The recombination of propargyl radicals is thought to be an important route to the formation of benzene both in planetary atmospheres and in flames. 1,3-Butadiene is one likely source of propargyl radical in such environments. We have carried out a study of the primary and secondary products of photodissociation of 1,3-butadiene following excitation near 220 nm in a supersonic expansion. Photoexcitation occurred inside a one-centimeter long reaction tube affixed to the nozzle of the pulsed valve, providing a 20μs window during which primary dissociation products could undergo recombination before expanding. The major primary products in the 118 nm ionization time-of-flight mass spectrum were C₃H₅, C₄H₄, and C₄H₃. The recombination of two C₃H₅ radicals, giving C₆H₆, was shown to be the major secondary reaction channel. Other secondary products were C₅H₆, C₇H₇, and C₇H₈. The primary and secondary products were characterized by resonant two-photon ionization and resonant ion-dip infrared spectroscopies.