[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

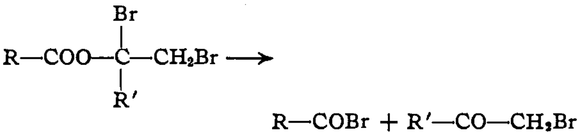
Bromination of Some Alkenyl Esters[1]

BY STEFAN J. SLANINA, G. F. HENNION AND J. A. NIEUWLAND

Introduction

It was reported in a previous communication[2] that 2-acetoxyheptene-1 added bromine readily to form an unstable bromide with distinct lachrymatory properties. We have investigated this bromination reaction in greater detail and are now able to describe its course. By brominating vinyl acetate at various temperatures between 5 and 70° Weibel and Nieuwland[3] obtained 1,2-dibromoethyl acetate in yields which increased with rising temperatures. Based on the quantity of vinyl acetate used they reported yields of 30 and 42% at the mentioned lower and higher temperatures, respectively. Morrison and Shaw[4] stated that the ease of bromination of vinyl acetate in aqueous solution is the basis of a method of analysis used in their Laboratory.

We have added bromine to the butyl and amyl homologs of vinyl acetate at temperatures below zero and have isolated from the reaction mixture two products in each instance: a monobromomethyl alkyl ketone and an acyl bromide. Apparently the alkyl group in the alpha position of the vinyl group resulted in the formation of an unstable dibromo ester which underwent spontaneous cleavage as illustrated by the following equation



$$R—COO—\overset{\overset{\displaystyle Br}{|}}{\underset{\underset{\displaystyle R'}{|}}{C}}—CH_2Br \longrightarrow R—COBr + R'—CO—CH_2Br$$

The yields of monobromo ketones were about 75% of the theoretical. Appreciably smaller yields of acyl bromides were obtained, probably because of further bromination. The bromo ketones were colorless liquids which slowly darkened on exposure to light. The study of halogenation of alkenyl esters was handicapped because of the extreme lachrymatory character of the products.

Experimental

Reagents.—The alkenyl esters were prepared from the appropriate alkylacetylene and acid as previously described by Hennion and Nieuwland.[5] The chloroform used as a solvent was dried over calcium chloride and distilled before use.

Bromination of 2-(Chloroacetoxy)-hexene-1.—A one-liter three-necked flask was equipped with a reflux condenser, a motor-driven mercury-sealed stirrer, thermometer and dropping funnel. Into the flask was placed a solution of 266 g. (1.5 moles) of 2-(chloroacetoxy)-hexene-1 in 150 g. of dry chloroform. A solution of 240 g. (1.5 moles) of bromine in 150 g. of dry chloroform was poured into the dropping funnel. The ester solution was cooled to −5° by means of an ice and salt mixture and the bromine solution added dropwise at such a rate that a temperature below zero was maintained. The addition of bromine required about an hour. The crude product was transferred to a one-liter round-bottomed flask provided with a 91-cm. Vigreux fractionating column. The chloroform was removed by slow distillation under a slight vacuum. The pressure was then reduced to 120 mm. and the chloroacetyl bromide distilled. The residue was distilled through a 41-cm. Vigreux column at a pressure of 30 mm. The fraction boiling between 80–100° (30 mm.) amounted to 216 g. This was redistilled through a short column and the fraction boiling at 86–88° (30 mm.) retained. The yield of 1-bromohexanone-2 was 186 g. or 67% of the theoretical. The chloroacetyl bromide fraction was redistilled at atmospheric pressure. The yield was 34 g. or 21% of the theoretical.

The following characteristics were determined for 1-bromohexanone-2: b. p. 86–88° at 30 mm.; n^{30}_{D} 1.4563; d_{30} 1.284; MR found 37.92, MR calcd. 37.69.

Anal. Calcd. for $C_6H_{11}BrO$: Br, 44.70. Found: Br, 43.64.

The identity of the chloroacetyl bromide was established by conversion to methyl chloroacetate with anhydrous methyl alcohol. The reaction was extremely vigorous and hydrogen bromide was evolved.

Bromination of 2-Acetoxyheptene-1.—A solution of 176 g. (1.125 moles) of the ester in 200 g. of chloroform was brominated as described above. The acetyl bromide formed was distilled from the product together with the chloroform and treated immediately with aniline in the cold. In this manner 41 g. of acetanilide was obtained which corresponds to a 30% yield of acetyl bromide. The residue which remained after distilling the acetyl bromide and chloroform was fractionated *in vacuo* and yielded 173 g. of 1-bromoheptanone-2. The following constants were determined for this ketone: b. p. 109–110° at 30 mm.; n^{25}_{D} 1.4644; d_{25} 1.268; MR found 42.31, MR calcd. 42.31.

Anal. Calcd. for $C_7H_{13}BrO$: Br, 41.40. Found: Br, 41.48.

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(1) Paper XI on the chemistry of the alkylacetylenes and their addition compounds; previous paper, THIS JOURNAL, 58, 796 (1936).

(2) Hennion, Killian, *et al.*, *ibid.*, 56, 1132 (1934).

(3) Weibel, M.S. Thesis, University of Notre Dame, August, 1931. Weibel reported the following constants for 1,2-dibromoethyl acetate: b. p. 94–95° at 22 mm.; n^{21}_{D} 1.503; d_{27} 1.912. *Anal.* Calcd. for $C_4H_6Br_2O_2$: Br, 65.18; mol. wt., 228.9. Found: Br, 65.4 and 65.5; mol. wt. (cryoscopic in benzene), 233.

(4) Morrison and Shaw, *Trans. Electrochem. Soc.*, 63, 446 (1933).

(5) Hennion and Nieuwland, THIS JOURNAL, 56, 1802 (1934).

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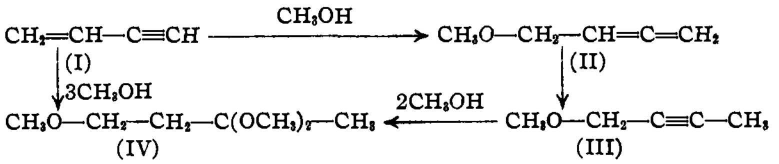
[6] Grignard and Perrichon, *Ann. chim.*, [10] 5, 22 (1926).

[Contribution from the Department of Chemistry, University of Notre Dame]

Addition of Methanol to Alkenyl Acetylenes[1]

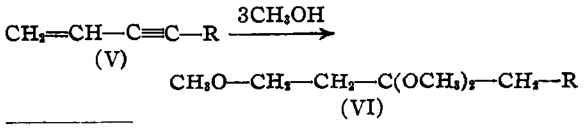
By D. B. Killian, G. F. Hennion and J. A. Nieuwland

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).



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

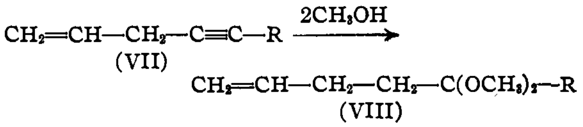
In an attempt to obtain further data on the mechanism of methanol addition to vinylacetylene, we have studied similar reactions with several allylalkylacetylenes (VII) and with vinylethylacetylene (V, R is C_2H_5). The latter behaved like vinylacetylene and added three molecules of methanol quite readily.



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

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.

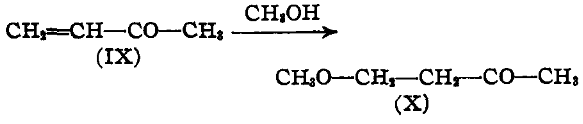
The allylalkylacetylenes (VII) reacted readily with methanol.



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

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.



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

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.