These values are in good agreement with those reported[6] 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 Perrichon[6]) 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-dibromethyl acetate.

NOTRE DAME, INDIANA RECEIVED MARCH 20, 1936

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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 Acetylenes[1]

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

It was shown in a recent communication[2] that vinylacetylene (I) reacts with methanol, in the presence of a catalytic mixture composed of mercuric oxide, boron fluoride and trichloracetic 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 ⟶ II ⟶ III ⟶ IV). Subsequent work[3] showed that 4-methoxy-2-butyne (III) adds methanol quite readily (III ⟶ IV).

$$\begin{tikzcd}
\underset{(I)}{CH_2{=}CH{-}C{\equiv}CH} \arrow[r, "CH_3OH"] \arrow[d, "3CH_3OH"'] & \underset{(II)}{CH_3O{-}CH_2{-}CH{=}C{=}CH_2} \arrow[d] \\
\underset{(IV)}{CH_3O{-}CH_2{-}CH_2{-}C(OCH_3)_2{-}CH_3} & \underset{(III)}{CH_3O{-}CH_2{-}C{\equiv}C{-}CH_3} \arrow[l, "2CH_3OH"']
\end{tikzcd}$$

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 vinylethylacetylene (V, R is C_2H_5). The latter behaved like vinylacetylene and added three molecules of methanol quite readily.

$$\underset{(V)}{CH_2{=}CH{-}C{\equiv}C{-}R} \xrightarrow{3CH_3OH} \underset{(VI)}{CH_3O{-}CH_2{-}CH_2{-}C(OCH_3)_2{-}CH_2{-}R}$$

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.

$$\underset{(VII)}{CH_2{=}CH{-}CH_2{-}C{\equiv}C{-}R} \xrightarrow{2CH_3OH} \underset{(VIII)}{CH_2{=}CH{-}CH_2{-}CH_2{-}C(OCH_3)_2{-}R}$$

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.

$$\underset{(IX)}{CH_2{=}CH{-}CO{-}CH_3} \xrightarrow{CH_3OH} \underset{(X)}{CH_3O{-}CH_2{-}CH_2{-}CO{-}CH_3}$$

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

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[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 R	R′	Product Name	Mol. formula
1	C_4H_9—	CH_2=CH—CH_2—	5,5-Dimethoxy-1-nonene	$C_{11}H_{22}O_2$
2	C_5H_{11}—	CH_2=CH—CH_2—	5,5-Dimethoxy-1-decene	$C_{12}H_{24}O_2$
3	C_6H_5—	CH_2=CH—CH_2—	5,5-Dimethoxy-5-phenyl-1-pentene	$C_{13}H_{18}O_2$
4	C_2H_5—	CH_2=CH—	1,3,3-(?)-Trimethoxyhexane	$C_9H_{20}O_3$

TABLE II

PROPERTIES OF METHOXY KETALS

No.	B. p., °C.	Mm.	Density	n_D	MR Calcd	MR 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 Calcd.	% Methoxyl Found	Mol. wt. Calcd.	Mol. wt. Found	[P] Calcd.	[P] 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 Sugden[5] and the parachors calculated by means of his formula.

Experimental

Reagents.—The allylalkyl- and arylacetylenes and the vinylethylacetylene were available from previous studies.[6,7] Methyl vinyl ketone was prepared from vinylacetylene as 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 $(C_2H_5)_2O{\cdot}BF_3$ and 2 ml. of anhydrous methanol. After warming the pasty 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^{23}_D 1.4041, d^{23} 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-one[9] 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-one[10] 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—CH_2—CH_2—CH=CH_2

R	B. p., °C.	Mm.	Density	n_D	M. p. semicarbazone, °C.
C_4H_9—	75–77	19	0.836^{25}	1.4330^{25}	88–89
C_5H_{11}—	86–88	15	$.838^{22}$	1.4365^{22}	
C_6H_5—	127–129	21	$.984^{25}$	1.5240^{25}	157

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(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).

(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 vinylethylacetylene 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. Vinylethylacetylene 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 Lignins[2]

BY ELWIN E. HARRIS

In a former publication[3] 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 publication[4] except for the oak which was first extracted with alcohol according to the modification of Ritter and Barbour[5] 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 Hibbert[7] 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

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[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).