AD-A138 146 PREPARATION OF FLUOROMETHYLENE OLEFINS(U) IOWA UNIV IOWA CITY D J BURTON 28 DEC 83 ARO-16382.16-CH DAAG29-79-C-0060 1/1

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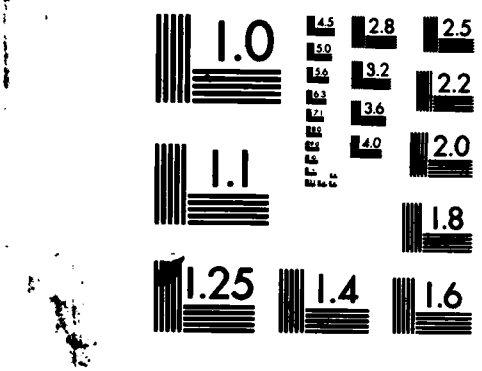


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19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

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|---|---|
| Dienes | Fluoromethylene Olefins |
| Conjugated Dienes | Metal Stabilized Ylides |
| Fluoroolefins | Ylide-carbene Reactions |
| Olefins | Wittig Reaction |
| | Difluorocarbene |

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

The purpose of this investigation were : (1) to investigate the preparation of metal stabilized ylides and their utility in the preparation of fluoromethylene olefins, and (2) to investigate ylide-carbene reactions as a route to difluoromethylene olefins which avoids the limitations of the classical Wittig reaction. During the course of these investigations several new and novel reactions of difluorocarbene were discovered as well as a new and unique chain-extention reaction for the preparation of fluoroolefins and conjugated dienes.



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# PREPARATION OF FLUOROMETHYLENE OLEFINS

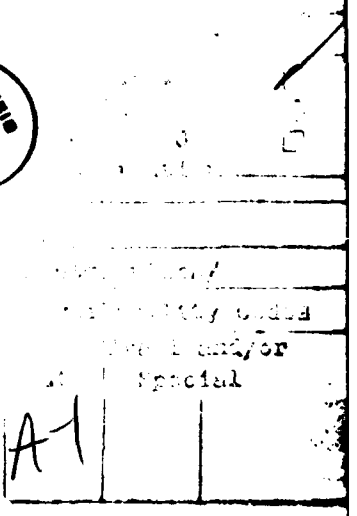
FINAL REPORT

Donald J. Burton

December 28, 1983

U.S. Army Research Office

University of Iowa



Research Report:

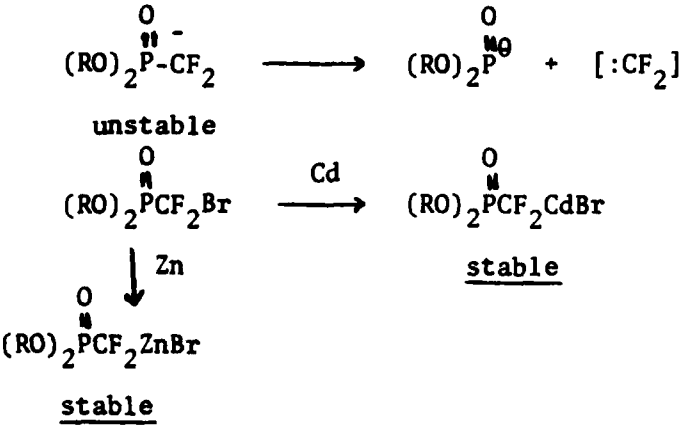
I. Statement of Problem:

The purposes of this investigation were: (1) to investigate the preparation of metal stabilized ylides and their utility in the preparation of fluoromethylene olefins, and (2) to investigate ylide-carbene reactions as a route to difluoromethylene olefins which avoids the limitations of the classical Wittig reaction.

During the course of these investigations we discovered several new and novel reactions of difluorocarbene as well as a new and unique chain-extention reaction for the preparation of fluoroolefins and conjugated dienes.

II. Summary of Important Results:

A. Our work on the preparation of metal-stabilized ylides yielded four significant publications. We were able to prepare stable zinc and cadmium complexes of the difluoromethy phosphonates ylide (cf. Publications #3 and 13). In contrast to the instability of difluoromethylene ylide (even at low temperatures) these metal stabilized ylides were thermally stable (Cd reagent to 60°C, Zn reagent to 100°C).




More importantly, the metal stabilized reagents mimic the unstable ylide in their chemical reactions and can be utilized in synthetic applications in which the free unstable ylide fails.

$$(RO)_2\overset{O}{\overset{\|}{P}}CF_2ZnBr + R'C(O)Cl \longrightarrow (RO)_2\overset{O}{\overset{\|}{P}}CF_2\overset{O}{\overset{\|}{C}}R' + ZnBrCl$$

Cf. Publication #3

Similarly, the analogous phosphonium ylide $[R_3\overset{+}{P}-\overset{-}{C}F_2]$ is unstable and can only be generated and captured insitu via dehalogenation of bromodifluoromethyl-phosphonium salts with tertiary phosphines. However, if the olefin product is

$$[Ph_3\overset{+}{P}CF_2Br]Br^- + Ph_3P: + PhC(O)CF_3 \xrightarrow{70^\circ} F_2C=C(Ph)CF_3$$

reactive towards the tertiary phosphine [utilized in generation of the ylide], the product is destroyed in a competitive side reaction with the tertiary phosphine.

However, we have no demostrated that metal-stabilized ylides can circumvent this difficulty, and the preparation of highly reactive fluoroolefins is now possible via the use of these reagents.

$$[Ph_3\overset{+}{P}CF_2Br]Br^- + Ph_3P: + C_6F_5C(O)CF_3 \longrightarrow F_2C=C(C_6F_5)CF_3 \qquad 0\%$$

$$[Ph_3\overset{+}{P}CF_2Br]Br^- + Cd + C_6F_5C(O)CF_3 \longrightarrow F_2C=C(C_6F_5)CF_3 \qquad 83\%$$

Cf. Publication #12

Similar utility of metal dehalogenation of phosphonium salts was employed in the initial development of a chain-extension reaction of fluoroolefins.

$$[Ph_3\overset{+}{P}CF_2Br]Br^- + Hg + F_2C=C(Ph)CF_2CF_3 \longrightarrow Ph_3\overset{+}{P}CF_2CF=C(Ph)CF_2CF_3]Br^-$$

$$\downarrow H_2O$$

$$CF_2=CFC(Ph)=CFCF_3$$

Cf. Publication #14

This novel reaction delineates the first unequivocal chain-extension method for the preparation of homologous fluoroolefins or dienes.

B. Our work on ylide-carbene chemistry has produced a novel route to difluoromethylene olefins in which all the phosphorus-containing moities can be readily recycled. Thus, the major limitation (formation of $Ph_3PO$) of the classical Wittig reaction is avoided.

This method utilizes the ylide in a dual role - initially as a base to generate difluorocarbene insitu, and secondly as a nucleophilic trapping agent for the electrophilic carbene.

$$Ph_3\overset{+}{P}\text{-}\overset{-}{C}R_2 + CHF_2Cl \longrightarrow [Ph_3\overset{+}{P}\text{-}CHR_2]Cl^- + [:CF_2]$$

$$Ph_3\overset{+}{P}\text{-}\overset{-}{C}R_2 + [:CF_2] \longrightarrow Ph_3P: + F_2C{=}CR_2$$

Overall Reaction: (sum of the two reactions above)

$$2\ Ph_3\overset{+}{P}\text{-}\overset{-}{C}R_2 + CHF_2Cl \longrightarrow [Ph_3\overset{+}{P}CHR_2]Cl^- + Ph_3P: + F_2C{=}CR_2$$

Note:

1) No $Ph_3PO$ is produced.
2) The $[Ph_3\overset{+}{P}CHR_2]Cl^-$ + $Ph_3P$ produced in the reaction can be readily recycled to give additional ylide. Thus, the expensive phosphorus reagents are not consumed.
3) Reaction is general and easily scaled up.
4) Cf. publication #1 for full details of this definitive paper.

C. The olefins obtained from the metal-stabilized ylide work and the ylide-carbene work provided us excellent model compounds to study the mechanism of the fluoride ion catalyzed isomerization of fluoroolefins. The mechanism of this process (concerted or carbanion) has been the subject of extensive

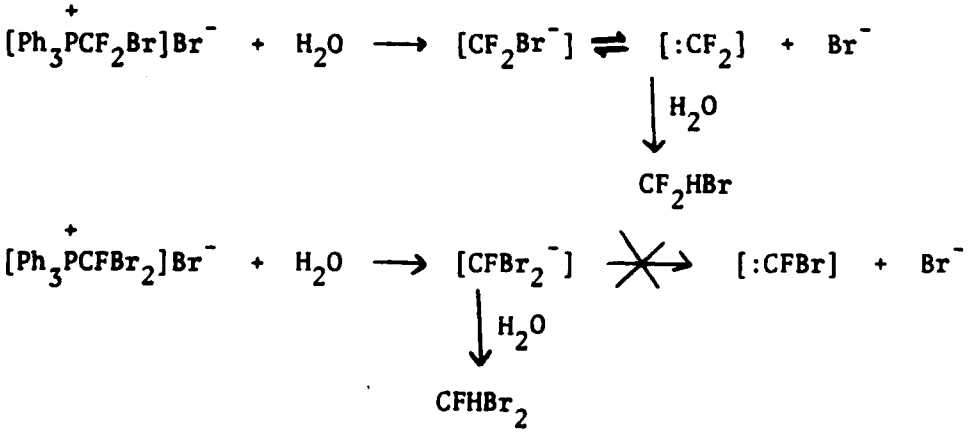
$$F_2C{=}C(Ph)CF_2CF_3 + F^- \longrightarrow CF_3C(Ph){=}CFCF_3 + F^-$$

controversy. A detailed kinetic study of a series of 2-aryl-F-butenes gave unequivocal evidence in support of the carbanion mechanism. However, we did discover that there was a two step mechanism involved in the formation of the carbanonic intermediate, and a change in the rate limiting step was determined by the type of substituent present on the aryl ring.

This work provides the first unequivocal evidence for a carbanion intermediate in this type of catalytic reaction.

Full details are described in publication #11.

D. The mechanism of hydrolysis of fluorine-containing phosphonium salts was probed with the use of radioactive bromide. The mechanism (carbene or carbanion) depends upon the rate of collapse of the initially formed methide ion vs. the rate of protonation of the methide ion. For the bromodifluoromethyl phosphonium salts, unequivocal evidence was obtained for difluorocarbene as a transient intermediate. For dibromofluoromethyl phosphonium salts, unequivocal evidence to support a carbanion intermediate was obtained. Thus, the mechanism of hydrolysis of these fluorinated phosphonium salts has been established as:




Publications #2 and 9 detail these results.

E. Othr carbene chemistry suggested by these results resulted in the work detailed in publications #9, #6, #7, and #4.

F. The work detailed in parts A and B led us to explore other routes to fluoro-olefins and ylides. These works are detailed in publications #15, #16, #10; and #5.

III. Publications:

List of Publications:


1. Ylide-Carbene Chemistry Synthesis of 1,1-Difluoro-1-Alkenes. Donald J. Burton and Gregory A. Wheaton, J. Organic Chemistry, 48, 917-927 (1983).

2. The Hydrolysis of Dibromofluoromethyl Triphenylphosphonium Bromide. Donald J. Burton, R.M. Flynn, R.G. Manning and R.M. Kessler, J. Fluorine Chemistry, 21, 371-376 (1982).

3. A Useful Zinc Reagent For The Preparation of 2-Oxo-1,1-Difluoroalkylphosphonate Donald J. Burton, Takashi Ishihara, and Masamichi Maruta, Chemistry Letters, 755-758 (1982).

4. Preparation, Stability, and Acidity of Difluoromethylene Bis-Phosphonic Acid. D.J. Burton, D.J. Pietrzyk, T. Ishihara, T. Fonong, and R.M. Flynn, J. Fluorine Chemistry, 20, 617-626 (1982).

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6. Difluoromethylene Exchange In The Preparation of Fluorinated Bis-Phosphonates. Donald J. Burton and Richard M. Flynn, J. Fluorine Chemistry, 20, 121-126 (1982).

7. Preparation of Halo-F-Methanes Via Potassium Fluoride-Halogen Cleavage of Halo-F-Methyl Phosphonium Salts. D.J. Burton, S. Shin-ya and H.S. Kesling, J. Fluorine Chemistry, 20, 89-97 (1982).

8. Synthesis of Bromodifluoromethyl Phenyl Sulfide, Sulfoxide, and Sulfone. Donald J. Burton and Denise M. Wiemers, J. Fluorine Chemistry, 18, 573-582 (1981).

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10. Tributylarsonium-2,2,3,3,4,4-hexafluorocyclobutane Ylide. Preparation and Cleavage. Donald J. Burton and Paul D. Vander Valk, J. Fluorine Chemistry, 18, 413-416 (1981).

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12. Metal Dehalogenation Route To Reactive Fluoroolefins. D.J. Burton, H.S. Kesling and D.G. Naae, J. Fluorine Chemistry, 18, 293-298 (1981).

13. Preparation, Stability, Reactivity, and Synthetic Utility of a Cadmium Stabilized Complex of Difluoromethylene Phosphonic Acid Ester. Donald J. Burton, Ryutaro Takei, and Seiji Shin-ya, J. Fluorine Chemistry, 18, 197-202 (1981).

14. Difluoromethylene Chain-Extension Reactions. Preparation of Fluorinated Alkenes and Alkadienes From Olefin Precursors. Donald J. Burton, Yoshio Inouye and James A. Headley, J. Am. Chem. Soc., 102, 3980-3982 (1980).

15. The Preparation of Alpha, Halo, Beta, Beta-Difluorostyrenes. D.J. Burton, A.L. Anderson, R. Takei, H.F. Koch and T.L. Shih, J. Fluorine Chemistry, 16, 229-235 (1980).

16. Convenient Procedures For Conversion of Carbonyl Compounds To gem-Difluoroolefins and Their Selective Reductions To Monofluoroolefins. Sei-ichi Hayashi, Takeshi Nakai, Nobuo Ishikawa, Donald J. Burton, Douglas G. Naae, and H.S. Kesling, Chemistry Letters, 983-986 (1979).

## IV. Participating Scientific Personnel

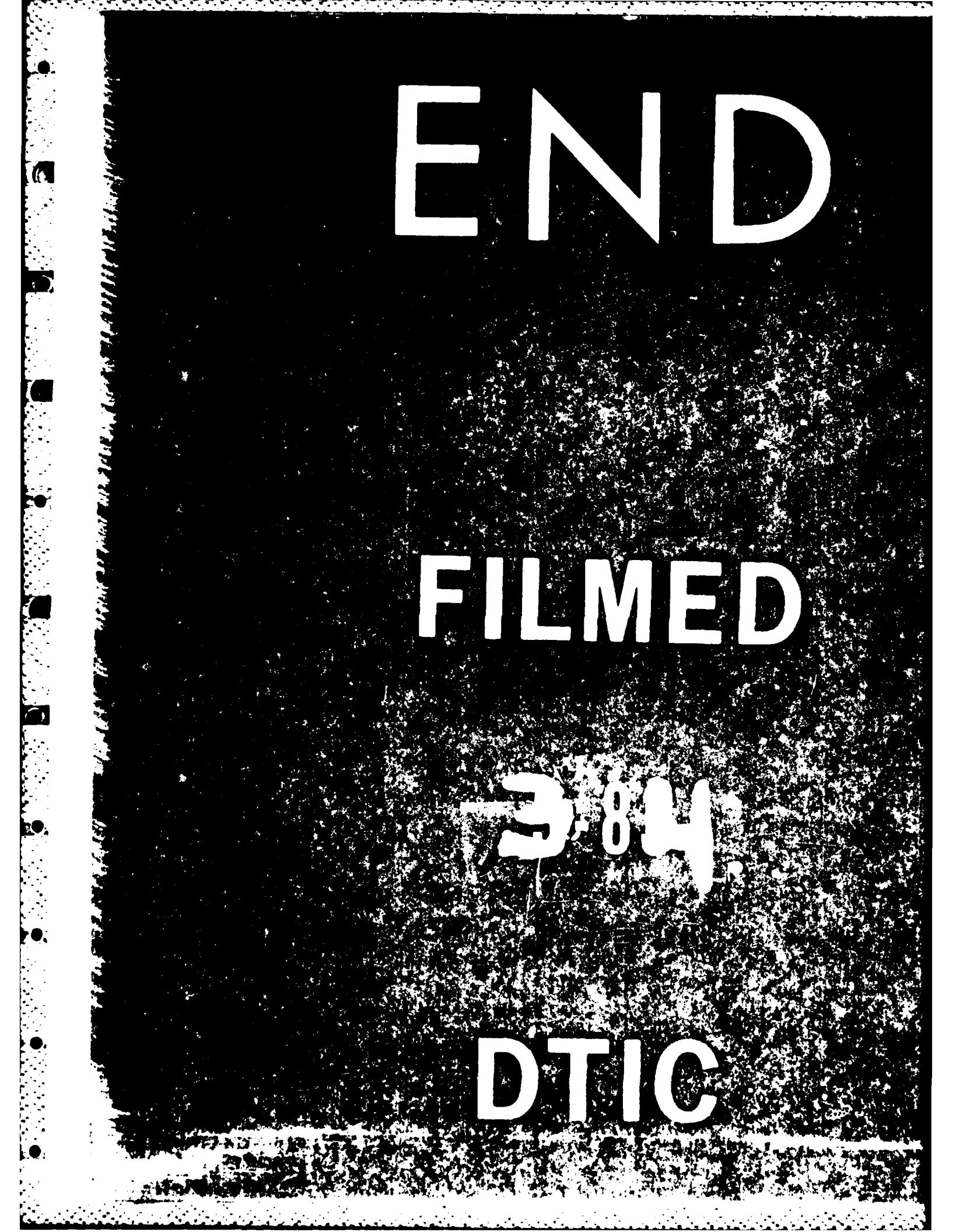
| | |
|---|---|
| Professor Donald J. Burton | * G.S. Shaw |
| Dr. T. Ishihara | J. Yao |
| Dr. C. Buss | ** D. Wiemers |
| Dr. Seiji Shin-ya | ** S.W. Hansen |
| Dr. Allan Bailey | |

* received Ph.D. degree

** will receive Ph.D. degree in 1984

## V. Appendices:

Copies of each publication (16) that resulted from this project.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