Molecular bromine reacts with alkenes. For example, ethylene reacts with bromine to yield 1,2-dibromoethane (figure, line [1]):

For purposes of understanding this transformation, molecular bromine may be interpreted as being endowed with the characteristics of an electrophile—nucleophile pair, Br⁺—Br⁻ [2]. The reaction then is seen as one between a nucleophile (the π bond of ethylene) and an electrophile (formally Br⁺), from which is displaced the nucleophile bromide ion [3]. Lest this be considered as a particularly novel idea, it should be remembered that one of the classical reactions of inorganic chemistry is the reaction of hydroxide ion with a diatomic molecular halogen to give the corresponding hypohalous acid and halide ion [4].

What is the product species of line [3] in the above figure, and how does it react further to give 1,2-dibromoethane? We might imagine it as the cation depicted...
in line [5], below, which could react by simple combination with bromide ion. However, this would invoke a primary carbocation — an entity that we have taken pains to label as unlikely. Instead, let us remember that bromine is a large atom, with free electrons in outer orbitals, and we consider instead the alternative possibility of line [6], a bromonium ion in which bromine is bonded to both carbon atoms of the double bond, and which can suffer subsequent attack by bromide ion to break a C—Br bond of the three-membered ring by rear-side displacement (and consequent inversion of configuration at the center of attack):

In fact, the mechanism of line [6] gains elegant support from stereochemical experiments conducted with Z- and E-2-butene, for which the observed results are as follows. From the reaction of Z-2-butene with molecular bromine only chiral (S,S and R,R) 2,3-dibromobutane, as a racemic mixture, is obtained. No achiral 2,3-dibromobutane is found. In direct contrast, from the reaction of E-2-butene with molecular bromine only achiral 2,3-dibromobutane, and no chiral 2,3-dibromobutane, is observed. The net result in each case may be interpreted as apparent trans addition of bromine to the double bond:
trans addition of molecular bromine to Z- and E-2-butene

Consider what the mechanism of line [6] predicts for Z-2-butene (see figure below). Whether the molecular bromine is approached by the top face or the bottom face of Z-2-butene, the same — achiral — bromonium ion must be formed, a consequence of the fact that the two faces of the alkene are homomorphous. The reaction then will be completed by attack of bromide ion in each of two possible ways, leading to the two enantiomeric forms of the chiral product in equal amount. It is important to understand explicitly that no mechanism can be considered which could allow leakage to the achiral product. Thus, an open secondary carbocation, similar to the primary carbocation in line [5] above, could be attacked by bromide ion on either cationic face, with the result of just such leakage. The bromonium ion provides such an attractive mechanistic solution precisely because the three-membered ring precludes C—C bond rotation, while at the same time it demands exactly the rear-side displacement to complete the reaction, and the accompanying inversion (emphasized graphically by the C-I-P descriptors), that the observed stereochemical findings impose inexorably on any viable proposal:
Furthermore, a front-side attack by bromide ion on the bromonium ion also would predict the incorrect result, amounting to overall cis addition, rather than the observed trans addition of molecular bromine to the alkene.

Starting now with E-2-butene, as delineated in the next figure, the same mechanism predicts that an enantiomeric pair of bromonium ions will be formed as a result of approach to molecular bromine by the two faces of the alkene, because the
faces are enantiomorphous; however, each of the subsequent two possible attacks by bromide ion on each of the enantiomeric bromonium ions will yield achiral 2,3-dibromobutane, again in perfect accord with the observation of overall trans addition. Once more, the mechanism rigorously does not permit stereochemical leakage, in this case to chiral 2,3-dibromobutane.

\[ \text{E-2-butene and molecular bromine yield only achiral (R,S) 2,3-dibromobutane, in agreement with a bromonium ion mechanism} \]
As a final note, it should be recognized that the addition reaction of bromine to alkenes (trans addition) is stereochemically complementary to the debromination of 1,2-dibromoalkanes with zinc (trans elimination; Segment 13.06).

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