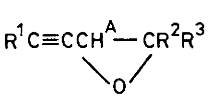
Chemical Behaviour of αβ-Acetylenic α′-Hydroxy Quaternary Ammonium Salts in Basic Media

By Roland Epsztein* and Nicole Le Goff

(*Laboratoire de Chimie Organique Biologique, Université de Paris-Sud, Centre d'Orsay Bâtiment* 420, 91405 *Orsay Cédex, France*)

Summary According to the nature of their substituents hydroxy-ammonium salts, $R^1C\equiv CCH(NMe_3{}^+I^-)CR^2R^3$-OH, when treated with a weak base in aqueous solution, are either cleaved into a carbonyl compound and a quaternary prop-2-ynylic ammonium compound, or cyclize to form an oxiran or a furan.

We recently reported a general method of synthesis of α-amino-βγ-acetylenic alcohols, $R^1C\equiv CCH(NR^4{}_2)CR^2R^3OH$.[1] As we were interested in the possibility of using these compounds as intermediates for other syntheses, especially of oxirans,[2] we have investigated the chemical properties of their quaternary salts, in particular their reactions in the presence of a weak base such as potassium carbonate (Table).



(1)

$R^1C\equiv CCHNMe_3{}^+I^-$

(2)

R^2COR^3

(3)

(4)

Table. Reactions of hydroxy acetylenic ammonium salts with aqueous K_2CO_3.[a]

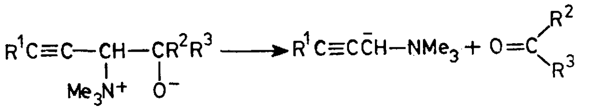
Salt $R^1C\equiv CCH(NMe_3{}^+I^-)CR^2R^3OH$			
R^1	R^2	R^3	Product(s)
Oxiran formation			
C_5H_{11}	Me	Me	(**1a**)[b]
C_5H_{11}	$-[CH_2]_5-$		(**1b**)[b]
Cleavage			
C_5H_{11}	Ph	Me	(**2a**) + (**3a**)
C_5H_{11}	Ph	Ph	(**2b**) + (**3b**)
H	$-[CH_2]_5-$		(**2c**) + (**3c**)
H	$-[CH_2]_2CHBu^t[CH_2]_2-$		(**2d**) + (**3d**)
Furan formation			
C_5H_{11}	H	H	(**4a**)
C_5H_{11}	H	C_7H_{15}	(**4b**)
C_5H_{11}	H	Ph	(**4c**)
Cleavage + furan formation			
H	H	Ph	(**4d**) + (**2e**) + (**3e**)

[a] Typical conditions: the ammonium salt was heated in aqueous solution with 1 equiv. of K_2CO_3 for 1—2 h at 90 °C.
[b] The oxirans (**1a**) and (**1b**) were obtained in 70% yield: (**1a**), b.p. 105 °C at 15 mmHg, δ (H^A; CCl_4; Me_4Si) 2·92; (**1b**), b.p. 95 °C at 0·1 mmHg, δ (H^A) 2·93.

The results in the Table show that oxirans will be formed in the reaction of these ammonium salts with aqueous K_2CO_3 if R^1, R^2, and R^3 are not hydrogen and R^2 and R^3 are not aromatic. If R^1, R^2, R^3 are not hydrogen and R^2 (and possibly also R^3) are aromatic, cleavage into a ketone and a prop-2-ynylic ammonium salt occurs. If R^1 only is hydrogen, cleavage also occurs. If R^1 is not hydrogen and R^2 (and possibly also R^3) are hydrogen, cyclization into a furan occurs almost quantitatively. In the particular case $R^1 = R^2 = H$, $R^3 = Ph$, cleavage and furan formation occur in competition. The results seem to be independent of the configuration of the substrates.

The tendency of β-acetylenic secondary alcohols to cyclize into furan derivatives when the α-C atom bears an electron-withdrawing group has already been observed.[3] The particular ease with which it occurs here is due to the enhanced inductive effect of the ammonium group, thus explaining why this reaction can be preferred to the expected oxiran formation. However, oxiran formation also seems to take place more readily here than in other cases where it requires more drastic conditions.[2]

We assume that the cleavage reaction proceeds *via* an ammonium ylide (A),[4] although it is difficult, so far, to draw any definite conclusion on the reasons why it takes place, in preference to or together with the cyclization. However, it seems reasonable to suppose that, in addition to the electron-withdrawing effects of both alkynyl and ammonium groups which weaken the bonds at the propynylic C atom, relief of strain and gain in energy due to the formation of a conjugated carbonyl derivative play a part in facilitating this reaction. The fact that it takes place even more readily when $R^1 = H$ is more difficult to explain, unless the increased inductive effect of the ethynyl group[5] plays a decisive part.



(A)

(*Received, 17th June* 1977; *Com.* 598.)

---

[1] R. Epsztein and F. Mercier, *Synthesis*, 1977, 183.
[2] A. Weissberger, 'Heterocyclic Compounds,' Interscience, New York, 1964.
[3] S. Holand and R. Epsztein, *Bull. Soc. chim. France*, 1971, 1694; F. Mercier and R. Epsztein, *ibid.*, 1973, 3393.
[4] A. W. Johnson, 'Ylid Chemistry,' Academic Press, New York, 1966, 251.
[5] G. B. Barlin and D. D. Perrin, *Quart. Rev.*, 1966, **20**, 75.