Objectives

After completing this section, you should be able to

1. write an equation to illustrate the acidic cleavage of an ether.
2. identify the products formed when a given ether is cleaved by a strong acid.
3. identify the reagent needed to bring about cleavage of a given ether.
4. deduce the structure of an unknown ether, given the products of acidic cleavage of the ether.
5. write the detailed mechanism for the acidic cleavage of a given ether.

Study Notes

There are a number of points in this section that require additional explanations.

First, if an excess of HI (or HBr) is used in the cleavage reaction, the alcohol formed is converted by a nucleophilic substitution reaction to the appropriate alkyl halide:

$$ROH + HI \rightarrow RI + H_2O$$

In view of this substitution, some textbooks simplify the overall cleavage process as:

$$R\ce{-}O\ce{-}R' + 2HI \rightarrow RI + R'I + H_2O$$

Second, we should consider in detail how certain ethers (those containing tertiary alkyl, benzyl or allyl groups) cleave by an $S_{N}1$ mechanism:
Finally, notice that an aryl alkyl ether will always produce a phenol and an alkyl halide, never an aryl halide and an alcohol. This is because we rarely see a nucleophile attacking an aromatic ring carbon in preference to an aliphatic carbon:

\[
\text{nucleophile will not attack here}
\]

As phenols do not undergo nucleophilic substitution reactions, even if an excess of HX is used, the products from the cleavage of an aryl alkyl ether are a phenol and an alkyl halide. Diaryl ethers are not cleaved by acids.

The most common reaction of ethers is cleavage of the C–O bond by strong acids. This may occur by S\(_{N}\)1 or E1 mechanisms for 3º-alkyl groups or by an S\(_{N}\)2 mechanism for 1º-alkyl groups. Some examples are shown in the following diagram. The conjugate acid of the ether is an intermediate in all these reactions, just as conjugate acids were intermediates in certain alcohol reactions.

1. \[
\begin{align*}
\text{O} & \quad \text{CH}_3 \\
\text{SN}_2 & \\
\text{CH}_3 & \quad \text{O} \\
\text{CH}_3 & \quad \text{H} \\
\text{I} & \quad \text{H}_2\text{O}
\end{align*}
\]

2. \[
\begin{align*}
\text{H}_2\text{C} & \quad \text{CH}_2 \\
\text{CH}_2 & \quad \text{CH}_2 \\
\text{SN}_2 & \\
\text{H}_2\text{C} & \quad \text{H}_2\text{O}
\end{align*}
\]

3. \[
\begin{align*}
\text{O} & \quad \text{CH}_3 \\
\text{SN}_2 & \\
\text{CH}_2 & \quad \text{H}_2\text{C} \\
\text{H}_3 & \quad \text{O} \\
\text{H}_2\text{O}
\end{align*}
\]

4. \[
\begin{align*}
\text{CH}_3 & \quad \text{O} \\
\text{CH}_3 & \quad \text{H}_2\text{COH} \\
\text{E1} & \\
\text{H}_2\text{C} & \quad \text{CH}_3
\end{align*}
\]

The first two reactions proceed by a sequence of S\(_{N}\)2 steps in which the iodide or bromide anion displaces an alcohol in the first step, and then converts the conjugate acid of that alcohol to an alkyl halide in the second. Since S\(_{N}\)2 reactions are favored at least hindered sites, the methyl group in example #1 is cleaved first. The 2º-alkyl group in example #3 is probably cleaved by an S\(_{N}\)2 mechanism, but the S\(_{N}\)1 alternative cannot be ruled out. The phenol formed in this reaction does not react further, since S\(_{N}\)2, S\(_{N}\)1 and E1 reactions do not take place on aromatic rings. The last example shows the cleavage of a 3º-alkyl group by a strong acid. Acids having poorly nucleophilic conjugate bases are often chosen for this purpose so that E1 products are favored. The reaction shown here (#4) is the reverse of the tert-butyl ether preparation described earlier.
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