[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY, AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Allylic Rearrangements. XV. The Carbonation of Butenylmagnesium Bromide

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In the course of independent investigations in these Laboratories, studies have been made of the products resulting from the carbonation of the Grignard reagent derived from crotyl and methylvinylcarbinyl bromides.

At the University of California, Los Angeles, this work was carried out as part of an extensive program of research on the nature of the allylic Grignard reagent and its reactions with a variety of substances. The approach, therefore, was one which gave detailed attention to all of the products formed in the reaction. On the other hand, certain studies now in progress at Princeton University on the reactions of the isomeric olefinic acids $R{-}CH{=}CH{-}CH_2CO_2H$(I), $R{-}CH(CO_2H){-}CH{=}CH_2$(II), led to an investigation of the carbonation of allylic Grignard reagents with particular attention being focused on the acidic components of the reaction mixture, since it appeared that a convenient method of the synthesis for at least one and perhaps both of the isomerides I and II would be available if the reaction proved successful.

Previous attempts to obtain unsaturated monocarboxylic acids by carbonating allylic Grignard reagents have met with only moderate success. Thus Houben[1] was able to obtain but an 11% yield of 3-butenoic acid when magnesium was allowed to act on allyl bromide in an atmosphere of carbon dioxide. Using the same technique Gilman and Harris[2] obtained a similarly low yield of 2-phenyl-3-butenoic acid from cinnamyl chloride. Subsequent experiments by Gilman and co-workers[3] in which a stream of carbon dioxide was passed into a previously prepared solution of the Grignard reagent gave only slightly better results.

In the present work the Grignard reagent was prepared by the action of magnesium on a mixture of crotyl and methylvinylcarbinyl bromides and the carbonation was carried out by two different methods. (1) A dilute ethereal solution of the butenylmagnesium bromide was poured rapidly onto a large excess of solid carbon dioxide and, after decomposition of the complexes, alkaline extraction and careful fractionation a good yield (75%, based on the Grignard reagent) of practically pure 2-methyl-3-butenoic acid was obtained. The acid, b. p. 95.5° (35 mm.), was converted to its chloride, b. p. 55–58° (110 mm.), and thence to the crystalline amide, m. p. 98°. Catalytic hydrogenation of the latter compound gave 2-methylbutanoamide, m. p. 110°.

(2) The carbonation of butenylmagnesium bromide by the procedure of Arnold[4] followed by decomposition of the complexes gave on direct fractionation of the ethereal layer (without alkaline extraction) 2-methyl-3-butenoic acid (63%), b. p. 94° (30 mm.). Other fractions consisted of lesser amounts of octadienes, b. p. 52–53° (100 mm.), a dibutenyl ketone (13%), b. p. 93–94° (100 mm.), and a high boiling residue, b. p. 100–115° (30 mm.), which may be alcoholic material. The principal fraction, as well as the intermediates containing acidic substances, gave α-phenylethylamine salts,[5] all of which melted at 118–120° without recrystallization. The structure of the acid was confirmed by isomerization with strong alkali to 2-methyl-2-butenoic acid (tiglic acid), m. p. 64°, and by hydrogenation to 2-methylbutanoic acid; anilide, m. p. 109°. The structures of the other products have not yet been elucidated.

These results using butenylmagnesium bromide show that the carbonation of an allylic Grignard reagent may give good yields of acids provided that a large excess of carbon dioxide and a low reaction temperature are used. It is also to be noted that such reactions apparently lead exclusively to acids of type II rather than I. Not only in the present studies, but also in the experiments of Gilman and Harris,[2,3a] no appreciable amounts of the latter type of acid were formed.

Experimental Part

Materials.—The mixture of butenyl bromides used in these experiments was prepared by the method of Claisen and Tietze[6] from a mixture of crotyl alcohol and methylvinylcarbinol purchased from the Shell Chemical Company. The butenyl bromide mixture boiled at 90–105° (39–51° (100 mm.)) and had $n^{20}\text{D}$ 1.4781 corresponding to the composition 80% crotyl bromide, 20% methylvinylcarbinyl bromide.[7] Magnesium turnings were prepared as needed from bars of the pure metal.

A. Action of Carbon Dioxide on Butenylmagnesium Bromide (J. F. L.).—A dilute ethereal solution of the Grignard reagent was prepared from the butenyl bromide (67.5 g., 0.5 mole) according to the procedure of Young, Prater and Winstein.[8] The yield of Grignard reagent was 82% (estimated by titration of an aliquot portion with standard hydrochloric acid). This solution (555 cc.) was poured rapidly onto 400 g. of solid carbon dioxide broken into small lumps. After the excess of solid carbon dioxide had evaporated, the mixture was treated with ice and concentrated hydrochloric acid (75 cc.) to decompose the

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(*) Abbott Laboratories Research Fellow 1943–44.

(1) Houben, *Ber.*, **36**, 2897 (1903).

(2) Gilman and Harris, THIS JOURNAL, **49**, 1825 (1927).

(3) (a) Gilman and Harris, *ibid.*, **53**, 3541 (1931); (b) Gilman and McGlumphy, *Bull. soc. chim.*, **43**, 1322 (1928).

(4) Arnold, Bank and Liggett, THIS JOURNAL, **63**, 3444 (1941).

(5) Buehler, Carson and Edds, *ibid.*, **57**, 2181 (1935).

(6) Claisen and Tietze, *Ber.*, **59**, 2344 (1926).

(7) *Cf.* Winstein and Young, THIS JOURNAL, **58**, 104 (1936).

(8) Young, Prater and Winstein, *ibid.*, **55**, 4908 (1933).

magnesium complex. The ethereal layer was then removed and the aqueous residue saturated with salt and extracted three times with ether, these extracts being united with the original ethereal solution of the product. The resulting solution was extracted three times with 100-cc. portions of 10% sodium carbonate solution. The united carbonate extracts were washed with ether, acidified with concentrated hydrochloric acid, saturated with salt, and extracted four times with ether. The united ethereal extracts were dried over anhydrous sodium sulfate. Removal of the ether by distillation gave 33 g. of the crude organic acid.

The crude product (65 g.) obtained from two such runs was freed from a small amount of residual water by mixing it with 100 cc. of benzene and removing the benzene by distillation at 100 mm. The residue from this treatment was subjected to fractionation at 35 mm. through a 1-m. column packed with Fenske spirals. Fractions were collected as follows

1	94.5°	1.5 g.	$n^{25}\text{D}$	1.4213
2	95.5°	52.0 g.	$n^{25}\text{D}$	1.4210
Holdup		9.0 g.		

The holdup was distilled from a small Claisen flask at 17 mm. The bulk of the material (6.2 g.) distilled at 80.5° and had $n^{25}\text{D}$ 1.4210. The remainder distilled at 80.5–90° and had $n^{25}\text{D}$ 1.4230. If the impurity in this fraction was 3-pentenoic acid, b. p. 93° (14 mm.), $n^{25}\text{D}$ 1.4346,[9] the amount present could not be more than 0.34 g. (13% of this fraction) or 0.5% of the total amount of the product obtained. Titration of the acid in aqueous solution gave the values 100.3, 100.5 for the equivalent weight (calcd. for $C_4H_8O_2$, 100.1).

The acid (8 g.) was warmed on the water-bath for twenty minutes with 10 g. of phosphorus trichloride. At the end of this time the upper layer of crude acid chloride was decanted into a small Claisen flask and distilled under reduced pressure. The bulk of the material (7 g.) distilled at 55-58° (110 mm.).

The acid chloride so prepared was taken up in 100 cc. of absolute ether, and ammonia gas was passed into the solution for one-half hour. The precipitated ammonium chloride was removed by filtration and the solution evaporated to dryness. The amide so obtained was purified by recrystallization from a mixture of benzene and petroleum ether, 5.0 g., m. p. 98°.

Anal. Calcd. for C_5H_9ON: N, 14.13. Found: N, 13.8.

The amide (1.0 g.) was dissolved in 25 cc. of alcohol and hydrogenated over 0.05 g. of Adams catalyst. The uptake of hydrogen was rapid and ceased after twenty minutes (98%). The catalyst was removed by filtration and the solution evaporated to dryness under diminished pressure. The crystalline residue melted at 110°, and the melting point was not depressed on admixture with an authentic specimen of 2-methylbutanoamide, m. p. 110°.

B. Action of Carbon Dioxide on Butenylmagnesium Bromide (J. D. R.).—The Grignard reagent (0.91 mole) was prepared as previously reported[6] in 84% yield[10] from butenyl bromide, magnesium turnings and dry ether in the relative mole quantities 1, 3 and 12, respectively. Of this 0.32 mole was carbonated smoothly by the procedure of Arnold[4] over a period of two hours.

The magnesium complexes were decomposed by ice and saturated ammonium chloride, the mixture acidified with dilute hydrochloric acid and the resulting ethereal layer of the products dried over magnesium sulfate. After evaporating the bulk of the ether, fractionation through a 70-cm. column[11] packed with small glass helices gave the following cuts:

Fraction	B. p., °C.	Press., mm.	Wt., g.	$n^{20}\text{D}$
1	34– 35	753	5.2	....
2	46– 52	100	0.8	1.4232
3	52– 53	100	2.1	1.4239
4–6	53– 85	100	2.2	1.4253–1.4351
7	93– 94	100	1.8	1.4371
8–11	94–118	100	2.7	1.4388–1.4352
12–13	118–119	100	7.54	1.4251–1.4235
14	94	30	8.1	1.4226
15–16	94–115	30	4.69	1.4390–1.4625

Residue 1.5 g.

Fraction 1 is diethyl ether and Fractions 2–6 consist mainly of octadienes formed by the coupling of the butenylmagnesium bromide with butenyl bromide. Except for carbon–hydrogen analysis on Fraction 3, these were not further investigated.

Anal. Calcd. for C_8H_{14}: C, 87.19; H, 12.80. Found: C, 85.69; H, 12.85.

Fraction 7 gave a positive test with 2,4-dinitrophenylhydrazine reagent and the analysis indicated that the material was a dibutenyl ketone.

Anal. Calcd. for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 77.23; H, 10.10.

Fractions 11, 14 and 16, but not Fraction 7, gave nicely crystalline α-phenylethylamine salts[5] which without recrystallization melted from 118–120°. A sample crystallized from ethyl acetate for analysis showed m. p. 119.5–120.5°.

Anal. Calcd. for $C_{13}H_{19}O_2N$: C, 70.55; H, 9.11. Found: C, 70.22; H, 8.78.

The structure of the acid (Fraction 14) was confirmed in the following ways.

(1) Hydrogenation of a 2.13-g. sample over platinum oxide in ethyl acetate gave 2-methylbutanoic acid, b. p. 90–95° (35 mm.), $n^{20}\text{D}$ 1.4069; yield 1.9 g. (90%). Somewhat less than the theoretical amount of hydrogen was absorbed (83%). The saturated acid was identified by conversion to the anilide m. p. 109° (lit., 105.5–106.5°,[12a] 108°,[12b] 110–111°[12c]).

(2) A small sample of the acid was refluxed with 60% potassium hydroxide solution for ten minutes.[13] After dilution, acidification and purification of the product there was obtained tiglic acid, m. p. 64° (lit.,[14] 64°).

Anal. Calcd. for $C_5H_8O_2$ (2-methyl-3-butenoic acid): C, 59.98; H, 8.05; neut. eq., 100.1. Found: C, 59.35; H, 8.24; neut. eq., 104.2.

Investigation of the higher boiling material which is probably an alcoholic substance is in progress.

Summary

1. From the reaction of carbon dioxide with butenylmagnesium bromide 2-methyl-3-butenoic acid was obtained in excellent yield. No detectable amounts of the isomeric 3-pentenoic acid were isolated. Other non-acidic substances were formed in the reaction.

2. It is indicated that good yields of acids from carbonation of allylic Grignard reagents may be obtained by using a low reaction temperature and a large excess of carbon dioxide.

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(9) Constants determined for a sample of pure 3-pentenoic acid prepared by the method of Linstead, Noble and Boorman, *J. Chem. Soc.*, 557 (1933).

(10) If very vigorous stirring is used, such as that afforded by a Model L "Lightning" mixer driving a large Hershberg stirrer, the time of addition may be cut to three hours or less without apparent diminution in the yield of Grignard reagent.

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

(12) (a) Underwood and Gale, *ibid.*, **56**, 2117 (1934); (b) Schwartz and Johnson, *ibid.*, **53**, 1065 (1931); (c) Verkade, *Rec. trav. chim.*, **36**, 204 (1916).

(13) *Cf.* Kon and Linstead, *J. Chem. Soc.*, **127**, 616 (1925).

(14) Young, Dillon and Lucas, THIS JOURNAL, **51**, 2528 (1929).

3. The present results are in accord with those of Gilman and Harris, who isolated 2-phenyl-3-butenoic acid from the carbonation of cinnamylmagnesium chloride.

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Allylic Rearrangement in the Reaction of Cuprous Cyanide with Butenyl Halides[1]

BY JOHN F. LANE, JAMES FENTRESS AND L. T. SHERWOOD, JR.

That cuprous cyanide reacts smoothly with allyl halides to give good yields of 3-butenonitrile is well known.[2] Until the present time, however, the reaction has not been extended to α- and γ-substituted allyl halides; *i. e.*

$$\mathrm{R{-}CHX{-}CH{=}CH_2\ (I),\ R{-}CH{=}CH{-}CH_2X\ (II)}\qquad (\mathrm{X = Cl, Br})$$

In connection with studies being carried out in this Laboratory on the preparation and reactions of isomeric olefinic acids of the type

$$\mathrm{R{-}CH(CO_2H){-}CH{=}CH_2\ (III)}$$
$$\mathrm{R{-}CH{=}CH{-}CH_2CO_2H\ (IV)}$$

it seemed desirable to investigate the action of cuprous cyanide on a pair of allylic isomerides such as I and II in the hope of producing the nitriles

$$\mathrm{R{-}CH(CN){-}CH{=}CH_2\ (V)}$$
$$\mathrm{R{-}CH{=}CH{-}CH_2CN\ (VI)}$$

corresponding to the acids III and IV.

Replacement of halogen by cyanide in such a system might proceed either by normal (bimolecular) substitution to give the expected nitrile from each isomeride

$$(1)\quad \mathrm{R{-}CH{=}CH{-}CH_2X + CuCN \longrightarrow R{-}CH{=}CH{-}CH_2CN + CuX}$$

or by an "ionic" mechanism

$$(2)\quad \mathrm{R{-}CH{=}CH{-}CH_2X \longrightarrow X^- + [R{-}CH{=}CH{=}CH_2]^+} \xrightarrow{\mathrm{CN^-}} \left\{\begin{array}{l}\mathrm{R{-}CH{=}CH{-}CH_2CN}\\ \mathrm{R{-}CH(CN){-}CH{=}CH_2}\end{array}\right.$$
$$\mathrm{(VII)}$$

to give a mixture of the isomeric nitriles V and VI.[3] In the latter event the composition of the mixture obtained should be independent first of the isomeric halide (I or II) used, and second of the nature of X. There remains also the possibility that the replacement might proceed by an "inverse" (bimolecular) substitution process[3c] to give from each isomeric halide the nitrile corresponding to the other form

$$(3)\quad \mathrm{R{-}CH{=}CH{-}CH_2X + CuCN \longrightarrow R{-}CH(CN){-}CH{=}CH_2 + CuX}$$

Of these three types of substitution process, all of which are known in reactions involving allylic systems, the process 2 is most frequently encountered, since the high resonance energy of ions such as VII greatly facilitates reaction by this path.

We have investigated the action of cuprous cyanide on the butenyl halides ($\mathrm{R = CH_3}$, $\mathrm{X = Cl, Br}$) and have found that at 60–70°, regardless of the nature of the halide used, the same mixture of isomeric nitriles is always produced

$$\begin{array}{l}\mathrm{CH_3{-}CH{=}CH{-}CH_2X + CuCN}\searrow\\ \mathrm{CH_3{-}CHX{-}CH{=}CH_2 + CuCN}\nearrow\end{array}\left\{\begin{array}{l}\mathrm{CH_3{-}CH{=}CH{-}CH_2CN}\\ \mathrm{CH_3{-}CH(CN){-}CH{=}CH_2}\end{array}\right. + \mathrm{CuX}$$

After the two pure isomers had been isolated, it was possible to estimate the composition of this mixture by measurement of the refractive index. By this means we have determined that the mixture produced in each instance consisted of 91.5 ± 0.5% 3-pentenonitrile and 8.5 ± 0.5% 2-methyl-3-butenonitrile.

The simplest interpretation of these results is that the action of cuprous cyanide on halides such as I and II belongs to that class of allylic replacement reactions which are completely "ionic" in nature (mechanism 2 above). It has been pointed out,[3a] however, that assignment of such a mechanism may be most satisfactorily made only when the allylic reactants and products are not susceptible to thermal rearrangement under the conditions employed. While in the present investigation this requirement was fulfilled with respect to the products of the reaction, it could not be fulfilled with respect to the reacting halides. Even the butenyl chlorides, normally rather stable substances, are, under the conditions of the reaction (*i. e.*, at 60° in the presence of cuprous chloride), isomerized fairly rapidly to an equilibrium mixture containing 74.0 ± 0.5% 1-chloro-2-butene and 26.0 ± 0.5% 3-chloro-1-butene. The butenyl bromides, of course, are extremely labile substances which rearrange almost instantaneously at elevated temperatures to an equilibrium mixture containing 87% 1-bromo-2-butene and 13% 3-bromo-1-butene.[4]

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(1) Abstracted in part from Senior Theses presented to the Faculty of Princeton University by James Fentress and L. T. Sherwood, Jr., in partial fulfilment of the requirements for the degree of Bachelor of Arts.

(2) Bruylants, *Bull. Soc. Chim. Belg.*, **31**, 175 (1922); Breckpot, *ibid.*, **39**, 465 (1930); Supniewski and Salzberg, *Org. Syn.*, Coll. Vol. I, 38 (1932).

(3) (a) Young and Lane, THIS JOURNAL, **60**, 847 (1938); (b) Roberts, Young and Winstein, *ibid.*, **64**, 2157 (1942); (c) Hughes, *Trans. Faraday Soc.*, **37**, 627 (1941).

(4) Winstein and Young, THIS JOURNAL, **58**, 104 (1936).