

Ch 5, supplemental problems

Occasionally Ouellette lacks enough problems on basic material. One example is simple (one-step) aromatic substitution reactions, Sect 5.5. So here is a set of supplemental problems, to deal with that deficiency. Answers are on the back; you can also turn this in, if you would like.

Please let me know of other topics where such supplemental problem sets would be useful.

⇒ In all questions, show the structure and give the name of all organic compounds requested. For inorganic compounds, show proper chemical formula.

1. Write a balanced equation showing the reaction of 1 mol of bromine with benzene under aromatic substitution conditions (i.e., the slow reaction that occurs in the presence of Fe or FeBr_3).
2. Write a balanced equation showing the reaction of 1 mol of nitric acid, HNO_3 , with benzene under aromatic substitution conditions (i.e., with sulfuric acid catalyst). In such reactions, nitric acid behaves as HO-NO_2 .
3. What is the major organic product if benzene is mixed with Br_2 , under conditions typically used to test for alkenes (Ch 4)?

⇒ In the following group of questions, assume that the conditions allow for typical aromatic substitution reactions.

4. Reaction of bromine with toluene can yield three possible products, each with a single Br. What are they?
5. Reaction of bromine with p-xylene (1,4-dimethylbenzene) can yield only one possible product, with a single Br. What is it?
6. Give the major organic product of reacting benzene with “fuming sulfuric acid”. For this purpose, one can think of sulfuric acid as $\text{HO-SO}_3\text{H}$.
7. Give the major organic product of reacting ethyl chloride with p-xylene, under Friedel-Crafts alkylation conditions (i.e, with AlCl_3).

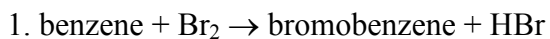
⇒ In the following group of questions, describe how you would make the requested compound in one aromatic substitution step.

8. 2-chloro-1,3,5-trimethylbenzene, from a hydrocarbon of your choice.
9. sec-butylbenzene, from benzene.

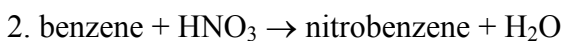
(Answers are on back.)

Answers

I have given the answers for some of these using only names of chemicals, not structures. Of course, you should be able to draw the structures of all the organic reactants and products. If there are cases where the answer key does not seem adequate, please let me know.



The equation shows several key features: Bromine is diatomic, one Br atom replaces one H on the ring, and that H shows up in a small molecule product -- HBr in this case.



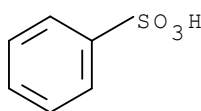
3. no reaction

4. 2-bromotoluene, 3-bromotoluene, 4-bromotoluene. You can also call these o, m, and p, respectively.

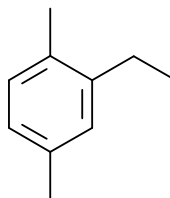
(Later, advanced, parts of the chapter talk about the preference for some of these products, but that is not core material. If you did take it into account, the o and p products would be favored in this case, since the methyl group of toluene is an o,p-directing group. But note that the question asked for three possible products.)

5. 2-bromo-1,4-dimethylbenzene. There is only one possible product because, in p-xylene, all four H on the aromatic ring are equivalent.

6. benzene sulfonic acid



7. 2-ethyl-1,4-dimethylbenzene

8. 1,3,5-trimethylbenzene + Cl₂ → 2-chloro-1,3,5-trimethylbenzene + HCl. (Need catalyst: Fe or FeCl₃)

9. Friedel-Crafts alkylation of benzene, using 2-chlorobutane (sec-butyl chloride).