ANALYTICAL DATA

Compound prepared	M. p. or b. p., mm., °C.	Nitrogen, % Calcd.	Nitrogen, % Found	Halogen, % Calcd.	Halogen, % Found	Sulfur, % Calcd.	Sulfur, % Found
Tetrahydrofurfuryl sulfonyl chloride	B. p. 112–113[4]	...	...	19.22	19.38	...	...
Tetrahydrofurfuryl sulfonamide	M. p. 81.5–82.5	8.48	8.37	...	...	19.42	19.65
S-Tetrahydrofurfuryl-isothiourea picrate	M. p. 153–153.5	17.98	17.93	...	...	...	...
S-Furfuryl-isothiourea hydrochloride	M. p. 142–143	14.54	14.50	18.40	18.43	16.64	16.97
S-Furfuryl-isothiourea picrate	M. p. 162	18.13	18.04	...	...	...	...
S-Methoxymethyl-isothiourea hydrochloride	M. p. 112	17.88	17.78	22.63	22.60	20.48	20.70
S-Methoxymethyl-isothiourea picrate	M. p. 163	20.00	19.82	...	...	...	...
S-Isoamoxymethyl-isothiourea hydrochloride	M. p. 134–135	13.16	13.08	16.67	16.36	15.07	15.20
S-*n*-Butoxymethyl-isothiourea hydrochloride	M. p. 118–120	14.09	13.95	...	...	...	...
S-Carbethoxymethyl-isothiourea hydrochloride	M. p. 112–113	14.10	14.15	17.85	17.75	...	...
S-β-Acetoxyethyl-isothiourea hydrochloride	M. p. 137–137.5	14.10	14.13	17.85	17.84	...	...
S-β-Acetoxyethyl-isothiourea picrate	M. p. 174.5–175.5	17.89	17.82	...	...	...	...
B-Acetoxyethyl sulfonyl chloride	B. p. 101–103[4]	...	...	19.01	19.00	...	...
S-β-Oxidodiethyl-isothiourea picrate	M. p. 209–210	20.58	20.45	...	...	...	...
Diethylether-β,β′-disulfonamide	M. p. 125–126	12.06	12.00	...	...	...	...

ration was chlorinated in 700 cc. of water below 10°. The yield of this sulfonyl chloride was 39.5 g. (70%); b. p. 112–114° at 6 mm.; $n^{25}\text{D}$ 1.4633.

2,4-Dinitrobenzenesulfonyl Chloride.[8]—By chlorinating a dilute aqueous solution of freshly prepared 2,4-dinitrophenyl isothiourea hydrochloride[9] (10 g.), we obtained the above sulfonyl chloride melting at 101–102°. It was purified by crystallization from a mixture of benzene and petroleum ether. The corresponding sulfonamide melted at 156–157°.

Summary

1. The method of preparing sulfonyl chlorides by chlorination of isothiourea in aqueous solution has been investigated further.

2. The practical application of this method of synthesis is influenced by the structure of the grouping attached to sulfur in the isothiourea.

3. Branched aliphatic substituents favor a competing reaction during chlorination leading to dissociation of the alkyl grouping substituted in the isothiourea, and oxidation of the sulfur to sulfate.

4. Isothioureas containing ether groupings and furfuryl attached to the sulfur failed to give the corresponding sulfonyl chlorides.

NEW HAVEN, CONN. RECEIVED SEPTEMBER 20, 1937

[8] Mohr, *J. prakt. Chem.*, [2] **34**, 123 (1886).

[9] Taylor and Dixon, *J. Chem. Soc.*, **125**, 243 (1924).

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

Allylic Rearrangements. VI. Effect of Solvent and Metal on the Coupling Reaction of Butenyl Bromides

BY WILLIAM G. YOUNG, JOHN FERO LANE, ABE LOSHOKOFF AND SAUL WINSTEIN

In previous papers from this Laboratory it was shown that the butene mixtures obtained from the formation and decomposition of butenylmagnesium bromides[1] and those obtained from the reaction of butenyl bromides on zinc in ethanol,[2] had similar but definitely different compositions. It was not certain whether those differences were due to the effect of solvent, metal or temperature on the allylic rearrangement. In order to settle this question it was essential to obtain butene mixtures by preparing and decomposing the Grignard reagent in several different ethers and by allowing various metals to react with the butenyl bromides in 80% ethanol. Before this work could be undertaken it was necessary to overcome the well-known tendency for alkenyl halides to undergo a coupling reaction of the Wurtz type.

It is the purpose of this paper to present work on the effect of metal, solvent and experimental conditions on the above-mentioned coupling reaction of butenyl bromides.

The Coupling Reaction During the Formation of Butenylmagnesium Bromides in Different Ethers.—Several investigators[3] have found that the coupling reaction may be eliminated partially by using a large excess of magnesium which is

[1] Young, Winstein and Prater, THIS JOURNAL, **58**, 289 (1936).

[2] Young and Winstein, *ibid.*, **58**, 441 (1936).

[3] (a) Gilman and McGlumphy, *Bull. soc. chim.*, **43**, 1322 (1928); (b) Gilman and Kirby, THIS JOURNAL, **51**, 3475 (1929); (c) Gilman and Zoellner, *ibid.*, **52**, 3984 (1930); (d) Gilman and Harris, *Rec. trav. chim.*, **50**, 3475 (1931); (e) Young, Prater and Winstein, THIS JOURNAL, **55**, 4908 (1933).

kept in contact with all parts of the reaction mixture by vigorous stirring. However, to obtain maximum yields of the Grignard reagent it is necessary to use the proper ratio of solvent to alkenyl halide. This ratio must be determined for each alkenyl halide and solvent being used. Accordingly, butenylmagnesium bromides have been prepared in *n*-propyl and isopropyl ethers at various ratios of solvent to bromide. The results are shown in Fig. 1 where the yield of Grignard reagent, based on the total bromide reacting, is plotted against the ratio of solvent to butenyl bromide. Thus a low yield of Grignard reagent indicates a high yield of coupling product and *vice versa*. The data previously found with ethyl and butyl ethers are also included.[3e]

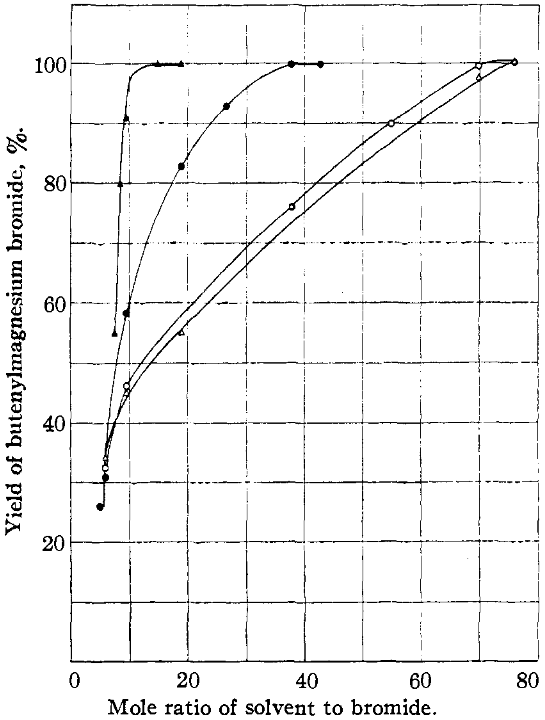

Fig. 1.—Effect of solvent on the yield of butenylmagnesium bromide: ▲, diethyl ether; ●, di-*n*-propyl ether; O, 10% diethyl + 90% diisopropyl ethers; △, dibutyl ether.

The tendency to undergo coupling increases in the order ethyl, propyl, and butyl or isopropyl ethers. However, the results with isopropyl ether are not strictly comparable for it was necessary to add some ethyl ether to cause the metal to react. Although propyl and butyl bromides gave 70–80% yields, the butenyl bromide gave no evidence of reacting in the pure isopropyl ether. Consequently a mixture of 10% ethyl and 90% isopropyl ethers was used.

The Coupling Reaction During the Treatment of Butenyl Bromides with Metals in 80% Ethanol.—Since the alkenylmetallic bromide would be expected to be decomposed to form butene as soon as it is formed in such a solvent as 80% ethanol, it was of interest to know whether special conditions were necessary to avoid the coupling reaction. With this in mind, a series of experiments was made with a butenyl bromide mixture and zinc in 80% ethanol. When 0.1 mole of butenyl bromide was dropped slowly into an equal quantity of boiling ethanol containing 0.3 mole of zinc dust the yield of coupled product was 53%. When vigorous stirring was used the yield of coupled product was 41%. Increasing the ratio of solvent to bromide to 2.5 (with stirring) gave 26% of coupled product. The use of a solvent–bromide ratio of 3.5 (with stirring) caused a drop in the yield of coupled product to 10–15%.

In studying the action of other metals on the butenyl bromide mixture in 80% ethanol the ratio of metal to bromide was approximately 3 and the

Table I

The Action of Metals on the Butenyl Bromide Mixture in 80% Ethanol[a]

Metal	Butene collected, stand. ml.	Yield of butene, %	Predominant reaction
Zinc (dust)	950	85	Reduction
Magnesium (turnings)	None	0.0	Coupling
Magnesium (amalgam)	None	.0	Coupling
Aluminum (amalgam)	695	62.0	Reduction
Sodium (amalgam)	None	0.0	Coupling
Iron[b] (filings)	None	.0	Coupling
Iron (powder)	None	.0	Coupling
Manganese[b] (coarse grains)	137	12.2	Coupling
Manganese[b] (50 mesh)	134.5	12.0	Coupling
Manganese (coarse grains)	97.5	8.7	Coupling
Chromium (coarse grains)	749	66.8	Reduction
Chromium (powder)	835	74.5	Reduction
Tin (turnings)	306	27.3	Coupling
Tin[b] (50 mesh)	597	53.4	Reduction
Copper (powder)	None	0.0	Coupling
Copper[b] (powder)	None	.0	Coupling
Silver (molecular)	None	.00	Coupling
Cobalt (filings)	...	...	No reaction
Cadmium (turnings)	241	21.5	Coupling
Cadmium[b] (turnings)	297	26.5	Coupling
Nickel (Raney catalyst)	None	0.0	Coupling

[a] 6.75 g. of an equilibrium mixture of crotyl and methylvinylcarbinyl bromides was used in each experiment. The mole ratios of metal to bromide and solvent to bromide were 3.0 and 3.5, respectively.

[b] These metals were washed with acid to produce a fresh surface.

ratio of solvent to bromide was 3.5. Vigorous stirring was maintained at all times. The results are summarized in Table I. Although only the yield of butene is listed, the yield of coupling product may be qualitatively estimated by subtracting the butene yield from 100%. Aluminum amalgam, zinc, chromium, and tin liberated butene rapidly and in good yields, while cadmium and manganese liberated it slowly and in poor yields. With chromium there was an inhibition period in which no gas was evolved. However, as soon as a blue-green color appeared in the reaction mixture butene was evolved rapidly. All of the other metals except cobalt reacted readily to give only the coupled product. Cobalt failed to react with the butenyl bromide mixture.

Experimental Part

Crotyl alcohol, b. p. 120–122°, $n^{25}\text{D}$ 1.4271, was prepared from crotonaldehyde by the aluminum isopropoxide method.[4]

Butenyl Bromide Mixture.—Crude butenyl bromide preparations made by several of the standard methods previously described[5] were combined and fractionally distilled at 93 mm. A small portion of each fraction was subjected to thermal rearrangement at 100° and all fractions were combined which gave the correct equilibrium refractive index of $n^{25}\text{D}$ 1.4767. This procedure eliminated traces of impurities. The combined sample was then allowed to rearrange at room temperature to an equilibrium mixture of 87% crotyl and 13% methylvinylcarbinyl bromides. This final equilibrium mixture which is referred to as the "butenyl bromide mixture" was used in all of the work described in this paper.

Purification of Ethers.—The dipropyl and diisopropyl ethers were purified, washed, dried and distilled as described for dibutyl ether.[3e]

Metals.—Commercial "C. P." preparations of aluminum, cadmium, chromium, cobalt, copper, iron, lead, magnesium and tin were used. Turnings, filings, and coarse and fine powders were used depending on the properties of the metal and the source of supply available. Whenever it seemed advisable the metals were treated with hydrochloric or nitric acids to produce a reactive surface.

Aluminum and Magnesium Amalgams.—Small pieces of thin sheet aluminum or turnings of magnesium were treated with dilute sodium hydroxide to produce a fresh surface. The metal was then washed several times with water and finally with ethanol. It was then treated with a 1% solution of mercuric chloride in ethanol for twenty seconds. The resulting amalgam was washed three times with ethanol and used immediately.

Nickel Powder.—The nickel powder used in this work was "Raney Catalyst" prepared according to the directions of Covert and Adkins.[6]

Preparation and Estimation of Butenylmagnesium Bromide.—The butenyl bromide mixture was converted into the Grignard reagent according to the procedure previously described.[3e] Care was taken to have the experimental conditions identical for all experiments so that the effect of solvent and of the changing the ratio of solvent to bromide could be evaluated. After all of the butenyl bromide had been added the reaction mixture was stirred for twenty minutes. Aliquot portions were then withdrawn and titrated with dilute nitric acid to estimate the Grignard reagent present. An excess of acid was added and the bromide ion was titrated with dilute silver nitrate solution. The percentage yield of Grignard reagent was based on the total bromide which had reacted.

The Action of Metals on the Butenyl Bromide Mixture in Boiling 80% Ethanol.—The metal (6–10 g.) and 20 ml. of 80% ethanol were placed in a 150-ml. cylindrical glass reaction vessel into which was sealed a 25-ml. dropping funnel and a 30-cm., all glass, water-jacketed condenser. A mechanical stirrer was inserted into the top of the reaction vessel and the reaction mixture was stirred rapidly to keep the metal in contact with all parts of the solution. The ethanol was heated to the boiling point and the butenyl bromide was added dropwise at such a rate as to keep the butene evolution under control. As the butene was evolved it passed through the condenser, a safety bottle and a 30-cm. tube of calcium chloride into a trap which was cooled with a mixture of solid carbon dioxide and alcohol. After the reaction was complete the butene was swept out of the system into the trap by a stream of nitrogen. The trap was then disconnected and the butene was vaporized and collected by displacement of water in a graduated cylinder. The volume of butene was corrected to standard conditions and the percentage yield calculated. In some experiments the hydrocarbon mixture formed as a result of the coupling reaction was isolated from the reaction vessel. The quantity obtained was essentially equal to that expected from the butenyl bromide which was not converted into butene. Consequently only the butene was measured in later experiments. The results of the experiments with the different metals are listed in Table I.

Summary

The preparation of butenylmagnesium bromide has been studied in *n*-propyl ether and in a mixture of 10% ethyl and 90% isopropyl ethers. The results are compared with previous work in ethyl and butyl ethers.

The action of several metals on an equilibrium mixture of crotyl and methylvinylcarbinyl bromides in 80% ethanol has been investigated.

LOS ANGELES, CALIF. RECEIVED AUGUST 28, 1937

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[4] Young, Hartung and Crossley, THIS JOURNAL, **58**, 100 (1936).

[5] Young and Lane, *ibid.*, **59**, 2051 (1937).

[6] Covert and Adkins, *ibid.*, **54**, 4116 (1932).