

SOLVOLYSIS REACTIONS OF PRIMARY  
 $\beta$ -ACETYLENIC BROMIDES<sup>1</sup>GERALD R. LAPPIN<sup>2</sup>*Received May 28, 1961*

Several reactions of primary  $\beta$ -acetylenic halides have been shown to involve a rearrangement, analogous to the allylic rearrangement, which has been called the propargylic rearrangement (1) and which involves the formation of allenic products as well as the expected acetylenic products. The hydrolysis of propargyl-magnesium halides (2) and the dehalogenation of propargyl halides (3) have been shown to give both acetylenic and allenic hydrocarbons. The carbonation of propargyl Grignard reagents gave both acetylenic and allenic acids (1, 2). The investigation herein described was instituted to discover whether a similar rearrangement occurred in some solvolysis reactions of primary  $\beta$ -acetylenic halides.

For allyl halides it has been shown that the reaction conditions determine whether or not rearrangement will occur in a given solvolysis. When butenyl halides were treated with methanolic sodium methoxide, conditions favoring  $S_N2$  mechanism, no rearrangement occurred but if the solvolysis was carried out in methanol alone, conditions favoring  $S_N1$  mechanism, partial rearrangement occurred (4). Similar results have been reported for the acetolysis of butenyl halides, potassium acetate in acetic anhydride giving no rearranged product while silver acetate in acetic acid gave partial rearrangement (5).

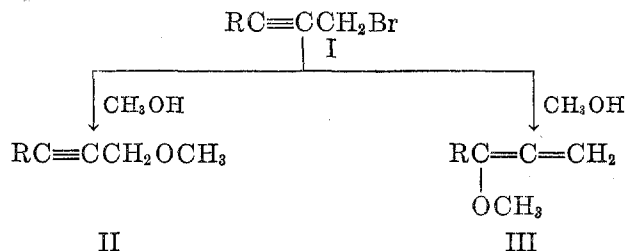
No solvolysis reaction of a primary  $\beta$ -acetylenic halide has been reported. The acetolysis of two tertiary  $\beta$ -acetylenic halides has been studied with conflicting results. When 3-chloro-3-methyl-1-butyne (6) or 4-chloro-4-methyl-2-pentyne (7) was reacted with silver acetate in ether only the normal acetylenic acetate resulted while silver acetate in acetic acid gave both acetylenic and allenic acetates. However, the very similar 4-chloro-4-methyl-2-pentyne gave only the normal acetate even with silver acetate in acetic acid (7). Reactions of such tertiary halides throw little light on the behavior of the primary halides because of the ready rearrangement of tertiary  $\beta$ -acetylenic halides to allenic halides (8, 9). Thus it is difficult to be certain whether the actual reagent was a mixture of isomers or whether the rearrangement occurred during the course of the reaction. Primary  $\beta$ -acetylenic halides do not suffer from this defect being stable towards rearrangement to allenic halides even under rather vigorous conditions (9).

The alcoholysis of a propargylic halide (I) might lead to either the unrearranged propargyl ether (II) or to the rearranged allenic ether (III). Ozonolysis

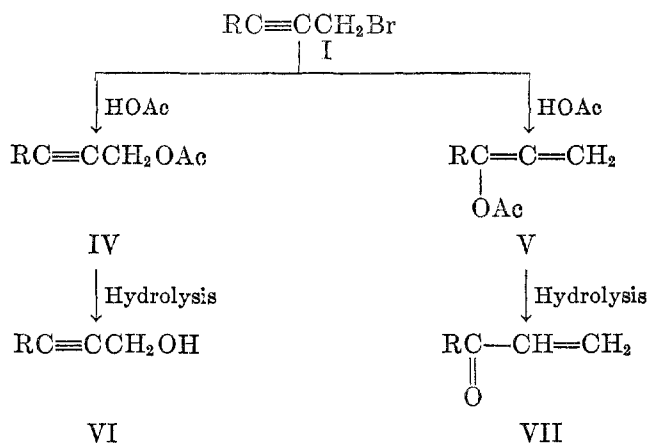
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should readily distinguish between II and III since only III would yield formaldehyde:



Similarly the acetolysis of a propargylic halide might lead to either a normal propargylic acetate (IV) or to the rearranged enol acetate (V). These should be readily distinguished by hydrolysis as IV would give the propargyl alcohol (VI) while V would give the keto form of the enol, the unsaturated ketone (VII).

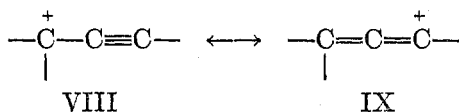


When 1-bromo-2-hexyne was refluxed with methanolic sodium methoxide, conditions favoring  $S_N2$  reaction without rearrangement, a nearly quantitative yield of 1-methoxy-2-hexyne was obtained. The complete absence of any rearrangement product of type III was established by demonstrating the absence of even traces of formaldehyde in the ozolysis product formed by treating the crude ether from the reaction with ozonized oxygen. When methanolysis was accomplished by refluxing the bromide in methanol solution and neutralizing the hydrogen bromide formed by frequent addition of either methanolic sodium methoxide or solid barium hydroxide, maintaining the solution as nearly neutral as possible as indicated by Methyl Red, again a nearly quantitative yield of unrearranged product (II) was obtained. When this ether was ozonized the ozonolysis product gave a very faint positive test for carbonyl (10) but no derivative of formaldehyde could be isolated. The maximum amount of rearranged product which could have been present, as estimated on the basis of this colorimetric test for carbonyl, was less than 0.01% of the total ether. It is quite possible that the trace of carbonyl detected was due not to formaldehyde but to

some trace impurity in the starting material or produced during the long heating involved in this reaction. Since the amount was insignificant no attempt was made to ascertain more definitely the identity or source of this carbonyl material. It was found, therefore, that even under conditions highly favorable to rearrangement no such rearrangement occurred in this solvolysis reaction.

Similar results were observed in the acetolysis of 1-bromo-2-heptyne. The reaction of this bromide with potassium acetate in acetic anhydride, with silver acetate in benzene, and with silver acetate in acetic acid all gave high yields of the normal ester, 2-heptynyl acetate (IV, R = C<sub>4</sub>H<sub>9</sub>). In each of these reactions the ester produced was hydrolyzed to produce pure 2-heptyne-1-ol as shown by refractive index comparison with an authentic specimen of the pure alcohol. In each case the hydrolysate gave a very weak positive test for carbonyl content (10) but inasmuch as the pure alcohol prepared by other methods gave the test to approximately the same extent this cannot be construed as evidence for the presence of even trace amounts of the enol acetate (V, R = C<sub>4</sub>H<sub>9</sub>). Here again, under conditions which would seem to be as favorable as possible to rearrangement the expected propargylic rearrangement failed to occur.

The results of this and other investigations bear out the conclusion that considerations based on the allylic rearrangement cannot be applied to the reactions of the propargylic system. Two basic differences between the two systems probably account for the differences in behavior. First, cyclic mechanisms such as have some times been proposed for certain allylic rearrangements are excluded by the linear geometry of the propargylic system. Second, the two contributing resonance forms of the carbonium ion produced from a  $\beta$ -acetylenic compound (VIII and IX) are not equivalent in structure.



In the allylic system the corresponding forms are essentially equivalent in structure. Thus the general conclusion that in the allylic system a reaction may involve either of the two forms of the resonance carbonium ion and thereby produce two products from a given reaction does not necessarily apply to the propargylic system. In fact, it seems very probable that, in the attack on the propargylic system by a nucleophilic reagent, form VIII would present the most favorable form for reaction or would result in a more stable intermediate activated complex. Thus nucleophilic substitutions in the propargylic system might well be expected to give rise chiefly to the normal unrearranged product. This conclusion appears to be in accord with the results of the solvolysis of primary  $\beta$ -acetylenic halides. In the solvolysis of tertiary  $\beta$ -acetylenic halides, where rearrangement does appear to occur, other factors alter the situation.

#### EXPERIMENTAL

*Reaction of 1-bromo-2-heptyne with sodium methoxide in methanol.* To 5.0 g. (0.21 g.-atom) of clean sodium in 500 ml. of absolute methanol was added 25.0 g. (0.14 mole) of 1-bromo-2-heptyne. The solution was refluxed with stirring for five hours and then concentrated to

100 ml. *in vacuo*. After cooling it was poured into 500 ml. of water and the product was extracted with ether. The ether solution was dried over sodium sulfate and the ether was removed under reduced pressure. Distillation of the residue through a 20-cm. Vigreux column gave 16.5 g. (91%) of 1-methoxy-2-heptyne, b.p. 88–90° at 58 mm.,  $n_D^{20}$  1.4332. Part of the product was redistilled from sodium through a 50-plate Podbielniak Miniature Hyper-Cal column using tetracosane as a chaser. There was no indication of two fractions, virtually all of the sample distilling at the constant temperature of 76° at 40 mm. and having a constant refractive index,  $n_D^{20}$  1.4332. Hennion and Bell (11) report  $n_D^{20}$  1.4329 for this compound which they prepared by another method.

A solution of 1.0 g. of the crude ether, taken before the first distillation, in 10 ml. of carbonyl-free absolute ethyl acetate (prepared by refluxing 100 ml. of absolute ethyl acetate with 1 g. of 2,4-dinitrophenylhydrazine and 1 drop of concentrated sulfuric acid for one hour followed by distillation of the ethyl acetate from the solution) was treated with a stream of ozonized oxygen containing about 2% ozone until the absorption of ozone ceased. The resulting ozonide solution was decomposed by hydrogenation at 0° over a palladium-on-charcoal catalyst and examined for the presence of carbonyl-containing products (10). The test was negative.

*Reaction of 1-bromo-2-hexyne with methanol.* A solution of 17.5 g. (0.10 mole) of the bromide in 250 ml. of absolute methanol was refluxed with stirring. The solution was maintained as near to neutrality as possible by constant titration with 0.2 molar methanolic sodium methoxide using Methyl Red as the indicator. The theoretical amount of base was added in 74 hours after which an excess of the sodium methoxide solution was added and refluxing was continued for five additional hours to insure complete reaction of the bromide. The solution was concentrated to 50 ml. *in vacuo* and worked up as before. Distillation through a 20-cm. Vigreux column gave 11.0 g. (86%) of 1-methoxy-2-heptyne, b.p. 89–91° at 60 mm.,  $n_D^{20}$  1.4332.

The crude product was ozonized and tested for carbonyl as described above. A very faint positive test was obtained which, by visual comparison to standard carbonyl solutions corresponded to an allene content of less than 0.01% in the crude product. No derivative for formaldehyde could be isolated from the ozonolysis product and qualitative tests for this substance were negative.

The reaction of 1-bromo-2-heptyne was also carried out using the same quantities of halide and methanol as used above but neutralizing the hydrogen bromide formed by the frequent addition of solid barium hydroxide. The yield of 1-methoxy-2-hexyne was 11.5 g. (90%).

*Reaction of 1-bromo-2-heptyne with potassium acetate in acetic anhydride.* A mixture of 17.5 g. (0.10 mole) of the bromide, 14.7 g. (0.15 mole) of anhydrous potassium acetate, and 50 ml. of acetic anhydride was heated with stirring at 100° for 100 hours. The dark solution was distilled *in vacuo* until most of the acetic anhydride had been removed and the residue was poured into cold water. The mixture was allowed to stand with stirring for one hour to hydrolyze the remaining anhydride after which the ester was extracted with ether. The ether solution was dried over potassium carbonate and the ether was removed under reduced pressure. The residue was distilled through a 20-cm. Vigreux column to give 12.6 g. (82%) of heptynyl acetate, b.p. 93–95° at 12 mm.,  $n_D^{20}$  1.4403. Hennion and Bell (11) report  $n_D^{20}$  1.4400 for this compound which they prepared by another method.

Saponification of 10 g. of this ester was carried out by refluxing with aqueous-alcoholic potassium hydroxide for five hours. The resulting mixture was neutralized with dilute hydrochloric acid and examined for presence of carbonyl-containing compounds (10). A very weak positive test was obtained corresponding to an enol acetate content of the original ester of no more than 0.01%. No derivative for a carbonyl containing compound could be isolated. The alcohol obtained by saponification of the ester was isolated in the usual manner and proved to be pure 2-heptyne-1-ol,  $n_D^{20}$  1.4899 without redistillation. Bartlett and Rosen (12) report for this compound  $n_D^{20}$  1.4898.

*Reaction of 1-bromo-2-heptyne with silver acetate in benzene.* A mixture of 17.5 g. (0.10 mole) of the bromide, 18.4 g. (0.11 mole) of recrystallized silver acetate, and 250 ml. of benzene was refluxed with stirring for 90 hours. After cooling the precipitated silver halide was removed and the benzene was taken off under reduced pressure. Distillation of the residue through a 20-cm. Vigreux column gave 14.0 g. (91%) of 2-heptyne-1-ol acetate,  $n_D^{20}$  1.4401.

Saponification of the ester as before gave a solution giving a very weak positive test for carbonyl from which could be isolated pure 2-heptyne-1-ol.

*Reaction of 1-bromo-2-heptyne with silver acetate in acetic acid.* A mixture of 17.5 g. (0.10 mole) of the bromide, 18.4 g. (0.11 mole) of recrystallized silver acetate, and 100 ml. of redistilled glacial acetic acid was heated at 90° for 100 hours. After cooling the solution sufficient sodium chloride was added to precipitate the excess silver and the silver halide was removed. The acetic acid solution was concentrated to 50 ml. *in vacuo* and poured into water. The ester was extracted with ether, the ether solution was dried over potassium carbonate, and the ether was removed under reduced pressure. Distillation of the residue gave 12.0 g. (78%) of heptynyl acetate,  $n_D^{20}$  1.4404.

Saponification and examination for carbonyl-containing compounds was carried out before. The test was again weakly positive but no carbonyl derivative could be isolated. Again pure 2-heptyne-1-ol was isolated from the saponification product.

#### SUMMARY

The methanolysis and acetolysis of 1-bromo-2-heptyne have been carried out under conditions favorable to  $S_N2$  as well as  $S_N1$  reactions. No rearrangement to allene derivatives resulted even under favorable conditions for such rearrangements.

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