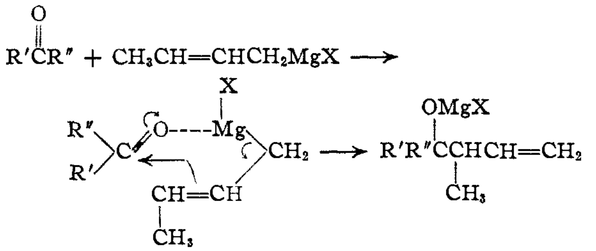
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Allylic Rearrangements. XXVIII. The Reaction of Butenylmagnesium Bromide with Hindered Ketones

BY K. W. WILSON,[1] JOHN D. ROBERTS[2]* AND WILLIAM G. YOUNG

Recent studies[3-5] of the addition reactions of the butenylmagnesium bromide have indicated that the butenyl Grignard reagent is probably best formulated as being exclusively crotylmagnesium bromide. The almost invariable formation of products containing α-methylallyl groups in carbonyl addition reactions has been suggested as due to the operation in the addition process of a six-membered cyclic mechanism.



It is particularly noteworthy that even with sterically hindered carbonyl groups of diisopropyl ketone[5a] and acetomesitylene,[5c] the Grignard reagent adds to give α-methylallylcarbinols.

In the present investigation, the reaction of butenylmagnesium bromide with several highly hindered ketones was studied to determine whether the degree of hindrance at the carbonyl position could be increased sufficiently so that the introduction of a crotyl group by the Grignard reagent would be favored over that of the more bulky α-methylallyl group. Benzophenone, isobutyrylmesitylene, dimesityl ketone, pentamethylacetone and hexamethylacetone were chosen as typical highly hindered ketones and, in each case, addition of the Grignard reagent was found to occur. Isolation and identification of the carbinol products were complicated by dehydration and cleavage reactions which usually occurred simultaneously.[6] The cleavage on heating of the carbinols to give butenes and the original ketones was previously observed with α-methylallylmethylmesitylcarbinol.[5c] Since it was found that α-methylallylmethylmesitylcarbinol gave only 2-butenes (*i. e.*, complete allylic rearrangement), the compositions of the butene mixtures were employed in the present work as a measure of the relative extent of formation of crotyl or α-methylallyl addition products. Although this method of analysis is complicated by the simultaneous dehydration reaction which may not occur with equal rates for both allylic isomers, the structural assignments are in agreement with those obtained by oxidative degradation.

It was found that butenylmagnesium bromide with benzophenone, isobutyrylmesitylene and pentamethylacetone gave principally, if not exclusively, α-methylallylcarbinols. The Grignard reagent added to dimesityl ketone but the structure of the product was not determined. Hexamethylacetone with butenylmagnesium bromide gave crotyldi-*t*-butylcarbinol. This reaction is the only one so far observed which gives a product corresponding exclusively to the primary form of the Grignard reagent, although about 15% of crotyldiisopropylcarbinol was obtained in the reaction with butenylmagnesium bromide and diisopropyl ketone.[5a,7]

The results of these experiments indicate that the processes by which α-methylallyl groups are furnished by the Grignard reagent are considerably favored over those which give rise to crotyl derivatives. However, the Grignard reagent may add so as to give a crotyl derivative with hexamethylacetone where steric hindrance to the cyclic introduction of an α-methylallyl group is at a maximum and no reaction competes with the 1,3-shift of a crotyl group. As in the earlier work,[4,5a-c] reduction of the carbonyl compounds by the butenyl Grignard reagent was never observed. This fact may be considered as evidence that the Grignard reagent exists entirely as a crotylmagnesium halide where the one β-hydrogen atom is unfavorably located on a double bonded carbon.[8]

Experimental

Butenylmagnesium Bromide with Isobutyrylmesitylene.—Isobutyrylmesitylene (0.25 mole) prepared by the method of Klages[9] was added with stirring to butenylmagnesium bromide.[3] A transient orange color similar to that observed in the reaction of benzylmagnesium chloride with acetomesitylene[5c] was noticed as each drop of ketone struck the Grignard solution. No butenes or other unsaturated volatile substances were formed in the reaction. After hydrolysis of the reaction mixture with water, the

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* Harvard University, National Research Fellow, 1945–1946.

[1] Present address, Chemistry Department, West Virginia University.

[2] Present address, Chemistry Department, Massachusetts Institute of Technology.

[3] Lane, Roberts and Young, THIS JOURNAL, **66**, 543 (1944).

[4] Roberts and Young, *ibid.*, **67**, 148 (1945).

[5] (a) Young and Roberts, *ibid.*, **67**, 319 (1945); (b) Young and Roberts, *ibid.*, **68**, 649 (1946); (c) Young and Roberts, *ibid.*, **68**, 1472 (1946).

[6] See Ramart-Lucas, *Ann. chim.*, [8] **30**, 349 (1913); Grignard and Escourrou, *Compt. rend.*, **176**, 1860 (1923); Grignard and Dubien, *Ann. chim.*, [10] **2**, 298 (1924); and Grignard and Chambret, *Compt. rend.*, **182**, 299 (1926), for similar observations.

[7] Less than 5% of crotyldiisopropylcarbinol was obtained using butenylmagnesium chloride and diisopropyl ketone. The differences in the product composition using different halides have not yet been elucidated.

[8] See Whitmore and George, THIS JOURNAL, **64**, 1239 (1942), for a correlation of the structure and reducing powers of alkyl Grignard reagents.

[9] Klages, *Ber.*, **37**, 928 (1904).

ether layer was separated and dried over magnesium sulfate. Distillation of the addition products at 6 mm. (b. p. about 128°) was accompanied by considerable decomposition and the distillate contained considerable quantities of the starting ketone. Molecular distillation at 2×10^{-3} mm. was also unsatisfactory. A portion of the crude reaction mixture was pyrolyzed at atmospheric pressure. Decomposition began at 155° and went briskly at 215°. The resulting butenes were condensed in a Dry Ice trap. Infrared analysis[10] of the butenes indicated 6 ± 5% butene-1, 24 ± 5% *trans*-butene-2, and 70 ± 5% *cis*-butene-2.

An attempt was made to synthesize the saturated carbinols corresponding to the expected addition products of butenylmagnesium bromide and isobutyrylmesitylene by the reaction of mesitylmagnesium bromide with *n*-butyl and *s*-butyl isopropyl ketones. In each case, no addition product was isolated, the only reaction observed being enolization of the ketones by the Grignard reagent.

Butenylmagnesium Bromide with Benzophenone.—A benzene solution containing 0.27 mole of benzophenone was added to an equivalent amount of butenylmagnesium bromide in ether. No color or unsaturated volatile material was detected during the course of the reaction. Preliminary tests on the addition product showed that decomposition took place at too low a temperature to permit distillation. Pyrolysis of the crude product began at 115° and proceeded rapidly at 200°. Infrared analysis[10] of the resulting butenes indicated 77% *trans*-butene-2 and 23% *cis*-butene-2.

Attempts to prepare solid derivatives of the addition product or the corresponding hydrogenated material were unsuccessful. For comparison *n*-butyl- and *s*-butyl-diphenylcarbinols were prepared by the addition of phenylmagnesium bromide to appropriate esters. *n*-Butyldiphenylcarbinol showed b. p. 134–135° (1.5 mm.), n^{27}_{D} 1.5661–1.5665.

Anal. Calcd. for $C_{17}H_{20}O$: C, 84.95; H, 8.33. Found: C, 84.75; H, 8.27.

The product from the reaction of propyl α-methylbutyrate and phenylmagnesium bromide dehydrated completely on distillation despite precautions to eliminate traces of acidic materials which might catalyze the reaction. The resulting 1,1-diphenyl-2-methylbutene-1 showed b. p. 123° (1.5 mm.) and n^{25}_{D} 1.5777.

Anal. Calcd. for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.20; H, 8.64.

Butenylmagnesium Bromide with Dimesityl Ketone.—A benzene solution of dimesityl ketone[11] (0.38 mole) was added with stirring to an equal quantity of butenylmagnesium bromide in ether solution. An intense magenta color developed, which gradually faded over a period of four hours. No enolization or reduction products could be detected and no unreacted Grignard reagent remained. The product obtained after hydrolysis of the Grignard complexes and removal of the solvent could not be crystallized and decomposed on distillation. Pyrolysis gave water but no butene. The ultraviolet spectrum of the organic pyrolysis product (b. p. *ca.* 180° at 4 mm.) showed that the material was not the original ketone and it seems likely that dehydration occurred in the pyrolysis reaction. The material was not further investigated.

Butenylmagnesium Bromide with Pentamethylacetone.—Pentamethylacetone and hexamethylacetone were prepared simultaneously by the method of Whitmore and Stahly,[12] using tetralin in place of toluene as a solvent. Pentamethylacetone (0.29 mole) was added with stirring to an equivalent amount of butenylmagnesium bromide. After four hours, the reaction mixture was decomposed with iced ammonium chloride solution, the ether layer separated and dried over magnesium sulfate. The addition products were distilled through a Podbielniak[13] column. The principal product showed b. p. 100° (17 mm.) and n^{20}_{D} 1.4651. The yield was 74% and the material absorbed 90% of the theoretical amount of hydrogen over platinum oxide. A small amount of higher boiling material was obtained which may have contained some isomeric addition product, but this amounted to less than 6% of the total product.

Pyrolysis of the principal product gave 100% *trans*-butene-2 as indicated by infrared analysis.[10] The structure of the addition product as α-methylallylisopropyl-*t*-butylcarbinol was confirmed by hydroxylation with performic acid[14] and cleavage of the resulting glycol with periodic acid. Formaldehyde was isolated as the methone derivative and no acetaldehyde was detected.

Butenylmagnesium Bromide with Hexamethylacetone.—Hexamethylacetone (0.18 mole) was added with stirring to an equal quantity of butenylmagnesium bromide. After one and one-half hours the mixture was decomposed with iced ammonium chloride. The product was distilled through a small column, b. p. 72° (2 mm.), n^{20}_{D} 1.4714–1.4720. The yield was 69%. On quantitative hydrogenation over platinum oxide 93% of the theoretical amount of hydrogen was absorbed. The structure of the addition product was established as crotyldi-*t*-butylcarbinol by the following experiments. Pyrolysis of the addition product proceeded smoothly at 215° and infrared analysis[10] indicated that pure butene-1 was formed. Cleavage of the carbinol by successive treatments with performic acid and periodic acid gave acetaldehyde which was isolated as the methone derivative. No formaldehyde was detected.

Summary

Butenylmagnesium bromide adds to benzophenone, isobutyrylmesitylene and pentamethylacetone to give principally, if not exclusively, α-methylallyl derivatives. Addition occurs to dimesityl ketone but the structure of the product has not been determined.

Butenylmagnesium bromide adds to hexamethylacetone to give crotyldi-*t*-butylcarbinol. This reaction is the first carbonyl addition reaction to give a pure crotyl derivative.

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[10] Wilson, Roberts and Young, THIS JOURNAL, **72**, 215 (1950).

[11] Kohler and Baltzly, *ibid.*, **54**, 4023 (1932).

[12] Whitmore and Stahly, *ibid.*, **55**, 4153 (1933).

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

[14] Swern, Billen, Findley and Scanlan, THIS JOURNAL, **67**, 1786 (1945); Swern, Billen and Scanlan, *ibid.*, **68**, 1504 (1946).