

These values are in good agreement with those reported⁶ in the literature.

Identification of Bromo Ketones.—The identity of the bromo ketones was established by means of the haloform reaction with sodium hypobromite. In this manner valeric and caproic acids were isolated and these were checked by their boiling points and neutralization equivalents. It was interesting to note that semicarbazones could not be obtained from the bromo ketones. In several instances, however, small amounts of amorphous products were obtained by treatment with semicarbazide in the usual manner, but only after long heating. Therefore the existence of the semicarbazone of 1-bromoheptanone-2 (m. p. 245–

248° reported by Grignard and Perrichon⁶) might be questioned.

Summary

Alkenyl esters of the type $R-COO-C(R')=CH_2$ (R' = alkyl group) were found to add bromine in the cold, forming dibromides which underwent spontaneous cleavage with the formation of bromo ketones and acyl halides. Three such esters have been thus brominated.

Previous work in this Laboratory showed that vinyl acetate ($R'=H$) added bromine to form chiefly 1,2-dibromomethyl acetate.

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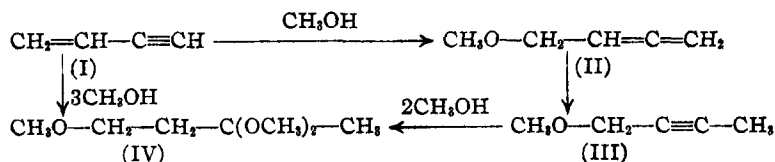
(6) Grignard and Perrichon, *Ann. chim.*, [10] **5**, 22 (1926).

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

Addition of Methanol to Alkenyl Acetylenes¹

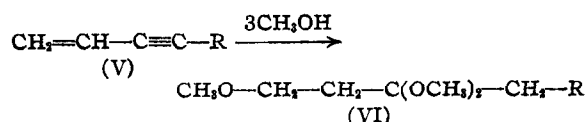
BY D. B. KILLIAN, G. F. HENNION AND J. A. NIEUWLAND

It was shown in a recent communication² that vinylacetylene (I) reacts with methanol, in the presence of a catalytic mixture composed of mercuric oxide, boron fluoride and trichloroacetic acid, to form trimethoxybutane (IV). The suggestion was made that the first molecule of methanol may



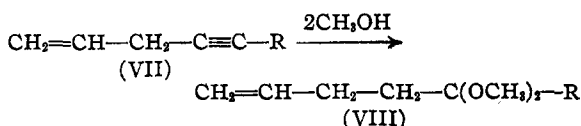
possibly add 1,4 followed by rearrangement and further methanol addition ($I \rightarrow II \rightarrow III \rightarrow IV$). Subsequent work³ showed that 4-methoxy-2-butyne (III) adds methanol quite readily ($III \rightarrow IV$).

In an attempt to obtain further data on the mechanism of methanol addition to vinylacetylene, we have studied similar reactions with several allylalkylacetylenes (VII) and with vinyl-ethylacetylene (V, R is C_2H_5). The latter behaved like vinylacetylene and added three molecules of methanol quite readily.



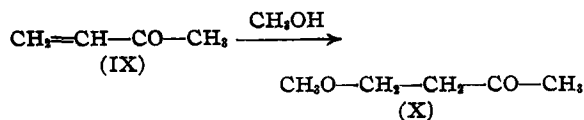
Divinylacetylene (V, R is $CH_2=CH-$), however, has been found to behave quite peculiarly. Reactions with methanol, when carried out in the usual manner, invariably resulted in rapid reduction of the catalytic mercuric salt accompanied by polymerization of the divinylacetylene. Addition of methanol to this acetylene has not been definitely observed. The abnormal behavior of divinylacetylene must remain unexplained for the present.

The allylalkylacetylenes (VII) reacted readily with methanol.



Three such acetylenes were studied, and in each instance, *methanol addition occurred at the triple bond only*, forming dimethoxy-1-alkenes (VIII).

In another experiment, vinylacetylene (I) was hydrated to methyl vinyl ketone (IX) and the reaction of the latter with methanol studied.



As was expected, addition of methanol at the double bond occurred forming 4-methoxy-2-butanone (X) when mercuric oxide and boron fluoride were used as catalysts. This was quite

(1) Paper XII on the chemistry of the alkyl acetylenes and their addition products; previous paper, *THIS JOURNAL*, **58**, 891 (1936).

(2) Killian, Hennion and Nieuwland, *ibid.*, **56**, 1786 (1934).

(3) Hennion and Nieuwland, *ibid.*, **57**, 2006 (1935). The work of Dykstra, *ibid.*, **57**, 2255 (1935), is also of interest in this connection.

TABLE I
 METHOXY KETALS OF DISUBSTITUTED ACETYLENES

No.	R—C≡C—R' taken		Name	Product	Mol. formula
	R	R'			
1	C ₆ H ₅ —	CH ₂ =CH—CH ₂ —	5,5-Dimethoxy-1-nonene		C ₁₁ H ₂₂ O ₂
2	C ₆ H ₁₁ —	CH ₂ =CH—CH ₂ —	5,5-Dimethoxy-1-decene		C ₁₂ H ₂₄ O ₂
3	C ₆ H ₅ —	CH ₂ =CH—CH ₂ —	5,5-Dimethoxy-5-phenyl-1-pentene		C ₁₃ H ₁₈ O ₂
4	C ₆ H ₅ —	CH ₂ =CH—	1,3,3-(?)-Trimethoxyhexane		C ₉ H ₂₀ O ₃

 TABLE II
 PROPERTIES OF METHOXY KETALS

No.	B. p., °C.	Mm.	Density	n _D	MR	
					Calcd.	Found
1	91-93	18	0.870 ²³	1.4325 ²³	55.82	55.64
2	104-106	16	.866 ²⁴	1.4347 ²⁴	60.44	60.26
3	117-118	16	.982 ²³	1.5011 ²³	61.45	61.84
4	80-82	19	.916 ²⁶	1.4185 ²⁶	48.70	48.52

 TABLE III
 ANALYSES OF METHOXY KETALS

No.	% Methoxyl		Mol. wt.		[P]	
	Calcd.	Found	Calcd.	Found	Calcd.	Found
1	33.33	33.03	186	185	492.2	486.2
2	30.99	30.67	200	196	531.2	533.2
3	30.10	29.35	206	198	509.1	506.3
4	52.83	50.67	176	172	445.2	447.4

likely a case of 1,4-addition. The addition of alcohols to methyl vinyl ketone with the aid of other catalysts was reported by Rothrock.⁴

These facts seem to indicate that conjugation of the triple and double bonds is a necessary condition for the addition of alcohols to the ethylenic linkage in alkenyl acetylenes. While the possibility of direct addition is not precluded, the 1,4-addition hypothesis is certainly quite reasonable. The evidence also indicates that conjugate alkadienes may quite likely behave in a manner analogous to the acetylenes in typical catalytic reactions. This type of reaction is being studied.

The new ketals prepared along with their physical properties and analyses are reported in Tables I, II and III. In these tables, R represents the alkyl or aryl group, and R' the allyl or vinyl group attached to the triple-bonded carbon atoms in the acetylene used.

Surface tensions were measured by the method of Sugden⁵ and the parachors calculated by means of his formula.

Experimental

Reagents.—The allylalkyl- and arylacetylenes and the vinyl ethylacetylene were available from previous studies.^{6,7} Methyl vinyl ketone was prepared from vinylacetylene as

(4) Rothrock, U. S. Patent 2,010,828 (1935).

(5) Sugden, *J. Chem. Soc.*, **125**, 27 (1924).

(6) Danehy, Killian and Nieuwland, *THIS JOURNAL*, **58**, 611 (1936).

(7) S. Doloretta Thorn, Hennion and Nieuwland, *ibid.*, **58**, 796 (1936).

described by Conaway.⁸ All other reagents were specially purified before use.

Addition of Methanol to Allyl Phenylacetylene.—Into a one-liter three-necked flask was weighed 1-2 g. of red mercuric oxide. To this was added 1 ml. of (C₂H₅)₂O·BF₃ and 2 ml. of anhydrous methanol. After warming the paste mass to dissolve part of the mercuric oxide, 26 g. (0.81 mole) of methanol, in which was dissolved 1 g. of trichloroacetic acid, was added. A further 26 g. of alcohol and 77 g. (0.54 mole) of allyl phenylacetylene was then added dropwise with constant stirring. This addition required about one hour. When no further reaction occurred, 1 g. of sodium dissolved in 25 ml. of methanol was added to neutralize acidity. The solid sludge was allowed to settle and the supernatant liquid decanted, and fractionated *in vacuo*. The yield of 5,5-dimethoxy-5-phenyl-1-pentene was 89 g. (80% of the theoretical).

The addition of methanol to the other acetylenes was accomplished in an analogous manner.

Addition of Methanol to Methyl Vinyl Ketone.—Using the same general technique described above, except for the omission of the trichloroacetic acid from the catalyst mixture, 65 g. (1.08 mole) of methyl vinyl ketone and 48 g. (1 mole plus 0.5 mole excess) of methanol reacted. The resulting mixture was refluxed on a water-bath for one hour and allowed to stand overnight. After neutralization with anhydrous potassium carbonate, the reaction product was fractionated. In this manner, 4-methoxy-2-butanone, b. p. 137-138° at 745 mm., *n*_D²⁵ 1.4041, *d*₄²⁵ 0.926, was obtained in 61% yield.

Proof of the Structure of the Methoxy Ketals of Disubstituted Acetylenes.—Hydrolysis of the ketals yielded the corresponding ketones which were identified by their physical properties and semicarbazones. In this manner 1-nonene-5-one⁹ was obtained by the hydrolysis of 5,5-dimethoxy-1-nonene. Similarly, 5,5-dimethoxy-5-phenyl-1-pentene, and 5,5-dimethoxy-1-decene yielded, respectively, 5-phenyl-1-pentene-5-one¹⁰ and 1-decene-5-one. The last of these compounds has not been previously described. Its constitution is, by analogy with the corresponding ketone derived from the allylbutylacetylene addition product, undoubtedly as indicated. The physical properties of these ketones are reported in Table IV.

 TABLE IV
 KETONES, R—CO—CH₂—CH₂—CH=CH₂

R	B. p., °C.	Mm.	Density	n _D	M. p. semi-carbazone, °C.
C ₄ H ₉ —	75-77	19	0.836 ²⁵	1.4330 ²⁵	88-89
C ₆ H ₁₁ —	86-88	15	.838 ²²	1.4365 ²²	
C ₆ H ₅ —	127-129	21	.984 ²⁶	1.5240 ²⁶	157

(8) Conaway, U. S. Patent 1,967,225 (1934).

(9) Helferich and Keiner, *Ber.*, **57**, 1616 (1924).

(10) Baeyer and Perkin, *ibid.*, **16**, 2132 (1883); Haller, Bauer and Ramart, *Ann. chim.*, [10] **2**, 270 (1924).

By analogy with vinylacetylene, it is believed that the structure of the methoxy ketal from vinyl ethylacetylene is 1,3,3-trimethoxyhexane. The quantity of material available was not sufficient definitely to prove its structure.

Summary

1. Substituted allylacetylenes add two molecules of methanol, in the presence of mercuric oxide, boron fluoride and trichloroacetic acid, to yield 5,5-dimethoxy-1-alkenes. Vinyl ethylacetylene reacts, under these conditions, to form a trimethoxyalkane analogous to the trimethoxybutane derived from monovinylacetylene.

2. Conjugation of the triple and double bonds in alkenylacetylenes is apparently necessary for the addition of methanol to the ethylenic linkage.

3. Using mercuric oxide and boron fluoride as a catalyst, methyl vinyl ketone reacts with methanol to yield 4-methoxy-2-butanone.

4. The addition of methanol to divinylacetylene has not been effected with mercury-boron fluoride catalysts in this Laboratory.

5. Further evidence in favor of 1,4-addition of oxy compounds to vinylacetylenes is presented.

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[CONTRIBUTION FROM THE FOREST PRODUCTS LABORATORY,¹ FOREST SERVICE, U. S. DEPARTMENT OF AGRICULTURE]

Some Characteristics of Wood Lignins²

BY ELWIN E. HARRIS

In a former publication³ it was reported that maple and spruce lignin isolated by the sulfuric acid method differed with respect to methoxyl content and reactions with chlorine. The present paper deals with an extension of the former work to determine if the same consistent differences exist in lignins from other species of hardwoods and softwoods. Lignins isolated by extraction with methyl alcohol acidified with hydrochloric acid were also included in this study.

The procedure used for the isolation of lignin by the sulfuric acid method was the same as that recommended in a previous publication⁴ except for the oak which was first extracted with alcohol according to the modification of Ritter and Barbour⁵ by which some materials not soluble in alcohol-benzene mixtures or water were removed.

The alcohol lignin was prepared by a modification of the Friedrich procedure,⁶ in which the material was subjected to mild hydrolysis and fractionation during purification. Brauns and Hibbert⁷ have more recently used methyl alcohol with acid as a means of removing lignin from wood.

As a further means of comparison, samples of the lignin by the two methods were methylated and chlorinated. Moist lignin was methylated by dimethyl sulfate in the presence of sodium hydroxide. Lignin, dried in a desiccator, was chlorinated with dry chlorine in dry carbon tetrachloride until it reached the second or light-colored stage. The chlorolignin showed about 20% increase in weight over the starting product.

Table I shows that, with the exception of the high yield of lignin from oak, a similarity exists among all the hardwood lignins. Another similarity exists among all the softwood lignins. Except for the methoxyl content of the fully methylated lignin and the chlorine content of chlorinated lignin, there are distinct differences between the hardwood and softwood lignins as shown especially in the average figures given in Table II.

The lignins isolated by the sulfuric acid method were partially soluble in alcohol or acetone: about 12% of hardwood and 2% of softwood lignin. These soluble fractions had the same methoxyl content, could be methylated to the same percentage of methoxyl, and gave chlorolignins with the same percentages of methoxyl and chlorine as the corresponding insoluble fraction from which they were separated.

The yield of extracted lignin, using methyl alcohol and hydrochloric acid, was low. This may be due to the fact that the reaction temperature was not high enough. To determine

(1) Maintained at Madison, Wis., in coöperation with the University of Wisconsin.

(2) Presented before the American Chemical Society at its 89th meeting in New York City, April 22-26, 1935.

(3) E. E. Harris, E. C. Sherrard and R. L. Mitchell, *THIS JOURNAL*, **56**, 889 (1934).

(4) E. C. Sherrard and E. E. Harris, *Ind. Eng. Chem.*, **24**, 103 (1932).

(5) G. J. Ritter and J. H. Barbour, *ibid.*, **7**, 238-240 (1935).

(6) A. Friedrich, *Z. physiol. Chem.*, **176**, 127-143 (1928).

(7) F. Brauns and H. Hibbert, *THIS JOURNAL*, **55**, 4720 (1933).