ADDITION OF ETHYL ALCOHOL TO TRIETHYL PROPARGYL AMMONIUM BROMIDE

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ABSTRACT

Rearrangement of propargyl amine salt, in the presence of a base was studied and it was concluded that this occurs through an allenic intermediate.

INTRODUCTION

Propargylic compounds, in the prescence of a base, rearrange themselves into allenic compounds. This is the so called, prototropic rearrangement which occurs through an anionic intermediate as the following[1]:

$$R_1R_2CHC{\equiv}CR_3 \xrightarrow[\text{base}]{\text{Proton acceptor}} \left[\begin{matrix} R_1R_2C^- - C{\equiv}CR_3 \\ R_1R_2C{=}C{=}C^- - R_3 \end{matrix}\right] \xrightarrow[(H_2O)]{\text{Proton donor}} R_1R_2CH{-}C{\equiv}CR_3 \ , \ R_1R_2C{=}C{=}CHR_3$$

Catalysts of varying basicity for this type of rearrangement include, sodamide, potassium hydroxide, potassium carbonate, potassium t-butoxide, and even some Lewis acids, e.g. $ZnCl_2$. Important factors affecting this type of rearrangement are: basicity, type of solvent, temperature, and the substituents (R_1 & R_2)[2].

So far, the rearrangements of the propargylic ethers[3], thioethers[2, 4], acids[5-7], esters [8-9] aldehydes and ketones[10-12], nitriles [13], phousphorous derivatives[14-16], amines[17-21], and miscellaneous propargylic compounds[23-24] have been studied. Common solvents include; ethyl alcohol, ether, and dimethyl sulfoxide (DMSO). However, solvents with higher basicity, e.g. NH_3 (dry) and amines, are preferred. Of course, the rearrangement can occur in the absence of a solvent (2). The temperature affects the rate of the rearrangement. In some instances, slow isomerization, in the presence of a strong base, occurs at temperatures below 0°C[2].

The prototropic rearrangement is possible if the substituent, R_3, is replaced by an active group (e.g. aryl group, ...). Otherwise, there is a mixture of the propargyl with the allene in equilibrium (propargyl $\rightleftharpoons$ allene),

and the allene being a quite minor product[2].

EXPERIMENTAL PROCEDURE

50 ml benzene and 4.4 g triethyl propargyl ammonium bromide(0.02 mole) in a 100 ml flask were refluxed for 10 minutes.After cooling the flask 0.46 g (0.02 mole)sodium was added and subsequently,20 ml dry ethanol was added dropwise.The mixture was refluxed for 12 hours.Benzene and extra alcohol were distilled off under vacuum and enough water was added in order to destroy sodium ethoxide.The aqueous solution was extracted,repeatedly with chloroform,and the product was crystallized. m.p.:165-166 C;Mass Spect: $\frac{m}{e}$ (164,166) ,136,138),(108-110), 56,45,and 30;IR Spect:3080 cm^{-1},2960 cm^{-1},1627 cm^{-1},and 1290 cm^{-1}; ^{1}HNMR spect.:(in $CDCl_3$)δ1.7(q,12H)with J_{H-H}= 10.5 Hz,4(qu ,8 H)with J_{H-H}= 10.5, 4.75(d,1 H)with J_{H-H}=2.33 Hz,and 4.95 (d,1 H)with J_{H-H}=2.33 Hz,δ 4.4(s,2H).

SPECTRAL ANALYSIS AND CONCLUSION

To determine the structure of the product,each of the two possible structures,I & II,were studied with the help of Mass,IR and ^{1}HNMR ,spectroscopies.

$$CH{\equiv}C{-}CH_2{-}N^+(\text{ring})\,Br^- + C_2H_5OH \xrightarrow{C_2H_5ONa/C_6H_6}$$

I,II

$CH_2 = C(OC_2H_5)CH_2{-}N^+(\text{ring})\,Br^-$;

$H_5C_2O{-}CH{=}CH{-}CH_2{-}N^+(\text{ring})\,Br^-$

II

Mass Spect:

The parent ion(M^+)was not seen in the spectrum,but from the observed masses(164,166),(136,138),and(108,110) it was concluded that there was a bromine atom in the molecule. The masses 56, 45,and 30 are indicators of species $C_3H_6N^+$,$C_2H_5O^+$, $CH_2{}^+NH_2$ respectively. Thus,no distinction could be made between I & II via mass spectrometry.

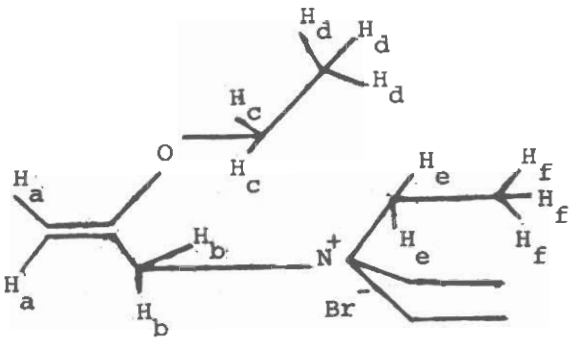
IR Spect:

The peaks at 3080 cm^{-1},2960 cm^{-1}, 1627 cm^{-1},and 1290 cm^{-1} are indica - tions of olefinic hydrogens , alkanic hydrogens,carbon-carbon double bond, and caron-oxygen single bond respectively. Therefore IR spect.can neither differentiate between I & II .

^{1}HNMR Spect:

The protons a and a' in structure I are diastereotopic and have a splitting like a AX system(AV/j=6 to 7). The two b protons are equivalent and are seen as a singlet. All in all, NMR of this compound should give seven different signals with the ratios of 1:1: 2:2:3:6:9. But,experimentally there appear the ratios of 1:1:2:8:12. The ratios 8 and 12 belong to protons c and e(8 H,quintet),and d and f(12 H, quartet). Two mixed triplet make a quartet(12 H)and two mixed quartet make a quintet(8 H). Therefore, the NMR spectrum agrees with structure I .

The structure II has all the protons b,c,d,e,f,and also 1 and 2 replacing a and a' in structure I.



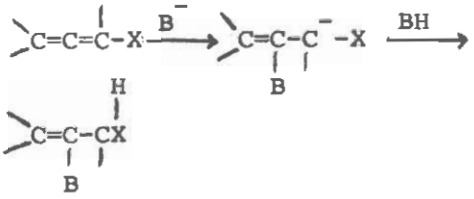
(I)

However,the splitting patterns for structure I and II are different from each other.

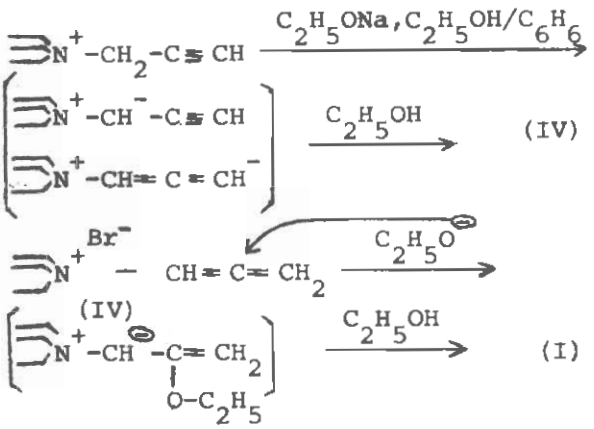
(d) (c) (b) (e) (f)
$CH_3-CH_2O-C(H_1)=C(H_2)-CH_2-N(CH_2-CH_3)_3$ (II)

The two b protons,should be seen as a doublet(not a singlet)and no. 2 proton should be seen as a multiplet. This analysis is different from what is seen in the spectrum.

Although allene(C_3H_4)and its homologs do not undergo any nucleophilic attack,the presence of strong electron-withdrawing groups(X)on allenes make the following type of reaction possible[24].



Electron withdrawing groups (X), e.g.nitriles[25],carboxylic acid[26], esters[27],carbonyls[28-30],and $(RO)_2PO$[31],activate the allenic bond favoring its attack by amines, alkoxy,etc.Although we have not isolated the allenic compound by the end of the reaction,we can postulate that the reaction first proceeds through a prototropic rearrangement with an allenic intermediate(IV)and a subsequent attack by the nucleophile on the allene would make compound(I).



ylide nitrogen

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