

### Diallylmethylcarbinyl Acetate

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In the course of a recent investigation we became interested in the problem of preparing  $\beta,\gamma$  unsaturated ketones by the reaction of allylmagnesium halides with acid chlorides. Blaise<sup>1</sup> has reported the preparation of such compounds by the reaction of allyl iodide, zinc and nitriles.

In a study of the reaction of allylmagnesium chloride with acetyl chloride the Grignard reagent was added to an ether solution of the acid chloride so as to reduce the possibility of carbinol formation through the action of excess Grignard reagent on the ketone formed. This attempt to isolate the  $\beta,\gamma$  unsaturated ketone by the use of the "inverse Grignard" procedure was unsuccessful. The product was not methyl allyl ketone<sup>1</sup> or diallylmethylcarbinol<sup>2</sup> but was instead the acetate of diallylmethylcarbinol. This ester was undoubtedly produced by the reaction of acetyl chloride with the halomagnesium alcoholate formed from one molecule of acid chloride and two molecules of Grignard reagent. It has been shown previously that magnesium alcoholates of tertiary alcohols can be made to react with acid halides or anhydrides to form esters.<sup>3</sup>

A reaction similar in character to that under consideration occurs between allylmagnesium bromide and nitriles giving alkyldiallylcarbinamines.<sup>4</sup> These compounds presumably are formed by the reaction of allylmagnesium bromide with the ketimine produced from the nitrile and allylmagnesium bromide.

(1) Blaise, *Bull. soc. chim.*, [3] **33**, 39 (1905).

(2) Saytzeff, *J. prakt. Chem.*, [2] **76**, 100 (1907).

(3) (a) Houben, *Ber.*, **39**, 1736 (1906); (b) Yabroff and Porter, *THIS JOURNAL*, **54**, 2453 (1932); (c) Fessler and Shriner, *ibid.*, **58**, 1384 (1936).

(4) (a) Allen and Henze, *ibid.*, **61**, 1790 (1939); (b) Henze, Allen and Leslie, *ibid.*, **65**, 87 (1943).

### Experimental

**Allylmagnesium Chloride.**—Twenty-five and one-half grams (0.33 mole) of allyl chloride was converted into the Grignard reagent according to the procedure described by Young and Eisner<sup>5</sup> for crotylmagnesium chloride. However, the low solubility of allylmagnesium chloride resulted in the production of a semi-solid mixture by the time the reaction was completed. When an additional 100 ml. of ether was added to the flask, the precipitated Grignard reagent could be conveniently transferred to a separatory funnel or flask without occluding magnesium. A yield of 84% of allylmagnesium chloride was obtained. This was determined by titrating an aliquot portion with acid according to the method of Gilman and co-workers.<sup>6</sup>

**The Reaction of Allylmagnesium Chloride with Acetyl Chloride.**—The allylmagnesium chloride suspension in ether was added dropwise to a solution of 26.3 g. (0.34 mole) of acetyl chloride in 50 ml. of ether which was being stirred vigorously and cooled in an ice-bath. The Grignard reagent was added just rapidly enough to promote slow refluxing of the ether. Stirring was continued for an hour after all of the Grignard reagent had been added. The reaction mixture was poured on cracked ice. After the ice had melted, the ether layer was separated, washed with dilute alkali and with water, and dried. After the ether had been removed, the residue was fractionated under reduced pressure from a modified Claisen flask. The distillate (10.6 g.) proved to be diallylmethylcarbinyl acetate; b. p. 126–129° (192 mm.),  $n_{20}^{20}$  1.4408,  $d_{20}^{20}$  0.9005, *MR* calcd. 49.21, *MR* found 49.31. *Anal.* Calcd. for  $C_{10}H_{18}O_2$ : C, 71.39; H, 9.59. Found: C, 71.04; H, 9.80.

**Saponification of the Ester.**—The diallylmethylcarbinyl acetate was difficult to saponify just as the esters of other tertiary alcohols reported by Redemann and Lucas.<sup>7</sup> The saponification equivalent obtained from the standard procedure of Redemann and Lucas was 371 compared to a calculated value of 168.2. This represents 45.5% saponification. Another run at 100° for forty-five minutes gave a saponification equivalent of 189 (88.5% saponification).

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

(6) Gilman, Wilkinson, Fishel and Myers, *ibid.*, **45**, 150 (1923).

(7) Redemann and Lucas, *Ind. Eng. Chem., Anal. Ed.*, **9**, 521 (1937).