test for bromine ion was positive. The compound could not be purified without decomposition.

Anal. Calcd. for $C_{16}H_{12}N_2OBr_2$: C, 47.09; H, 2.96; N, 6.86. Found: C, 47.65, 47.30; H, 3.20, 3.15; N, 6.98, 6.98.

2-Phenyl-4-(α-bromobenzal)-5-glyoxalidone.—The hydrobromide described above dissolves completely in 2 *N* sodium hydroxide solution. Neutralization with dilute acetic acid precipitated the free glyoxalidone. The compound crystallized from 2-pentanol as long yellow needles melting at 230°. The compound gave a positive test for bromine after fusion with sodium.

Anal. Calcd. for $C_{16}H_{11}N_2OBr$: C, 58.73; H, 3.39; N, 8.56. Found: C, 58.77, 58.74; H, 3.36, 3.40; N, 8.57, 8.42.

Because of damage to the spectrograph at the University of Colorado and lack of repairs due to war conditions, the absorption spectra of these compounds cannot be reported. It is hoped that complete absorption spectra data may be reported later.

Summary

1. Improved procedure for the preparation of 2-phenyl-4-benzal-5-oxazolone (azlactone) and of 2-phenyl-4-benzal-5-glyoxalidone are described.

2. The synthesis and properties of ω-2-phenyl-4-(α-bromobenzyl)-4-bromo-5-glyoxalidone are reported.

3. The isolation and properties of α-2-phenyl-4-(α-bromobenzyl)-4-bromo-5-glyoxalidone are reported.

4. The synthesis and properties of 2-phenyl-4-(α,α-dibromobenzyl)-4-bromo-5-glyoxalidone hydrobromide are reported.

5. The synthesis and properties of 2-phenyl-4-(α-bromobenzal)-5-glyoxalidone and hydrobromide are reported.

FT. COLLINS, COLORADO RECEIVED DECEMBER 13, 1945

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

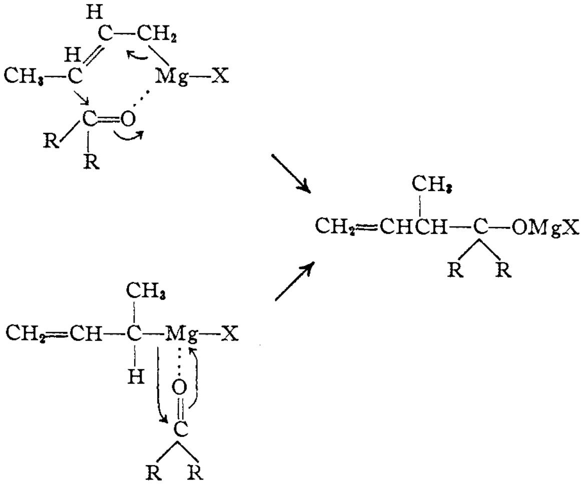
Allylic Rearrangements. XX. Some Addition Reactions of Butenylmagnesium Bromide

BY WILLIAM G. YOUNG AND JOHN D. ROBERTS[1]

Preceding studies of the butenyl Grignard reagent have indicated a striking tendency on the part of the reagent to introduce an α-methylallyl group in coupling reactions with allylic chlorides[2] and in addition reactions to aldehydes,[3,4] ketones[4] and carbon dioxide.[5] Even with highly-hindered ketones as diisopropyl ketone and acetomesitylene[6] the reaction products are predominantly α-methylallyl derivatives.

We have now turned to the investigation of other types of addition reactions of butenylmagnesium bromide and find that with phenyl isocyanate, ethyl formate and ethyl orthoformate the reaction products correspond almost exclusively to the secondary form of the Grignard reagent. With ethyl orthoformate some (<4%) of the diethyl acetal of 3-pentenal was obtained but in the other reactions none of the products resulting from the introduction of the primary butenyl group by the Grignard reagent was detected.

As one of several possible working hypotheses it is possible to account for the results of the addition and coupling reactions by considering the butenyl Grignard reagent (formulated as RMgBr) as being almost exclusively either crotyl or α-methylallylmagnesium bromide depending on the mechanism of the transfer of the butenyl radical to give a α-methylallyl derivative as the reaction product. Choosing a carbonyl addition reaction as an example we have



Similar mechanisms have been suggested for other Grignard reactions.[7,8]

Assuming that butenylmagnesium bromide is a single substance, it appears likely that a possible choice between consideration of the reagent as a crotyl or α-methylallyl derivative might be afforded by a study of the products from the 1,4-addition of the reagent to an α,β-unsaturated

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[1] Abbott Laboratories Research Fellow, 1943–1944.

[2] Young, Roberts and Wax, THIS JOURNAL, **67**, 841 (1945).

[3] Ou Kuin-Houo, *Ann. chim.*, [11] **13**, 175 (1940).

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

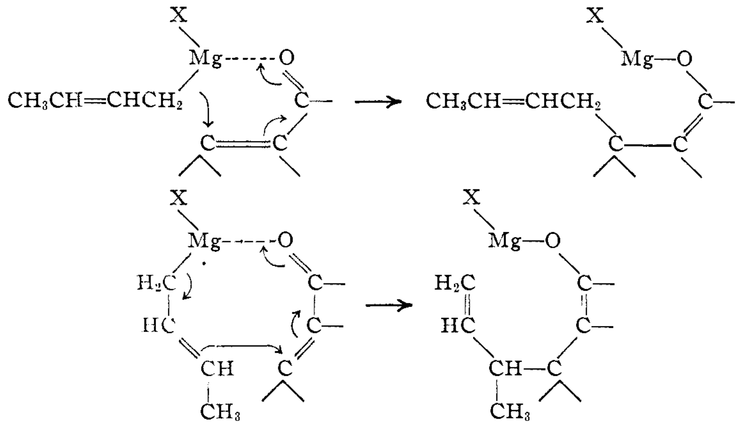
[5] Lane, Roberts and Young, *ibid.*, **66**, 543 (1944).

[6] Young and Roberts, *ibid.*, **66**, 2131 (1944); **67**, 319 (1945).

[7] Johnson in Gilman, "Organic Chemistry," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1943, Chap. XXV, pp. 1879–1883.

[8] Whitmore and George, paper presented before the Division of Organic Chemistry at the Atlantic City Meeting of the American Chemical Society, September, 1941.

carbonyl compound if the generally accepted mechanism[7,8] for 1,4-addition of Grignard reagents is correct. Thus, for crotylmagnesium bromide a crotyl derivative would result if the reaction mechanism involved a six-membered ring while a α-methylallyl derivative would be formed only from a process involving a less-favored eight-membered ring.



Similarly, α-methylallylmagnesium bromide might be expected to give a α-methylallyl derivative if it were the principal form of the Grignard reagent.

We have investigated the reaction of butenylmagnesium bromide with phenyl vinyl ketone, as Kohler[9] has reported that ethyl- and phenylmagnesium bromides gave only 1,4-addition products with this ketone. In our experiments the principal product was a polymeric substance and no 1,4-addition products could be definitely characterized. In view of the failure of this experiment we turned to the reaction of the butenyl Grignard with *t*-butyl cinnamate as means of obtaining a 1,4-addition product. Frostich, Baumgarten and Hauser[10] have shown that phenylmagnesium bromide adds in the 1,4-manner to *t*-butyl cinnamate and we have obtained similar results with *n*-butylmagnesium bromide. In striking contrast the reaction of the butenyl Grignard reagent with *t*-butyl cinnamate gave no significant amount of 1,4-addition products and no excess of Grignard reagent was present after the addition of one mole of the ester to two moles of organomagnesium halide. It is significant that whatever mode of 1,2-addition is available to the butenyl Grignard reagent this process is much more favored when a 1,4-addition path is possible than is true for a saturated or aromatic Grignard reagent. This fact might be taken to indicate that the 1,2-addition mechanisms of saturated and allylic Grignard reagents are different and, hence, that if the butenyl Grignard reagent is predominantly one form it is most likely to be primary since α-methylallyl derivatives are the products of carbonyl addition reaction.[3,4,5,6] Further evidence on this question will be considered in later papers.

Experimental

Butenylmagnesium bromide was prepared by the previously reported method,[5] filtered from excess magnesium and standardized before using.

Butenylmagnesium Bromide with Phenyl Isocyanate.—To an ethereal solution of butenylmagnesium bromide (0.125 mole) was added dropwise a solution of 15 g. (0.125 mole) of phenyl isocyanate dissolved in 100 ml. of ether. After half an hour of stirring the mixture was poured into iced ammonium chloride solution and the ethereal layer separated and washed with water. The ether was evaporated and the product dried by distillation with benzene. The oily residue was crystallized from hexane, giving 16 g. (74%) of crude 2-methyl-3-butenoanilide. Crystallization of the crude product from alcohol–water mixture or simple distillation removed some tarry hexane-soluble impurity and gave 80–90% recoveries of the pure anilide, m. p. 90–91°. The material did not depress the melting point of anilide prepared from a known sample of 2-methyl-3-butenoic acid.[6]

Anal. Calcd. for $C_{11}H_{13}ON$: C, 75.39; H, 7.47. Found: C, 75.39; H, 7.60.

Butenylmagnesium Bromide with Ethyl Formate.—To 0.35 mole of butenylmagnesium bromide in 500 ml. of ether was added 13 g. (0.17 mole) of ethyl formate (b. p. 54°) dissolved in 100 ml. of dry ether. During the addition of the ester, the reaction mixture was kept in an ice-bath. After four hours of stirring the mixture was decomposed by pouring into iced ammonium chloride solution and the products isolated in the usual way. Fractionation through an efficient column[11] gave the following cuts.

TABLE I

Cut	Temp., °C.	Press., mm.	Wt., g.	$n^{20}D$	
1	42.5	125	2.8	1.4228	Octadienes
2	68.6	125	1.4	1.4394	
3	107.2	125	2.2	1.4525	Nonadienols
4	108.9	125	1.9	1.4529	
5	72.1	25	1.8	1.4546	
6	76.6	25	6.0	1.4549	
7	76.3	25	3.0	1.4554	
8[a]	77–80	20	3.0	1.4489	
Residue			1.4		

[a] Holdup, distilled from a small Claisen flask.

The distillation curve indicates the presence of two principal products boiling at least several degrees apart. The yield, assuming both materials to be nonadienols, was 18.6 g. (78%). Phenylurethans were readily prepared by mixing the alcohols with an equal weight of phenyl isocyanate with a drop or two of pyridine as catalyst.[12] After standing overnight, the derivatives were crystallized from petroleum ether. The urethan from Fraction 3 was obtained as heavy prisms, m. p. 79.5–81.5°.

Anal. Calcd. for $C_{16}H_{21}O_2N$: C, 74.10; H, 8.16. Found: C, 74.10; H, 8.34.

The derivative from Fraction 6 crystallized as fine needles, m. p. 67–68°.

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[9] Kohler, *Am. Chem. J.*, **42**, 375 (1909).

[10] Frostich, Baumgarten and Hauser, THIS JOURNAL, **66**, 305 (1944).

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

[12] Tarbell, Mallatt and Wilson, THIS JOURNAL, **64**, 2229 (1942).

Anal. Calcd. for $C_{16}H_{21}O_2N$: C, 74.10; H, 8.16. Found: C, 73.97; H, 8.18.

These urethans were readily hydrogenated over platinum oxide in ethyl alcohol. The urethans of the saturated alcohols were crystallized from petroleum ether. The product from Fraction 6 showed m. p. 89–91° while from Fraction 3 a urethan, m. p. 81–82°, was obtained.

Anal. Calcd. for $C_{16}H_{23}O_2N$ (Fraction 3): C, 72.96; H, 9.56. Found: C, 72.91; H, 9.34. Calcd. for $C_{16}H_{23}O_2N$ (Fraction 6): C, 72.96; H, 9.56. Found: C, 73.11; H, 9.70.

In order to establish the structure of the products, di-*s*-butylcarbinol, *s*-butyl-*n*-butylcarbinol and di-*n*-butylcarbinol were prepared.

Di-*n*-butylcarbinol was prepared in 72% yield according to the procedure of Coleman and Craig[13]; b. p. 104–105° (30 mm.). The product gave a phenylurethan, m. p. 48.5–50° after two crystallizations from hexane.

Anal. Calcd. for $C_{16}H_{23}O_2N$: C, 72.96; H, 9.56. Found: C, 73.53; H, 9.55.

n-Butyl-*s*-butylcarbinol was synthesized by the addition of 8 g. (0.09 mole) of α-methylbutyraldehyde[14] to 0.1 mole of *n*-butylmagnesium bromide. Fractionation of the products gave 3.8 g. (38%) of the alcohol; b. p. 106° (50 mm.), $n^{20}D$ 1.4330. Heat was evolved in the reaction of the alcohol with phenyl isocyanate but the derivative was not solid at room temperature.

Di-*s*-butylcarbinol was prepared by the addition of 36 g. (0.5 mole) of ethyl formate dissolved in 50 ml. of ether to a solution of one mole of *s*-butylmagnesium bromide in 300 ml. of ether. Olefin-containing gases were vigorously evolved. The products were isolated in the usual way and fractionation gave 18.2 g. (13%) of product; b. p. 93.3–99.8° (40 mm.), $n^{20}D$ 1.4377–1.4278.

The most satisfactory means of accounting for the fact that this synthetic sample of di-*s*-butylcarbinol appears to be a mixture of closely-boiling substances is that at least two of the three possible antipodes were formed in the reaction and that these boil at somewhat different temperatures. The phenylurethan of the alcohol was difficult to purify and after several crystallizations from hexane the melting point was 86–89°.

The melting point of the saturated urethan from Fraction 6 was not depressed by admixture with the urethan obtained from the di-*s*-butylcarbinol sample, indicating the higher-boiling material of the original product to be a di-α-methylallylcarbinol. As the low-boiling material is also a nonadienol it seems safe to infer that this compound also has the di-α-methylallylcarbinol structure and is an antipode of the higher-boiling product.

Butenylmagnesium Bromide with Ethyl Orthoformate.—The reaction was carried out by a procedure similar to that of McElvain, Clarke and Jones.[14a] To a stirred, refluxing, ethereal solution of butenylmagnesium bromide (0.27 mole) was added 49 g. (0.30 mole) of ethyl orthoformate (b. p. 144–145°). A white precipitate separated thirty minutes after the start of the addition. After ten hours of heating the reaction mixture was poured onto cracked ice and the ether layer decanted. A solution of 13 g. of acetic acid in 150 ml. of water was added slowly to the residue with cooling. The mixture was filtered and the filtrate extracted with ether. The combined ethereal extracts were washed with water and 10% sodium carbonate solution, then dried over potassium carbonate. On fractionation of the products the following cuts were taken, other than ether and octadienes (Table II).

Fractions 6–10 were recovered ethyl orthoformate ($n^{20}D$ 1.3905) and Fractions 11–21 were pentenal acetal. The yield of the latter material on the basis of unrecovered orthoester was 84%. The principal fractions were nearly constant-boiling but showed considerable changes in refractive index. That this behavior (similar to that observed in earlier work[6]) was due to double bond rather than skeletal isomerism was shown by hydrogenation of 20 g. of combined material of Fractions 14–19. The reduction proceeded smoothly in 25 ml. of ethanol over platinum oxide and 97% of the theoretical hydrogen was absorbed. The product was essentially constant-boiling, constant-index material; b. p. 155.1–155.3° (750 mm.), $n^{20}D$ 1.4022–1.4028; yield 18.6 g. (91%).

TABLE II

Fraction	Temp., °C.	Press., mm.	Wt., g.	$n^{20}D$	
6–10	135.9–148.3	748	11.6	1.4013–1.3962	Ethyl orthoformate
11–19	148.3–152.5	748	29.0	1.3997–1.4120	Pentenal acetal
20–21[a]	81–90	50	4.0	1.4138–1.4162	
22[a]	90–145	50	0.9	1.4252	
Residue (viscous oil)			4.2		

[a] Holdup, distilled from a small Claisen flask.

The identities of the various pentenal acetal fractions were established by hydrogenation in absolute alcohol, followed by hydrolysis with dilute acid and formation of solid derivatives with 2,4-dinitrophenylhydrazine. Fractions 12 and 19 gave identical derivatives, m. p. 127.5–128.0°, which did not depress the melting point (127.5–128.0°) of an authentic sample of the 2,4-dinitrophenylhydrazone of α-methylbutyraldehyde.[15]

Hydrogenation, hydrolysis and formation of derivatives of Fractions 21 and 22 gave poorly characterized solids which, on crystallization, gave 2,4-dinitrophenylhydrazones of m. p. 89–94°. *n*-Valeraldehyde 2,4-dinitrophenylhydrazone is reported to have m. p. 98°.[16] A generous estimate of the total corresponding to the primary form of the Grignard reagent would not be greater than 4%.

Conversion of the unsaturated acetal (Fraction 19) to a 2,4-dinitrophenylhydrazone gave different products depending on the conditions. Fraction 19 (0.5 ml.) was boiled with 0.5 g. of 2,4-dinitrophenylhydrazine in 13 ml. of 80% alcohol to which had been added one drop of concentrated hydrochloric acid. After all of the hydrazine had dissolved, the mixture was cooled and the product filtered. Recrystallization from boiling ethanol gave orange flakes, m. p. 122.8–123.5°.

Anal. Calcd. for $C_{11}H_{12}O_4N_4$: C, 49.99; H, 4.57. Found: C, 50.40; H, 4.79.

A similar procedure using 1 ml. of concentrated hydrochloric acid gave a bright red solid which was recrystallized from ethyl acetate; red needles, m. p. 215.5–217.5°. The strong acid undoubtedly catalyzed the isomerization of the β,γ-double bond of the aldehyde to the α,β-position. The assignment of the α,β-position for the double bond is consistent with the fact that 2,4-dinitrophenylhydrazones of α,β-unsaturated carbonyl compounds are generally bright red.[17]

The Action of Butenylmagnesium Bromide with Phenyl Vinyl Ketone.—The phenyl vinyl ketone was prepared by a modification of the method of Mannich.[18]

In a liter, three-necked flask, equipped with stirrer, thermometer and reflux condenser connected to a water separator, was placed 120 g. (1 mole) of acetophenone, 45 g. (1.5 moles) of paraformaldehyde, 120 g. (1.1 mole) of diethylamine hydrochloride, 1 ml. of concentrated hydrochloric acid, 250 ml. of nitromethane, 100 ml. of toluene and 50 ml. of absolute alcohol. The mixture was heated to rapid refluxing and the theoretical amount of water was taken off in about a half an hour. About 250 ml. of solvent were distilled off under reduced pressure keeping the boiler temperature below 50°. The flask was cooled and 800 ml. of dry ether added with vigorous shaking. The mixture was placed in a refrigerator overnight. The pasty

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[13] "Organic Syntheses," Coll. Vol. II, p. 179.

[14] Linstead and Mann, *J. Chem. Soc.*, 2069 (1930).

[14a] McElvain, Clarke and Jones, THIS JOURNAL, **64**, 1966 (1942).

[15] Morgan and Hardy (*Chem. Ind.*, **52**, 518 (1933)) report the melting point of this derivative as 120.5°.

[16] Allen, THIS JOURNAL, **52**, 2957 (1930).

[17] Buchman, Schlatter and Reims, *ibid.*, **64**, 2701 (1942); see also Roberts and Green, *ibid.*, **68**, 214 (1946).

[18] Mannich and Heilner, *Ber.*, **55**, 356 (1922).

solid was filtered, pressed down well, washed with dry ether and recrystallized from 250 ml. of acetone. The yield of diethyl-(β-benzoylethyl)-ammonium chloride was 113 g. (47%), m. p. 114°. By working up the mother liquor an additional 16 g. of product was obtained, raising the yield to 54%.

An intimate mixture of 124 g. (0.51 mole) of diethyl-(β-benzoylethyl)-ammonium chloride with 1 g. of hydroquinone was pyrolyzed at a pressure of 2 mm. in a distilling flask equipped with a stout capillary and heated by an electric mantle heater. A few crystals of hydroquinone were placed in the receiver. The ketone distilled at 70–90° during the reaction. Redistillation gave 38 g. (56%) of the pure ketone, b. p. 72–73° (3 mm.). A small sample was converted by reaction with phenylhydrazine to 1,3-diphenylpyrazoline; lustrous yellow needles from alcohol, m. p. 154–155°. Reported melting points for the pyrazoline derivative are 158[9] and 151°.[18]

To an ice-cold ethereal solution of 0.29 mole of butenylmagnesium bromide was added slowly a solution of phenyl vinyl ketone (38.1 g., 0.29 mole) dissolved in an equal volume of ether. A vigorous reaction took place and a gummy, dark orange precipitate separated. Near the end of the addition the thick, pasty mass stopped the stirrer. More powerful stirring was applied and after a half an hour 200 ml. of saturated ammonium chloride solution was added while cooling in an ice-bath. No excess Grignard reagent was present as no butene was liberated during the decomposition. The dark, pasty solid slowly dissolved and, after an hour, the mixture was almost colorless. The ether layer was separated and the residue extracted with ether. The combined extracts were dried over magnesium sulfate and the ether removed. The residue was distilled at 0.5–1.0 mm. until decomposition began to set in. The distillate amounted to 12.0 g. and the residue, which set to a hard, yellow glass on cooling, weighed 39 g. The recovery of organic material was 93% on the basis that one mole of the Grignard reagent added to the ketone.

The distillate was redistilled through a short Vigreux column taking two cuts: (1) b. p. 93–98° (3.5 mm.), n^{20}_{D} 1.5281; 5.3 g., and (2) b. p. 98–108° (3.5 mm.), n^{20}_{D} 1.5299, 6.4 g. No ketonic material could be isolated from Fraction 1 with Girard reagent. Fraction 2 gave a weak 2,4-dinitrophenylhydrazine test for carbonyl compounds and had the correct composition for the expected addition products (both 1,2- and 1,4-addition products should have the same molecular formula).

Anal. Calcd. for $C_{13}H_{16}O$: C, 82.93; H, 8.56. Found: C, 82.67; H, 8.71.

Attempts to prepare the semicarbazone or phenylhydrazone of the ketonic material were unsuccessful, giving intractable oils which were probably seriously contaminated with the 1,2-addition products. A few milligrams of a 2,4-dinitrophenylhydrazone was obtained, m. p. 160–161° after crystallization from acetic acid. This material was not identified.

Anal. Calcd. for $C_{19}H_{20}O_4N_4$: C, 61.94; H, 5.47. Found: C, 61.97; H, 5.65.

Reaction of Butenylmagnesium Bromide and *t*-Butyl Cinnamate.—To a solution of butenylmagnesium bromide (0.19 mole) was added over a half-hour period 20.4 g. of *t*-butyl cinnamate[19] dissolved in 50 ml. of dry ether. The mixture was allowed to stir for two and one-half hours at room temperature and at this point the Gilman test for Grignard reagent was negative. The mixture was poured into iced ammonium chloride solution and the ethereal layer separated and dried. The ether was evaporated and the residue distilled in a molecular still. At 5×10^{-4} mm. 18.4 g. of distillate was obtained with the bath temperature at 65–123°. The residue amounted to 5.4 g.

As the major interest was focused on the 1,4-addition products the following procedure was adopted which gave attention only to acidic compounds or their esters. The distillate (12.1 g.) was hydrogenated in ethanol over platinum oxide at room temperature. The absorption of hydrogen was 0.80 mole. The catalyst was filtered and a stream of dry hydrogen chloride passed into the filtrate for a few minutes. The acidic solution was refluxed for four hours, then 20 g. of potassium hydroxide and 100 ml. of alcohol were added and the mixture refluxed for an hour. The alcohol was distilled and the residue extracted with ether. The non-acidic material was not investigated. The alkaline residue was acidified and extracted with ether. From this extract was obtained 1 g. of cinnamic acid, m. p. 132.8–133.8°, 1 g. of an oil containing hydrocinnamic acid; *p*-bromophenacyl ester, m. p. 100–103° (authentic sample 104–105°) and a residual oil (0.15 g.) which formed an α-phenylethylammonium salt,[20] m. p. 137–139° and a poorly crystallized *p*-bromophenacyl ester; m. p. 49–53°. These derivatives depressed the melting points of the corresponding derivatives of β-*n*-butylhydrocinnamic acid but were not otherwise characterized as the unknown acid could not have amounted to more than 2–3% of the total product.

In contrast to the results obtained with butenylmagnesium bromide the reaction of 20.4 g. (0.1 mole) of *t*-butyl cinnamate with 0.2 of *n*-butylmagnesium bromide left a large excess of Grignard reagent and the 1,4-addition product, β-*n*-butylhydrocinnamic acid, was readily obtained after ester interchange and hydrolysis as described above; yield 8.8 g. (43%); b. p. 173–178° (8 mm.); *p*-bromophenacyl ester, m. p. 48–49°; α-phenylethylammonium salt, m. p. 130.5–131.5° after crystallization from ethyl acetate.

Summary

1. Butenylmagnesium bromide reacts with phenyl isocyanate, ethyl formate and ethyl orthoformate to give almost exclusively α-methylallyl derivatives.

2. Butenylmagnesium bromide gives almost no 1,4-addition products with phenyl vinyl ketone and *t*-butyl cinnamate, although simple saturated and aryl Grignard reagents add almost exclusively in the 1,4-manner to these compounds.

LOS ANGELES 24, CALIFORNIA

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[19] Abramovitch, Shivers, Hudson and Hauser, THIS JOURNAL, **65**, 986 (1943).

[20] Buehler, Carson and Edds, *ibid.*, **57**, 2181 (1935).