with nickel of a tertiary arsine oxide to the arsine has been carried out.

3. Attempts to prepare an arsinimine derived from sulfanilamide and tri-(3-amino-4-ethoxyphenyl)-arsine have not been successful.

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

Allylic Rearrangements. XVI. The Addition of the Butenyl Grignard Reagent to Some Simple Carbonyl Compounds[1]

BY JOHN D. ROBERTS[2] AND WILLIAM G. YOUNG

The nature of allylic Grignard reagents has been the subject of many investigations. Aside from those cases where the allylic double bond is included in an aromatic ring (as benzylmagnesium chloride) the structures of these substances are still open to question. For a simple primary–secondary allylic system it may be expected that the Grignard reagent will be primary (I), secondary (II) or a mixture of these forms.

$$RCH{=}CHCH_2MgX \text{ (I)} \qquad RCHMgXCH{=}CH_2 \text{ (II)}$$

Assignment of the correct structure is complicated by at least three possibilities: (a) allylic rearrangement during the formation of the reagent; (b) the establishment of an allylic equilibrium between the forms (I and II) after the Grignard reagent has been formed; or (c) rearrangement during the course of the reaction with specific addends. In certain cases the possibility of rearrangement of the reaction products must not be overlooked.

The evidence obtained from the reactions of cinnamylmagnesium chloride offers a typical example of the prevailing confusion as to the nature of the allylic Grignard reagent. For this system it has been reported that the hydrolysis of the reagent gives a mixture of propenyl- and allylbenzene,[3] that treatment with chloroamine gives only the primary amine[4] and that with carbon dioxide[5a] and acetaldehyde[5b] only those products derived from structure II are obtained. This may appear surprising, since chloroamine, carbon dioxide and acetaldehyde may be classified as "normal"[6] reagents in the reactions of benzylmagnesium chloride.

In previous communications[7a,b] from this Laboratory it has been shown that the hydrolysis of butenylmagnesium halides results in a mixture of butenes and that the composition of this mixture is independent of the ratios of the possible allylic forms of the halide. This evidence, along with the results of Lespieau and Heitzmann[8] and Prevost and Richard[9] on the coupling reactions of allylic bromides with magnesium, has indicated that the Grignard reagent is formed with rearrangement but that no rearrangement occurs on hydrolysis. In order to test the validity of the conclusions derived from the previous work, a study is being made of the reactions of butenylmagnesium bromide with a variety of substances with detailed attention to those reactions which might be expected to give insight into the structure of the reagent and the mechanisms by which it reacts. The present report presents some preliminary results of this study.

The addition of butenylmagnesium bromide to carbonyl compounds has not been extensively studied. Ou Kiun-Houo[5b] reported that acetaldehyde, propionaldehyde, acrolein and benzaldehyde gave rise to products derived from the secondary form (II) of the Grignard reagent. However, the yields were uniformly below 25%. It is thus possible that considerable amounts of the isomeric products may have been overlooked, although the carbonation[10] of butenylmagnesium bromide has been shown to lead exclusively to the acid corresponding to the secondary form of the Grignard reagent.

From the reactions of butenylmagnesium bromide with acetone, acetaldehyde and formaldehyde we have substantiated the conclusions of Ou Kiun-Houo[5b] that only those products are obtained which may be considered to be derived from the secondary form of the Grignard reagent. No detectable amounts of the isomeric products corresponding to the primary Grignard reagent were isolated. The yields were excellent, and it may be pointed out that the 81% conversion of acetone to 2,3-dimethyl-4-pentenol-2 far exceeds the figures for the analogous conversion of *s*-butylmagnesium bromide to 2,3-dimethylpentanol-2. The structures of the products were established by ozonization and hydrogenation to the saturated alcohols.

Although the composition of the butene mixture produced by hydrolysis of the butenyl Grignard reagent has been shown[7a,b] to be independent of the nature and composition of the starting allylic

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(1) Presented before the Division of Organic Chemistry of the American Chemical Society at New York City, September, 1944.

(2) Abbott Laboratories Research Fellow, 1943–44.

(3) Young, Ballou and Nozaki, THIS JOURNAL, **61**, 12 (1939).

(4) Coleman and Forrester, *ibid.*, **58**, 27 (1936).

(5) (a) Gilman and Harris, *ibid.*, **49**, 1825 (1927); **53**, 3541 (1931); (b) Ou Kiun-Houo, *Ann. chim.*, [11] **13**, 175 (1940).

(6) Austin and Johnson, THIS JOURNAL, **54**, 647 (1932).

(7) (a) Young, Winstein and Prater, *ibid.*, **58**, 289 (1936); (b) Young and Eisner, *ibid.*, **63**, 2113 (1941).

(8) Lespieau and Heitzmann, *Compt. rend.*, **200**, 1077 (1935).

(9) Prevost and Richard, *Bull. soc. chim.*, [4] **49**, 1369 (1931).

(10) Lane, Roberts and Young, THIS JOURNAL, **66**, 543 (1944).

halides, the fact that simple carbonyl compounds and carbon dioxide lead in each case to a single product indicates a different mechanism for this type of reaction and it therefore was desirable to demonstrate whether or not the addition products from carbon-oxygen double bonds would likewise be independent of the nature of the butenyl halide. This was found to be the case since the Grignard reagent prepared from methylvinylcarbinyl chloride gave only 2-methyl-3-butenoic acid on carbonation. Further, as it is well-known that the Grignard reagent is a complex mixture of substances[11] and also because it has been shown that the hydrolysis of dibutenylmagnesium[12] leads to a different mixture of butenes than that obtained from butenylmagnesium bromide, we have carbonated dibutenylmagnesium. Only 2-methyl-3-butenoic acid was isolated. Thus the equilibria in the Grignard solution of the type, $2RMgX \rightleftarrows R_2Mg + MgX_2$ appear to have no effect on the final products from addition to carbon-oxygen double bonds where no great amount of steric hindrance may be expected. Also, as formaldehyde and benzaldehyde have been classified as "abnormal" reagents and acetaldehyde, acetone and carbon dioxide as "normal" reagents in the reactions of benzylmagnesium chloride, it is clear that no correlation necessarily exists between the products obtained from the benzyl system and other types of allylic systems. Actually with butenylmagnesium bromide the above mentioned reactants lead to addition products derived solely from the secondary form of the Grignard reagent.

Experimental Part

Butenylmagnesium bromide was prepared by the previously reported method.[10] The reagent was filtered from the excess magnesium before use. The products were fractionated through efficient packed columns of either the Whitmore-Lux[13] or Podbielniak Heli-Grid[14] types.

The Action of Formaldehyde on Butenylmagnesium Bromide.—The Grignard reagent (0.35 mole) in dilute ethereal solution was treated with gaseous formaldehyde by the procedure of Gilman and Catlin.[15] Fractionation gave the following cuts: 1–6, 5.1 g., b. p. 65–108° (756 mm.), n^{20}_{D} 1.3962–1.4240; 7–10, 5.6 g., 108–120° (756 mm.), 1.4260–1.4265; 11–13, 11.8 g., 120–121° (756 mm.), 1.4261–1.4263; 14, 0.95 g., 71–72° (100 mm.), 1.4260.

Fractions 1–6 were octadienes formed by the coupling of the butenylmagnesium bromide with butenyl bromide and were not further investigated. Fractions 7–10 were mixtures of octadienes and pentenol, while Fractions 11–14 were pure pentenol. The yield considering Fraction 10 to be essentially pure product was 15.1 g. (50%).

Anal. Calcd. for $C_5H_{10}O$: C, 69.72; H, 11.70. Found: C, 68.12, 68.10; H, 11.70, 11.70.

The 3,5-dinitrobenzoate of the pure alcohol showed m. p. 57.5–58.0° and the melting point was not depressed by the 3,5-dinitrobenzoate obtained from the alkadiene-pentenol mixture of Fraction 7.

Anal. Calcd. for $C_{12}H_{12}O_6N_2$: C, 51.42; H, 4.31. Found: C, 51.36; H, 4.41.

The 3-nitrophthalate derivative (Fraction 13) showed m. p. 158–160°.

The structure of the pentenol was confirmed in the following ways. (1) Ozonolysis by the procedure of Whitmore and Church[16] gave formaldehyde but no acetaldehyde. (2) Hydrogenation of Fraction 14 (0.9 g.) in ethanol over platinum oxide went smoothly with the absorption of the theoretical amount of hydrogen. After removal of the solvent and thorough washing with water the product gave a 3,5-dinitrobenzoate, m. p. 67.5°, which did not depress the melting point of the derivative obtained from an authentic sample of 2-methylbutanol-1 (Eastman Kodak Co.). The product was thus 2-methyl-3-butenol-1 and none of the isomeric 3-pentenol-1 could be detected.

The Action of Acetone on Butenylmagnesium Bromide.—To 0.70 mole of the cold Grignard reagent was added a solution of 40 g. (0.70 mole) of acetone (b. p. 55.8°) dissolved in an equal volume of ether. After one-half hour of stirring the mixture was worked up in the usual way. Fractionation gave the following cuts: 1–6, 7.0 g., b. p. 64–93° (200 mm.), n^{20}_{D} 1.4245–1.4335; 7, 2.1 g., 93–94.5° (200 mm.), 1.4362; 8–12, 62.3 g., 94.5–94.9° (200 mm.), 1.4367–1.4369. Fractions 1–6 were octadienes, Fraction 7 was somewhat impure heptenol while Fractions 8–12 were the pure addition compound. The yield (including Fraction 7) was 64.5 g. (81%).

Anal. Calcd. for $C_7H_{14}O$: C, 73.62; H, 12.35. Found: C, 74.33; H, 12.49.

The dinitrobenzoate of the heptenol showed m. p. 78–79.5°.

Anal. Calcd. for $C_{14}H_{16}O_6N_2$: C, 54.53; H, 5.23. Found: C, 54.47; H, 5.52.

The structure of the heptenol was established as 2,3-dimethyl-4-pentenol-2 by ozonolysis which gave formaldehyde but no acetaldehyde and by hydrogenation to 2,3-dimethylpentanol-2.

The hydrogenation of Fraction 11 (15.7 g.) proceeded smoothly in methanol over platinum oxide at room temperature and 93% of the theoretical amount of hydrogen was absorbed. Fractionation gave 12.4 g. (80%) of 2,3-dimethylpentanol-2; b. p. 136.4–137.4° (uncor.), n^{20}_{D} 1.4262, n^{25}_{D} 1.4237. About 2.5 g. of material boiling from 112.9–136.4° was obtained which appeared to result from partial dehydration of the hydrogenation product. In an earlier run virtually all of the product dehydrated on distillation. Norton and Hass[17] report the following constants for 2,3-dimethylpentanol-2; b. p. 139°, n^{25}_{D} 1.4234.

Addition of Acetaldehyde to Butenylmagnesium Bromide.—To 0.45 mole of butenylmagnesium bromide was added 17.5 g. (0.4 mole) of freshly distilled acetaldehyde (b. p. 21.8°) dissolved in an equal volume of ether, while cooling in an ice-bath. After two hours of stirring, the products were isolated in the usual way.

Fractionation gave the following cuts: 1–9, 5.9 g., b. p. 71–123° (753 mm.), n^{20}_{D} 1.4149–1.4294; 10–11, 2.0 g., 123–126° (753 mm.), 1.4304–1.4309; 12–15, 24.9 g., 126–128° (753 mm.), 1.4315; 16, 3.53 g. 64–65° (100 mm.), 1.4338. Fractions 1–9 were octadienes. Fractions 10–11 were impure hexenol while 12–15 were the pure product. The total yield (Fractions 10–16) was 84%.

Anal. Calcd. for $C_6H_{12}O$ (Fraction 14): C, 71.94; H, 12.08. Found: C, 72.06; H, 11.99.

The hexenol formed a 3,5-dinitrobenzoate which showed m. p. 44.0–45.5° after crystallization from petroleum ether.

Anal. Calcd. for $C_{13}H_{14}O_6N_2$: C, 53.05; H, 4.79. Found: C, 52.85; H, 4.88.

The structure of the hexenol was established by hydrogenation to 3-methylpentanol-2 in ethanol over platinum oxide. The yield from 10 g. of unsaturated alcohol was 75% and the material showed b. p. 130.3–131.3° (uncor.) (lit.,[17] 134.2°) and n^{20}_{D} 1.4198. The melting points of the 3,5-dinitrobenzoate and the α-naphthylurethan of the satu-

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(11) See, for example, Evans and Pearson, THIS JOURNAL, **64**, 2865 (1942).

(12) Young and Pokras, *J. Org. Chem.*, **7**, 233 (1942).

(13) Whitmore and Lux, THIS JOURNAL, **54**, 3451 (1932).

(14) Podbielniak, *Ind. Eng. Chem.*, *Anal. Ed.*, **13**, 639 (1941).

(15) "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., 1941, Coll. Vol. I, 2d ed., p. 188.

(16) Whitmore and Church, THIS JOURNAL, **54**, 3710 (1932).

(17) Norton and Hass, *ibid.*, **58**, 2147 (1936).

rated alcohol were 44–47° (lit., 43.5°,[18] 41°[17]) and 74–75° (lit. 72°[19]), respectively.

Fraction 16 had a somewhat higher index than the pure product and the analysis shows this to be due probably to impurities other than hexenol. In any event hardly more than 5% of the total product could have been the isomeric 4-hexenol-2.

Anal. Calcd. for $C_6H_{12}O$: C, 71.94; H, 12.08. Found: C, 70.55; H, 12.17.

Carbonation of the Grignard Reagent Prepared from Methylvinylcarbinyl Chloride.—The Grignard reagent (0.29 mole) prepared from methylvinylcarbinyl chloride (b. p. 62.5–63.0°, $n^{20}\text{D}$ 1.1450) was carbonated by pouring the dilute ethereal solution onto a large excess of powdered solid carbon dioxide with stirring. The acidic material was isolated as previously described.[10] Fractionation gave 20.4 g. (70%) of pure 2-methyl-3-butenoic acid, b. p. 101.7–102.0° (50 mm.), $n^{20}\text{D}$ 1.4231–1.4233.

Carbonation of Dibutenylmagnesium.—A mixture of dry dioxane (200 g.) and a dilute ethereal solution of butenylmagnesium bromide (0.45 mole) was stirred overnight, then filtered by forcing the pasty mass by nitrogen pressure through a 90-mm. sintered glass filter. The filtrate was carbonated and worked up as in the preceding preparation. Fractionation gave 16.9 g. (37%) of 2-methyl-3-butenoic acid, b. p. 100.9–102.0° (50 mm.), α-phenylethylammonium salt, m. p. 120.5–121.5°.[10]

Summary

1. The addition of formaldehyde, acetaldehyde and acetone to butenylmagnesium bromide results in products of the type $CH_2{=}CHCH(CH_3)$-$C(R)(R')OH$. No detectable amounts of the isomeric unsaturated alcohols were isolated.
2. The carbonation of the butenyl Grignard reagent appears to be independent of the composition of the allylic isomers of the starting halides.
3. The carbonation of dibutenylmagnesium gives a product identical with that obtained from butenylmagnesium bromide.

LOS ANGELES, CALIFORNIA RECEIVED OCTOBER 16, 1944

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[18] Sutter, *Helv. Chim. Acta*, **21**, 1270 (1938).

[19] Cottle and Powell, THIS JOURNAL, **58**, 2270 (1936).

[CONTRIBUTION FROM THE WESTERN REGION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

Heat Contents at High Temperatures of Magnesium and Calcium Fluorides[1]

BY B. F. NAYLOR[2]

The determination of high-temperature heat content data for metallurgically important substances is part of the program of the Pacific Experiment Station of the Bureau of Mines. This paper presents data recently determined for magnesium and calcium fluorides. Measurements were made for each substance in both the solid and liquid temperature ranges, and the heats of fusion were determined.

Method and Materials

The heat contents were measured by the "drop" method. The apparatus and method were described previously.[3] The calorimeter was calibrated with electrical energy, measured in international joules, and the results were converted to the conventional thermochemical calorie by the relation,[4] 1 cal. = 4.1833 int. joules (NBS). During the measurements, the samples were enclosed in a platinum–rhodium alloy capsule, the heat content of which was known. To prevent loss of the samples at high temperatures, where they tended to "creep" out of the neck, the capsule was sealed with platinum.

Magnesium fluoride was prepared from Baker "C. P. Analyzed" magnesium oxide, containing less than 0.3% Ca and 0.5% SO_4, by treating with hot 48% HF for sixteen hours and then drying at 400°. Analysis for Mg by conversion to sulfate and weighing as $MgSO_4$ gave 38.97% Mg (theoretical 39.02%).

The calcium fluoride was natural fluorite having a very faint purple color. Analysis by treating the ground fluorite successively with HCl and H_2SO_4 and weighing as $CaSO_4$ gave 51.27% Ca (theoretical 51.33%).

Results

Experimental heat contents above 298.16°K. are listed in Table I. The column labeled T, °K. gives the absolute temperature of the sample before it was dropped into the calorimeter, while that marked $H_T - H_{298.16}$ lists the heat liberated per gram molecular weight in cooling from T to 298.16°K. The sample weights were corrected to vacuum, and the molecular weights accord with the 1941 International Atomic Weights.

No attempt was made to correct for the minor impurities present. The lack of premelting and sharp melting point of the calcium fluoride indicated very high purity. Some premelting was observed about 80° below the melting point of the magnesium fluoride, showing it to be somewhat less pure. The experimental heat-content values that appear to involve premelting have been designated "(p)" in Table I.

Heat content values read from smooth curves at 100° intervals, and corresponding graphically computed entropies are given in Table II.

In the region 1,320 to 1,440°K., calcium fluoride shows a decided increase in temperature co-

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[2] Chemist, Pacific Experiment Station, Bureau of Mines.

[3] J. C. Southard, THIS JOURNAL, **63**, 3142 (1941).

[4] E. F. Mueller and F. D. Rossini, *Am. J. Physics*, **12**, 1–7 (1944).