[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ALABAMA]

# MECHANISM OF RETROPINACOL-TYPE REARRANGEMENTS[1]

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The consensus of modern theories of rearrangement is that strained carbonium ions derived from carbinols, halides, olefins, etc., rearrange spontaneously when less-strained intermediates are formed by migration of alkyl or aryl groups (1). Such views do not account for the fact that considerably greater proportions of rearranged products are obtained from strained carbinols than from the corresponding olefins even though the same carbonium ion is considered to be involved during replacement of the hydroxyl group of a particular carbinol and addition of a hydrogen halide to the corresponding olefin. Likewise, these views fail to account for the fact that different hydrogen halides give different proportions of rearranged products when added to the same olefin. Thus, pinacolyl alcohol gives almost exclusively rearrangement products with hydrogen chloride (2), whereas *tert*-butylethylene gives about 60% rearrangement products with hydrogen chloride and 10% with hydrogen iodide (3).

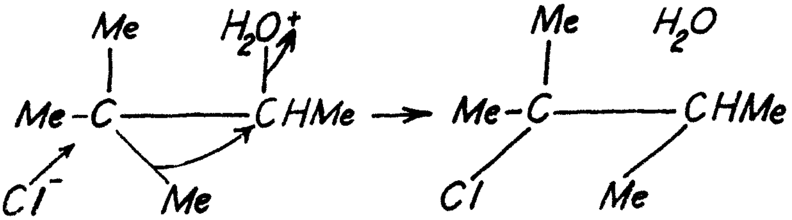

FIG. 1

When the common view-point is modified, however, to consider that, first, a carbonium ion does not rearrange *per se* but may be rearranged by base attack, and second, an oxonium ion can be rearranged in similar manner, many apparent anomalies become logical. In spite of the fact that Winstein has inferred such a mechanism (4) from the work of Bartlett (5), no one has followed this reasoning to the logical explanation of apparently anomalous results as is done in the following descriptions of probable reaction mechanisms for the cases cited above.

When pinacolyl alcohol is reacted with hydrogen chloride, an oxonium ion is formed. Some of this loses water to give an equilibrium mixture of oxonium (I) and carbonium (II) ions. That remaining as oxonium ion is converted almost exclusively to rearrangement products because normal $S_N2$ attack is too hindered to be significant. Instead of attacking the oxonium carbon atom, the

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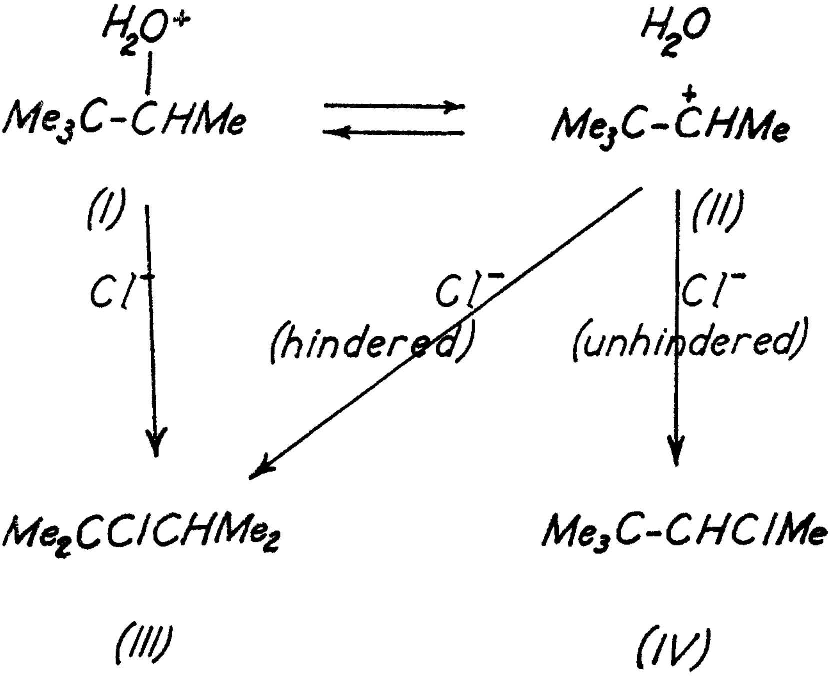
chloride ion attacks, by default, the *beta*, or neo, carbon atom and displaces a methyl carbanion. This readily attacks the back face of the oxonium carbon atom to give a rearranged product (III) because there is no hindrance to such attack. (See Figure 1.) The carbonium ion portion of the equilibrium mixture gives rise to the same proportions of rearrangement products as does *tert*-butylethylene, for the carbonium ion probably is the only intermediate involved when a hydrogen halide is added to the latter. In this instance, a considerable amount of unrearranged product (IV) results from simple neutralization of the carbonium ion, thereby demonstrating that the base is not necessarily hindered from attacking the carbonium carbon atom. However, an attacking base which is so located that it is hindered from such a reaction may neutralize the carbonium ion indirectly by means of a methyl carbanion which it displaces by attacking the *beta*, or neo, carbon atom, thereby yielding a rearranged product. Thus the difference in amounts of rearranged product from pinacolyl alcohol and from *tert*-butylethylene may now be explained on a fundamental basis. Carbinols form mixtures of oxonium ions and carbonium ions. The oxonium ions may be highly hindered from normal attack and lead to rearranged products. The carbonium ions are relatively unhindered and consequently lead to greater amounts of normal products. Because olefins form only carbonium ions, smaller amounts of rearranged products are to be expected. Since a smaller base will have greater access to the neo carbon atom, it is not surprising that hydrogen chloride adds to *tert*-butylethylene with formation of more rearrangement products than does hydrogen iodide, for the chloride ion is considerably smaller than the iodide ion.



The accessibility of the *beta* carbon atom is an important factor in accounting for many apparent anomalies. Viewing the mechanism of the retropinacol-type rearrangement as involving a base attack at the *beta* carbon atom, it follows that hindrance to such attack will result in reaction taking place to a greater extent through the carbonium ion intermediate, thereby forming less rearrangement products. This hindrance may be of two types:

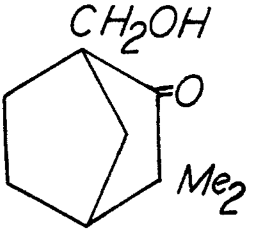
(a) The result of bulky substituents which shield the *beta* carbon atom and/or the result of a bulky attacking base, and

(b) The result of electrostatic repulsion by electron-dense substituents located in a position to shield the *beta* carbon atom from a rearranging base attack. In this type the electron density of the base also is significant.

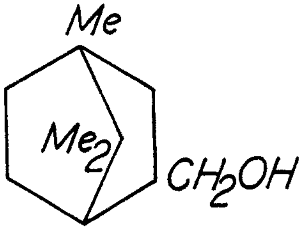
Hindrance to base attack at the *beta* carbon atom accounts for many cases frequently pointed out as anomalous. For example, Wheland considers the rearrangement of carbonium ions *per se* as being a completely successful view in that it permits correlation of a large number of facts and does not appear to be in direct conflict with known facts "although it may perhaps occasionally lead one to expect the formation of a rearranged product which is not actually obtained (sic)" (6). Likewise, Whitmore points out the "radical difference" between pentaglycol, $Me_2C(CH_2OH)_2$, and neopentyl alcohol in that the former is not rearranged by hydrogen bromide (7). Other cases in which rearranged products might be expected but are not actually obtained are discussed below. For instance, 10-hydroxyfenchone (V) is not rearranged on treatment with phosphorus pentachloride (8) because the *beta* carbon atom is located at a cage-head of a bicyclo (2.2.1) system, and, therefore, is protected from base attack. Less obvious is the hindrance afforded by the distorted methylene bridge and its substituents when 3-hydroxymethylcamphane (VI) is dehydrated without rearrangement by syrupy phosphoric acid (9), whereas dehydration of cycloheptyl carbinol with oxalic acid or zinc chloride leads to rearrangement (10). With the commonly accepted views of cationic rearrangements, the strained bicyclic compound would be expected to lead to more rearrangement products than the relatively strainless monocyclic one. Conversion of 8-hydroxycamphane (VII) (11) and tricyclol (VIII) (12) into the corresponding chlorides by phosphorus pentachloride also take place without the formation of rearranged products. Likewise, 2,10-dichlorocamphane (IX) yields the unrearranged dihydroxy compound with silver oxide in boiling dilute alcohol (13) and the corresponding dibromide yields 10-bromo-2-camphanol with silver hydroxide in aqueous acetone (14). Similarly, thionyl chloride converts 3-hydroxymethylcamphor (X) into 3-chloromethylcamphor (14).

Besides pentaglycol, the following show non-rearrangement, probably because of the high electron density of the neo carbon atom substituents: Pentaerythritol on reaction with hydrogen bromide and the resultant bromide on conversion to the original poly-alcohol (15); pentaglycerol, $MeC(CH_2OH)_3$, on conversion to the tribromide (16); and $\gamma$-1-piperidylneopentyl alcohol on conversion to the corresponding chloride with thionyl chloride (17). Of course, the larger bulk of the substituted groups helps somewhat to shield the neo carbon atom.

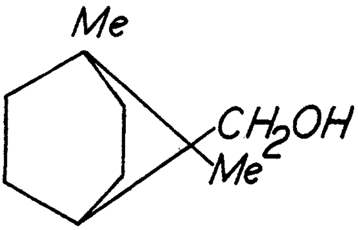
The literature is replete with further data supporting this view of the retropinacol-type rearrangements. The examples cited, however, seem adequate to establish the validity of the proposed mechanism. The utility of this mechanism is evident from the foregoing discussion of probable reaction mechanisms.



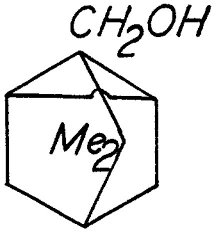
(V)



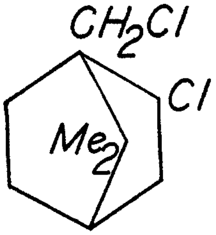
(VI)



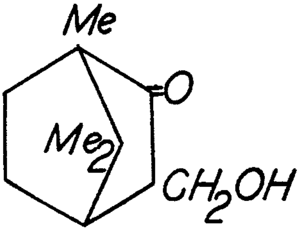
(VII)



(VIII)



(IX)



(X)

In conclusion, it appears that:

1. The rearrangement of carbonium ions *per se* is not a completely successful view of retropinacol-type rearrangements. With such views rearranged products are expected in many cases in which they are not obtained. Nor do such views have quantitative value.

2. Considering retropinacol-type rearrangements to be the result of an attack by a secondary base (carbanion) displaced by $S_N2$ base attack at the *beta*

carbon atom not only accounts for all cases of such rearrangement but also accounts for those cases in which rearrangement fails to take place. Further, this view has more than qualitative value in accounting for varying proportions of rearranged products under different conditions.

3. Shielding the *beta* carbon atom, either by bulky groups or by electron-dense neighbors, hinders base attack at that carbon and, hence, hinders rearrangement.

## SUMMARY

Contrary to current views, strained cations do not rearrange *per se* but are rearranged by base attack at the *beta* carbon atom. Oxonium ions form little unrearranged products from the normal $S_N2$ attack when the base is sterically hindered; instead, an unhindered carbanion attacks when it is displaced by base attack at the *beta* carbon atom. Normal and rearranging base attacks may likewise occur with carbonium ions with the great difference that the carbonium carbon atom is relatively unhindered and greater proportions of normal products are obtained. Access of the *beta* carbon atom to base attack and, probably, strength of the base determine the proportion of rearrangement products. Rearrangement can be prevented by shielding the *beta* carbon atom by either bulky or electron-dense groups. Size and electron density of attacking base must be considered conjointly with shielding groups. Many "anomalous" cases of failure of the retropinacol-type rearrangement to occur are shown to result from protection of the *beta* carbon atom.

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