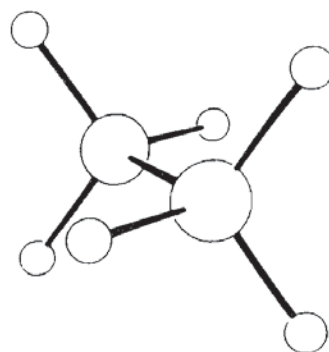


ANDREW STREITWIESER, JR.
CLAYTON H. HEATHCOCK

INTRODUCTION TO ORGANIC CHEMISTRY

THIRD EDITION



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Introduction to Organic Chemistry

Andrew Streitwieser, Jr.

Clayton H. Heathcock

UNIVERSITY OF CALIFORNIA, BERKELEY

Macmillan Publishing Company *New York*

Collier Macmillan Publishers *London*

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Printed in the United States of America

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Macmillan Publishing Company
866 Third Avenue, New York, New York 10022

Collier Macmillan Canada, Inc.

Library of Congress Cataloging in Publication Data

Streitwieser, Andrew,
Introduction to organic chemistry.

Includes index.

I. Chemistry, Organic. I. Heathcock, Clayton H.

II. Title.

QD251.2.S76 1985 547 84-15399

ISBN 0-02-418140-4 (Hardcover Edition)

ISBN 0-02-946720-9 (International Edition)

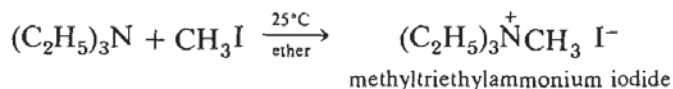
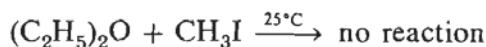
Printing: 1 2 3 4 5 6 7 8 Year: 5 6 7 8 9 0 1 2 3

ISBN 0-02-418140-4

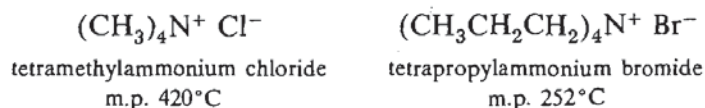
23.5 Quaternary Ammonium Compounds

A. Tertiary Amines as Nucleophiles

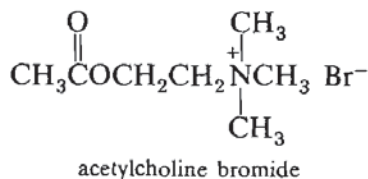
Recall that there is a correlation between Lewis basicity and the nucleophilicity of a species (Section 9.4). Amines are more basic than alcohols or ethers, and they are also more nucleophilic. For example, a mixture of diethyl ether and methyl iodide does not react under ordinary conditions, but triethylamine and methyl iodide react violently at room temperature. If the reaction is carried out in a solvent to moderate its vigor, the product, which is a tetraalkylammonium iodide, may be obtained in good yield.



Such compounds, which have four alkyl groups replacing the four hydrogens of the ammonium ion, are called **quaternary ammonium compounds**. Since they are ionic, they are generally water soluble and have fairly high melting points. They often decompose at the melting point.



Quaternary ammonium compounds are important as intermediates in some reactions that we shall encounter and also occur in nature. Acetylcholine, which is important in the neural transport system of mammals, is an example.

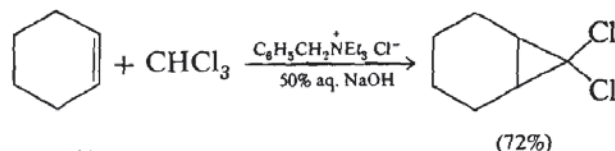


Quaternary ammonium hydroxides are as basic as alkali hydroxides. They decompose on heating (Hofmann degradation; Section 23.7.E) and find use as base catalysts in organic systems.

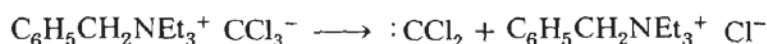
B. Phase-Transfer Catalysis

In Section 11.6.F we learned that chloroform reacts with strong bases to form dichlorocarbene, which can then add to double bonds to give dichlorocyclopropanes. If a solution of cyclohexene in chloroform is stirred with 50% aqueous sodium hydroxide, only small yields of the cyclopropane are formed. The hydroxide ion stays in the aqueous phase, and the only reaction that occurs is at the interface between the organic and aqueous phases. However, if a small amount of benzyltriethylammonium chloride is added to the heterogeneous mixture, rapid reaction occurs and 7,7-dichlorobicyclo[4.1.0]heptane is isolated in 72% yield.

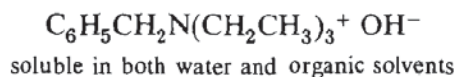
Sec. 23.5

Quaternary
Ammonium
Compounds

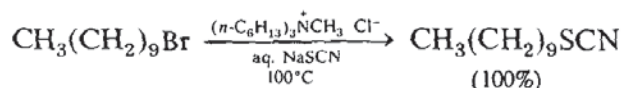
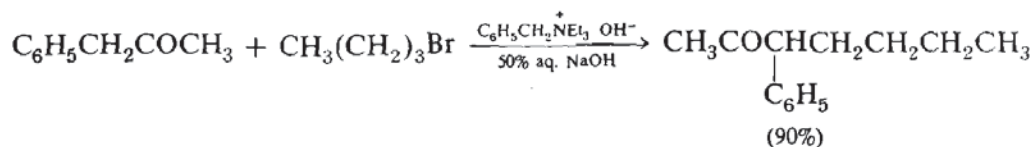
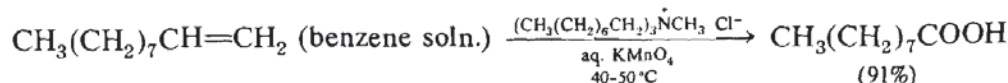
To understand what has happened, we need to recognize that although the quaternary ammonium compound is a salt soluble in water, it also has a large organic group and has solubility in organic solvents as an *ion pair*. Although the quaternary ammonium chloride was used because of its availability and greater convenience in handling, chloride ion is swamped by the large excess of hydroxide ion in the aqueous solution. In the heterogeneous mixture some benzyltriethylammonium hydroxide ion pairs are distributed into the chloroform layer. Hydroxide ion is especially reactive in this medium because of the reduced hydrogen bonding. Dichlorocarbene is produced in the chloroform solution, in which there also is a high concentration of cyclohexene.



The benzyltriethylammonium chloride ion pairs diffuse into the aqueous phase, where the ammonium ion can again pick up a hydroxide ion and begin the cycle anew. The key to the procedure is the solubility of the quaternary ammonium salt in both water and organic solvents.



The technique is called **phase-transfer catalysis** and can be applied to a number of different types of reaction. The general procedure is to use concentrated solutions with an aqueous and an organic phase. The quaternary ammonium salt used need only have organic groups that are sufficiently large to provide solubility in organic solvents. Among the ones commonly used are tetrabutylammonium, methyltriocetylammmonium, and hexadecyltrimethylammonium salts. Some additional examples of applications of phase-transfer catalysis are given below.



Note that the examples include alkylation, oxidation, and displacement reactions, that the anions are not restricted to hydroxide ion and that various temperatures may be used.

EXERCISE 23.7 For each of the three foregoing examples of phase-transfer catalysis, what species are in the aqueous phase? In the organic phase? Which species are passing from one phase to another?