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Most of the answers for this chapter in the back of the book are adequate. Only those needing further clarification are listed here.

**16-13** The point of this exercise is to get you used to seeing symmetry in molecules. When symmetry is present atoms become identical. Can you find the planes of symmetry present in the three dibromobenzenes?

**16-16** Because the nitro group and the sulfonic acid group are meta directors, it does not matter which first place on the benzene.

**16-19** Note that Friedel-Crafts alkylation will not work as rearrangement will occur, resulting in a tertiary carbocation.

**16-20** Note that the nitro group is sufficiently deactivating so that Friedel-Crafts alkylation and acylation do not occur on benzene rings with this substituent present.

**16-25** Note that deactivating groups direct substitution to the ring NOT bearing the substituent whereas activating groups direct substitution to the same ring. When an activating group is present on one ring and a deactivating group is on the other ring, reaction occurs on that ring bearing the activating group. However, the basic preference of the naphthalene ring for substitution at C1 (and C4, C5, and C8 when other substituents are present) remains.

- a) With a nitro group on one ring, substitution occurs on the other ring and follows the preference of naphthalene for substitution next to the bridgehead carbons (C5 & C8). This is the case for both 1- and 2-nitronaphthalene.
- b) With a nitro group on one ring and a methoxy on the other, substitution occurs on the ring bearing the activating substituent. Here, the powerfully activating methoxy group overwhelms the bias of the naphthalene itself and substitution occurs at C5 and C8, ortho and para to the methoxy group.
- c) With two tertiary butyl groups present at C1 and C6, substitution is sterically blocked at C2, C5, C7, and C8. Of the remaining carbons, only C4 is activated by the alkyl group at C1.

An alternate way of approaching this problem is to realize that in the intermediate cation formed in addition of an electrophile to naphthalene, there will be little delocalization of the cation into the other ring as that will lead to loss of aromaticity of BOTH rings. Substitution at C1 affords an allylic cation whereas that at C2 does not.

