

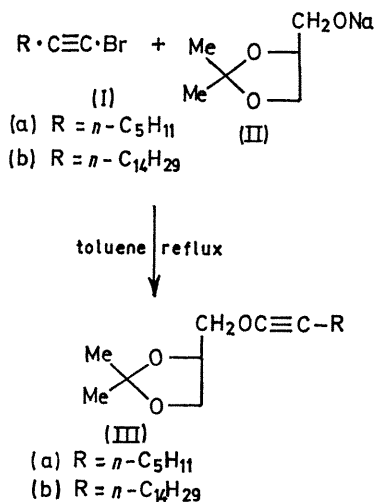
Unusual Products from an Alkoxide Ion and a 1-Bromoalk-1-yne: Evidence for a Vinylidene Carbene Intermediate

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Summary Sodium 2,2-dimethyl-1,3-dioxolan-4-methanolate (II) reacts with 1-bromohept-1-yne by hydrogen abstraction at C-3 giving *n*-butylvinylidenecarbene (VIII) which reacts with the alcohol corresponding to (II) to give unusual products (IV—VII) that can be explained by nucleophilic attack on the ambident zwitterion-carbene, by prototropic shifts, and by insertion into the C-H bond on the carbon atom bearing the hydroxy-group.

PLASMALOGENS¹ contain a *cis* vinyl ether linkage at position 1 and therefore partial hydrogenation of the corresponding acetylenic ether (III) would provide a convenient stereospecific synthesis. While Preobrazhenskii and his co-workers² have claimed the preparation of (IIIa) by Scheme 1 a recent attempt to repeat this procedure was reported to give instead only the isomeric allene (IV).³

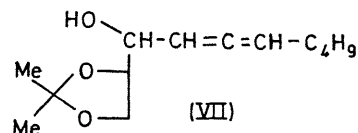
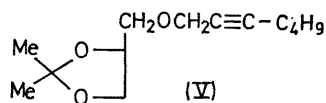
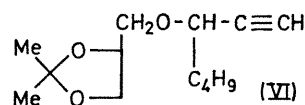
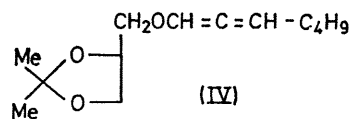


SCHEME 1

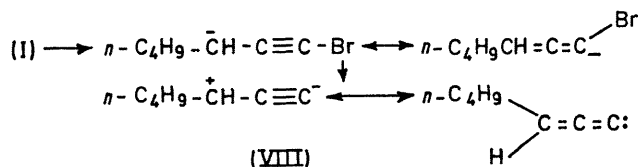
Re-investigation using gas chromatography (g.l.p.c.) gave a mixture of the four compounds (IV), (V), (VI), and (VII) (mixture of stereoisomers) in the ratio 6:2:1:11 (total yield 19%) under these reaction conditions. The components were isolated by a combination of distillation and preparative g.l.p.c.† No evidence for the formation of (III) could be found by g.l.p.c., t.l.c., or by i.r. analysis of the crude reaction mixture. The alcohol (VII) was air-sensitive and thermally labile which may explain why previous workers failed to detect this compound.

A priori, (IV) and (V) could be derived from (IIIa) by base-catalysed isomerization;⁴ however the formation of (VI) or (VII) cannot be explained in this manner. An alternative interpretation involves hydrogen abstraction at position 3 of the bromoalkyne (I) (Scheme 2) and formation

of the ambident zwitterion-carbene (VIII)⁵ which then reacts with alcohol and/or alkoxide at both C-1 and C-3

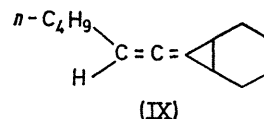


giving (IV) and (VI), respectively. The acetylenic ether (V) could then be derived from (IV) by a prototropic propargylic rearrangement under the basic reaction conditions.⁶



SCHEME 2

When the solvent was changed to cyclohexene or toluene-cyclohexene (3:1), the major product was the allenic cyclopropane (IX) formed in competition with (IV—VII) and thereby demonstrating the intermediacy of (VIII). This compound (IX) could also be obtained in 8% yield by



treatment of (I) with an equimolar quantity of potassium *t*-butoxide in refluxing cyclohexene.

† Satisfactory analytical and spectral data were obtained for all compounds reported herein. 1-Bromohept-1-yne was freshly distilled and carefully checked for impurities prior to use. In particular the absence of 1-bromohepta-1,2-diene and 1-bromohept-3-yne was established by spectral methods.

In a later communication the Russian workers extended the method to a longer carbon chain and using refluxing xylene as solvent reported a 6% yield of (IIIb), but no allenic ether. Duplication of these conditions gave a product distribution very similar to our results obtained in toluene with slightly smaller quantities of (IV). Analogous results were achieved with 1-bromohexadec-1-yne (Ib).

The postulated carbene intermediate satisfactorily accounts for the formation of (IV—VI), but the origin of the allenic alcohol (VII) remains uncertain. In the presence of cyclohexene the ratio of compounds (IV—VII) was

unchanged while the yield decreased significantly, suggesting that the allenic alcohol may also be derived, at least indirectly, from (VIII). A reasonable explanation for such a transformation involves insertion of the carbene into the C—H bond on the carbon atom bearing the hydroxy-group of the alcohol corresponding to (II). A detailed description, and evidence for this and other insertion reactions of (VIII) are presented in the following communication.

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