Answer: $\frac{5}{36}$

What we want to knowis the probability that the king and the bishop share a diagonal when randomly placed on the chess board: $\mathbb{P}$(king and bishop share diagonal). This probaility can be computed by conditioning on the position of the king. We do this by dividing the chess board into concentric "square rings". It is easy to see that all squares in a ring have the same number of squares in their diagonals, for example the squares in the outer ring have 7 other squares in their diagonal, and the four squares on the inner ring have 13 other squares on their diagonal. Now we can write:

$$\mathbb{P}(\text{king and bishop share diagonal}) = \sum_i \mathbb{P}(\text{king and bishop share diagonal}|\text{king is on ring i})$$

Since the position of the bishop and the king are independent we can write this as:

$$\sum_i \mathbb{P}(\text{king is on ring i})\mathbb{P}(\text{king and bishop share diagonal})$$

Now by counting the number of squares in each ring, and the size of the diagonals one can easily compute these chance. $\frac{28}{64} \cdot \frac{7}{63} + \frac{20}{64} \cdot \frac{9}{63} + \frac{12}{64} \cdot \frac{11}{63} + \frac{4}{64} \cdot \frac{13}{63} = \frac{5}{36}$