,6-trichloro-s-triazine to give either 2,4-dichloro-6-(4,6-dichloropyrimidin-2-yldimethylmalonyl)-s-triazine; the 2-chloro-4,6-bis(4,6-dichloropyrimidin-2-yldimethylmalonyl)-s-triazine; or the 2,4,6-tris(4,6-dichloropyrimidin-2-yldimethylmalonyl)-s-triazine. (Figure 2) The three different pyrimidine malonate triazines, designated PMT, $(PM)_2T$ and $(PM)_3T$, respectively, are readily identified by their characteristic NMR spectra (figure 3).

Unfortunately, further coupling of the halogenated pyrimidine malonyl triazines shown in figure 2 does not take place under analogous conditions because the reactivity of the halogen on the substituted pyrimidine rings is much less than that of the halogen on the subsituted s-triazine rings. This is clearly shown by the fact that while 4,6-dichloro-2-dimethylmalonyl-s-triazine undergoes hydrolysis of the chlorine atoms at ambient temperature in aqueous DMSO solvent (figure 4), the chlorine atoms of 4,6-dichloro-2-dimethylmalonylpyrimidine do not undergo hydrolysis even at high temperature in aqueous DMSO.

By adding the appropriate mole ratio of 2,4,6-trichloro-s-triazine to sodiourea in one case, and to sodioethylene glycol in another case, the mono and tri urea derivatives, and the mono and tri ethylene glycol derivatives were formed. These compounds in order were: 2,4-dichloro-6-ureido-s-triazine; 2,4,6-triureido-s-triazine; 2,4-dichloro-6-(β-hydroxyethoxy)-s-triazine; and 2,4,6-tris(β-hydroxyethoxy)-s-triazine. These four compounds were identified by their characteristic NMR spectra, as well as their IR spectra. Both the triurea and triethylene glycol derivatives of s-triazine were treated in solution with sodium, respectively, to form the corresponding anion, and then reacted with s-triazine in order to couple another triazine ring with either the urea or ethylene glycol as the bridging group. As yet, we have

not had the opportunity to entirely purify and spectroscopically study the products, but initial NMR spectra of the crude products indicates that small amounts of the coupled products were formed. Evidence for this comes from hydrolysis of the products in aqueous DMSO-d6 in the NMR tube. In both cases, NMR peaks were observed to from near 11 to 12 ppm downfield from reference tetramethylsilane, as expected for hydrolysis of a dichloro-substituted triazine as shown previously in figure 4. It appears that if only the initial reactants were present, this peak would not have occurred upon hydrolysis.

Because guanidine derivatives of halogenated s-triazines promise potential for use as energetic materials, much time was spent on methods for their synthesis. Because the protons on guanidine are not hardly acidic at all, the method of displacing a hydrogen on guanidine with an alkali metal prior to reaction with trichloro-s-triazine requires rigorous conditions. The literature indicates that by reacting potassium amide in liquid ammonia with guanidine nitrate, dipotassium guanidine precipitates from solution. We attempted to prepare the dipotassium guanidine in this manner in a cooled glass vessel containing liquid ammonia under a nitrogen atmosphere, followed by filtration under nitrogen. The liquid ammonia solutions proved very difficult to work with, and Rodney Briggs ended up with what appeared to be a mixture of the dipotassium guanidine, potassium guanidine, as well as some residual potassium amide. This gray solid was then added to dry tetrahydro-furan solvent, and a solution of trichloro-s-triazine in the dry THF was added. Workup of this reaction by the student involving multiple passes through a chromatographic column produced a very small quantity of oily product whose infrared spectrum (figure 5) possesses some absorption expected for a guanidine derivative of s-triazine. This experiment will have to be repeated under more carefully controlled conditions if a pure analytical sample is to be obtained.

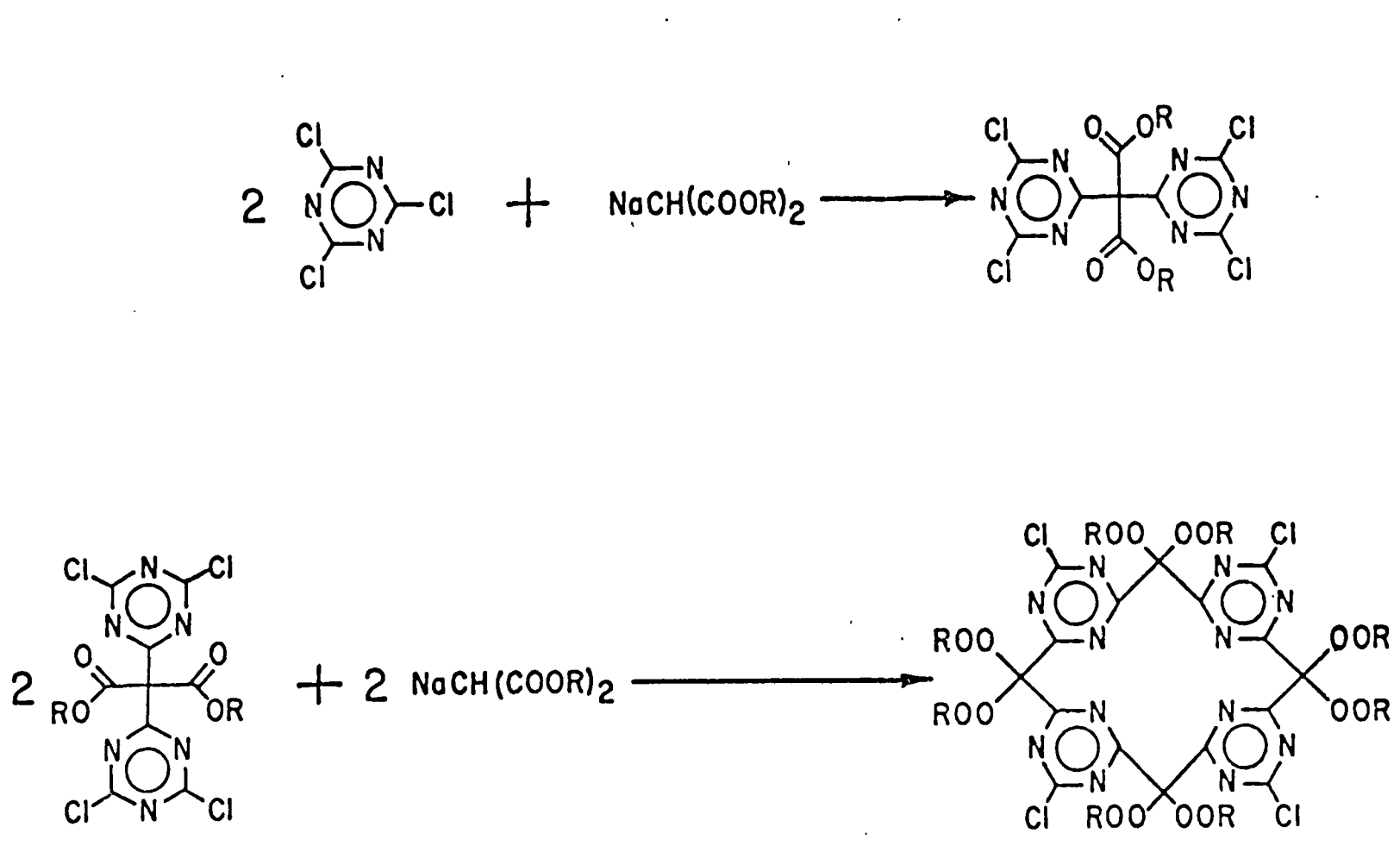


Figure 1. The Reaction of 2,4,6-Trichloro-s-triazine with Sodium 4,6-Dichloro-s-triazin-2-yldimethylmalonate.

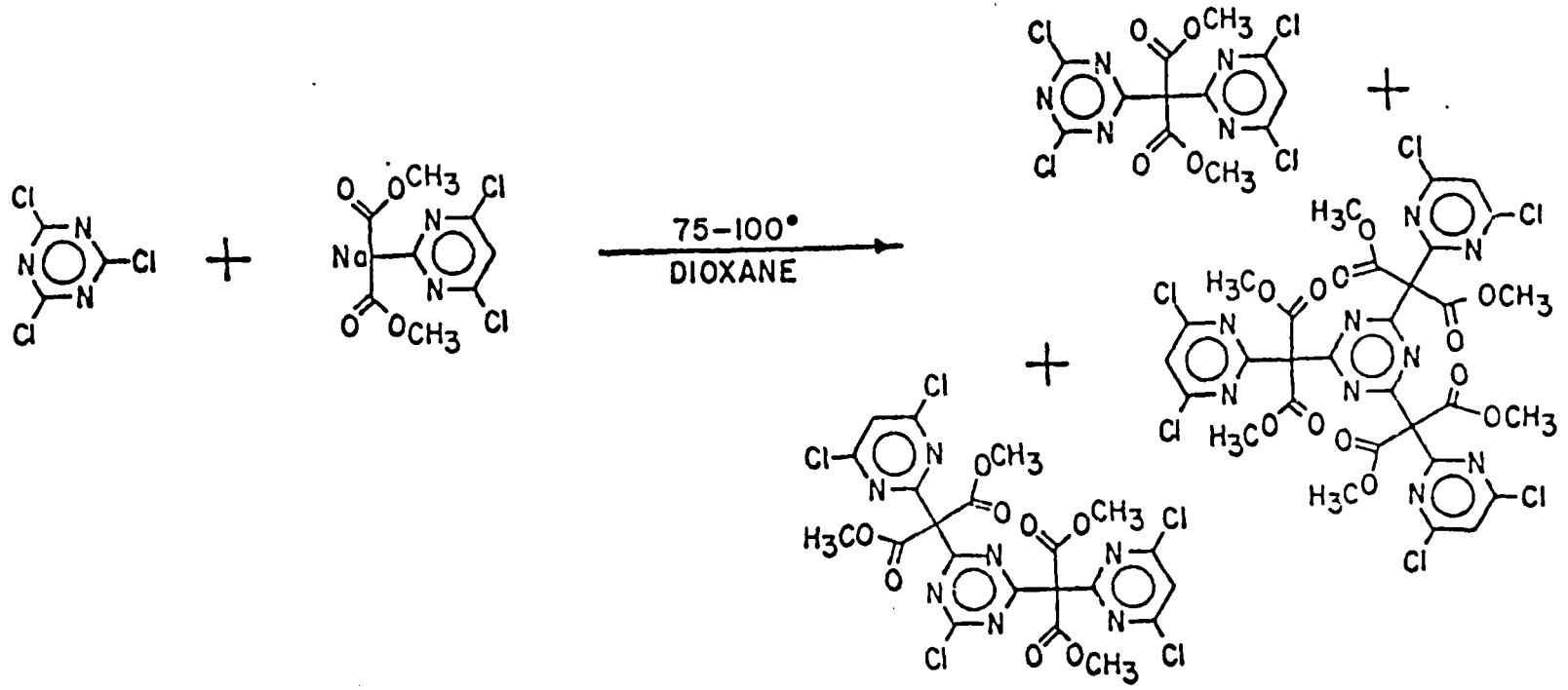


Figure 2. The Reaction of 2,4,6-Trichloro-s-triazine with Sodium 4,6-Dichloropyrimidin-2-yldimethylmalonate.

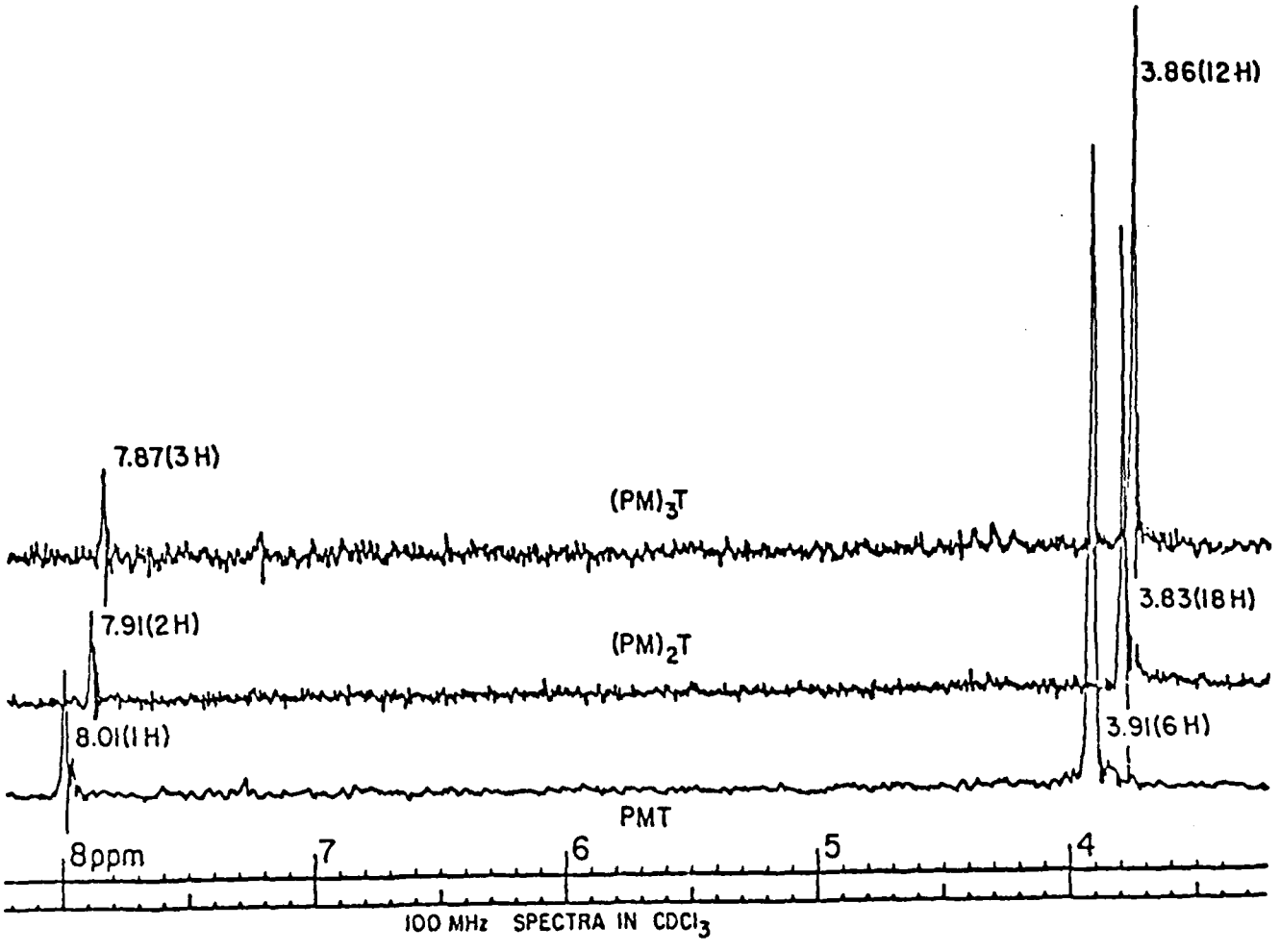


Figure 3. The NMR Spectra of the (4,6-Dichloropyrimidin-2-yldimethylmalonyl)-s-triazines.

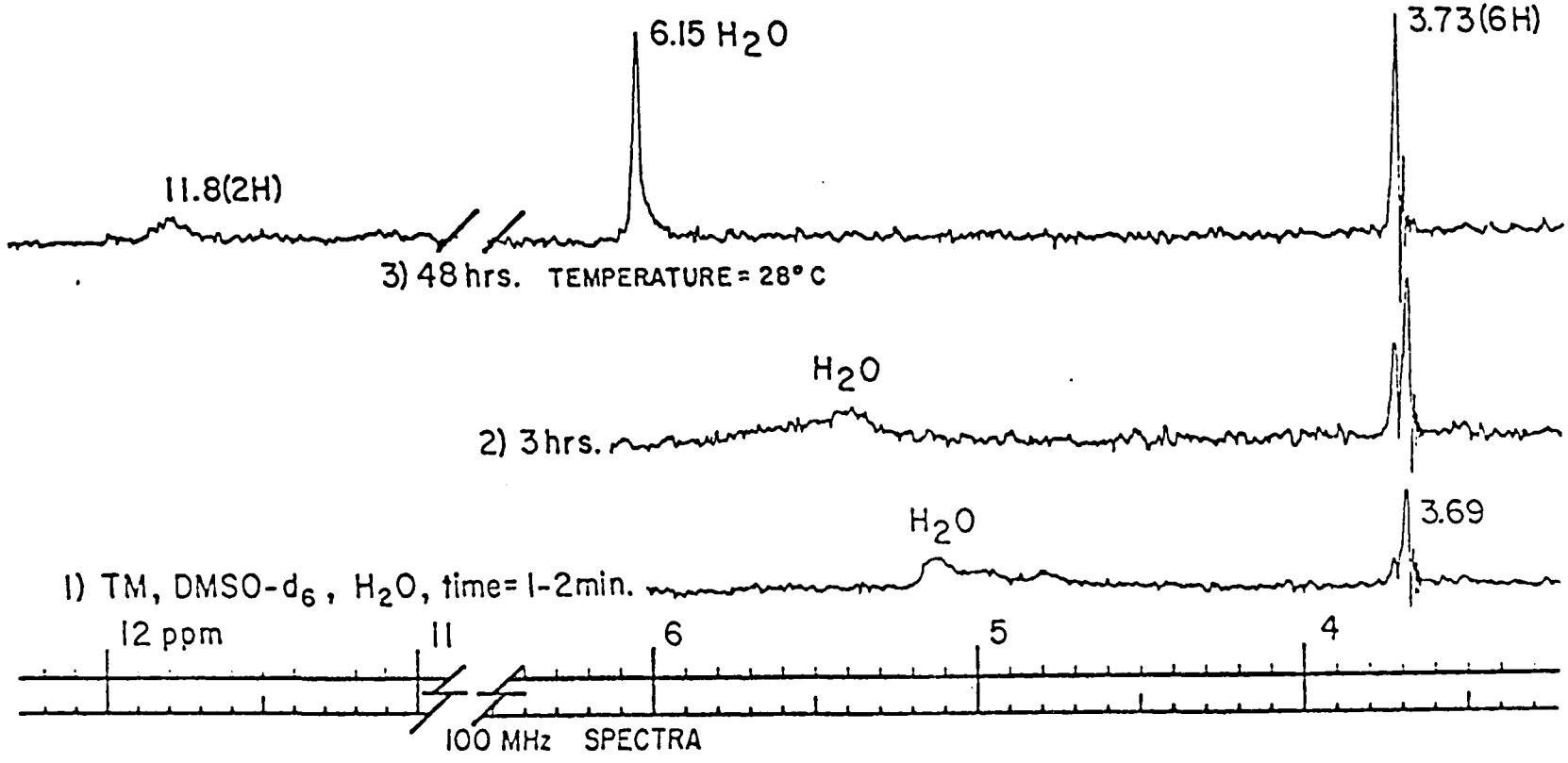


Figure 4. NMR Spectra of 4,6-dichloro-2-dimethylmalonyl-s-triazine Hydrolysis in DMSO.

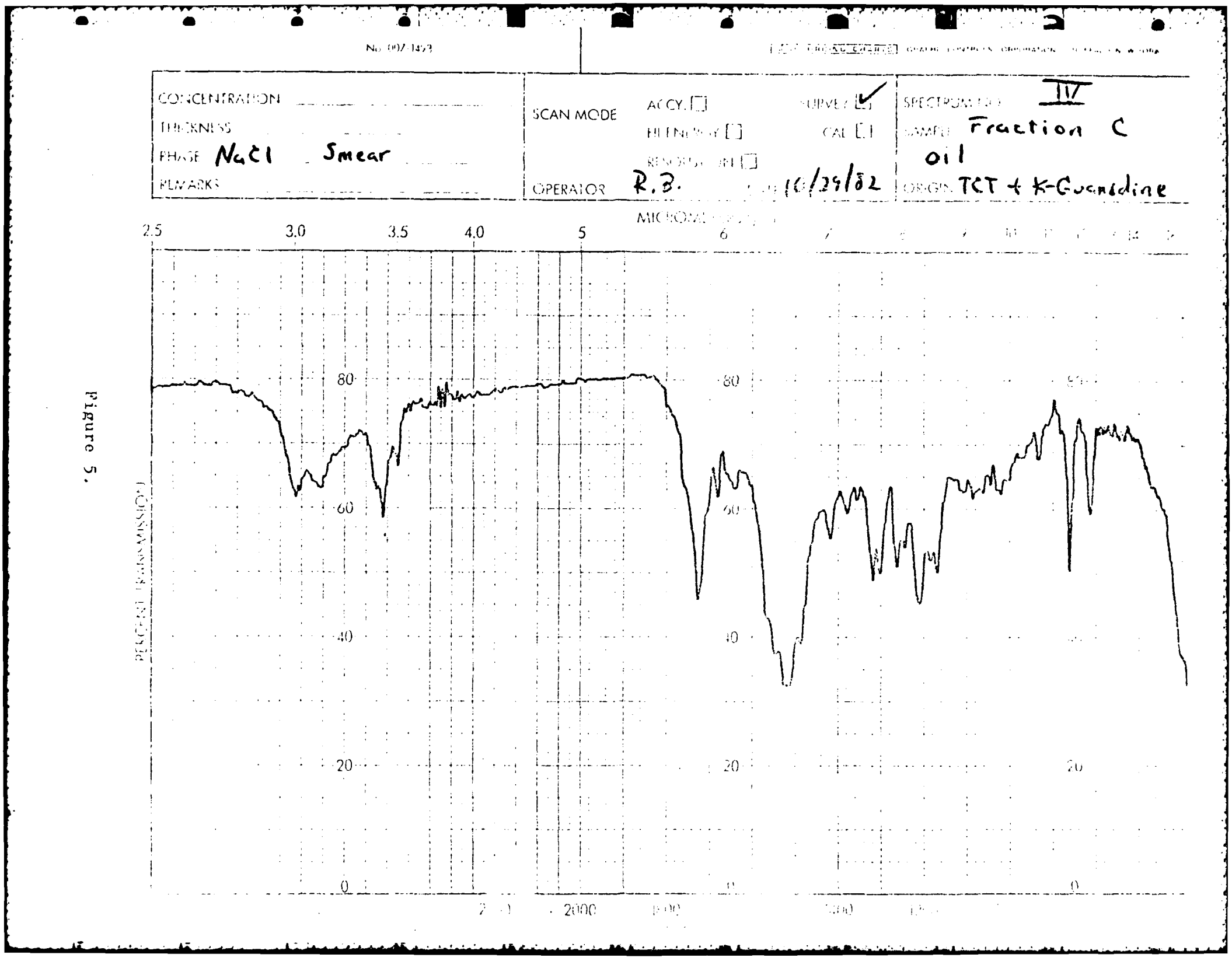

CONCENTRATION
THICKNESS
PHASE NaCl Smear
REMARKS
SCAN MODE
ACCY.
SURVEY
CAL
OPERATOR R.B.
10/29/82
IV
Fraction C
oil
TCT + K-Guanidine
MICRONS
2.5
3.0
3.5
4.0
5
6
80
60
40
20
0
2000

Figure 5.