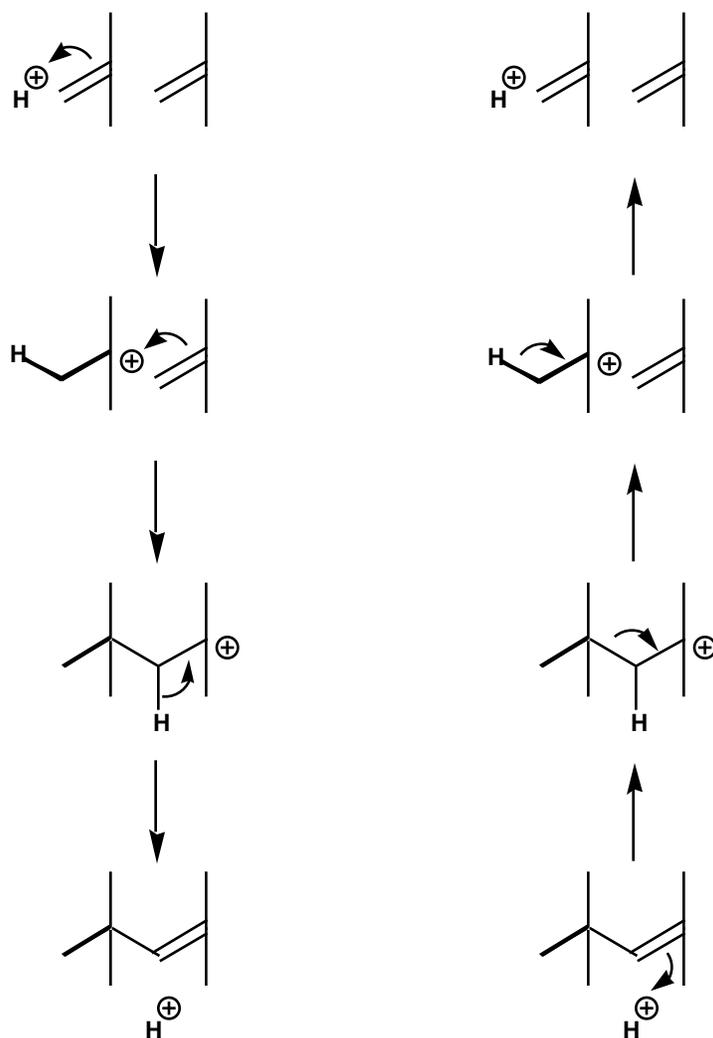


Text Related to Segment 15.02 ©2002 Claude E. Wintner

Under appropriate reaction conditions — a not-too-strong-not-too weak medium of 60% H_2SO_4 is cited here just as an example — isobutylene forms a dimer by the following sequence:

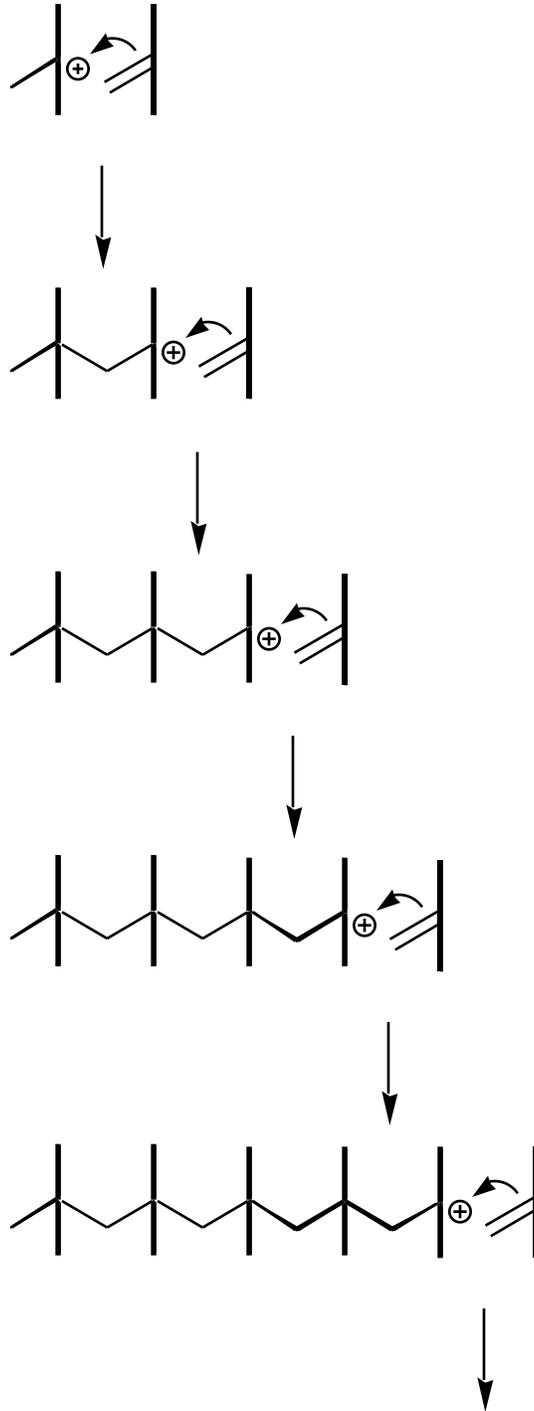


"arrow pushing" for dimerization and fragmentation

One molecule of isobutylene is protonated to give the tertiary carbocation. With no other satisfactory nucleophile at hand, in a closed system the best available base is another molecule of isobutylene itself, which donates electrons to the carbocation, forming in turn a new carbocation that loses a proton to yield the dimer. Once again

there is a choice between two cations, and again it is the more stable tertiary cation that must be formed. Thus, the product stems from the application of the more-stable-carbocation rule twice in succession. (The final double bond may form in either of two positions; only one outcome is shown here.) The reverse of this sequence, termed *fragmentation*, is observed when the dimer is heated in acid in an open system, from which isobutylene can escape. The fragmentation must be initiated by addition of a proton to the double bond of the dimer, again to form the more stable, tertiary, carbocation. The figure shows the "arrow pushing" that is used to keep track of the electron flow in the dimerization and fragmentation processes. (Remember that the curved arrow signifies the movement of two electrons; remember also that electrons move *toward* electron deficient sites.)

Under very strongly acidic conditions the process of isobutylene addition can be repeated many times, leading to polymerization, as shown in the next figure. In fact, this is one of the basic methods that can be used in the production of so-called butyl rubber. Furthermore, of extraordinary significance in biological systems, the rather straightforward ideas outlined here for the steps in dimerization and polymerization are the ones that govern the processes of biosynthesis of all isoprenoid natural products.



acid catalyzed polymerization of isobutylene