

AD-A042 885

MASSACHUSETTS INST OF TECH CAMBRIDGE DEPT OF CHEMISTRY F/G 7/3
THE GENERATION OF GEM-DIFLUOROALLYLLITHIUM BY THE TRANSMETALATI--ETC(U)
JUL 77 D SEYFERTH, K R WURSTHORN N00014-76-C-0837

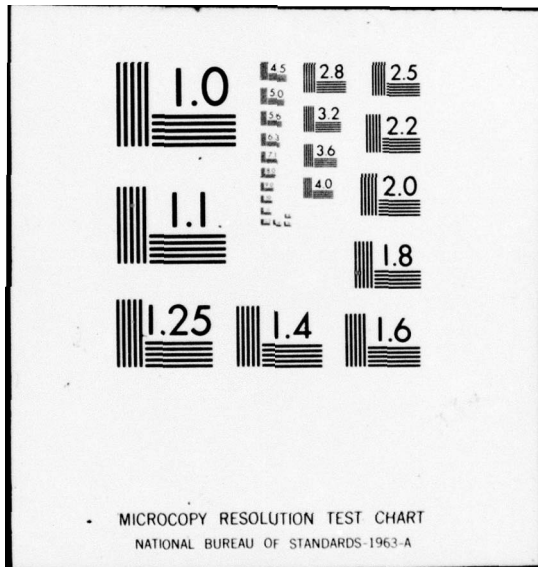
UNCLASSIFIED

NL

1 of 1
ADA042885



END
DATE
FILMED
9-77
DDC



UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) THE GENERATION OF GEM-DIFLUOROALLYLLITHIUM BY THE TRANSMETALATION REACTION.	5. TYPE OF REPORT & PERIOD COVERED Technical Report, Interim	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Dietmar/Seyferth, Karl R./Wursthorn	8. CONTRACT OR GRANT NUMBER(s) N00014-76-C-0837	9. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 053-618
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry Massachusetts Institute of Technology Cambridge, Massachusetts 02139	10. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy Arlington, Virginia 22217	11. REPORT DATE Jul 1977
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy Arlington, Virginia 22217	12. NUMBER OF PAGES 128 p.	13. SECURITY CLASS. (of this report) UNCLASSIFIED
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)
Approved for Public Release, Distribution Unlimited

DDC
RECEIVED
AUG 15 1977
A

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

18. SUPPLEMENTARY NOTES
To be published in the Journal of Organometallic Chemistry

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)
organolithium compounds
organofluorine compounds
organotin compounds
organosilicon compounds

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)
3,3-Difluoroallyltrimethyltin was prepared by reaction of chlorodifluoromethane with the ylide reagent $Ph_3P=CHCH_2SnMe_3$. gem-Difluoroallyllithium, which was generated by the reaction of n-butyllithium with 3,3-difluoroallyltrimethyltin in THF at -95° , was of very limited stability at that temperature. However, in situ procedures and alternate incremental addition procedures allowed its application in the synthesis of 1,1-difluoroallylsilanes from chlorosilanes and of $CH_2-CHCF_2C(OH)Et_2$ from 3-pentanone.

ADA 042885

FILE COPY

220007

Handwritten signature

Office of Naval Research
Arlington, Virginia 22217

Attn: Code 472 (2)

ONR Branch Office
715 Broadway
New York, NY 10003
Attn: Scientific Dept., (1)

ONR Branch Office
495 Summer Street
Boston, MA 02210
Attn: Dr. L.H. Peebles (1)

Director, Naval Research
Laboratory
Washington, D.C. 20390
Attn: Library, Code 2029 (6)
Technical Info. Div. (1)

Director, Naval Reserach
Laboratory
Washington, D.C. 20390
Attn: Code 6100, 6170 (1)

The Asst. Secretary of the
Navy (R&D)
Department of the Navy
Room 4E736, Pentagon
Washington, D.C. 20350 (1)

Commander, Naval Air Systems
Comand
Department of the Navy
Washington, D.C. 20360
Attn: Code 310C (1)

Defense Documentation
Center
Building 5, Cameron Station
Alexandria, Virginia 22314
(12)

U.S. Army Research Office
P.O.Box 12211
Research Triangle Park
North Carolina 27709
Attn: CRD-AA-IP (1)

Commander
Naval Undersea Research &
Development Center
San Diego, CA 92132
Attn: Technical Library,
Code 133

Naval Weapons Center
China Lake, CA 93555
Attn: Head, Chemistry Div.

Office of Naval Research
Arlington, Virginia 22217

Attn: Code 1021P (6)

ONR Branch Office
1030 East Green Street
Pasadena, CA 91106
Attn: Dr. R.J. Marcus (1)

Naval Civil Engineering
Laboratory
Port Hueneme, CA 93041
Attn: Mr. W.S. Haynes (1)

Professor O. Heinz
Dept of Physics & Chemistry
Naval Postgraduate School
Monterey, CA 93940

Dr. A.L. Slafkosky
Scientific Advisor
Commandant of the Marine Corp
(Code RD-1)
Washington, DC 20380 (1)

Dr. W.N. Lipscomb
Dept of Chemistry
Harvard University
Cambridge, MA 02138 (1)

Dr. R.M. Grimes
Dept of Chemistry
University of Virginia
Charlottesville, VA 22903 (1)

Dr. M. Tsutsui
Dept of Chemistry
Texas A&M University
College Station, TX 77843 (1)

Dr. C. Quicksall
Dept of Chemistry
Georgetown University
37th & O Streets
Washington, D.C. 20007 (1)

Dr. M.F. Hawthorne
Dept of Chemistry
University of CA
Los Angeles, CA 90024 (1)

Dr. D.B. Brown
Department of Chemistry
University of Vermont
Burlington, Vermont 05401 (1)

ONR Branch Office
536 S. Clark Street
Chicago, Illinois 60605
Attn: Dr. George Sandoz (1)

ONR Branch Office
760 Market Street, Rm 447
San Francisco, CA 94102
Attn: Dr. P.A. Miller (1)

Dr. Alan Siedle
National Bureau of Standards
Dept of Commerce
Chemistry Section
Washington, D.C. 20375 (1)

Dr. W.B. Fox
Naval Research Laboratory
Chemistry Division
Code 6130
Washington, DC 20375 (1)

Dr. R.J. Lagow
University of Texas
Dept of Chemistry
Austin, TX 78712 (1)

Dr. A. Cowley
University of Texas
Dept of Chemistry
Austin, TX 78712 (1)

Dr. W. Hatfield
University of North Carolina
Dept of Chemistry
Chapel Hill, NC 27514 (1)

Dr. M.H. Chisholm
Princeton University
Dept of Chemistry
Princeton, NJ 08540 (1)

Dr. B. Foxman
Department of Chemistry
Brandeis University
Waltham, MA 02154 (1)

OFFICE OF NAVAL RESEARCH
CONTRACT N00014-76-C-0837

Task No. NR 053-618

THE GENERATION OF GEM-DIFLUOROALLYLLITHIUM BY THE
TRANSMETALATION REACTION

by

Dietmar Seyferth and Karl R. Wursthorn

Prepared for Publication
in the
Journal of Organometallic Chemistry

Massachusetts Institute of Technology
Department of Chemistry, 18-411
Cambridge, Massachusetts 02139

July 29, 1977

Reproduction in whole or in part is permitted for
any purpose of the United States Government

*Approved for Public Release; Distribution Unlimited

*This statement should also appear in Item 10 of Document Control
Data- DD Form 1473. Copies of form available from cognizant
contract administrator.

THE GENERATION OF GEM-DIFLUOROALLYLLITHIUM
BY THE TRANSMETALATION REACTION

Dietmar Seyferth and Karl R. Wursthorn

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139 (USA)

ACCESSION for	
NTIS	White Section <input checked="" type="checkbox"/>
DDC	Buff Section <input checked="" type="checkbox"/>
UNANNOUNCED	<input type="checkbox"/>
JUSTIFICATION.....	
BY.....	
DISTRIBUTION/AVAILABILITY CODES	
Dist.	AVAIL. and/or SPECIAL
A	

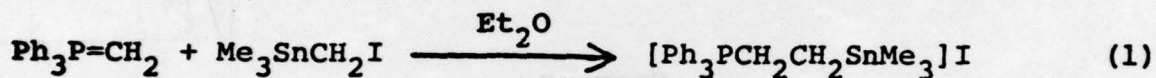
Summary

3,3-Difluoroallyltrimethyltin was prepared by reaction of chlorodifluoromethane with the ylide reagent $\text{Ph}_3\text{P}=\text{CHCH}_2\text{SnMe}_3$. gem-Difluoroallyllithium, which was generated by the reaction of n-butyllithium with 3,3-difluoroallyltrimethyltin in THF at -95° , was of very limited stability at that temperature. However, in situ procedures and alternate incremental addition procedures allowed its application in the synthesis of 1,1-difluoroallylsilanes from chlorosilanes and of $\text{CH}_2=\text{CHCF}_2\text{C}(\text{OH})\text{-Et}_2$ from 3-pentanone.

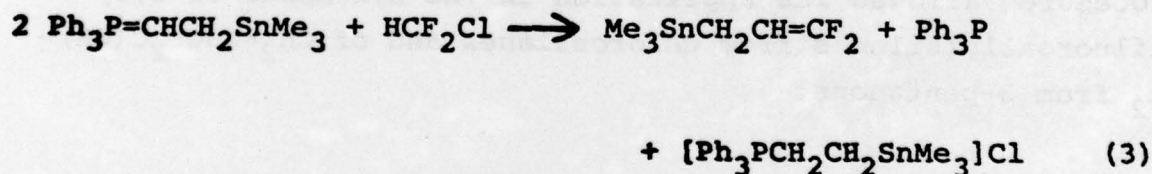
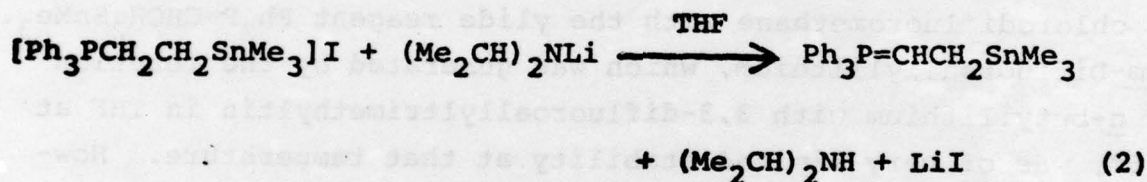
gem-Dichloroallyllithium, which can be prepared in good yield by the transmetalation reaction between $\text{Ph}_3\text{PbCH}_2\text{CH}=\text{CCl}_2$ and n-butyllithium in THF and which is stable in THF below -80° , is an ambident nucleophile which shows unusual regioselectivity in its reactions with carbonyl compounds (1). We have extended our studies of allyllithium chemistry to gem-difluoroallyllithium, a reagent, which, if accessible, would permit the synthesis of diverse unsaturated organofluorine compounds and whose regioselectivity in C=O addition would be of interest to examine.

An appropriate starting material of type $\text{CF}_2=\text{CHCH}_2\text{Z}$ or $\text{ZCF}_2\text{CH}=\text{CH}_2$ is required for the preparation of gem-difluoroallyllithium either by direct lithiation ($\text{Z}=\text{H}$), ether cleavage with metallic lithium ($\text{Z}=\text{PhO}$) or transmetalation ($\text{Z}=\text{R}_3\text{Sn}$, R_3Pb , RHg). We have developed a procedure based on the latter reaction using $\text{Me}_3\text{SnCH}_2\text{CH}=\text{CF}_2$ as the difluoroallyl anion source.

The 3,3-difluoroallyltrimethyltin required for this study was prepared in good yield using a trimethyltin-substituted Wittig reagent (eq. 1-3). In the first reaction of this



1



sequence, ethereal triphenylphosphinemethylene is added to an ether solution of iodomethyltrimethyltin (2). The phosphonium halide which precipitates, 1, generally is contaminated with 10-15% of $[\text{Ph}_3\text{PCH}_3]\text{I}$. It can be purified by fractional crystallization to give analytically pure material, mp 122.5-123.5° (dec). However, for use in the eq. 2,3 sequence it need not be purified, as the $\text{CH}_2=\text{CF}_2$ formed from the $[\text{Ph}_3\text{PCH}_3]\text{I}$ impurity (via $\text{Ph}_3\text{P}=\text{CH}_2$) is too volatile to interfere

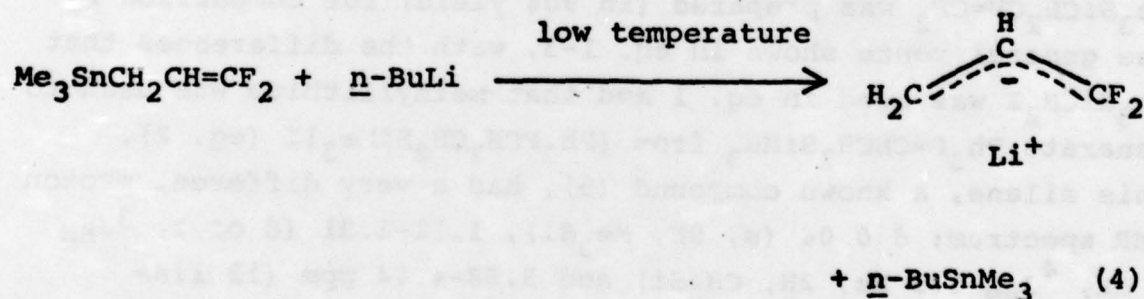
in product isolation.

In the second step of this sequence the phosphonium salt is added to the cooled (ice bath) THF solution of lithium diisopropylamide* in THF to give a cranberry-red ylide solution.

* Organolithium reagents, e.g., PhLi, cannot be used since they attack at tin as well as at the protons α to phosphorus.

Removal of the diisopropylamine formed in reaction 2 is essential in order to obtain good product yields in the subsequent step and to effect this, the volatiles are removed at 0.02 torr and 50° by trap-to-trap distillation into a receiver at -196°. The ylide which remains is redissolved in diethyl ether and treated, at 0°, with one-half molar equivalent of chlorodifluoromethane, following the procedure of Burton (3). The precipitated phosphonium salt is filtered and the filtrate is distilled. The product, $\text{Me}_3\text{SnCH}_2\text{CH}=\text{CF}_2$, bp 129-131°, $n^{25\text{D}}$ 1.4465, is obtained in 74% yield and triphenylphosphine is recovered from the distillation residue in 79% yield.

Further experiments examined the preparation of gem-difluoroallyllithium from 3,3-difluoroallyltrimethyltin (eq. 4).



All experiments which were carried out to preform a solution of this reagent in this manner, prior to addition of the substrate, at temperatures between -95° and -130°, have failed thus far. The transmetalation does occur since n-

butyltrimethyltin is formed in good yield (73% in one such experiment which was carried out at -95° , together with a 12% recovery of unconverted $\text{Me}_3\text{SnCH}_2\text{CH}=\text{CF}_2$). However, chlorosilanes can be converted to 1,1-difluoroallylsilanes in high yield by an in situ procedure in which n-butyllithium in hexane (~ 2 molar equivalents) is added slowly at -95° to a mixture of ~ 1 molar equivalent of $\text{Me}_3\text{SnCH}_2\text{CH}=\text{CF}_2$ and ~ 4 molar equivalents of R_3SiCl in THF. Prepared in this manner were $(n\text{-C}_3\text{H}_7)_3\text{SiCF}_2\text{CH}=\text{CH}_2$ (86%), $\text{PhMe}_2\text{SiCF}_2\text{CH}=\text{CH}_2$ (75%) and $\text{Me}_3\text{SiCF}_2\text{CH}=\text{CH}_2$ (64%) (yields by GLC after trap-to-trap distillation of the reaction mixture and concentration of the distillate).

It is of interest to note that the products had the structures shown, and not the isomeric $\text{R}_3\text{SiCH}_2\text{CH}=\text{CF}_2$ structure. It would appear that as in the case of the gem-dichloroallyllithium-trimethylchlorosilane reaction, which gives $\text{Me}_3\text{SiCCl}_2\text{CH}=\text{CH}_2$ exclusively (4), these reactions of gem-difluoroallyllithium are subject to kinetic control of product formation. The structure of the $\text{R}_3\text{SiCF}_2\text{CH}=\text{CH}_2$ products was indicated clearly by their proton NMR spectra which showed only complex multiplets in the vinyl region (~ 4.9 - 6.4 ppm), in addition to the resonances due to the R groups. In addition, the isomeric $\text{Me}_3\text{SiCH}_2\text{CH}=\text{CF}_2$ was prepared (in 90% yield) for comparison by the general route shown in eq. 1-3, with the differences that $\text{Me}_3\text{SiCH}_2\text{I}$ was used in eq. 1 and that methyllithium was used to generate $\text{Ph}_3\text{P}=\text{CHCH}_2\text{SiMe}_3$ from $[\text{Ph}_3\text{PCH}_2\text{CH}_2\text{SiMe}_3]\text{I}$ (eq. 2). This silane, a known compound (5), had a very different proton NMR spectrum: δ 0.04 (s, 9H, Me_3Si), 1.11-1.31 (d of t, $^3\text{J}_{\text{HH}}$ 9 Hz, $^4\text{J}_{\text{FH}}$ 1.5 Hz, 2H, CH_2Si) and 3.68-4.44 ppm (12 line pattern, $^2\text{J}_{\text{HH}}$ 9 Hz, $^3\text{J}_{\text{FH(cis)}}$ 3 Hz, $^3\text{J}_{\text{FH(trans)}}$ 24 Hz, 1H, =CH) (in CCl_4 , CHCl_3).

The in situ procedure could not be applied successfully to the difluoroallylation of carbonyl compounds since the rate of attack of n-butyllithium at $\text{C}=\text{O}$ appears to be greater than its rate of attack at tin. A successful addition of gem-

difluoroallyllithium to 3-pentanone, however, could be effected by a procedure in which a solution of $\text{Me}_3\text{SnCH}_2\text{CH}=\text{CF}_2$ (~ 6 mmol) in THF, cooled to -95° , was treated alternately with 1 mmol portions each of *n*-butyllithium in hexane (over a 15 sec. period, with 30 sec. of stirring) and 3-pentanone (followed by 3 min. of stirring). This procedure of 1 mmol alternate additions was repeated identically at 3 min. intervals until 25 mmol of each reactant had been added. The product alcohol was isolated and characterized as its trimethylsilyl ether, $\text{CH}_2=\text{CHCF}_2\text{Cet}_2\text{OSiMe}_3$, and was obtained in 75% yield.

These experiments have demonstrated that gem-difluoroallyllithium, although it is of very limited stability at -95° , can serve as a useful reagent, giving difluoroallyl group transfer in high yield, provided that appropriate procedures are used. Our further studies will examine its reactions with other substrates. Of special interest will be a study of its reactions with other carbonyl compounds. Its reaction with 3-pentanone parallels that of gem-dichloroallyllithium, which reacts with dialkyl ketones to give products of type $\text{R}_2\text{C}(\text{OH})\text{CCl}_2\text{CH}=\text{CH}_2$ exclusively (1). It may be expected that gem-difluoroallyllithium will show similar regioselectivity, with the direction of addition to $\text{C}=\text{O}$ being determined in the main by substrate electronic factors.

The availability of $\text{Ph}_3\text{P}=\text{CHCH}_2\text{SnMe}_3$ and $\text{Ph}_3\text{P}=\text{CHCH}_2\text{SiMe}_3$ provides a new and useful route for the synthesis of allylic tin and silicon compounds by Wittig reactions of our ylides with aldehydes and ketones. A separate report will detail our investigations in this area (6).

Acknowledgments. This work was supported in part by the Office of Naval Research. Gifts of chemicals from Cincinnati Milacron Chemicals, Inc. and M&T Chemicals, Inc. are gratefully acknowledged.

References

1. D. Seyferth, G.J. Murphy and R.A. Woodruff, J. Amer. Chem. Soc., 96 (1974) 5011.
2. (a) D. Seyferth and S.B. Andrews, J. Organometal. Chem., 30 (1971) 151; (b) D. Seyferth, S.B. Andrews and R.L. Lambert, Jr., J. Organometal. Chem., 37 (1972) 69.
3. G.A. Wheaton and D.J. Burton, Tetrahedron Lett. (1976) 895.
4. D. Seyferth, G.J. Murphy and R.A. Woodruff, J. Organometal. Chem., 66 (1974) C29.
5. (a) V.F. Mironov, O.M. Rad'kova, V.D. Sheludyakov and V.V. Shcherbinin, Dokl. Akad. Nauk, SSSR, 207 (1972) 207; (b) V.D. Sheludyakov, V.V. Shcherbinin, N.A. Viktorov and V.F. Mironov, Zh. Obshch. Khim., 44 (1974) 1935.
6. D. Seyferth, K.R. Wursthorn and R.E. Mammarella, J. Org. Chem., in press.

