[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Allylic Rearrangements. VIII. The Action of Magnesium on Cinnamyl Chloride[1]

BY WILLIAM G. YOUNG, GERALD BALLOU AND KENZIE NOZAKI

Within recent years several investigators have prepared Grignard reagents by the action of magnesium on halides containing the three carbon system, $-\overset{|}{C}=\overset{|}{C}-\overset{|}{C}X$, and have studied their reaction with a variety of reagents. Benzyl,[2] naphthyl,[3] cinnamyl[4] and butenyl halides[5] have received particular attention. The experimental facts may be summarized as follows
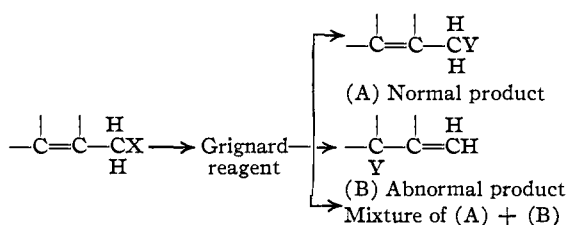

where X is a halogen and Y is a radical introduced by the action of the reactant with the Grignard reagent. If the double bond is part of a ring structure, product (B) may undergo a proton migration to give the product (C), $-\overset{|}{C}=\overset{|}{C}-\overset{H|}{C}H$, as in the case of benzyl chloride reactions. The fact that only normal or abnormal products are obtained in some cases while mixtures of both products are isolated in others, has led to much speculation regarding the mechanism of the reactions.

In spite of the fact that abnormalities may arise due to allylic rearrangement before, during or after the formation of the Grignard reagent, the tendency has been to assume the formation of the normal Grignard reagent and to classify reactants as normal, abnormal or partially abnormal according to the character of the final products. On the other hand, in the case of cinnamyl chloride reactions Gilman and Harris[4a,b] have accepted carbon dioxide as a normal reactant and concluded that the Grignard reagent is the secon-

dary isomer, $C_6H_5-\overset{H|}{C}-\overset{H}{C}=\overset{H}{C}H$ since the literature did not at that time contain any data which conflicted with that assumption. More recently, however, Coleman and Forrester[4c] have reported the formation of cinnamylamine from the reaction of the Grignard reagent with chloroamine, a reactant which behaves normally with both benzyl- and α-naphthylmagnesium chlorides. If carbon dioxide and chloroamine are normal reactants, it seems probable that the Grignard reagent from cinnamyl chloride consists of a mixture of both allylic forms
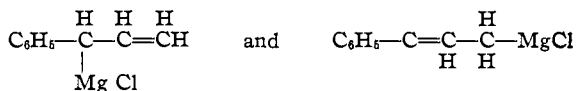
This conclusion is consistent with the finding that the butenyl Grignard reagent[5b] is a mixture of both primary and secondary forms. Since the hydrolysis of the butenyl metallic complex[5b,6] does not involve rearrangements, it appeared profitable to study the hydrolysis of the so-called cinnamylmagnesium chloride in the same manner. The results indicate that this reagent consists of approximately 73% secondary and 27% primary forms. It is of interest to note that both forms occur in sufficient quantity to account for the yields of phenylvinylacetic acid[4a,b] and of cinnamylamine[4c] which were reported.

Discussion of Results.—The method used in determining the composition of the Grignard reagent from cinnamyl chloride consisted of the hydrolysis of the reagent to form a hydrocarbon mixture which could be analyzed. As might be expected, the mixture is composed of a high boiling fraction containing hydrocarbons formed by coupling of the Grignard reagent with cinnamyl chloride and a lower boiling fraction of allylbenzene, $C_6H_5CH_2CH=CH_2$ and propenylbenzene, $C_6H_5CH=CHCH_3$ contaminated with a small amount of propylbenzene. Analysis of this lower boiling fraction was accomplished by controlled oxidation with potassium permanganate in pyridine by a method similar to that described by

(1) This work was accomplished with the aid of a grant from the Board of Research of the University of California.

(2) (a) Gilman and Kirby, THIS JOURNAL, **54**, 345 (1932); (b) Austin and Johnson, ibid., **54**, 647 (1932).

(3) Gilman and Kirby, ibid., **51**, 3475 (1929).

(4) (a) Gilman and Harris, ibid., **49**, 1825 (1927); (b) Gilman and Harris, ibid., **53**, 3541 (1931); (c) Coleman and Forrester, ibid., **58**, 27 (1936).

(5) (a) Young and Prater, ibid., **54**, 404 (1932); (b) Young, Winstein and Prater, ibid., **58**, 289 (1936).

(6) Young, Kaufman, Loshokoff and Pressman, ibid., **60**, 900 (1938).

TABLE I

SUMMARY OF RESULTS OBTAINED DURING THE STANDARDIZATION AND TESTING OF THE METHOD OF ANALYSIS

Run	Phenyl-acetic acid moles × 10³	Sodium acetate moles × 10³	% Phenyl-acetic acid in mixture	Total acid HBz + HAc found, moles × 10³	% Difference between total acid found and calcd.	Benzoic acid extracted moles × 10³	% Loss of benzoic acid during analysis
1	1.190	1.010	54.2	2.230	+1.4	1.135	4.6
2	0.785	1.210	39.4	2.000	+0.25	0.761	3.2
3	1.819	0.141	88.3	2.070	+0.5	1.764	2.9
4	1.013	...	100.0	1.003	−1.0	0.972	3.1
5	1.710	...	100.0	1.701	−0.5	1.653	2.9
6	1.102[a]	...		1.098	−0.4	1.070	2.6
7	...	...		0.002	...	...	...
8	0.819[b]					0.796	2.8
9	1.091[b]					1.061	2.9
10	1.842[b]					1.794	2.7
11	0.992[c]			0.988	−0.4	0.962	3.0

[a] Benzoic acid was used in place of phenylacetic acid.   [b] The benzoic acid was extracted from sulfuric acid solution to test extraction part of the method.   [c] Allylbenzene was used in place of phenylacetic acid.

Smith and Spoehr[7] for the oxidation of carotene. It was possible to convert the propenylbenzene into benzoic acid and acetic acid, and the allylbenzene into benzoic acid and carbonic acid, without oxidizing the propylbenzene. The analysis was based on the fact that both benzoic and acetic acids may be steam distilled and later separated by distribution between water and ether. The method was developed and tested using mixtures of phenylacetic and acetic acids or benzoic acid alone. The results are summarized in Table I. (See experimental part for detailed discussion of the method.)

The hydrocarbon mixtures from the preparation and hydrolysis of so-called cinnamylmagnesium chloride were analyzed. The results are listed in Table II. Experiments 1 and 2 were made on a hydrocarbon sample which had been standing in the laboratory for several months. While the analysis was being carried out it was found that the refractive index of the sample had changed from $n^{25}D$ 1.5145 to $n^{25}D$ 1.5241 during the period it had been stored in the laboratory. This was entirely unexpected since portions of the sample previously had been subjected to heating at 75° for several days without changing in physical properties. Further examination revealed that the change in refractive index was due to the presence of polymerized material. The analytical results are listed since they indicate either that rearrangement accompanies the polymerization process or that the propenylbenzene polymerizes faster than the allylbenzene. Experiments 3–5 were made on a freshly prepared hydrocarbon mixture. This sample contained approximately

(7) Smith and Spoehr. J. Biol. Chem., **86**, 755 (1930).

27% propenylbenzene and 73% allylbenzene, which corresponds to 27% and 73% to cinnamyl and phenylvinylcarbinylmagnesium chlorides, respectively.

TABLE II

SUMMARY OF RESULTS ON THE ANALYSIS OF THE HYDROCARBON MIXTURE OF PROPENYLBENZENE AND ALLYLBENZENE

Expt.	Moles of hydrocarbon mixture × 10³	Moles of volatile acids obtained × 10³	Moles of benzoic acid found (corr.) × 10³	% Propenyl-benzene (primary Grignard reagent)	% Allylbenzene (secondary Grignard reagent)
1	1.414[a]	1.680	1.395	21.2	78.8
2	1.912[a]	2.282	1.888	21.2	78.8
3	1.639	2.024	1.598	26.6	73.4
4	1.629	1.980	1.557	27.1	72.9
5	1.660	2.025	1.610	25.8	74.2
			Mean	26.5	73.5 ± 0.4

[a] This hydrocarbon was found to be partially polymerized before analysis.

The existence of both primary and secondary forms of the Grignard reagent is not required to account for the experimental facts presented here and by Gilman[4a,b] and Coleman[4c] provided the reagent exists as an ionic resonating system

$$[C_6H_5—CH—CH=CH_2^- \rightleftharpoons C_6H_5—CH=CH—CH_2^-] + MgCl^+$$
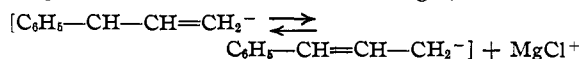
which is capable of reacting in different ways depending on the character of the reactants carbon dioxide, water and chloroamine. However, several facts favor the existence of both forms of the Grignard reagent rather than the ionic form just mentioned. For example, it has been possible to predict[5b] the composition of the hydrocarbons obtained when butenyl bromides are allowed to

couple with the butenyl Grignard reagent by assuming that the composition of the butene mixture obtained by the hydrolysis of the Grignard reagent is a measure of the composition of the Grignard reagent itself. Likewise, it has been pointed out[6] that if the resonating ionic form of the butenyl Grignard reagent were present it would be possible to introduce into the reaction mixture other metallic ions than those produced by the ionization of the metallic complex and bring about a competition between two metallic ions in coördinating with the resonating butenyl ions. The result would be a different mixture of butenes than that expected from either metallic ion alone. Experiments[8] of this type using metals of widely different character failed to produce new mixtures of butenes. Accordingly, dissociation of the metallic complex to give a resonating negative ion does not occur.

Experimental Part

Cinnamyl Chloride.—Cinnamyl alcohol, purchased from Givaudan-Delawanna, Inc., was converted into cinnamyl chloride by the action of sulfuryl chloride according to the method of Gilman and Harris,[9] and also by the action of hydrogen chloride. Although the yield by the former method was more satisfactory, 69–75% compared to 60%, nevertheless the products from both methods appeared to be the same: b. p. (5 mm.) 101.5–103.4°; degree of unsaturation by the method of Frances,[10] 99%.

Preparation of the Grignard Reagent from Cinnamyl Chloride.—Four-tenths of a mole of freshly distilled cinnamyl chloride treated with magnesium according to the method of Gilman and Harris,[9] gave only 31% yields of the Grignard reagent. Changing the ratios of chloride: magnesium: ether to 1:4:15 increased the yield to 44%, however, while ratios of 1:4:30 resulted in a yield of 70%. This failure to reproduce previously reported yields under specified conditions is not unexpected. Work in this Laboratory on other unsaturated halides, which are prone to couple, has shown that different preparations of halide and ether do not usually produce the same yields of the Grignard reagent, especially when carried out by different experimenters. Gilman[9] also has observed this and notes that the age of the cinnamyl chloride is important. However, all of our experiments were made with freshly distilled material.

Hydrolysis of the Grignard Reagent.—The freshly-prepared Grignard reagent from cinnamyl chloride was decanted from excess magnesium and hydrolyzed by the dropwise addition of 3 N sulfuric acid. The ether layer was separated, washed first with dilute sodium bicarbonate solution, then with water and dried over anhydrous calcium chloride. After removal of the ether the hydrocarbon mixture was separated by fractionation through a 30-cm.

Vigreux column at 1.5 mm. pressure, into fraction A, 12.4 g., b. p. 26.5–29.0°, $n^{20}D$ 1.5180, d^{20}_4 0.8942, mol. wt., 119.1,[11] degree of unsaturation 94%; fraction B, 0.6 g., b. p. 29–33°, $n^{20}D$ 1.5416; and a high boiling residue, C, 30 g. Based on the Grignard reagent present before hydrolysis, the combined yield of fractions A and B was 47% and of fraction C (coupled product) 81%.

Analysis of the Hydrocarbon, Fraction A

(a) **Isolation of the Saturated Impurity.**—In order to determine what impurity was causing fraction A to have a low unsaturation value, 4.0 g. of the fraction was brominated. On heating the resulting product at 1.5 mm. pressure a volatile liquid, 0.2 g., was obtained which possessed physical properties $n^{20}D$ 1.4941 and molecular weight[11] 121, which agree well with those of propylbenzene.

(b) **Estimation of the Allyl and Propenylbenzene Content of Fraction A by Oxidation with Potassium Permanganate.**—One-tenth to 0.3 g. of hydrocarbon fraction A and 1–2 g. of potassium permanganate were placed in a 150-ml. Pyrex test-tube with 75 ml. of pyridine purified with hot alkaline permanganate. The test-tube was stoppered with a lead foil covered cork and suspended in the vapors of refluxing amylene at 40° for eight hours. The reaction tube was then fitted with a capillary tube and a Kjeldahl connecting bulb and the pyridine was removed by distillation at reduced pressures to avoid the formation of volatile acids due to the oxidation of pyridine. The residue in the tube was acidified with 50 ml. of 2 N sulfuric acid. Solid oxalic acid was then added slowly until all of the permanganate was reduced. Great care was exercised in the latter operation to avoid mechanical losses during the escape of the carbon dioxide. The excess oxalic acid was titrated at 50° with dilute permanganate. The benzoic and acetic acids formed by the oxidation of the hydrocarbon were then isolated by steam distillation from the reaction tube through the connecting bulb and an ordinary condenser into a flask immersed in ice water. The volume of solution in the tube was maintained at 10–15 ml. by dropwise addition of water as the distillation proceeded. The distillation was discontinued after 400 ml. of distillate had been collected. The total volatile acids were then estimated by ordinary acidimetry. The neutralized solution was made alkaline and carefully evaporated at reduced pressure to a volume of 50 ml. This concentrate was transferred quantitatively to a separatory funnel, acidified with an excess of 3 N sulfuric acid and extracted with three 40-ml. portions of acid-free ether. The combined ether extracts after being washed with three 50-ml. portions of water to remove any acetic acid, were titrated with standard sodium hydroxide to determine the amount of benzoic acid which had been extracted. A 3% positive correction was then made in the numerical value for the moles of benzoic acid found. This corrected value was subtracted from the total moles of volatile acids to estimate the acetic acid produced by the oxidation of the hydrocarbon. The number of moles of acetic acid is a direct measure of the number of moles of propenylbenzene in the hydrocarbon sample, while the moles of benzoic acid minus the moles of acetic acid gives the number of moles of allylbenzene in the sample.

(8) Unpublished work.

(9) Gilman and Harris, *Rec. trav. chim.*, **50**, 1052 (1931).

(10) Frances, *Ind. Eng. Chem.*, **18**, 821 (1926).

(11) Smith and Young, *J. Biol. Chem.*, **75**, 289 (1927).

Standardization of the Method of Analysis.—As a means of standardizing and testing the analytical method described above, runs were made using weighed amounts of phenylacetic acid and sodium acetate in various proportions as shown in Table I. Columns 2 and 3 list the moles of phenylacetic acid and sodium acetate subjected to the oxidation and isolation process, while column 4 gives the percentage of phenylacetic acid in the mixture. Column 5 shows the total volatile acids isolated and column 6 gives the percentage difference between the moles of volatile acids isolated and those calculated for each mixture examined. Column 7 contains the number of moles of benzoic acid isolated and column 8 gives the percentage difference between the moles of benzoic acid isolated and the number of moles calculated from the phenylacetic acid used. In runs 1–5 it became evident that approximately 3% of the benzoic acid was lost during the analysis. This was at first thought to be due to incomplete oxidation of the phenylacetic acid. However, when benzoic acid was substituted for the phenylacetic acid (run 6) the same loss was recorded. In runs 8, 9 and 10 solutions of benzoic acid were subjected to the standard extraction process with the same loss occurring as in the entire analytical procedure. Since the loss was proportional to the amount of phenylacetic acid present even though the percentage of this acid in the mixture was varied from 40–100% it was concluded that a 3% correction could be applied to the amount of benzoic acid isolated from the oxidation of the

hydrocarbon mixture provided the moles of hydrocarbon taken corresponded to moles of phenylacetic and acetic acids used in the test runs. Run 7 was a blank made to show that no volatile acid is produced by oxidation of the pyridine under the conditions used in the analytical method. Run 11 using allylbenzene shows that no acetic acid is produced by the oxidation of this hydrocarbon. Propenylbenzene was not used in the standardization process since there is no agreement in the literature with respect to the physical properties of this compound. Hence no guaranteed criterion of purity was available.

Summary

An allylic rearrangement producing a mixture of 27% cinnamyl and 73% phenylvinylmagnesium chlorides has been shown to occur when cinnamyl chloride is converted into the Grignard reagent. The composition of the Grignard reagent has been estimated by measuring the composition of the hydrocarbon mixture obtained on hydrolysis of the Grignard reagent. The hydrocarbon mixture has been analyzed by quantitative oxidation with potassium permanganate in pyridine at 40° to a mixture of benzoic acid and acetic acid.

Sodium Saccharin as a Reagent for the Identification of Alkyl Halides

By Lynne L. Merritt, Jr., Stanley Levey and Harold B. Cutter

Many reagents have been suggested for the identification of alkyl halides. None are entirely satisfactory, either because of the experimental difficulties involved or because their application is not general. The most satisfactory are the N-alkyl-*p*-bromobenzenesulfon-*p*-anisides,[1] and the S-alkyl thiourea picrates.[2]

Sodium saccharin, as has long been known, reacts with alkyl halides to give N-alkyl saccharins.[3–5]

When the reaction is carried out in butyl carbitol–water solution, well crystallized derivatives are formed. The reaction does not take place with tertiary compounds nor with branched chain chlorides.

Experimental Part

Preparation of N-Alkyl Saccharins.—A mixture of 6 g. of sodium saccharin, 1 cc. of the alkyl halide, 25 cc. of butyl

carbitol and 4 cc. of water is refluxed for thirty minutes. If the halide is a chloride, or methyl bromide, 3.5 g. of potassium iodide is added to the mixture. After refluxing, the mixture is poured into 300 cc. of water and the resulting suspension cooled in an ice-bath. The N-alkyl saccharin usually crystallizes. If an oil is obtained, it is separated and warmed in a small beaker until no odor of alkyl halide can be detected. It is then dissolved in a little hot alcohol, and water added until a slight cloudiness results. On cooling the material crystallizes. The derivatives are recrystallized from aqueous alcohol.

The yield of N-alkyl saccharin varies from 0.5 to 0.8 g., except in the case of *i*-butyl, where only about 0.25 g. is obtained and crystallization is difficult.

n-Propyl- and *i*-butylsaccharin have melting points differing by only 1°, but a mixture of the two shows a depression of from 8 to 10°. The same is true of allyl saccharin and bromoethyl saccharin.

Ethylene dibromide requires refluxing for one hour. The yield is about 0.5 g. of bromoethyl saccharin, very little of the disaccharide compound being formed. Longer refluxing—three hours—yields about 20% of a compound melting at 253–254°, presumably the disaccharinoethane.

No derivatives could be obtained with methyl, ethyl, isopropyl, secondary butyl chlo-

(1) H. B. Gillespie, This Journal, 56, 2740 (1934).
(2) Brown and Campbell, J. Chem. Soc., 1699 (1937).
(3) Eckenroth, Hugo and Koerppen, Ber., 29, 1048 (1896).
(4) C. Fahlberg and R. List, ibid., 20, 1596 (1887).
(5) Eckenroth, Hugo and Klein, ibid., 29, 329 (1896).