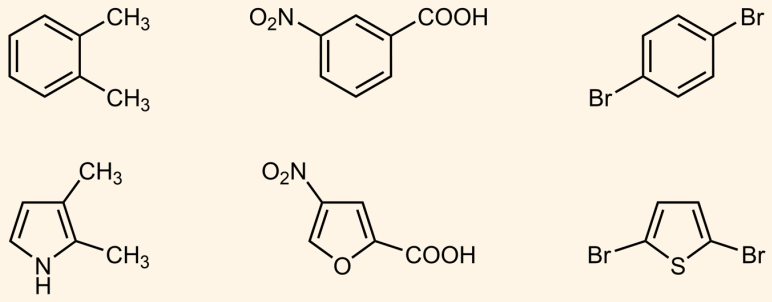
CONCEPT: DIRECTING EFFECTS IN SUBSTITUTED PYRROLES, FURANS, AND THIOPHENES

o, *m*, *p* in 5-Membered Heterocycles

- *Ortho*, *meta*, and *para* terms are limited to substituted benzene rings.
  - □ However, _____ numerical relationships exist for 5-membered aromatic heterocycles.

Relative Substituent Positions



- Substituent relative positions are assigned through the ___ skeleton, not through the _____.

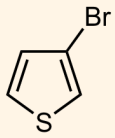
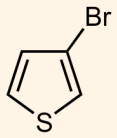
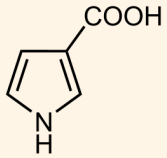
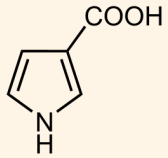
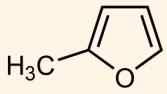
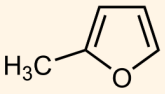
Directing Effects in Substituted Pyrroles, Furans, and Thiophenes

Directing Groups

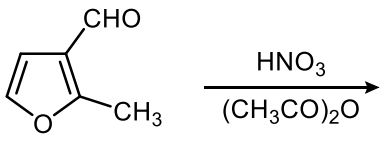
ortho/*para*	*meta*
—N:	—NO_2
—O:	—NR_3^+
—N=O	—SO_3H
—R	—CN
—X	—C=O

- **RULE 1:** Directing effects are the same as EAS on benzene rings (__/__/__).
  - □ **Recall:** For disubstituted rings, the most _____ group takes precedence.
- **RULE 2:** C__ substitution is always preferred.

EAS Directing Effects

Reactant	Reagents	Directing Effect	Product
	Br_2 / CH_3COOH	Br → ___ S → ___	
	HNO_3 / CH_3COOH	COOH → ___ N → ___	
	SO_3 / Pyridine	CH_3 → ___ O → ___	

EXAMPLE: Nitration of the following compound gives a single product. Draw the structure of that product.



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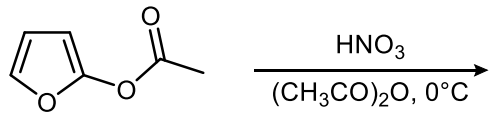
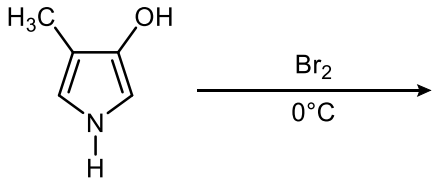
PRACTICE: Write a mechanism for the formation of the mononitrated product of the following reaction.



PRACTICE: Predict the product of the following EAS reaction.



PRACTICE: How can the following compound be synthesized using benzene as the starting material?