

B-1534

Final Report

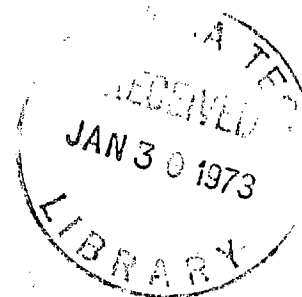
October 4, 1967

Petroleum Research Fund Grant No. 630-A, A⁴

STUDIES UPON CARBANIONS

Principal Investigator: Erling Grovenstein, Jr.
Georgia Institute of Technology

Period of Grant: July 1, 1960 - December 31, 1963
June 1, 1964 - September 30, 1967



Work under this grant has involved the work of seven graduate students as indicated by the summary of personnel given in Table I.

In the course of the present work it was discovered that 2,2,3-triphenylpropyllithium undergoes ready rearrangement in tetrahydrofuran solution when warmed from -65 to 0° to give 1,1,3-triphenylpropyllithium. The more ready rearrangement of 2,2,3-triphenylpropyllithium than of 2,2,2-triphenylethyllithium and the preferred migration of benzyl over phenyl in the former are interpreted as supporting a carbanion mechanism of rearrangement.¹ The carbanion rearrangement of 2,2,3-triphenylpropyllithium was shown to occur, according to tracer studies, by an intermolecular process—apparently by cleavage into benzyllithium and 1,1-diphenylethylene followed by recombination of these components to give 1,1,3-triphenylpropyllithium. In contrast the rearrangement of 2,2,2-triphenylethyllithium is via an intramolecular process.^{2,3} Also both the Stevens and Sommelet rearrangements of dibenzyltrimethylammonium halide brought about by benzyllithium- α -C¹⁴ in tetrahydrofuran are judged to be intramolecular rearrangements since no radioactivity can be detected in the products.³ Rearrangement of 2-m-biphenyl-2,2-bis(p-biphenyl)ethyllithium gives a product which is at least 98% 1-m-biphenyl-1,2-bis(p-biphenyl)ethyllithium. The much higher

Table I

Summary of Personnel on PRF 630-A,A4

<u>Name</u>	<u>Age</u> *	<u>Undergraduate School</u>	<u>County</u>	<u>Degree Granted (Date)</u>	<u>Dates Supported</u>
(1) Yao Ming Cheng	26	Taipei Inst. of Technology	Taiwan (Free China)	MS (1967)	July 1964-Aug. 1964 July 1965-March 1966
(2) William E. Davis	32	Middlebury College (Vermont)	U.S.A.	**	Sept. 1962-August 1963 July 1965-August 1965 April 1966-August 1967
(3) Thomas H. Longfield	28	Blackburn College (Illinois)	U.S.A.	**	July 1967-Sept. 1967
(4) H. Randall Munson, Jr.	27	U. of Maryland	U.S.A.	None	Sept. 1960-June 1961 Sept. 1961-Dec. 1961
(5) Lynn C. Rogers	23	U. of Oklahoma	U.S.A.	MS	Sept. 1960-Aug. 1962
(6) Gary Wentworth	26	Rensselaer Polytechnic Inst.	U.S.A.	Ph.D.	April 1962-August 1963 June 1964-Dec. 1965
(7) Laray P. Williams, Jr.	27	Emory University	U.S.A.	Ph.D.	July and Aug. 1960 July 1961

* Age at which last support was received
** Degree work still in progress

migratory aptitude of p-biphenyl than of m-biphenyl is taken to indicate that migration of an aryl group in such organolithium compounds occurs in a carbanion by way of a cyclic or bridged transition state or intermediate.⁴

The cleavage of 2,2-dimethylpropyltrimethylammonium, 2,2,2-triphenylethyltrimethylammonium, and 3,3,3-triphenylpropyltrimethylammonium iodides with sodium in liquid ammonia at -33° gives a mixture of products which have been carefully analyzed. The results are accounted for on the basis that electronic rather than steric factors are of dominant importance in determining the ease of cleavage of groups from quaternary nitrogen. In liquid ammonia solution the 2,2,2-triphenylethyl anion in part rearranges to the more stable 1,1,2-triphenylethyl anion but is largely protonated to give 1,1,1-triphenylethane.⁵ A study of the cleavage of quaternary ammonium salts of the type $\text{Ph}(\text{CH}_2)_n\text{NCH}_3^+\text{X}^-$ by sodium in liquid ammonia is underway.⁶ The first member of this series ($n = 0$) gives traces of methane but mostly benzene and a hydrocarbon whose structure is under investigation.

The reaction of 4-chloro-1,1,1-triphenylbutane with various alkali metals has been studied in order to learn about the chemistry of the 4,4,4-triphenylbutyl alkali metal compounds.⁷ With lithium metal in tetrahydrofuran, 4,4,4-triphenylbutyllithium can be prepared at -60° ; warming this compound to room temperature gives primarily 1,1,1-triphenylbutane. With potassium metal in refluxing tetrahydrofuran (65°) 1,1-diphenyl-1,2,3,4-tetrahydronaphthalene was obtained in about 75% yield (provided that only a short reaction time, 10 minutes, was allowed). With cesium-potassium alloy at -40° followed by addition of methanol, some 40% yield of 9-phenyl-9-n-propylfluorene, 20% of 1,1,1-triphenylbutane, 10% of 1,1,4-triphenylbutane, and 20% of a 9-phenyl-9-n-propyldihydrofluorene were obtained. These diverse products show the rich chemistry of this system. The formation of 1,1,4-triphenylbutane indicates that a carbanion rearrangement with

1,4-migration of phenyl has occurred in the reaction with cesium.

The reaction of 3,3,3-triphenylpropanoic acid with hydrazoic acid in presence of sulfuric acid was undertaken in an attempt to prepare 2,2,2-triphenylethylamine which was needed in one of the above studies. The reaction, however, took an abnormal course and hence this reaction and that of 3,3-diphenylindan-1-one with hydrazoic acid in presence of sulfuric acid has been studied in some detail. These reactions both give a mixture of 4,4-diphenyl-2-oxotetrahydroquinoline, : an isomer apparently 4,4-diphenyl-1-oxotetrahydroisoquinoline, and a red product 2,3-diphenylindone. It is concluded that under the reaction conditions 3,3,3-triphenylpropanoic acid cyclizes to 3,3-diphenylindan-1-one prior to reaction with hydrazoic acid.⁸

- (1) E. Grovenstein, Jr., and L. P. Williams, Jr., J. Am. Chem. Soc., 83, 2537 (1961).
- (2) E. Grovenstein, Jr., and G. Wentworth, ibid., 85, 3305 (1963).
- (3) E. Grovenstein, Jr., and G. Wentworth, ibid., 89, 1852 (1967).
- (4) E. Grovenstein, Jr., and G. Wentworth, ibid., 89, 2348 (1967).
- (5) E. Grovenstein, Jr., and L. C. Rogers, ibid., 86, 854 (1964).
- (6) W. E. Davis, Jr., Ph.D. thesis in progress.
- (7) Yao-Ming Cheng, M.S. Thesis, Georgia Institute of Technology, 1967.
- (8) E. Grovenstein, Jr., W. E. Davis, Jr., and L. C. Rogers, manuscript in preparation.