product. In the preparation of β-*n*-butylamino-α-phenylethyl alcohol further distillation yielded a small quantity of 4,*n*-butyl-2,6-diphenylmorpholine.

β-Dialkylamino-α-phenylethyl Alcohols.—Method A: A mixture of 0.2 mole of styrene oxide and 0.3 mole of the secondary amine was refluxed for four hours and then distilled to obtain the desired β-dialkylamino-α-phenylethyl alcohol.

Method B: An alternative procedure was to add 0.33 mole of styrene chlorohydrin over a one-half hour period to a boiling mixture of 0.33 mole of the secondary amine and 50 cc. of water containing 42 g. (0.5 mole) of sodium bicarbonate. After refluxing seven hours, the mixture was cooled and extracted with benzene. Distillation of the benzene extract yielded the desired β-dialkylamino-α-phenylethyl alcohol.

β-Dialkylamino-α-phenylethyl Esters.—Method C:[11] Acetates were prepared by refluxing the β-dialkylamino-α-phenylethyl alcohols with acetic anhydride containing sodium acetate.

Method D: Other esters were obtained by boiling a toluene solution of the amino alcohol and acid in question in the presence of *p*-toluenesulfonic acid, while the water was removed continuously by means of a Dean and Stark trap.

β-Alkoxy-α-phenylethyl Alcohols.—Method E: To a boiling solution of 20 g. (0.36 mole) of potassium hydroxide in 200 cc. of the corresponding alcohol was added 40 g. (0.26 mole) of styrene chlorohydrin over a five-minute period. After refluxing for one hour, the mixture was diluted with water, acidified with acetic acid and then extracted three times with benzene. Distillation of the combined benzene extracts yielded the desired β-alkoxy-α-phenylethyl alcohol.

Method E_1: β-Ethoxy-α-phenylethyl alcohol was also prepared in the same way from styrene bromohydrin.

Method F: An alternative procedure was to add 0.2 mole of styrene oxide over a fifteen minute period to 0.3 mole of the boiling alcohol containing 1 cc. of 85% phosphoric acid or two drops of concentrated sulfuric acid. After refluxing four more hours, the mixture was cooled, washed with enough aqueous sodium bicarbonate to neutralize the acid, and then distilled. In this case from 12 to 27% of diphenyldioxane was always isolated as a by-product.

β-Alkoxy-α-phenylethyl Esters.—These were prepared by the identical procedures (Methods C and D) used for the synthesis of the β-dialkylamino-α-phenylethyl esters.

Styrene Glycol Diesters.—A mixture of 0.2 mole of styrene oxide, 0.6 mole of the acid in question (0.4 mole in the case of lauric acid), 0.5 g. of *p*-toluenesulfonic acid and 100 cc. of toluene was refluxed eleven hours while the water was removed in a Dean and Stark trap. After cooling, it was washed with enough aqueous sodium bicarbonate to neutralize the sulfonic acid and then distilled to obtain the diester.

Compounds Prepared.—The methods of synthesis, physical properties and analyses of the compounds prepared are summarized in Table I.

Summary

Styrene oxide reacts with primary and secondary amines to give good yields of the corresponding β-alkylamino- or β-dialkylamino-α-phenylethyl alcohols.

In the presence of mineral acids it reacts with alcohols to give β-alkoxy-α-phenylethyl alcohols and with organic acids to give styrene glycol diesters.

Thirteen new esters of the β-dialkylamino- and β-alkoxy-α-phenylethyl alcohols have been prepared and characterized.

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[11] Shriner and Fuson, "Identification of Organic Compounds," John Wiley and Sons, New York, N. Y., 1940, p. 137.

[CONTRIBUTION FROM THE CENTRAL RESEARCH DEPARTMENT, MONSANTO CHEMICAL COMPANY]

Vapor Phase Reactions of Styrene Chlorohydrin

BY WILLIAM S. EMERSON AND EDWARD P. AGNEW

When treated with steam in the presence of such widely different catalysts as alumina or calcium carbonate on silica, ethylene chlorohydrin has been reported to give acetaldehyde in good yield.[1] The same result has been effected with an aqueous suspension of magnesium oxide.[2] Similarly ethylene dichloride reacted with steam in the presence of a surface catalyst to give a mixture of acetaldehyde and vinyl chloride.[3]

Styrene chlorohydrin, $C_6H_5CHOHCH_2Cl$, was selected as a suitable unsymmetrical chlorohydrin for the detailed study of this type of reaction. In spite of the presence of steam the principal reaction of styrene chlorohydrin (I) over an acid catalyst, such as phosphoric acid on silica gel, was one of dehydration to yield β-chlorostyrene (II). This is in contrast to the reported reaction with acid in the liquid phase to give acetophenone,[4] and to the preparation of biacetyl by treating methyl vinyl ketone with hypochlorous acid and then mineral acid.[4]

In the presence of more neutral catalysts, such as silica skeleton, calcium carbonate on silica gel or sodium metaphosphate on silica gel, hydrolysis of styrene chlorohydrin predominated, although some dehydration still occurred, since the principal reaction product, phenylacetaldehyde (III), was always contaminated with some β-chlorostyrene (II). This reaction probably proceeds by much the same mechanism as the reaction of isobutylene with aqueous chlorine under pressure to produce isobutyraldehyde.[5] The probable course of the styrene chlorohydrin reaction was hydrolysis to styrene glycol (V), followed by dehydration and rearrangement of this latter compound to phenylacetaldehyde. The postulated intermediate, styrene glycol, gave phenylacetaldehyde in good yield, under the nearly neutral conditions employed above, or, better, in the presence of an acid catalyst such as phosphoric acid on pumice.

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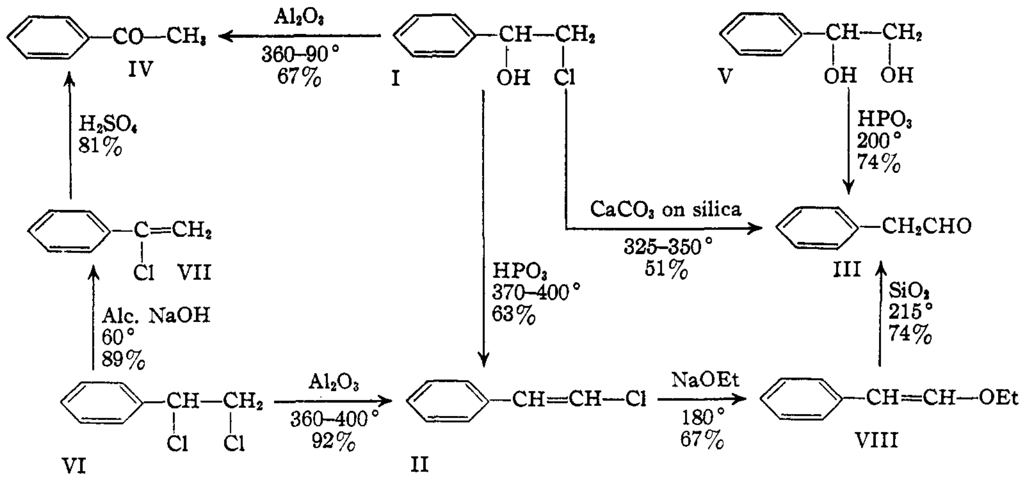
[1] Amos and Hooker, U. S. Patent 2,208,557; *C. A.*, **35**, 135^9 (1941).

[2] Ziese, U. S. Patent 2,245,377; *C. A.*, **35**, 5907^7 (1941).

[3] Amos, U. S. Patent 2,183,036; *C. A.*, **34**, 1995^3 (1940).

[4] Eberhardt and Stadler, U. S. Patent 2,246,299; *C. A.*, **35**, 5914^7 (1941).

[5] Kautter, U. S. Patent 2,060,086; *C. A.*, **31**, 418^6 (1937).



This type of reaction has previously been reported as occurring in the liquid phase,[6] although under these conditions it is very difficult to prevent further condensation to β-phenylnaphthalene.[7,8] In the presence of a basic catalyst such as alumina, styrene chlorohydrin was dehydrohalogenated and rearranged to acetophenone (IV). Under these same conditions styrene dichloride (VI) yielded β-chlorostyrene (II). This loss of the α-chlorine atom is surprising, since at 60° in alcohol solution dehydrohalogenation of styrene dichloride with sodium hydroxide gives α-chlorostyrene (VII). Apparently increase in temperature enhances the activity of the α-chlorine atom to a far greater extent than it does the activity of the α-hydrogen atom. The identity of the α-chlorostyrene (VII) was checked by hydrolysis to acetophenone (IV) using 80% sulfuric acid. A similar hydrolysis (no yield given) using hydrochloric acid has been reported previously.[9,10] The β-chlorostyrene (II) was converted to β-ethoxystyrene (VIII) by a modification of the method of Erlenmeyer.[11] This compound was then hydrolyzed to phenylacetaldehyde (III) by treatment with steam in the vapor phase.

Experimental

Apparatus.—The following apparatus was used for all of the vapor phase experiments. A quartz tube 21.5" long and $^{15}/_{16}$" o. d. was wrapped with Nichrome resistance wire for most of its length and then lagged with asbestos. It was packed with about 5" of carborundum at the bottom and then to within 4" of the top with the catalyst for the experiment in question. For operation it was set in a vertical position with a bulb condenser at the bottom. At the top it was equipped with a triple entrance inlet tube, so that a thermocouple could be introduced into the middle of the tube, while steam and an organic liquid were being added. The steam, a large excess of which was used in all cases, was generated in a large flask, while the organic liquid was dropped from a funnel equipped with a pressure equalizer. A suction flask immersed in an ice-bath served as the receiver. In this way the system could be evacuated to any desired pressure.

Starting Materials.—The preparation of styrene chlorohydrin has been described previously.[12] Styrene dichloride and β-chlorostyrene were prepared by chlorinating styrene in carbon tetrachloride solution at 40–50° and then fractionating the resulting mixture. The ratio of styrene dichloride to β-chlorostyrene was about 3 to 1, if care was taken to stop the chlorination before any chlorine added to the β-chlorostyrene to form α,β,β-trichloroethylbenzene. The styrene glycol was prepared by hydrolyzing styrene chlorohydrin with boiling aqueous sodium bicarbonate. After distillation, the crude product was crystallized from benzene.

β-Chlorostyrene from Styrene Chlorohydrin.—The tube was packed with silica gel impregnated with phosphoric acid. While steam was passed through the catalyst bed, 25 g. of styrene chlorohydrin was added over a forty-five minute period. The temperature was 370–400°, the pressure 95–115 mm. The passage of steam was continued for fifteen minutes before the tube was allowed to cool. It was then washed out with benzene. The washings were combined with three benzene extracts of the mixture in the receiver and the entire solution distilled to yield 14 g. (63%) of β-chlorostyrene, b. p. 88–100° (18 mm.), n^{25}_{D} 1.5719 (n^{25}_{D} 1.5736[13]).

Phenylacetaldehyde from Styrene Chlorohydrin.—The technique was the same as that in the previous experiment except that the tube was packed with silica skeleton. From an experiment run at 360–390°, 105–115 mm. and with a ninety minute addition time for the 25 g. of styrene chlorohydrin there was obtained 8 g., b. p. 86–97° (17 mm.), n^{25}_{D} 1.5407. In addition 11 g. (44%) of styrene chlorohydrin, b. p. 110–130° (17 mm.), n^{25}_{D} 1.5515, was recovered. The 2,4-dinitrophenylhydrazone of the first fraction melted at 115–117° after one crystallization from alcohol. (Shriner and Fuson give 121° for phenylacetaldehyde 2,4-dinitrophenylhydrazone[14]). If the refractive index of β-chlorostyrene is taken as 1.5736 (n^{25}_{D} 1.5736)[13] and that of phenylacetaldehyde as 1.5230 ($n^{19.6}_{\mathrm{D}}$ 1.5255),[15] and one assumes a straight line function of refractive index for mixtures of these two compounds, this product contained a 27% yield of the aldehyde together with 13% of the β-chlorostyrene.

In another run using a calcium carbonate on silica gel catalyst, a temperature of 325–350°, a pressure of 105–125 mm. and a seventy-five minute addition time for 75 g. of styrene chlorohydrin, there was obtained 36 g. b. p. 88–98° (16 mm.), n^{25}_{D} 1.5324, together with a recovery of

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(6) Zincke, *Ann.*, **216**, 286 (1882).

(7) Zincke and Breuer, *ibid.*, **226**, 23 (1884).

(8) Carter and Van Loon, THIS JOURNAL, **60**, 1077 (1938).

(9) Béhal, *Bull. soc. chim.*, [2] **50**, 632 (1888).

(10) Urion and Namias, *ibid.*, [5] **3**, 2333 (1936).

(11) Erlenmeyer, *Ber.*, **14**, 1868 (1881).

(12) Emerson, THIS JOURNAL, **67**, 516 (1945).

(13) Biltz, *Ann.*, **296**, 259 (1897).

(14) Shriner and Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1940, p. 188.

(15) Heilbron, "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1938, Vol. III, p. 375.

21 g. (28%) of styrene chlorohydrin, b. p. 98–134° (16 mm.), n^{25}_D 1.5496. Calculated on the same basis as employed previously, fraction I consisted of a 51% yield of phenylacetaldehyde contaminated with 10% of β-chlorostyrene.

Phenylacetaldehyde from Styrene Glycol.—In this case the catalyst was silica gel impregnated with phosphoric acid. A solution of 50 g. of styrene glycol in 75 cc. of alcohol was added over an eighty-minute period at a temperature of 200–225° and a 105–125 mm. pressure. Distillation of the product yielded 32 g. (74%) of phenylacetaldehyde, b. p. 92–96° (20 mm.), n^{25}_D 1.5242 ($n^{19.6}_D$ 1.5255[15]).

Acetophenone from Styrene Chlorohydrin.—The vapor phase apparatus previously described was packed with activated alumina. At a temperature of 360–390° and a pressure of 115–125 mm., 25 g. of styrene chlorohydrin was dropped through during a ninety-five minute period. Distillation yielded 13 g. (67%) of acetophenone, b. p. 83–90° (16 mm.), n^{25}_D 1.5327 (n^{25}_D 1.5319[16]).

β-Chlorostyrene from Styrene Dichloride.—In this experiment the tube was packed with activated alumina and maintained at 360–400° and a pressure of 85–105 mm. During an eighty-minute period, 35 g. of styrene dichloride was added. Distillation yielded 25.5 g. (92%) of nearly pure β-chlorostyrene, b. p. 82–87° (16 mm.), n^{25}_D 1.5700 (n^{25}_D 1.5736[13]).

α-Chlorostyrene from Styrene Dichloride.—To a solution of 99 g. (2.5 moles) of sodium hydroxide in 377 cc. of ethyl alcohol and 124 cc. of water was added over a three-quarter hour period 333 g. (1.9 moles) of styrene dichloride. During the addition and for four hours thereafter the mixture was stirred at 50–60°. It was then diluted with water and the product removed by extraction with benzene. When this benzene solution was distilled, 234 g. (89%) of α-chlorostyrene was collected at 80–83° (21 mm.), n^{25}_D 1.5600 ($n^{24.5}_D$ 1.5590[17]).

Acetophenone from α-Chlorostyrene.—A mixture of 20 g. of α-chlorostyrene and 100 g. of 80% sulfuric acid was agitated for four hours at 60°. After cooling, it was diluted with water and extracted with benzene. Distillation yielded 14 g. (81%) of acetophenone, b. p. 93–95° (19 mm.), n^{25}_D 1.5289.

β-Ethoxystyrene from β-Chlorostyrene.—A solution of 6 g. (0.26 mole) of sodium in 65 cc. of absolute alcohol and 34 g. (0.25 mole) of β-chlorostyrene was heated for five and one-half hours in an autoclave at 175–182°. The cooled bomb was opened and washed with benzene. When this solution was distilled, 24 g. (66%) of β-ethoxystyrene was collected at 96–108° (16 mm.), n^{25}_D 1.5440 ($n^{21.2}_D$ 1.5502[18]), d^{25}_{25} 0.973 ($d^{21.4}_4$ 0.9714[18]).

Phenylacetaldehyde from β-Ethoxystyrene.—The tube was packed with silica skeleton. In the usual fashion 25 g. of β-ethoxystyrene was added over a forty-five minute period, while the temperature was maintained at 215–225° and the pressure at 135–150 mm. Distillation yielded 15 g. (74%) of phenylacetaldehyde, b. p. 85–95° (17 mm.), n^{25}_D 1.5263.

Summary

The vapor phase reactions of styrene chlorohydrin in the presence of steam have been examined.

In the presence of an acid catalyst dehydration to β-chlorostyrene occurs.

With a neutral catalyst, while there is some dehydration, the principal reaction is hydrolysis to styrene glycol which, in turn, loses water to form phenylacetaldehyde.

In the presence of a basic catalyst styrene chlorohydrin is dehydrohalogenated to acetophenone.

In contrast to liquid-phase dehydrohalogenation where α-chlorostyrene is produced, vapor-phase dehydrohalogenation of styrene dichloride yields β-chlorostyrene.

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[16] V. E. Lucas, private communication.

[17] Auwers, *Ber.*, **45**, 2795 (1912).

[18] Auwers, *ibid.*, **44**, 3520 (1911).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Relative Reactivities of Organometallic Compounds of the Alkaline Earth Group[1]

BY HENRY GILMAN AND LAUREN A. WOODS

The recent availability of organostrontium compounds[2] together with the presently described procedure for the preparation of diethylbarium made possible an examination of the relative reactivities of organometallic compounds of the alkaline earth group.[3]

Among the numerous procedures[4] which have been used to determine the relative reactivities of organometallic compounds, one of those used earlier in a related study with organoalkali compounds[5] appeared to be particularly suitable. In that study, reactions of phenylethynylalkali compounds were carried out with benzonitrile. The phenylethynylmetallic compounds were selected because of their generally low order of reactivity compared with other RM compounds. Benzonitrile was chosen as the reactant because the nitrilo group reacts slower than most organic functional groups which undergo reaction with RM compounds.[6] Slow-reacting combinations were desirable in order to measure with some accuracy the time required to use up the highly reactive organometallic compounds of the alkaline earth group when a definite excess of benzonitrile was used. Color Test I[7] was used to determine the disappearance of RM compound.

$$[C_6H_5{\equiv}C]_2M + C_6H_5CN \xrightarrow{(HOH)} C_6H_5C{\equiv}C{-}COC_6H_5$$

The present rate studies show the following

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[1] Paper LVII in the series "The Relative Reactivities of Organometallic Compounds"; the preceding paper is in THIS JOURNAL, **66**, 1515 (1944).

[2] Gilman, Meals, O'Donnell and Woods, THIS JOURNAL, **65**, 268 (1943).

[3] See Grüttner, Dissertation, Berlin, 1914, for the preparation of ethylbarium compounds from barium amalgam and ethyl iodide.

[4] A general account of some procedures is given in Gilman "Organic Chemistry," pp. 518–520 of Vol. I, John Wiley & Sons, Inc., New York, N. Y., 1943.

[5] Gilman and Young, *J. Org. Chem.*, **1**, 315 (1936).

[6] Entemann and Johnson, THIS JOURNAL, **55**, 2900 (1933).

[7] Gilman and Schulze, *ibid.*, **47**, 2002 (1925).