13:17:44 OCA PAD INITIATION - PROJECT HEADER INFORMATION 02/07/88

Active

Project #: G-33-603 Cost share #: Rev #: 0
Center # : R6431-0A0 Center shr #: OCA file #:
Work type : RES
Contract#: R-21 Mod #: Document : GRANT
Prime #: Contract entity: GTRC

Subprojects ? : N
Main project #:

Project unit: CHEM Unit code: 02.010.136
Project director(s):
HOUSE H O CHEM

Sponsor/division names: RESEARCH CORPORATION / PORT WASHINGTON, NY
Sponsor/division codes: 500 / 021

Award period: 871125 to 891124 (performance) 891124 (reports)

Sponsor amount	New this change	Total to date
Contract value	24,600.00	24,600.00
Funded	12,300.00	12,300.00
Cost sharing amount		0.00

Does subcontracting plan apply ?: N

Title: DERIVATIVES OF 1,8 -DIPHENYLANTHRACENE AS POTENTIAL CATALYSTS OR REAGENTS...

PROJECT ADMINISTRATION DATA

OCA contact: E. Faith Gleason 894-4820

Sponsor technical contact

BRIAN ANDREEN, GRANTS PROGRAM COORD.
(602)296-6771
6840 EAST BROADWAY BOULEVARD
TUSCON, ARIZONA 85710-2815

Sponsor issuing office

DR. JOHN. P. SCHAEFER, PRESIDENT
(602)296-6400
6840 EAST BROADWAY BOULEVARD
TUSCON, ARIZONA 85710-2815

Security class (U,C,S,TS) : ONR resident rep. is ACO (Y/N): N
Defense priority rating : supplemental sheet
Equipment title vests with: Sponsor GIT X

Administrative comments -
INITIATION. 2-YEAR GRANT, 1ST YEAR INSTALLMENT OF $12,300 HAS BEEN RECEIVED.

GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION

NOTICE OF PROJECT CLOSEOUT

Closeout Notice Date 07/18/90

roject No. G-33-603 Center No. R6431-0A0

roject Director HOUSE H O School/Lab CHEMISTRY

ponsor RESEARCH CORPORATION/PORT WASHINGTON, NY

ontract/Grant No. R-21 Contract Entity GTRC

rime Contract No.

itle DERIVATIVES OF 1,8 -DIPHENYLANTHRACENE AS POTENTIAL CATALYSTS OR REAGENTS

ffective Completion Date 900614 (Performance) 900614 (Reports)

loseout Actions Required:	Y/N	Date Submitted
Final Invoice or Copy of Final Invoice	Y	
Final Report of Inventions and/or Subcontracts	N	
Government Property Inventory & Related Certificate	N	
Classified Material Certificate	N	
Release and Assignment	N	
Other	N	

Comments

ubproject Under Main Project No.

ontinues Project No.

istribution Required:

Project Director	Y
Administrative Network Representative	Y
GTRI Accounting/Grants and Contracts	Y
Procurement/Supply Services	Y
Research Property Managment	Y
Research Security Services	N
Reports Coordinator (OCA)	Y
GTRC	Y
Project File	Y
Other	N
	N

School of Chemistry
(404) 894-4002 (Tel.)
(404) 894-7452 (Fax)

Georgia Institute of Technology
Atlanta, Georgia 30332
A Unit of the University System of Georgia

July 3, 1990

Dr. John W. Robson
Grants Program Associate
Research Corporation
6840 East Broadway Blvd.
Tuscon, Arizona 85710-2815

Dear Dr. Robson:

Enclosed are two copies of the Terminal Research Report for my Research Corporation Grant numbered R-21. This report has been signed both by me and by a repesentative of the Georgia Institute of Technology.

Please let me know if you need any other information at this time.

Sincerely yours,

Herbert O. House
Professor of Chemistry

ams

REPORT OF RESEARCH CORPORATION GRANT

R-21

(Submit original and one legible copy)

Please check one)

☐ Interim Report

☒ Terminal Report

Reply to: 6840 E. Broadway
Tucson, Arizona 85710

NSTITUTION AND ADDRESS Georgia Institute of Technology
Atlanta, GA 30332

'RINCIPAL INVESTIGATOR Herbert O. House PHONE (404)894-4044

CADEMIC RANK AND DEPARTMENT Professor, School of Chemistry

HORT TITLE OF RESEARCH SUPPORTED BY GRANT

Derivatives of 1,8-Diphenylanthracene as Potential Catalysts or Reagents for Asymmetric Synthesis

STARTING DATE June 15, 1988

UMMARY OR PRINCIPAL FINDINGS AND THEIR SIGNIFICANCE (State succinctly in language understandable to one not necessarily xpert in this field. Include extent to which original goals have been realized and any changes to original plan made or contemplated.)

The initial goal of this program, the synthesis of various 1,8-diaryl-2,7-dimethylanthracenes, requires reasonable quantities of the precursor, 1,8-dichloro-2,7-dimethylanthracene. Much of the time during the past two years has been devoted to developing a good workable synthesis for this precursor. Of the various methods examined (detailed in my Interim Progress Report), the method we are now using consists of the following steps: (1) reaction of isoprene with benzoquinone followed by oxidation to form 6-methyl-1,4-naphthoquinone; (2) reaction of 6-methyl-1,4-naphthoquinone with isoprene followed by oxidation to form a mixture of comparable amounts of the isomeric 2,6- and 2,7-dimethylanthraquinones; (3) separation of the isomeric dimethylyanthraquinones by acetone extraction follow by fracional crystallization; (4) chlorination of the 2,7-isomer by reaction of the quinone with chlorine at about 100°C in sulfuric acid solution; (5) separation of the desired 2,7-dimethyl-1,8-dichloroanthraquinone by a combination of column chromatography and recrystallization; (6) reduction of the dichlorodimethyl quinone with zinc in aqueous ammonia followed by treatment with acid to dehydrate the crude alcohol product forming 1,8-dichloro-2,7-dimethylanthracene.

In the course of this study, we found that earlier literature reports describing the preparations of 1,8-dichloro-2,7-dimethylanthraquinone and of 1,5-dichloro-2,6-dimethylanthraquinones had not given pure compounds. Thus, we have obtained pure samples of these quinones for the first time. By use of the reduction procedure noted above, each of these quinones was reduced to the corresponding dichloro-dimethyl-anthracene. The next phase of this work will involve the nickel-catalyzed coupling of the above 1,8-dichloro-2,7-dimethylanthracene precursor with phenylmagnesium bromide and with xylylmagnesium bromide. The latter coupled product will be used to prepare the chiral molecule that is the objective of this research.

While the above methodology was being developed, we also devoted some time to the development of a synthesis for 4-bromo-2-keto-bicyclo-[2.2.2]-octane, a possible precursor for the unknown and presumably very highly strained enone, 2-keto-delta-3,4-bicyclo-[2.2.2]-octene, that we expect to have unusual physical and chemical properties. The synthesis involved the following steps: (1) a Diels-Alder reaction of 2-methoxybutadiene with 3-buten-2-one to form 1-methoxy-4-acetylcyclohexene; (2) cyclization of the enol ether with anydrous p-toluenesulfonic acid to form 4-methoxy-2-keto-bicyclo-[2.2.2]-octane; (3) reaction of the bridgehead methyl ether with boron tribromide to form the corresponding ketone with a bromine at the bridgehead. With this bromo ketone in hand we are beginning to explore methods that might be used to generate (and then trap) the very strained enone mentioned above.

STUDENT PARTICIPATION (Give names of students working on the project, their roles in the research, their achievements and their career plans.)

Jay Holt - graduate student now completing his third year of graduate study toward a PhD in chemistry. All of the experimental work on this project has been performed by Mr. Holt.

PAPERS AND SCIENTIFIC TALKS (Give titles and references to papers and talks resulting from the work. Attach two copies of any reprints acknowledging Research Corporation support, if not previously forwarded.)

None yet.

OTHER SUPPORT (List amounts and sources — including institutional—of other contributions received or expected.)

None other than limited support by the Georgia Tech School of Chemistry for services and supplies.

EXPENDITURE OF RESEARCH CORPORATION GRANT FUNDS (List cumulative expenditures.)

a. Equipment, supplies (Itemize major expenditures)
$1796.35 - purchase of chemicals and expendable supplies during the period June 15, 1988 to June 14, 1990

b. Stipends (Academic status, rates, periods of appointment)
$11,199.96 - Research Assistantship (6-15-88 to 6-14-89)
$11,599.96 - Research Assistantship (6-15-89 to 6-14-90)

c. Other expenditures (Itemize and give purpose)
None

Signature of principal investigator — Date July 3, 1990

Signature of authorized officer of institution (required for terminal report only) — Date July 10, 1990

E. FAITH GLEASON
ASST. TO VP/GEN. MGR.
Name and position of authorized officer of institution

REPORT OF RESEARCH CORPORATION GRANT

R-21

(Submit original and one legible copy)

Please check one)

☐ Interim Report

☒ Terminal Report

Reply to: 6840 E. Broadway
Tucson, Arizona 85710

NSTITUTION AND ADDRESS Georgia Institute of Technology
Atlanta, GA 30332

RINCIPAL INVESTIGATOR Herbert O. House

PHONE (404)894-4044

CADEMIC RANK AND DEPARTMENT Professor, School of Chemistry

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R-21

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$11,599.96 - Research Assistantship (6-15-89 to 6-14-90)

c. Other expenditures (Itemize and give purpose)
None

Signature of principal investigator — Date: July 9, 1990

Signature of authorized officer of institution (required for terminal report only) — Date: July 10, 1990

E. FAITH GLEASON
ASST. TO VP/GEN. MGR.
Name and position of authorized officer of institution

The terminal report must be approved by an authorized officer of the institution.