Carbonium Ions. XXIII. Chain Elongation in the Rearrangement of 2,3-Dimethyl-4-penten-2-ol to 2-Methyl-3-hexen-2-yl Cation

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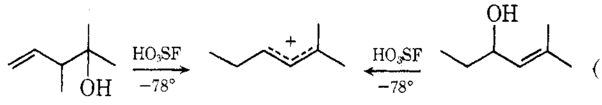
Received September 25, 1974

The 2-methyl-3-hexen-2-yl cation (I) is formed on addition of 2,3-dimethyl-4-penten-2-ol (II) to HO_3SF at −78°, eq 1. Ion I is the dominant product as evidenced by 90% of the nmr band areas being attributable to I. A novel feature of eq 1 is the elongation of the five-carbon chain of II to the six-carbon chain of I. This type of elongation does not seem to have been observed heretofore in allyl cation rearrangements[1] and will probably be uncommon because it would involve going from more branched to less branched carbonium ions.



(1)

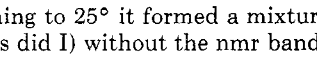
II I

The rearrangement cannot have taken place by H migration alone and paths involving H migration and 1,2-alkyl shifts are unlikely. The only attractive paths are those involving cyclopropylcarbonium ions and rearrangements of these ions of the type exemplified by the scrambling of methylene groups in the cyclopropylmethyl cation.[2] At least two paths involving this type of rearrangement can be constructed.

Structure I was assigned on the basis of its nmr spectrum: triplet at 1.29 (J = 6.5 Hz, ~3 H on C-6), unresolved quartet at 2.96 (2.0 H on C-5), singlet at 3.06 (6.0 H on *gem*-dimethyl), doublet at 7.74 (J = 14.5 Hz, 1.0 H on C-2), doublet at 9.60 (J = 14.5 Hz, 1.0 H on C-3). The band at 9.60 was broadened by coupling with the H on C-4. The band positions are in accord with precedent.[1]

The identification of I was confirmed by its independent synthesis by addition of 5-methyl-4-hexen-3-ol to HO_3SF at −78°, eq 1. This formation was quantitative.

It had been anticipated that II would form the 2,3-dimethyl-3-penten-2-yl cation, III, as the first stable observable cation. The question thus arose as to whether III was an intermediate in the formation of I. This was not the case. Addition of 2,3-dimethyl-3-penten-2-ol (IV) to HO_3SF at −40° produced III, eq 2. Ion III was stable at −40°. On warming to 25° it formed a mixture of cyclopentenyl cations (as did I) without the nmr bands of I ever appearing. This formation of cyclopentenyl cation mixtures is a common fate of carbonium ions.[3]



(2)

IV III

The identification of III rested on its mode of formation and nmr spectrum: singlet at 2.23 (3.0 H on C-3), a broad unresolved pair of bands at 2.75 (6.0 H of the *gem*-dimethyl), doublet at 3.11 (J = 6 Hz, 3.1 H on C-5), quartet at 9.55 (J = 6 Hz, 1.0 H on C-4). These are typical for allyl cations[1] and are in agreement with structure III.

It is remarkable that the two alcohols II and IV, which differ only in the position of the double bond, produce entirely different stable allyl cations, I AND III, on addition to HO_3SF at −78°.

Experimental Section

Nmr Spectra. Spectra were recorded on a Varian A-60 instrument. Spectra of ions I and III were recorded at −40°. Tetramethylammonium chloride (δ 3.10) was used as the internal standard in HO_3SF. Band positions are expressed in δ.

Carbonium Ion Precursors. 2,3-Dimethyl-4-penten-2-ol (II) was commercially available from Aldrich Chemical Co., Milwaukee, Wis. 2,3-Dimethyl-3-penten-2-ol[4] (IV) was prepared from CH_3Li and 3-methyl-3-penten-2-one. The nmr spectrum in CCl_4 consisted of a singlet (6 H, *gem*-dimethyl) at 1.22, an overlapping singlet and doublet (6 H, remaining two methyl groups) at 1.45–1.77, a singlet (H on OH) at 2.47, and a multiplet (H on C-4) from 5.20 to 5.77. The J coupling constants between hydrogens on C-4 and C-5 could not be accurately determined but both were in the same 6–7-Hz range. The boiling point (82–83° at 72 Torr) was in agreement with that reported (84–86° at 85 Torr[4]).

5-Methyl-4-hexen-3-ol[5] was prepared by $LiAlH_4$ reduction of 5-methyl-4-hexen-3-one. The nmr spectrum in CCl_4 consisted of a triplet (J = 6.5 Hz, 3 H on C-6) at 0.83, a multiplet (2 H on C-5) from 1.06 to 1.62, a pair of doublets (J = 1.5 Hz, 6 H on *gem*-dimethyl) at 1.65 and 1.70, a singlet (H on OH) at 3.07, a multiplet (H on C-4) from 3.93 to 4.35, and a multiplet (H on C-3) from 4.95 to 5.27. The boiling point (58° at 13 Torr) was in agreement with that reported (63–65° at 22 Torr[5]).

Acknowledgments. Support of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the National Science Foundation is gratefully acknowledged.

Registry No.—I, 53567-43-4; II, 19781-52-3; IV, 53555-58-1; 3-methyl-3-penten-2-one, 565-62-8; 5-methyl-4-hexen-3-ol, 53555-59-2; 5-methyl-4-hexen-3-one, 13905-10-7.

References and Notes

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A New Method for the Preparation of 4-Acylpyrazoles. The Reaction of C(α),N Dianions of Phenylhydrazones with Acid Chlorides

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Received September 6, 1974

The 1,4 dianions of phenylhydrazones having an α-hydrogen atom, such as dilithioacetophenone phenylhydrazone, have been condensed with esters[1] and nitriles[2] to give, after acid cyclization, numerous pyrazoles, especially 3,5-disubstituted pyrazoles.

It was of interest to treat these dianions with aroyl chlorides in order to determine the effect of these more reactive electrophilic reagents and to compare the results with those already obtained for esters and nitriles. When the dilithiophenylhydrazones **1** were treated with benzoyl, *p*-chlorobenzoyl, and *p*-toluoyl chlorides, followed by acid cyclization, 4-acylpyrazoles **2a–j** were obtained instead of 3,5-disubstituted pyrazoles **3**.