residue was distilled by heating under a pressure of 0.005 mm., the bath temperature being slowly raised to 75°; 1.0 cc. of a colorless, fluid distillate, b. p. 32–35° (0.005 mm.) (132–134° with decomposition at atmospheric pressure) was collected (methyl pyruvate boils at 137°). It burned without puffing and gave a definite but not strong peroxide test with neutral potassium iodide. It was incompletely water-soluble and the water extract was acidic and peroxidic. Since the peroxidic methyl methacrylate before concentration contained no acidic, water-soluble peroxide, this product was assumed to be a secondary product. The residue from the distillation was a nonperoxidic gum. In several attempts to repeat this experiment vigorous explosions occurred.

No clean-cut method was found for reducing the peroxide before isolation. It was attempted to hydrogenate peroxide and monomer both with Raney nickel but the methyl methacrylate could not be quantitatively hydrogenated under mild conditions. Shaking the peroxidic monomer with bisulfite caused instant polymerization in the aqueous phase. Shaking with ferrous salts gave incomplete reduction, as shown by subsequent potassium iodide tests. Liberation of iodine followed by decolorization with thiosulfate was also incomplete with more iodine obtained at each repetition. The addition of hydroquinone to the peroxidic monomer produced on concentration a residue of peroxide contaminated with quinone.

The degradation products in peroxidic methyl methacrylate can be titrated with dichloramine-T using *o*-tolidine as an indicator. There appears to be no reaction of this reagent with the peroxide.

Summary

Evidence is presented that polymeric peroxides are formed when vinyl monomers react with oxygen or air. The structure of these peroxides has been established for methyl methacrylate and styrene. It is suggested that they result from an interpolymerization of the vinyl monomer with oxygen. This has been shown to be consistent with the inhibitory action of oxygen in vinyl polymerizations.

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

Allylic Rearrangements. XVII. The Reactions of Butenylmagnesium Bromide with Active Hydrogen Compounds

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

Previous work has shown that while the butenyl Grignard reagent has a striking tendency to form α-methylallyl derivatives in a wide variety of coupling and carbonyl addition reactions,[3] hydrolysis with dilute sulfuric acid gives a mixture of butenes. It has been demonstrated that the composition of the butene mixture is independent of the ratio of allylic isomers in the starting butenyl halides[4] and that similar butene mixtures are produced using butenylmagnesium chlorides and bromides.[5] The average composition of the butene mixtures formed in these experiments was 17.2 ± 3.3% *trans*-butene-2, 26.5 ± 1.4% *cis*-butene-2, and 56.4 ± 2.0% butene-1. In contrast to the mixture of butenes produced by dilute aqueous acid hydrolysis, it has been found that cleavage of the Grignard reagent with phenylacetylene gives almost pure butene-1.[3]

In the present investigation, the reaction of the butenyl Grignard reagent has been studied with a wide variety of active hydrogen compounds to see if this type of reaction can be correlated with the earlier formulations of the structure and reaction mechanisms of the butenylmagnesium halides.[3]

Experimental Results and Discussion

The butene mixtures were analyzed with a Beckman IR-2 Infrared Spectrophotometer. Considerable difficulty was experienced in completely removing the butenes from the reaction mixtures. Consequently, the values for butene-1 may be too high by as much as 5%. Analyses were made in duplicate in nearly all experiments and, in many cases, two or more separate runs were made with each active hydrogen compound. The results are given in Table I.

It is apparent that in the cleavage of butenylmagnesium bromide the nature of the active hydrogen compound employed has a marked influence on the composition of the resulting butene mixtures. Water and alcohols give comparable butene mixtures. Carboxylic acids and hydrogen chloride give considerably more butene-1 than alcohols or water. No regular variation of the compositions of the mixtures with acid strength is apparent. Ammonium iodide, dibenzenesulfonylmethane, benzhydryl mesityl ketone and phenylacetylene[3] give quite different butene mixtures, which are unlike those obtained with water, acids or alcohols. Considerably less butene-1 is formed in the absence of a solvent for the Grignard reagent but little variation in composition is noted on substitution of dibutyl ether, benzene or heptane for diethyl ether.[6]

In our opinion, the results of the present study are not inconsistent with our earlier formulation of the Grignard reagent as crotylmagnesium bromide.[3] In general, the reactions of the butenylmagnesium halides have considerable resemblance

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[3] Young and Roberts, THIS JOURNAL, **68**, 1472 (1946). This paper gives references to earlier work on the coupling and carbonyl addition reactions.

[4] Young, Winstein and Prater, *ibid.*, **58**, 289 (1936).

[5] Young and Eisner, *ibid.*, **63**, 2113 (1941).

[6] Considerably greater variations with benzene and heptane might be found if it were possible to remove all of the coördinated diethyl ether from the Grignard reagent by distillation.

TABLE I

BUTENES FROM THE REACTION OF BUTENYLMAGNESIUM BROMIDE WITH ACTIVE HYDROGEN COMPOUNDS

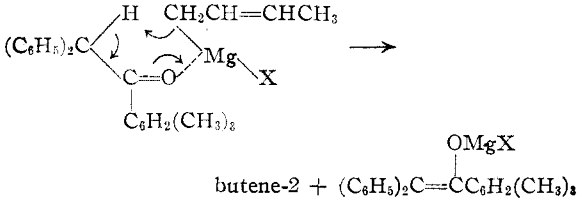
Reagent	Solvent	Analyses	% *trans*-Butene-2[a]	% *cis*-Butene-2[a]	% Butene-1[a]
2 *N* H_2SO_4	None	6	21.1 ± 0.7[b]	28.6 ± 1.4[b]	50.3 ± 1.6[b]
2 *N* H_2SO_4	Diethyl ether	2	13.5 ± 0.5	16.6 ± 0.1	69.9 ± 0.4
2 *N* H_2SO_4	Dibutyl ether	5	13.1 ± 1.4	14.3 ± 0.8	72.9 ± 2.1
2 *N* H_2SO_4	Benzene	1	13.6	10.0	76.4
2 *N* H_2SO_4	Heptane	2	12.4 ± 0.7	11.0 ± 0.9	76.5 ± 1.5
Ethanol	None	2	19.8 ± 0.4	25.4 ± 0.2	54.8 ± 0.6
Acetic acid	None	1	15.2	19.1	65.7
s-Butyldiisopropylcarbinol	Diethyl ether	2	17.8 ± 0.6	13.7 ± 1.0	68.5 ± 1.6
Acetic acid	Diethyl ether	4	10.0 ± 0.9	10.1 ± 1.1	80.0 ± 0.5
Trichloroacetic acid	Diethyl ether	2	7.7 ± 0.6	6.2 ± 0.1	86.3 ± 0.7
Chloroacetic acid	Diethyl ether	2	3.3 ± 0.8	4.8 ± 2.6	92.2 ± 1.6
Hydrogen chloride	Diethyl ether	3	10.1 ± 2.4	6.5 ± 1.9	83.4 ± 4.1
Ammonium iodide[c]	Diethyl ether	2	28.4 ± 0.6	30.1 ± 0.1	41.5 ± 0.5
Benzhydryl mesityl ketone	Diethyl ether and benzene	3	2.7 ± 2.8	35.9 ± 7.2	61.4 ± 4.4
Dibenzenesulfonylmethane	Diethyl ether	1	(32[d,e])		68[d]

[a] Average deviations from the mean are given. [b] Young, Winstein and Prater (ref. 4) report 17.2 ± 3.3% *trans*-butene-2, 26.5 ± 1.4% *cis*-butene-2 and 56.4 ± 2.0% butene-1. [c] Anhydrous ammonium iodide. [d] Analyzed by the method of Dillon, Young and Lucas, THIS JOURNAL, **52**, 1953 (1930). [e] Approximately equal *cis*- and *trans*-butene-2.

to those obtained with many other allylic compounds which react giving more or less rearrangement depending on the experimental conditions.[7] With the Grignard reagent and strong ionizing substances, such as water, acids and alcohols, a mixture of products results, while with phenylacetylene, or in addition to carbonyl compounds, essentially only one product is obtained. The situation, of course, is quite different from that observed in the usual nucleophilic reactions[7] of allylic compounds since the normal (or non-ionizing) reactions proceed without rearrangement in the nucleophilic case but are postulated to go with *complete* rearrangement in the Grignard reactions via electrophilic attack on the double bond at the γ-position of the Grignard reagent, following preliminary coördination with magnesium, to give exclusively α-methylallyl derivatives. This formulation is in agreement with the fact that the usual reactions of carbon–carbon double bonds generally involve electrophilic rather than nucleophilic reagents.[8]

Detailed analysis of the results of the reaction of butenylmagnesium bromide with various active hydrogen compounds is rendered difficult by the possibility that several mechanisms may be involved. Besides possible direct electrophilic attack at the α- or γ-positions of the Grignard reagent, cleavage may well be preceded in many cases by preliminary coördination with the active hydrogen compound. Such coördination would probably involve unshared electron pairs on the active hydrogen compound and the magnesium atom of the Grignard and, in favorable circumstances, might result in different butene mixtures through the formation and reaction of a more or less free butenyl carbanion in competition with a concerted cyclic mechanism which gives only butene-1. Furthermore, it is not now possible to exclude mechanisms involving reactions between coördination complexes and other molecules of Grignard reagent or active hydrogen compounds.

The reactions with benzhydryl mesityl ketone and dibenzenesulfonylmethane were chosen since it was expected that butenylmagnesium bromide might react with these substances to give butenes without rearrangement by a six-membered cyclic mechanism.



The results indicate that this mechanism does not operate exclusively with either of these reactants. It is unlikely that any appreciable reaction occurred through enolic forms of the compounds since extensive work[9] on similar sulfur compounds has failed to show the existence of enol forms, and the infrared spectrum of solid benzhydryl mesityl ketone showed no hydroxyl band. The abnormally high proportion of *cis*-butene-2 obtained with benzhydryl mesityl ketone is particularly significant since it indicates the operation of a different mechanism for the formation of butene-2 than that which obtains for reagents such as water, acids or alcohols. If the cyclic mechanism shown above is responsible for this different behavior, it may mean that the crotyl radical of the Grignard reagent is actually present as the *cis*-form. Ex-

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[7] See Roberts, Young and Winstein, THIS JOURNAL, **64**, 2157 (1942), and Young and Andrews, *ibid.*, **66**, 421 (1944), for discussion and examples of the effect of reaction conditions on the extent of rearrangement in reactions involving simple allylic systems.

[8] Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., New York, N. Y., 1940, pp. 147-152.

[9] Arndt and Martius, *Ann.*, **499**, 228 (1932); Böhme and Fischer, *Ber.*, **77**, 237 (1944).

planation of these results will depend on additional experimental evidence.

Experimental

The reactions between butenylmagnesium bromide and active hydrogen compounds were run in a 250-ml. or 500-ml. three-necked flask equipped with dropping funnel, condenser and sealed stirrer. The vessel was flushed with dry nitrogen and the desired quantity of Grignard reagent added with a pipet. In some experiments, the ether was distilled and other dry solvents added. The liquid active hydrogen compounds were added directly to the Grignard reagent from the dropping funnel, while solid substances were added as ether or benzene solutions. The butenes were caught in a Dry Ice-cooled trap connected to the top of the condenser. One trap was sufficient if the rate of generation of butenes was not greater than 0.1 mole in twenty minutes. The dibenzenesulfonylmethane was only slightly soluble in ether (0.8 g. in 100 ml. at the boiling point) and was extracted into the reaction flask from a Soxhlet apparatus, the condenser of which was connected to the butene trap. After the reactions were complete, the contents of the trap were distilled into ampoules containing anhydrous potassium carbonate or magnesium sulfate, which were then sealed until the butene mixture was analyzed. Gaseous impurities, if present, were removed during this distillation. In some runs much ether was present and the butenes were concentrated by fractionation through a small column with sintered glass walls. In each case, the final samples in the ampoules distilled completely with the warmth of the hand. The yields of butenes as estimated by bromine titration in the sulfuric acid hydrolyses were above 75%, even using as small as 0.01 mole quantities of Grignard reagent.

The infrared method for analyzing the butene mixtures was based on that described by Brattain, Rasmussen and Cravath.[10] The operating conditions used in this work for the Beckman IR-2 Spectrometer are summarized in Table II.

TABLE II

OPERATING CONDITIONS FOR BECKMAN INFRARED SPECTROPHOTOMETER

Component	λ, microns	Slit width, mm.	Press., mm.	Shutter
Butene-1	5.4	0.07	400	Metal
cis-Butene-2	14.3	1.15	200	Glass
trans-Butene-2	10.4	0.27	100	Glass
Diethyl ether	8.8	0.18	20	Metal

No isobutylene was detected in the butene mixtures formed in the experiments listed in Table I. With samples containing large amounts of ether, care was necessary to insure that the gas was properly mixed before taking a sample for analysis. In general, the accuracy of the butene analysis was decreased considerably in the presence of much ether.

Preparation of Dibenzenesulfonylmethane.—The following procedure gives a much better yield than the method previously described.[11] To a solution of 15 g. (0.065 mole) of dithiophenylmethane[11] in a mixture of 65 ml. each of acetic acid and acetic anhydride was added with stirring 35 ml. of 30% hydrogen peroxide over a two-hour period while the mixture was cooled in an ice-bath. The mixture was stirred for eight hours at room temperature, then allowed to stand for three days. The excess hydrogen peroxide was decomposed by stirring with a small quantity of manganese dioxide and the solvent removed under reduced pressure at room temperature. The solid residue of dibenzenesulfonylmethane was recrystallized from an alcohol–water mixture. The yield was 18 g. (94%), m. p. 122°.

Summary

A study has been made of the composition of the butene mixtures resulting from the reaction of butenylmagnesium bromide with active hydrogen compounds. The composition of the butene mixtures is dependent on the solvent and the structure of the active hydrogen compound.

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[10] Brattain, Rasmussen and Cravath, *J. Applied Phys.*, **14**, 418 (1943).

[11] Shriner, Struck and Jorison, THIS JOURNAL, **52**, 2067 (1930).