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The Preparation of Crotylmagnesium Bromide. The Effect of Solvents on the Yield of Crotyl and Allylmagnesium Bromides[1]

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In a previous communication[2] the authors reported the formation of mixtures of crotyl and vinylmethyl carbinyl bromides during the preparation of butene from *trans* crotonaldehyde. The most promising method of studying these allylic mixtures of bromides is to convert them into the Grignard reagent, since this reagent may be quickly decomposed to form butene mixtures which may be analyzed.[3] In view of the importance of the Grignard reagent for this purpose we are presenting in this paper an account of the preparation of crotylmagnesium bromide in diethyl and dibutyl ethers.

Crotylmagnesium bromide heretofore has never been isolated as a distinct preparation. Braun and Shermacker[4] have reported that this reagent couples with additional crotyl bromide to give 2,6-octadiene almost exclusively. This coupling phenomenon is common with allyl halides and with β substituted allyl halides. It is only recently that Gilman and coworkers have successfully prepared Grignard reagents from this type of compounds.[5] Like other β substituted allyl halides, crotyl bromide requires special conditions in order to obtain maximum yields of the Grignard reagent. Although these conditions are different for each solvent it is possible to obtain excellent yields of crotylmagnesium bromide[6] in both diethyl and dibutyl ethers.

Experimental Procedure

The Preparation of Crotyl Alcohol.—Crotyl alcohol, b. p. 117–119°, was obtained from the reduction of crotonaldehyde with zinc and acetic acid, with magnesium chloroethylate or with platinum catalyst and hydrogen. It always contained some butyl alcohol, 5–50%, which could not be removed by distillation. Since any attempt to separate crotyl and butyl alcohols might bring about molecular rearrangements, the mixtures were carried through the Grignard stage without previous separation. At this stage the undesirable butyl constituent was eliminated as butane. Consequently, the

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(1) Preliminary experiments on this investigation were performed by the senior author while serving as a National Research Council Fellow in Chemistry at Stanford University and were continued at the University of California at Los Angeles. This paper was presented at the Pasadena meeting of the American Association for the Advancement of Science, June 19, 1931.

(2) Young and Prater, THIS JOURNAL, **54**, 404 (1932).

(3) Dillon, Young and Lucas, *ibid.*, **52**, 1953 (1930).

(4) Braun and Shermacker, *Ber.*, **56**, 538 (1922).

(5) (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**, 1052 (1931).

(6) Although we are obviously working with crotyl bromide containing some vinyl methyl carbinyl bromide the expressions "crotyl bromide" and "crotylmagnesium bromide" are used for simplicity throughout this paper.

alcohol mixtures were analyzed for crotyl content by titration with bromine before being used.

Preparation of Crotyl Bromide.[6]—Crotyl bromide contaminated with butyl bromide was prepared from mixtures of crotyl and butyl alcohols by the action of phosphorus tribromide in pyridine, according to the procedure of Kirrmann as modified by Prévost.[7] The boiling range of the product varied from 4–10° depending on the amount of butyl bromide present. The crotyl bromide content of the product was assumed to be the same as the crotyl alcohol content of the original alcohol mixtures. The assumed compositions were later verified by the slow addition of bromine to the bromide mixtures over a period of forty-eight to sixty hours (see Table I for the composition of these mixtures). The crotyl bromide used for the experiments listed in Table II was prepared, free from butyl bromide, by the action of hydrobromic acid, saturated at 0°, on mixtures of crotyl and butyl alcohols according to Charon's method.[8]

Purification of Solvents.—Two sources of dibutyl ether were used: Eastman product, b. p. 141–142°, and a product prepared in this Laboratory. The ether was refluxed with acidified potassium permanganate, washed with water and sodium bicarbonate and dried with calcium chloride. Before it was distilled it was refluxed with molten sodium for several hours to remove the last traces of butyl alcohol; b. p. 142°.

Dry diethyl ether was prepared in the customary manner.

Preparation of Crotylmagnesium Bromide.[6]—The crotylmagnesium bromide was prepared in a nitrogen-filled dry flask which was fitted with a dropping funnel, a mercury-sealed mechanical stirrer, and an upright spiral condenser which was protected with a phosphorus pentoxide tube. The magnesium turnings were *vigorously* stirred with sufficient ether, ethyl or butyl, to cover them while an ether solution of crotyl bromide was added dropwise over a period of two to four hours. In the experiments listed in Table II, where the crotyl bromide[6] was free from butyl bromide, the yield of RMgX was determined by titration of aliquot portions of the ether solution.[9] However, if mixtures of crotyl and butyl bromides were used the solvent was removed at reduced pressures and the RMgX mixture was decomposed with 2 normal sulfuric acid. The resulting mixtures of butane and butene were passed through a purification train of 23% perchloric acid, soda lime and calcium chloride, and into a bromination flask where the butene was trapped as dibromobutane. The yield of crotylmagnesium bromide was based on the weight of dibromobutane obtained after the latter had been washed, dried and distilled. In order to locate the cause for low yields in the early experiments some of the Grignard reagents were treated with dilute nitric acid and analyzed for bromide ion (see experiments 3 and 4, Table II). The results proved that sufficient time had been allowed for all of the crotyl bromide to react to form either crotylmagnesium bromide or 2,6-octadiene. The lower yield of RMgX was due to interference by the coupling reaction and not to incomplete reaction of the crotyl bromide.

Discussion of Results

Diethyl Ether in the Preparation of Crotylmagnesium Bromide.[6]—The experiments on the preparation of crotylmagnesium bromide in diethyl ether are listed in Table I. It is evident from experiments 1–4 that crotyl bromide exhibits a greater tendency to couple with the Grignard reagent than does allyl bromide, thus leading to smaller percentage yields of RMgX under the same conditions. However, the yield of crotylmagnesium bro-

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(7) (a) Kirrmann, *Bull. soc. chim.*, [4] **39**, 698 (1926); (b) Prévost, *Ann. chim.*, [10] **10**, 147–81 (1928).

(8) Charon, *Ann. chim. phys.*, [7] **17**, 233 (1897).

(9) See Gilman, Wilkinson, Fishel and Meyers, THIS JOURNAL, **45**, 150 (1923).

mide may be improved rapidly by increasing the time of addition of the bromide and the ratio of solvent to bromide, as well as using 20–30 mesh magnesium turnings which are prepared just before use (see experiments 6–8). Magnesium–copper alloy has a detrimental effect on the yield of the Grignard reagent just as it does with allylmagnesium bromide.[10]

TABLE I

CROTYLMAGNESIUM BROMIDE[6] IN DIETHYL ETHER[e]

Expt.	Crotyl bromide in mixture, %	Moles of crotyl bromide[6]	Mole ratio Solvent Bromide	Mole ratio Mg Bromide	Time for bromide addition, min.	Yield of RMgX, %	Notes
1	50	0.10	7.5	3.0[b]	200	27.7[a]	
2	..	0.374	7.5	3.0[c]	95	72.5	Duplicate of Gilman's experiments using allyl bromide in place of crotyl bromide
3	..	0.200	7.5	3.0[c]	205	90.0	
4	70	0.374	7.5	3.0[c]	205	55.0	Duplicate of 3 using crotyl bromide
5	50	0.20	7.5	3.0[d]	205	3.0	
6	50	0.40	8.5	3.0[c]	275	80.0	
7	63	0.40	9.5	3.0[c]	275	91.0	
8	99.5	0.20	9.5	3.0[c]	275	90.0	Duplicate of 7 using pure crotyl bromide

[a] The same procedure as recommended by Gilman for allylmagnesium bromide. [b] Commercial magnesium turnings. [c] 20–30 mesh magnesium turnings prepared just before use from a bar 99.5% pure. [d] Magnesium–copper alloy: 88% Mg–12% copper. [e] Duplicate or triplicate runs of experiments 4–8 agreed within 2%.

TABLE II

CROTYL[6] AND ALLYLMAGNESIUM BROMIDE IN DIBUTYL ETHER[e]

Expt.	Moles of bromide	Mole ratio Solvent Bromide	Mole ratio Magnesium Bromide	Time for bromide addition, min.	Yield of RMgX, %	Notes
1	0.08[c]	6.1[d]	3.0	175	34.0	
2	.10[c]	9.5	3.0	180	45.0	
3	.10[c]	19.0	3.0	180	52.0	Total Br^- = 101% Medium stirring
4	.05[c]	38.0	6.3	180	62.0	Total Br^- = 100.2% Medium stirring
5	.035[c]	76.0	9.2	205	73.0	Medium stirring
6	.05[c]	38.0	6.3	180	77.0	Rapid stirring
7	.03[c]	76.0	11.0	157	95.7	Rapid stirring
8	.03[c]	76.0	12.0	170	100.2	Excellent stirring
9	.20[a]	4.7[b]	3.0	75	56.0	
10	.10[a]	9.5	3.0	190	77.5	
11	.05[a]	19.0	6.0	165	83.0	Rapid stirring
12	.05[a]	38.0	6.0	170	82.0	Medium stirring
13	.035[a]	38.0	12.0	180	99.0	Excellent stirring

[a] Allyl bromide. [b] This mole-ratio gives the same concentration in moles of bromide per cc. of solvent as the 7.5 mole ratio in diethyl ether. Compare yield with Experiment 3, Table I. [c] Crotyl bromide[6] (99.5% unsaturation). [d] This mole ratio gives the same concentration in moles of bromide per cc. of solvent as the 9.5 mole ratio in diethyl ether. Compare experiments 7 and 8, Table I. [e] Duplicate runs agreed within 2–5% when the rate of stirring was accurately controlled.

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(10) Johnson and Adkins, THIS JOURNAL, **53**, 1520 (1931); **54**, 1943 (1932).

Dibutyl Ether as a Solvent for Preparing Unsaturated Alkylmagnesium Bromides.—In studying the decomposition of crotylmagnesium bromides prepared from crotyl bromides having different sources, we were unable to prevent traces of diethyl ether from being carried over with the hydrolysis products. As a result dibutyl ether was investigated as a solvent since it is less volatile and has been used effectively to replace diethyl ether for preparing saturated alkylmagnesium halides.[11] It was found that the yield of RMgX was greatly affected by this change in solvents. We therefore determined the optimum conditions for obtaining maximum yields of RMgX using allyl bromide before proceeding with crotyl bromide, which is difficult to prepare in quantity. The results from both bromides are listed in Table II. The tendency to coupling is far more pronounced in dibutyl than in diethyl ether, especially with crotyl bromide. It is necessary to use much larger ratios of solvent and of magnesium to bromide in order to obtain yields of RMgX which correspond to those with diethyl ether. Extremely vigorous stirring is necessary when using butyl ether. The advantage gained by using an increased ratio of solvent to bromide will be lost if the magnesium is not kept in intimate contact with all parts of the solution during the entire run (compare experiments 4 and 5 with 3, 6, 7, 8, and 12 with 11 and 13).

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Summary

Crotylmagnesium bromide has been isolated for the first time. The use of the reagent in the study of mixtures of crotyl and vinyl methyl carbinyl bromides is discussed. Optimum conditions are reported for obtaining excellent yields of crotylmagnesium bromide in both diethyl and dibutyl ethers. The effect of solvent on the yields of both crotyl and allylmagnesium bromides is discussed.

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[11] Marvel, Blomquist and Vaughn, THIS JOURNAL, **50**, 2810 (1928).