Laboratory Experiments for an Introductory Course in Organic Chemistry

Nicholas D. Cheronis

Wright Junior College, Chicago, Illinois

The chief objective in an introductory course of organic chemistry is the selection of pertinent facts and the arrangement of these in such a manner as to develop and illustrate the fundamental principles of the carbon compounds. The laboratory work in most courses consists largely of experiments in which the sole object is to attempt one preparation after another. In a previous paper[1], a series of experiments was described to show both general group properties and reactions as well as difference in reactivity. The paper is a further elaboration of such a laboratory course. The plan followed is the arrangement of the compounds of carbon into groups which show related properties. The usual separation into aliphatic and aromatic compounds is avoided. For instance, in the monohalogen compounds, if we write R-X, where X is a halogen, for the general formula of the organic monohalide, it is possible to treat first all reactions which are common to the monohalides and then to show how the radical R influences the rate of reaction of the compound. The experiments on two units are described in this paper: hydrocarbons and the monohalides.

Experiments on Hydrocarbons: The preparation of n-butane by the use of the Grignard reagent illustrates the reduction of a monohalide to the hydrocarbon and introduces the student to a simple reaction which later will be found applicable to the preparation of other groups of organic compounds. The preparation of n-butyl magnesium bromide is made according to standard method[2], using 0.1 moles of the reagent. The hydrocarbon is generated by the addition of water to the Grignard reagent and collected by water displacement after passing the gas through an empty bottle immersed in an ice mixture, then through sulfuric acid. The usual tests on combustibility, action of bromine and potassium permanganate are made on the samples collected. The experiment can be used as demonstration.

The Wurtz-Fittig reaction[3] illustrates the preparation of a hydrocarbon by the union of two radicals when two monohalogens are reduced under anhydrous conditions. Ethyl benzene is prepared using 20 g. of bromobenzene, 17.3 of ethyl bromide, 40 cc. of dry ether and 9 g. of sodium. Yields of 45-65% are obtained by the students.

Methane and benzene are prepared by test tube experiments which illustrate the removal of the carboxyl group. Five grams of sodium acetate or sodium benzoate are heated with two grams of soda lime in an ignition tube. The unsaturated hydrocarbons are introduced by means of amylene and cyclohexene. The former is easily prepared by the careful dropwise addition of 2 cc. of sulfuric acid to 5 cc. of ter-amyl alcohol well cooled. Cyclohexene is prepared by distilling a mixture of 50 cc. of cyclohexanol with 8 cc. of sulfuric acid. This is followed by a brief study of the properties of acetylene and benzene.

The unit is closed with a study and contrast of reaction properties of several hydrocarbons from each group. Ten drops of each of the following hydrocarbons are used in each test: pentane, isopentane, pentene, hexane, cyclohexane, cyclohexene, cyclohexadiene, benzene, toluene and naphthalene. The reaction of these towards of the following reagents is studied: neutral or alkaline 0.04% potassium permanganate, 2% bromine solution in carbon tetrachloride, concentrated nitric acid, and concentrated sulfuric acid. These experiments illustrate the rapid reaction of the unsaturated, the relative inertness of the saturated and the relation of benzene to the other six-carbon cyclic hydrocarbons. The reactions of cyclohexene and cyclohexadiene with bromine and pottasium permanganate are instantaneous, and explosive with nitric and sulfuric acids. Yet benzene (cyclohexatriene) exhibits a stability characteristic of the saturated structures. Later, the various theories to account for this stability are presented.

Experiments on Monohalides: In this unit which follows that of hydrocarbons a number of experiments are used to illustrate the general methods of preparation and characteristic reactions of the monohalogens. The preparation of the alkyl halides by the reaction of the monohydroxy alcohols with aqueous hydrogen halides[4] is easily illustrated by mixing 5 cc. of the three butanols with 10 cc. of concentrated hydrochloric acid. The tertiary chloride separates out immediately while the secondary and primary require addition of zinc chloride and heating. The preparation is related to the application of the law of mass action to: $R{-}OH + HX \rightleftharpoons R{-}X + HOH$.

The formation of halides by the direct halogenation of the hydrocarbons is illustrated by a demonstration of bromination of benzene. Halogenation of hydrocarbons in general is discussed, including the use of catalysts, methods of introducing the chlorine or bromine and products formed. The preparation of n-butyl bromide using the sodium bromide method[5] is performed by the student with the main objective of obtaining a good yield. This is followed by a series of tests designed to illustrate a number of general reactions such as hydrolysis, ammonolysis, removal of halogen acid, etc. It is also possible to show differences in the reactivities of the various groups of halides. The tests on hydrolysis of n-butyl, sec-butyl, ter-butyl, n-amyl, cyclohexyl, phenyl, benzyl and naphthyl chlorides has been described[6]. The ammonolysis of monohalides is illustrated by the action of 1 g. of methyl iodide, n-amyl bromide and ter-amyl bromide with 5 cc. of saturated solution of ammonia in 90% methanol. Methyl iodide forms mostly quaternary salt; n-amyl a mixture of amines, and ter-amyl mostly olefins. The action of alcoholic potassium hydroxide on: n-amyl, ter-amyl, cyclohexyl, phenyl and benzyl chlorides illustrates the condition for olefin formation as well as differences in the relative stability of the halides.

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[1] Nicholas D. Cheronis, "Reactivity Experiments for An Introductory Course in Organic Chemistry;" J. Chem. Ed., 14, 480 (1937).

[2] Geman, Zoellner and Dickey; J. Am. Chem. Soc. 51, 1579 (1929), Org. Syntheses Coll. Vol. 1, 182.

[3] Wurtz, Ann. 44, 275 (1855); Fittig and Lonig, Ann. 144, 277 (1867) Schorlemmer, Ann. 144, 184 (1867).

[4] Norris, J. F., Organic Syntheses, Coll. Vol. 1, 137 (1932). Kamm and Marvel, J. Am. Chem. Soc., 42, 299 (1920).

[5] Organic Syntheses, Coll. Vol. I, p. 26, (1932).

[6] Ibid, J. Chem. Ed., 14, 480 (1937).