Markovnikov’s Rule: In an addition reaction of a protic acid HX (hydrogen chloride, hydrogen bromide, or hydrogen iodide) to an alkene or alkyne, the hydrogen atom of HX becomes bonded to the carbon atom that had the greatest number of hydrogen atoms in the starting alkene or alkyne.

*We will use Butene and H-Br as an example

Notice how the Hydrogen from the H-Br attaches at the terminal carbon of the alkene because that carbon originally had 2 hydrogens whereas the carbon on the other side of the double bond only has one.

Anti-Markovnikov’s Rule: In an addition reaction of a generic electrophile HX to an alkene or alkyne, the hydrogen atom of HX becomes bonded to the carbon atom that had the least number of hydrogen atoms in the starting alkene or alkyne.

Notice that the Hydrogen from the H-Br is now attached at the carbon of the alkene that had only 1 hydrogen thus does not follow Markovnikov’s rule and is the minor product.

Peroxide Effect: In the presence of Peroxide for H-Br, the reaction will always yield the Anti-Markovnikov product.

*We will use ROOR as our impurity for this example

*Notice how the product is the Anti-Markovnikov.

* This “Peroxide Effect” applies only to HBr in the presence of Peroxide.

Adding peroxide causes 100% anti-Markovnikov addition.
References

http://web.chem.ucla.edu/~harding/IGOC/A/anti_markovnikov_addition.html

http://www.chem.ucla.edu/~harding/IGOC/M/markovnikovs_rule.html

Chemistry 14D Lecture Supplement by Professor Steven Hardinger, UCLA First edition, page 139.

https://www.youtube.com/watch?v=wnKf5Z5Xzl&hl=es-ES&gl=ES&t=244s - Alkene + HBr + ROOR or H2O2 Peroxides Reaction Mechanism by The Organic Chemistry Tutor