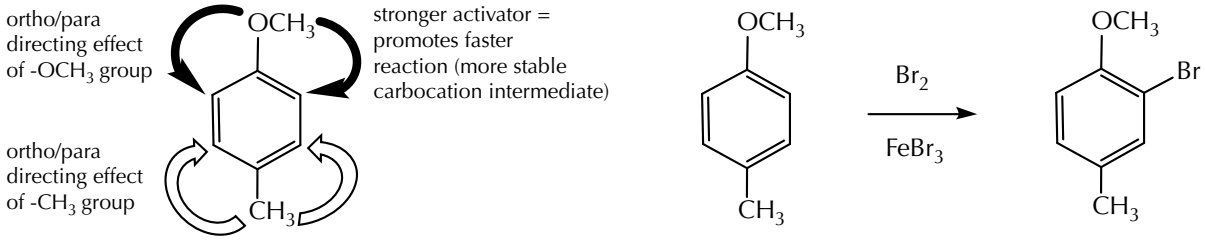
Figure 1054

Electrophilic aromatic substitution: intramolecular competition (directing effects not reinforcing).

1-methoxy-4-methylbenzene



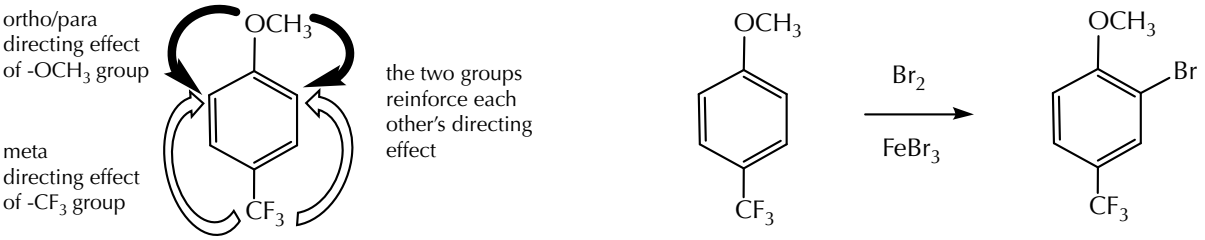
Both of these groups are ortho/para directors. In 1-methoxy-4-methylbenzene, the para position with respect to both of them is blocked, and so the competition is between which of the two possible ortho substitution products is predicted. In the methoxy versus methyl competition, the EAS reaction rates promoted by the methoxy group (a strong activator) are faster than methyl (a mild activator), and so the directing effect of the methoxy group wins out over that of the methyl group, and the 2-bromo product is predicted to be the major isomer over the 3-bromo regioisomer.

Sometimes, the directing effects of two different substituent groups are coincident, reinforcing one another, which makes predicting the outcome easier. The reaction of 1-(trifluoromethyl)-4-methoxy-benzene with bromine with ferric bromide is a nice contrast to the reaction with 1-methoxy-4-methylbenzene (Figure 1055).

Figure 1055

Electrophilic aromatic substitution: intramolecular competition (directing effects reinforcing).

1-(trifluoromethyl)-4-methoxybenzene



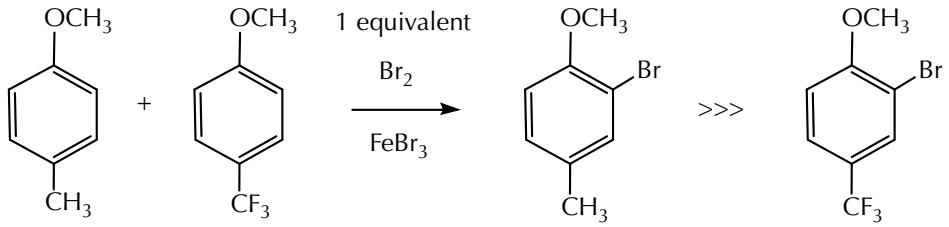
The methoxy group is still a strong activator and ortho/para director, and the trifluoromethyl group is a mild deactivator and a meta director. In this case, both of the substituent groups are directing the in-coming electrophile to the same position on the ring, and the 2-bromo product is anticipated.

Another question for an intermolecular comparison might be: How do the relative rates of these two bromination reactions compare? Is the bromination of 1-(trifluoromethyl)-4-methoxy-benzene faster or slower than that of 1-methoxy-4-methylbenzene?

Both molecules carry the methoxy group, and so the difference is between the EAS reaction rate effect of a methyl group and a trifluoromethyl group (Figure 1056).

Figure 1056

Electrophilic aromatic substitution: intermolecular competition (disubstituted rings).



plus unreacted starting materials