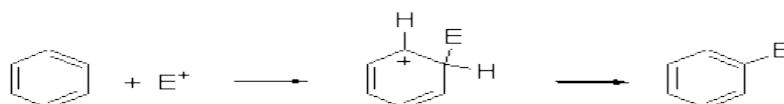


ELECTROPHILIC AROMATIC SUBSTITUTION IS REALLY ADDITION-ELIMINATION

We have all learned about aromatic substitution as proceeding via the following mechanism



(Worse yet – many of us have taught this for years!) Well, Galabov, Zou, Schaefer and Schleyer pour a whole lot of cold water on this notion in their recent *Angewandte* article.¹ Modeling the reaction of benzene with Br_2 and using B3LYP/6-311+G(2d,2p) for both the gas phase and PCM simulating a CCl_4 solvent, attempts to locate this standard intermediate led instead to a concerted substitution transition state **TS1** (see Figure 1).

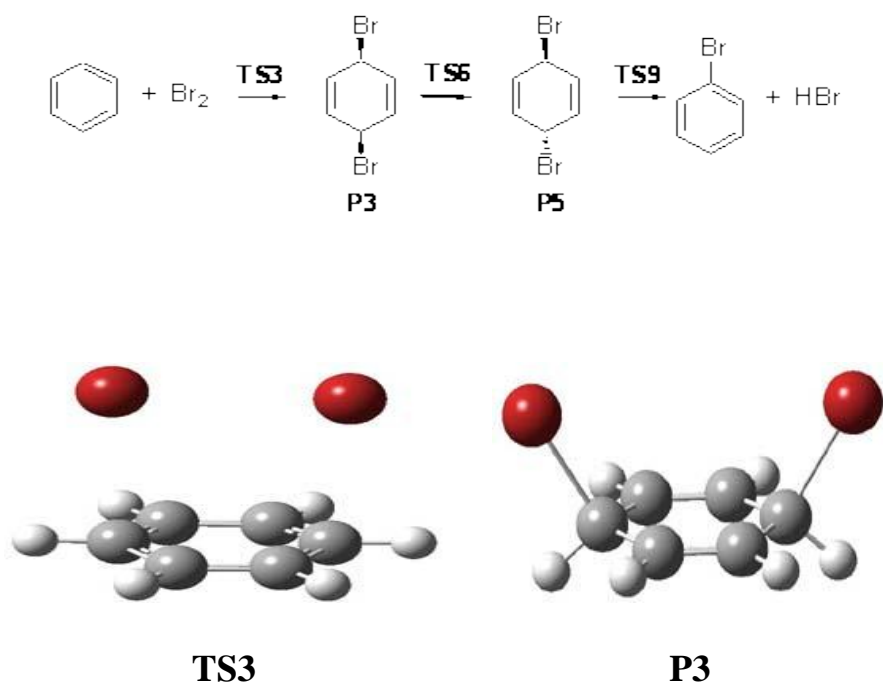


TS1

Figure 1. PCM/B3LYP/6-311+G(2d,2p) optimized transition state along the concerted pathway

However, this is not the lowest energy pathway for substitution. Rather and addition-elimination pathway is kinetically preferred. In the first step Br_2 adds in either a 1,2 or 1,4 fashion to form an intermediate. The lower energy path is the 1,4 addition, leading to **P3**. This intermediate then undergoes a syn,anti-isomerization to give **P5**. The last step is the elimination of HBr from **P5** to give the product, bromobenzene. This mechanism is shown in Scheme 2 and the critical points are shown in Figure 3.

Scheme 1



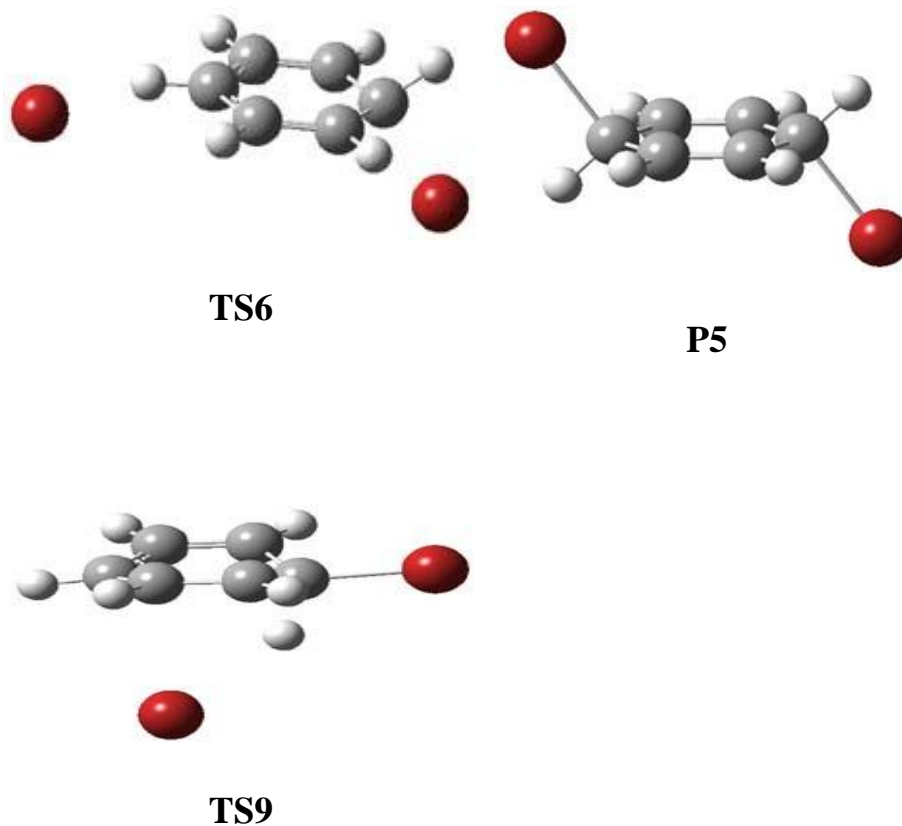


Figure 2. PCM/B3LYP/6-311+G(2d,2p) optimized critical points along the addition-elimination pathway

The barrier for the concerted substitution process through **TS1** is 41.8 kcal mol⁻¹ (in CCl₄) while the highest barrier for the addition-elimination process is through **TS3** of 39.4 kcal mol⁻¹.

Now a bit of saving grace is that in polar solvents, acidic solvents and/or with Lewis acid catalysts, the intermediate of the standard textbook mechanism may be competitive.

Source: <http://comporgchem.com/blog/?p=1757>