

way. A migration of acyl between sulfur and nitrogen occurred upon saponification.

3. Each of these isomeric pairs of mixed diacyl derivatives upon thermal decomposition at

250° yields a single benzothiazole. In each case this benzothiazole is the same as that obtained upon saponification at room temperature.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Reaction of Allyl Bromide with Acetylenic Grignard Reagents¹

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The reaction of allyl bromide with Grignard reagents was first reported by Tiffeneau² and has been used by numerous investigators³ for the synthesis of hydrocarbons containing an olefinic linkage at a terminal carbon atom.

Grignard and his co-workers⁴ have described allyl, *n*-amyl allyl and phenylallylacetylenes prepared from the corresponding acetylenic Grignard reagent and allyl bromide. In a subsequent publication, Grignard⁵ has reported that the preparation of allylacetylene from allyl bromide and monomagnesium acetylene bromide could not be repeated since the monomagnesium bromide of acetylene apparently was not formed as previously observed. However, no such difficulty occurred in the preparation of the Grignard reagent of an alkylacetylene or in the preparation of the corresponding allylacetylene.

Using the usual Grignard technique, attempts in these laboratories to synthesize alkyl allyl and aryl allyl acetylenes have failed without exception. For example, when allyl bromide was added to an ethereal solution of *n*-butylacetylenemagnesium bromide, no reaction was observed. After standing for twenty-three days at room temperature with frequent agitation, part of the mixture was hydrolyzed and fractionated and yielded only allyl bromide and *n*-butylacetylene. A small amount of cuprous chloride was added to the remainder of the mixture. A vigorous, rapid reaction ensued, and the mixture separated into two layers. Fractionation of the upper layer without hydrolysis yielded *n*-butylallylacetylene. The lower layer was poured into a dilute acid-ice

mixture, dried and fractionated whereupon a small additional amount of *n*-butylallylacetylene was obtained.

In another experiment, anhydrous acetone was added to the mixture of *n*-butylacetylenemagnesium bromide and allyl bromide. Upon hydrolysis and fractionation, the original quantity of allyl bromide was recovered and 1,1-dimethyl-2-heptyn-1-ol,⁶ not previously prepared, was obtained in high yield, indicating that the *n*-butylacetylenemagnesium bromide originally present had not reacted with the allyl bromide.

Refluxing an alkylacetylene Grignard reagent and allyl bromide in benzene or di-*n*-amyl ether for periods varying from two to twelve hours did not effect reaction. Using cuprous chloride, the appropriate alkyl or arylacetylene Grignard reagent in ethereal solution and allyl bromide, *n*-amyl, *n*-butyl, phenyl and vinyl allylacetylenes have been prepared and described. The physical constants of these compounds are reported in the table.

In general, these reactions seem to be catalyzed by both cuprous and cupric halides and cuprous cyanide. Cuprous bromide and cuprous chloride produce the highest yields of the substituted allylacetylenes. Copper bronze, cuprous and cupric sulfide apparently do not catalyze these reactions.

The pronounced effect of impurities in the magnesium on the course of the reaction of the Grignard reagents has been noted frequently.⁷ This might account, at least in part, for the different results obtained in these laboratories and abroad.

(1) Ninth paper on the alkylacetylenes and their addition compounds; previous paper, *J. Org. Chem.*, **1**, in press (1936).

(2) Tiffeneau, *Bull. soc. chim.*, [3] **29**, 1156 (1903); *Compt. rend.*, **139**, 481 (1904).

(3) For numerous references see Mulliken *et al.*, *THIS JOURNAL*, **57**, 1605 (1935).

(4) Grignard and Lapayre, *Bull. soc. chim.*, [4] **43**, 141 (1928); Grignard, Lapayre and Tcheoufaki, *Compt. rend.*, **187**, 517 (1928).

(5) Grignard and Lapayre, *ibid.*, **192**, 250 (1931).

(6) B. p. 92-93° (33 mm.); n_D^{20} 1.4479; d_4^{20} 0.855; MR_D : calcd. 43.29; found 43.87. *Anal.* Calcd. for $C_8H_{10}O$: C, 77.14; H, 11.52. Found: C, 76.40; H, 12.00.

(7) Gilman, *et al.*, *Rec. trav. chim.*, **54**, 584 (1935); Cusa and Kipping, *J. Soc. Chem. Ind.*, **53**, 213-214T (1934); Job, Reich and Dubien, *Bull. soc. chim.*, [4] **37**, 976 (1925); Job and Dubien, *ibid.*, [4] **39**, 583 (1926).

The catalytic reaction of acetylenic magnesium halides with other halogen derivatives is being studied in this Laboratory.

TABLE I
PHYSICAL CONSTANTS OF ALLYL ACETYLENES,
 $\text{CH}_2=\text{CH}-\text{CH}-\text{C}\equiv\text{CR}$

R	B. p., °C. Mm.	d_{25}^{25}	n_D^{25}	MR _D	
				Calcd.	Found
$\text{CH}_3-\text{CH}-$	109-110	750	0.787	1.4694	31.59 32.60
C_2H_5-	58	22	.777	1.4413	41.30 41.48
$\text{C}_6\text{H}_{11}-$	73-74	22	.785	1.4444	45.92 46.28
C_8H_5-	107-108	22	.932	1.5574	46.93 49.08

Experimental

Reagents.—The monoalkyl acetylenes used in this work were prepared by the modified Picon synthesis.⁸ Monovinyl acetylene was furnished by E. I. du Pont de Nemours and Co. Allyl bromide was prepared by the standard method from allyl alcohol.⁹ All other reagents were c. p. grade.

Preparation of *n*-Butylallylacetylene.—Into a three-necked, one-liter flask equipped with a motor-driven, mercury-sealed stirrer, a reflux condenser and a dropping funnel was added 26.5 g. (1.1 moles) of magnesium turnings, a crystal of iodine and 40-50 ml. of anhydrous ether. To this was added dropwise and with constant stirring 120 g. (1.1 moles) of ethyl bromide diluted with ether. When the reaction had ceased, 82 g. (1 mole) of *n*-butylacetylene diluted with an equal volume of ether was added dropwise. After the addition of all the acetylene, the contents of the flask were refluxed for one hour on a water-bath and 2 g. of anhydrous cuprous chloride was added. After cooling to room temperature, 133 g. (1.1 moles) of allyl bromide diluted with an equal volume of ether was added dropwise. When the addition was complete separation into two layers had occurred and a large amount of

flocculent, yellowish-green solid had precipitated. The mixture was refluxed for one hour and then poured into an ice-dilute hydrochloric acid mixture. The organic layer was separated, washed with water and dried over calcium chloride. Fractionation yielded 23 g. of a mixture of allyl bromide and *n*-butylacetylene and 95 g. of *n*-butylallylacetylene (88% yield based on acetylene used). *Anal.* Calcd. for C_9H_{14} : C, 88.54; H, 11.48. Found: C, 86.3; H, 11.3. The preparation of the other allylacetylenes described is similar except for the substitution of a liquid ammonia condenser¹⁰ for a water-cooled condenser in the preparation of vinylallylacetylene.

The Structure of Vinylallylacetylene.—Analysis for carbon and hydrogen by combustion was found to be impractical for this compound because of its extremely explosive character under the conditions obtaining during the combustion. One fused quartz tube was literally pulverized by a 0.2-g. sample at a moderately low temperature. The compound is readily oxidized by neutral permanganate but the main product of the oxidation is carbon dioxide. Molecular weight (cryoscopic in benzene): calcd. 92; found, 91.

Summary

1. Vinyl, phenyl, *n*-butyl and *n*-amyl allylacetylenes have been prepared in high yields from the corresponding acetylenic Grignard reagent and allyl bromide, using cuprous chloride as a catalyst. Without a catalyst no substituted allylacetylenes could be obtained.

2. Cuprous chloride and bromide used as a catalyst produce the highest yields of substituted allylacetylenes. Cupric halides and cuprous cyanide also catalyze the reaction.

(10) Vaughn and Pozzi, *J. Chem. Ed.*, **8**, 2433 (1931).

(8) Picon, *Compt. rend.*, **158**, 1346 (1914); **169**, 32 (1919).

(9) "Organic Syntheses," Vol. I, 1921, p. 3.

NOTRE DAME, INDIANA

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The Radiochemical Synthesis and Decomposition of Hydrogen Bromide

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The radiochemical formation of hydrogen bromide was first studied by Lind,¹ who found that the ion pair yield for a stoichiometric mixture was 0.54 at approximately 25°. Later Gillerot² determined the ion pair yield for synthesis at room temperature, and found that it depended upon the relative concentrations of hydrogen and bromine. He also demonstrated that the ion pair yield for decomposition was approximately 4.3. Working under slightly different conditions and using different values of the molecular ionization,

Lind and Ogg,³ found a value of 2.8. The ion pair yields for most radiochemical reactions which have been studied carefully⁴ are independent of the relative pressures of the reactants. The present unusual behavior combined with the detailed information available for the thermal and photochemical steps in the synthesis of hydrogen bromide made it appear that a careful study of this reaction might yield valuable information on the nature of radiochemical reactions in general.

(1) S. C. Lind, *Le Radium*, **8**, 289 (1911).

(2) R. Gillerot, *Bull. soc. chim. Belg.*, **39**, 503 (1930).

(3) Lind and Ogg, *Bodenstein Festband, Z. physik. Chem.*, 801 (1931).

(4) See Lind, "The Chemical Effects of Alpha Particles and Electrons," p. 101.