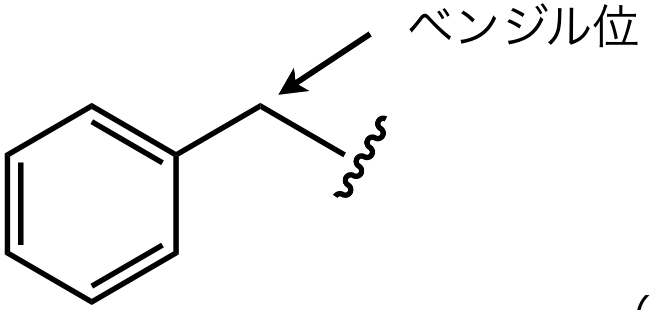
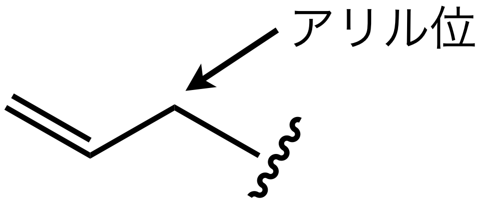
★★★

ベンジル化合物の反応

復習ポイント！
アリル化合物の特性

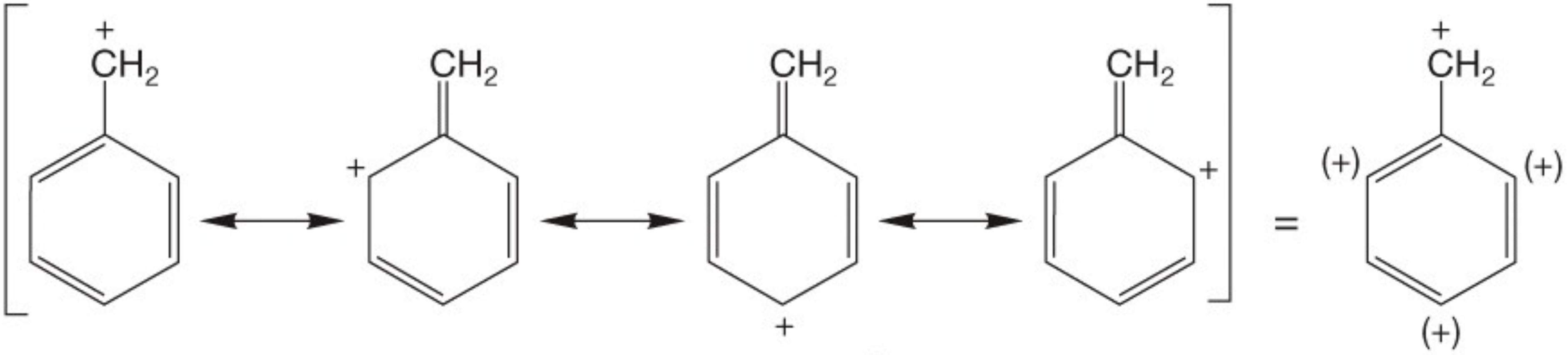
ベンジル基（PhCH$_2$–）を有する化合物はベンジル位で特別な反応性を示す





（アリル基（CH$_2$=CH–CH$_2$–）と似た挙動）

例えば、ベンジルカチオンはとても安定



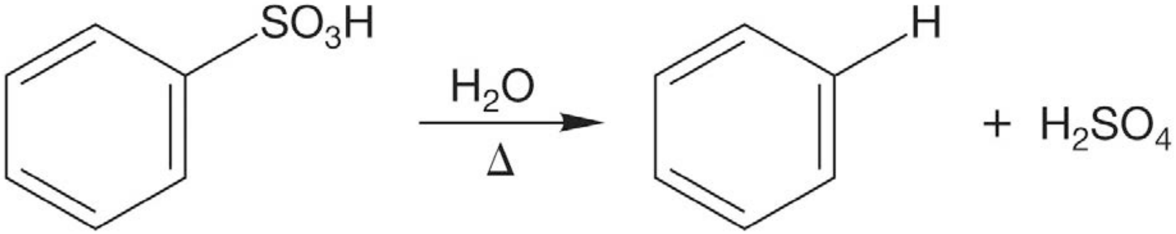
The benzyl cation—4 resonance forms

共鳴構造において、正電荷を帯びている
ベンゼン環上の炭素を(+)で示した

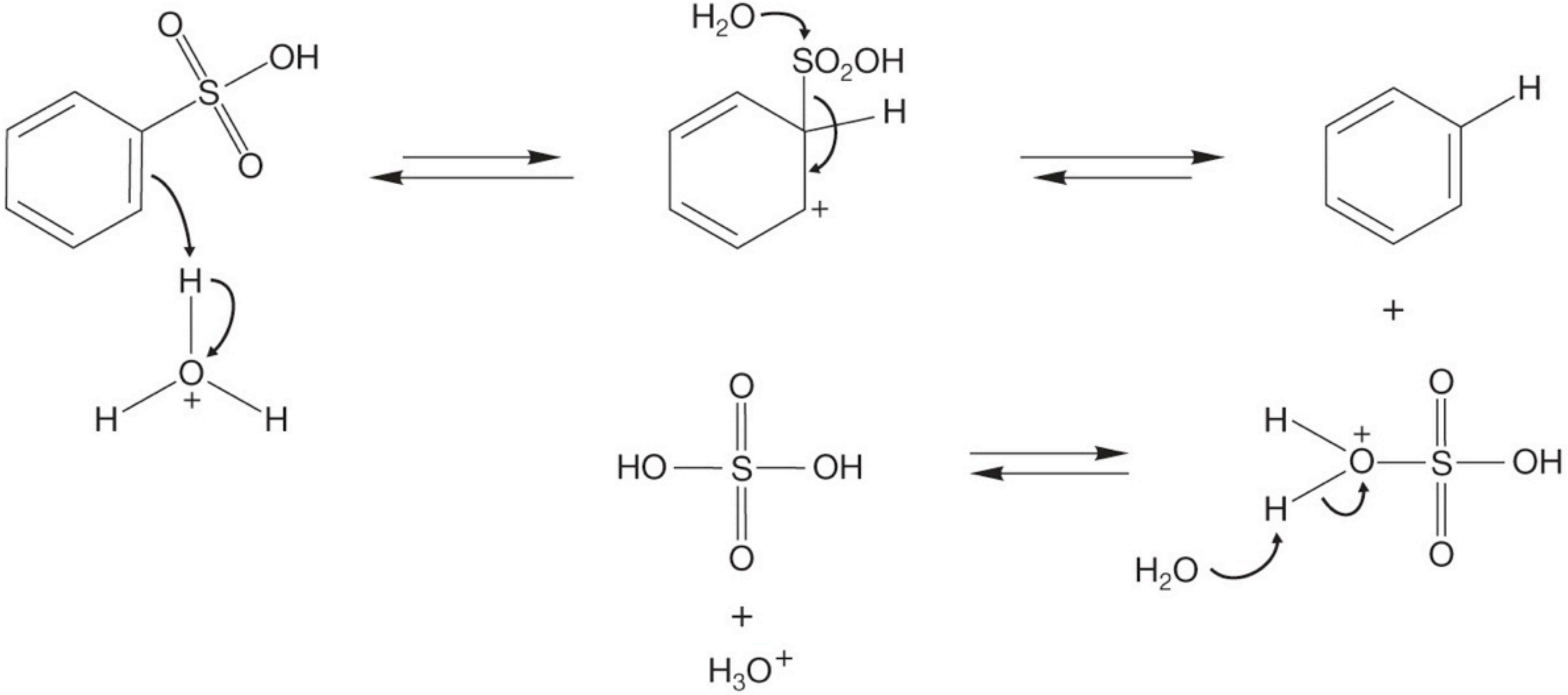
芳香族求電子置換反応の具体例

スルホン化は可逆：高温条件下で水と反応させると逆反応が進む

つまり、ベンゼンスルホン酸を熱水蒸気にさらすと、ベンゼンができる



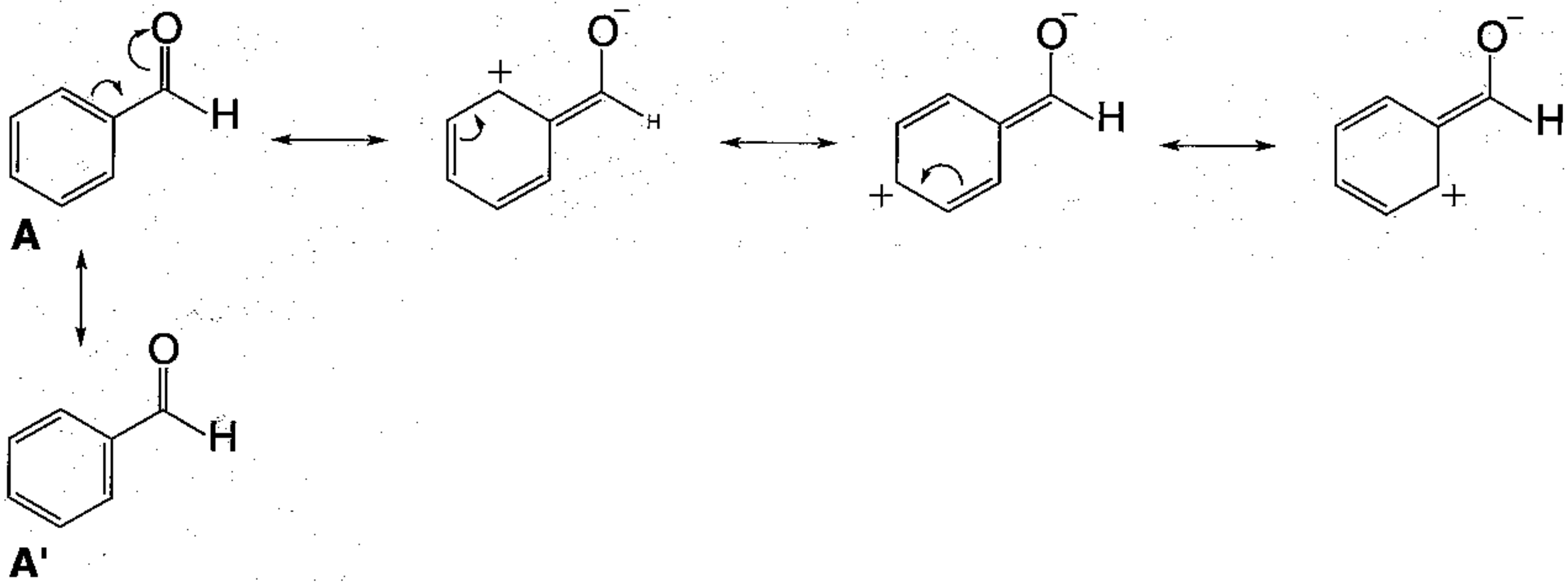
これも芳香族求電子置換反応の一種　　**反応機構を考えてみよう**



解答

1. benzaldehydeの共鳴構造式を示せ

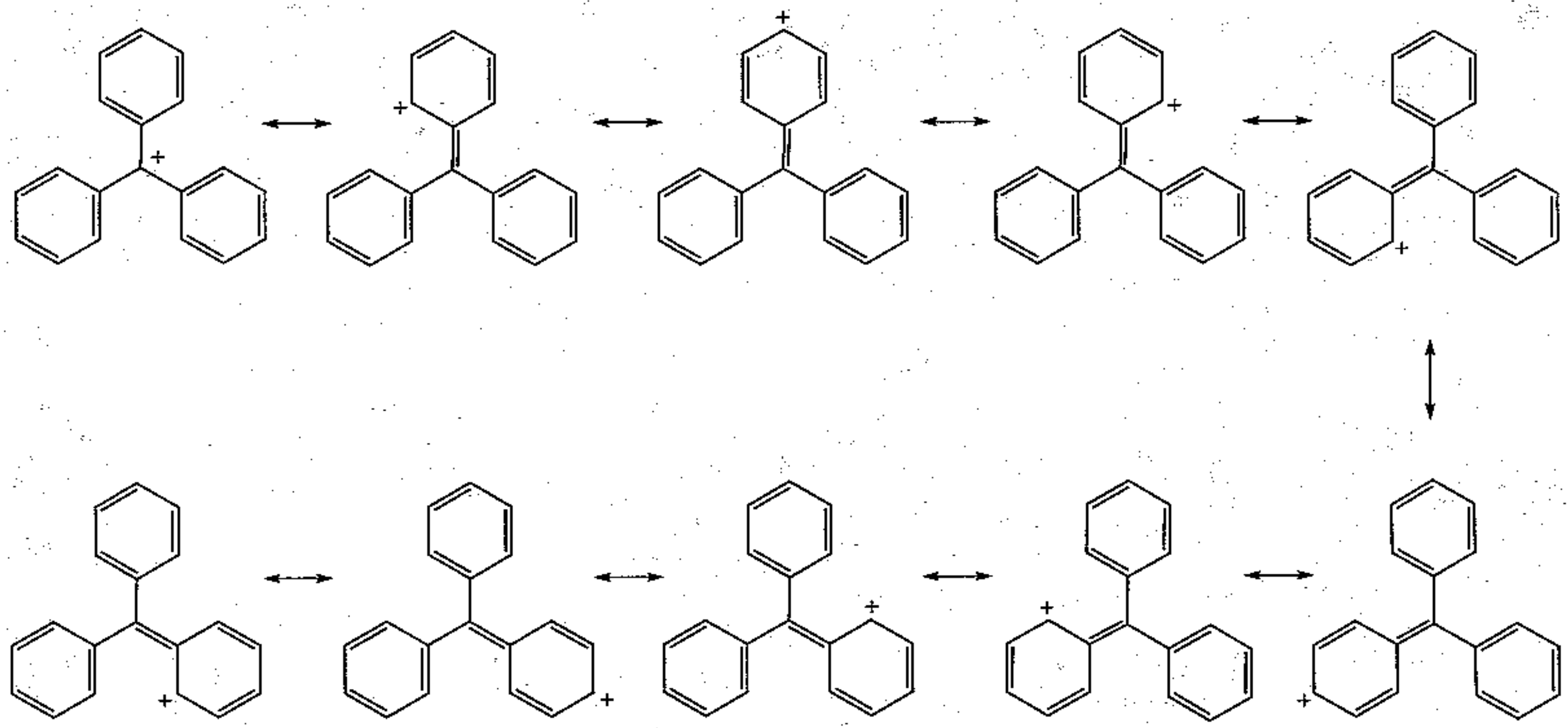
There are three contributing resonance structures of benzaldehyde (**A**) that introduce charge into the structure. There is one resonance structure (**A′**) that simply moves the aromatic ring double bonds. The important point is to recognize that the carbonyl group of benzaldehyde can withdraw electrons from the aromatic ring by resonance.



解答

2. trityl cationの共鳴構造式を示せ

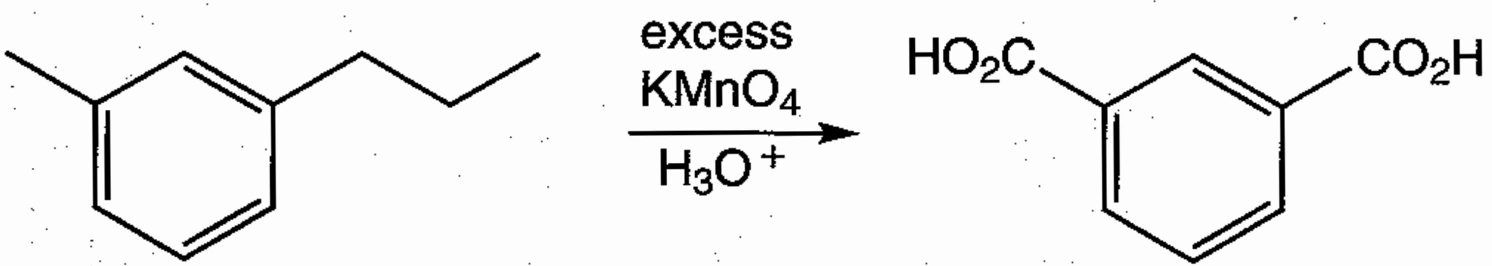
These are the 10 resonance structures that have the cation on different carbons. If you want to show resonance structures that just move the double bonds around the rings, then there are at least 30 more representations!



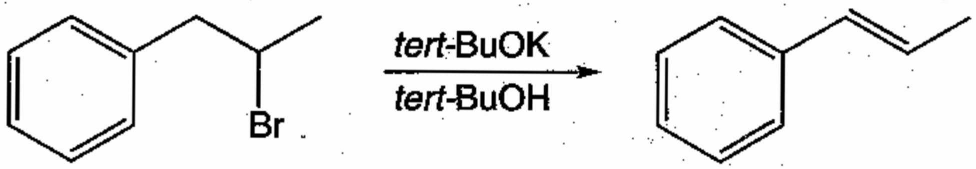
解答

3. 次の反応生成物は何か

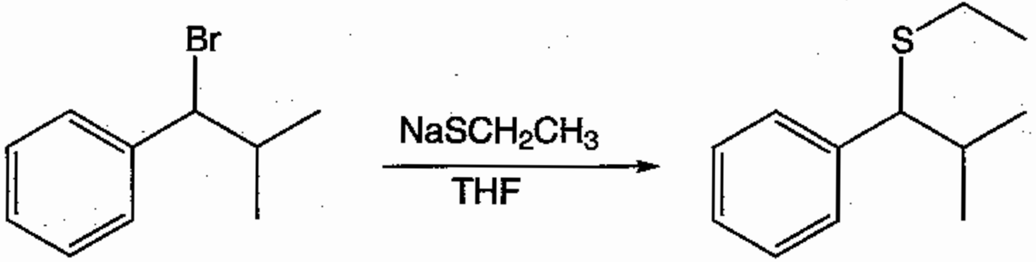
(a) Potassium permanganate oxidizes the alkyl side chains of an aromatic ring as long as there is at least one benzylic hydrogen.



(b) This reaction is a bimolecular elimination (*E*2). The major product is (*E*)-1-phenylpropene because it is the more stable product and therefore has a lower transition state leading to it. There might be a minor amount of the (*Z*) isomer and perhaps 3-phenylpropene.



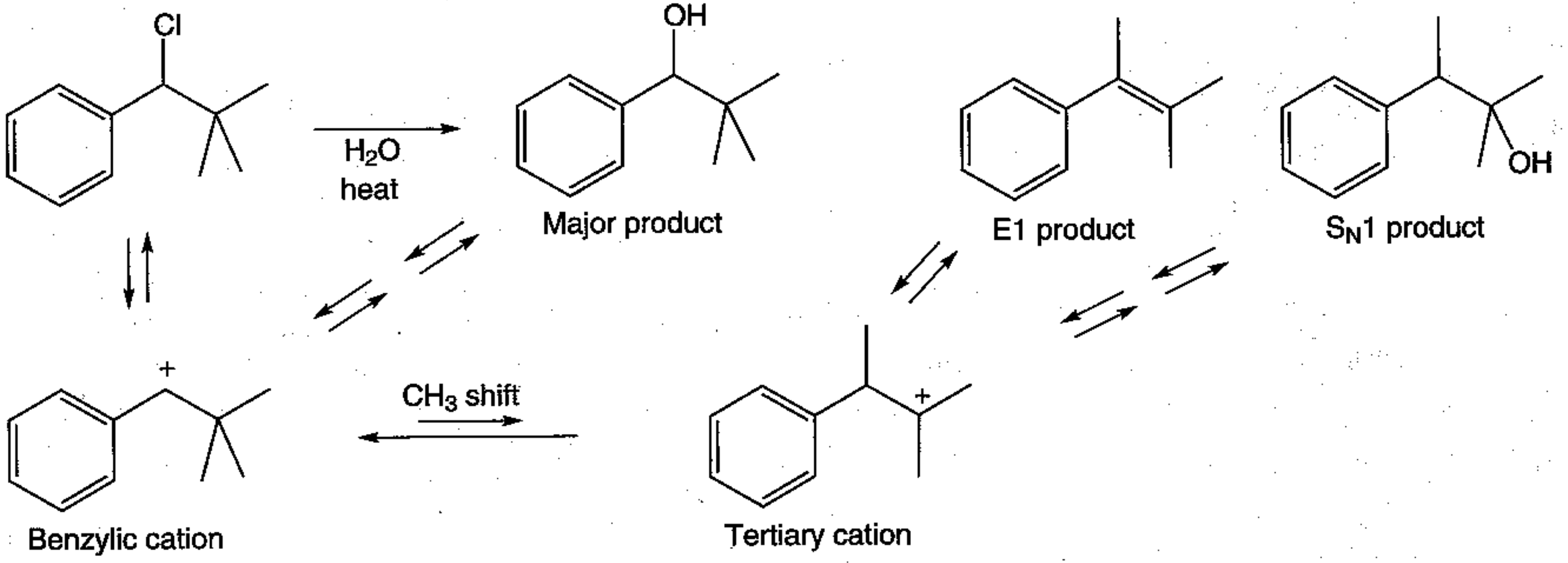
(c) This reaction is an S_N2 process. The reaction would presumably go with inversion.



解答

3. 次の反応生成物は何か

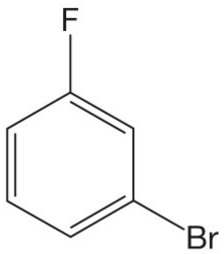
(d) This reaction is an S_N1 solvolysis. The relatively stable benzylic cation will be formed when the chloro group leaves. The water can be added in an S_N1 reaction and then be deprotonated to produce the major product. Rearrangement of the benzylic cation will not be favored because the methyl shift would give the less stable tertiary cation. Once the tertiary cation is formed, the E1 and S_N1 pathways will compete.



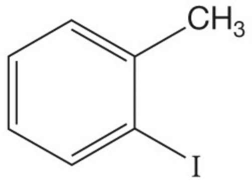
解答

4. 次の化合物を命名せよ

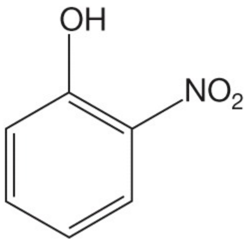
(a)



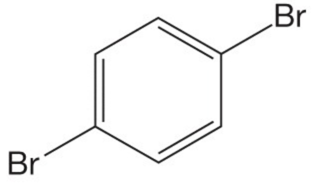
(b)



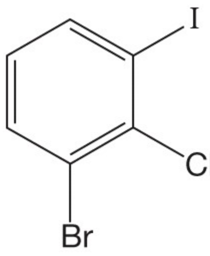
(c)



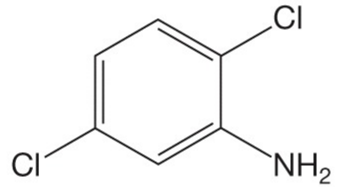
(d)



(e)



(f)



(a) *m*-bromofluorobenzene or 1-bromo-3-fluorobenzene

(b) *o*-iodotoluene or 2-iodotoluene

(c) *o*-nitrophenol or 2-nitrophenol

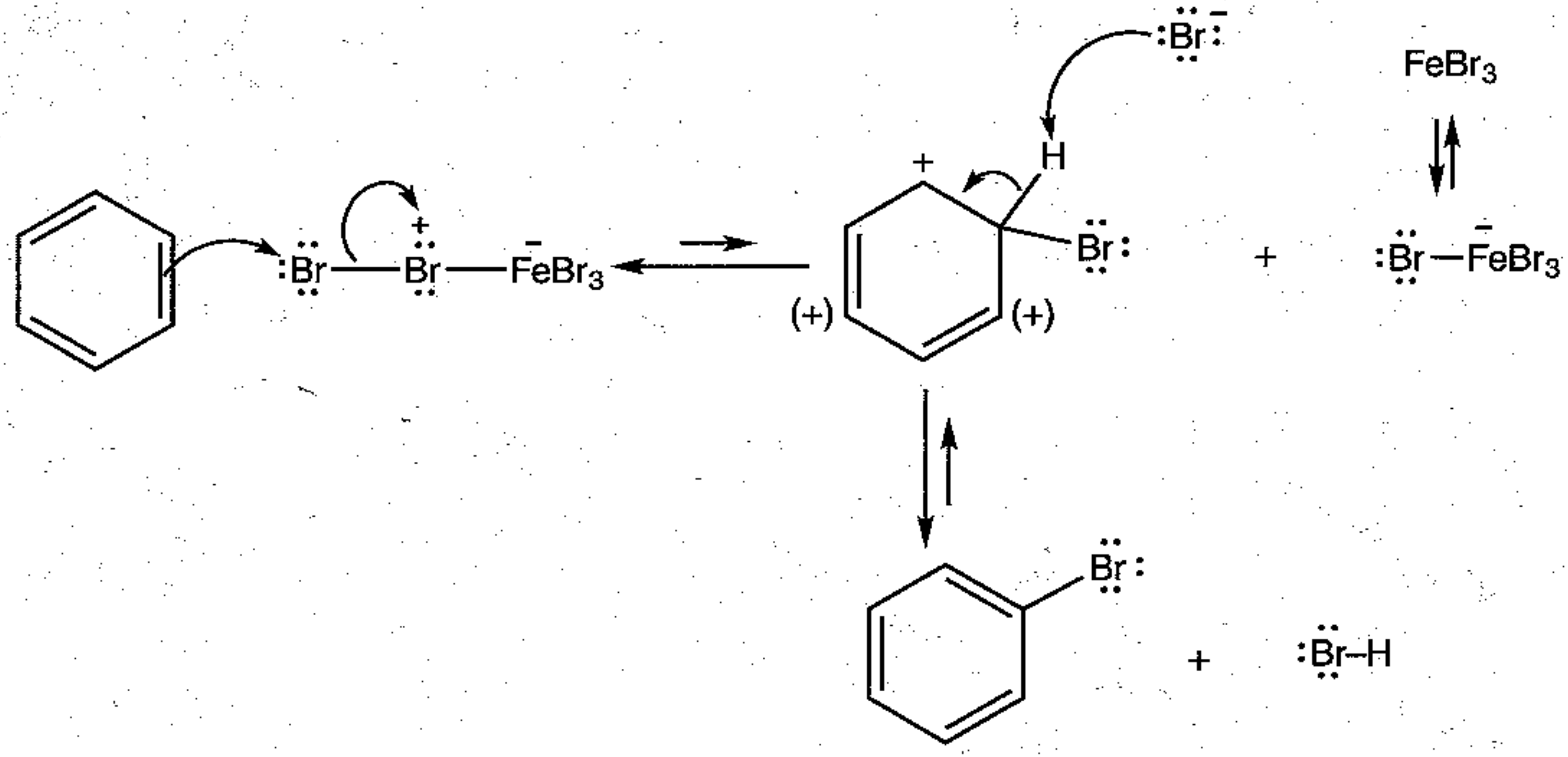
(d) *p*-dibromobenzene or 1,4-dibromobenzene

(e) 1-bromo-2-chloro-3-iodobenzene

(f) 2,5-dichloroaniline

解答

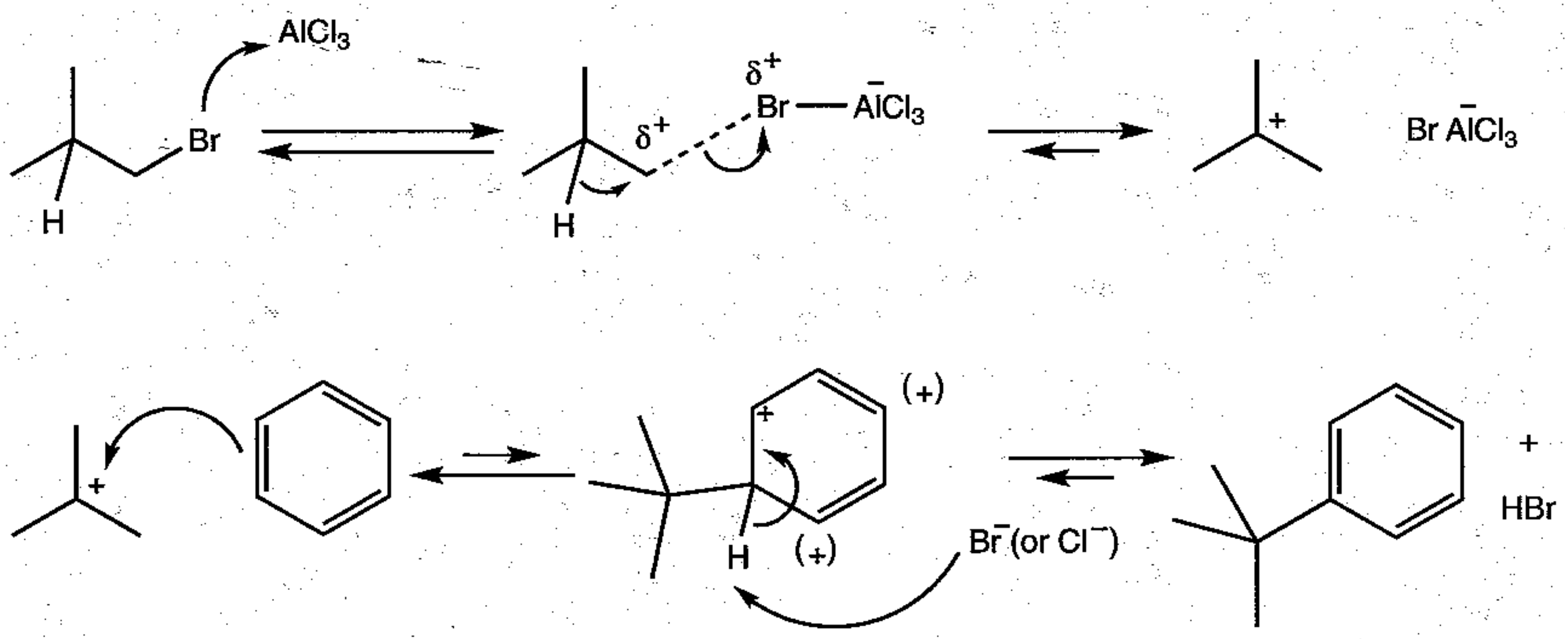
5. Br2とFeBr3を用いるbenzeneの臭素化の反応機構を示せ。



解答

6. 1-bromo-2-methylpropane、benzene、AlCl3を用いることで、tert-butylbenzeneを合成することができる。その反応機構を示せ。

tert-Butylbenzene will be the product whenever the *tert*-butyl cation is formed in the presence of benzene. Aluminum chloride forms a complex with the alkyl bromide that has partial positive charge on a primary carbon. A hydride shift in this complex produces the much more stable tertiary carbocation. Standard electrophilic substitution of benzene leads to *tert*-butylbenzene.

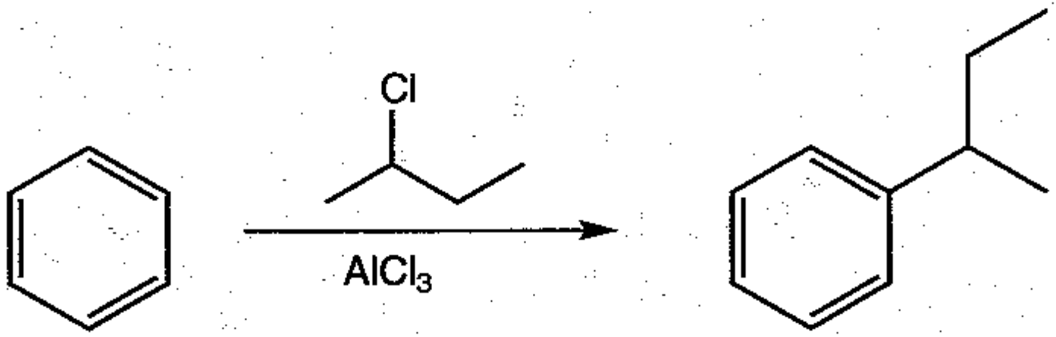


解答

7. 次の反応生成物は何か

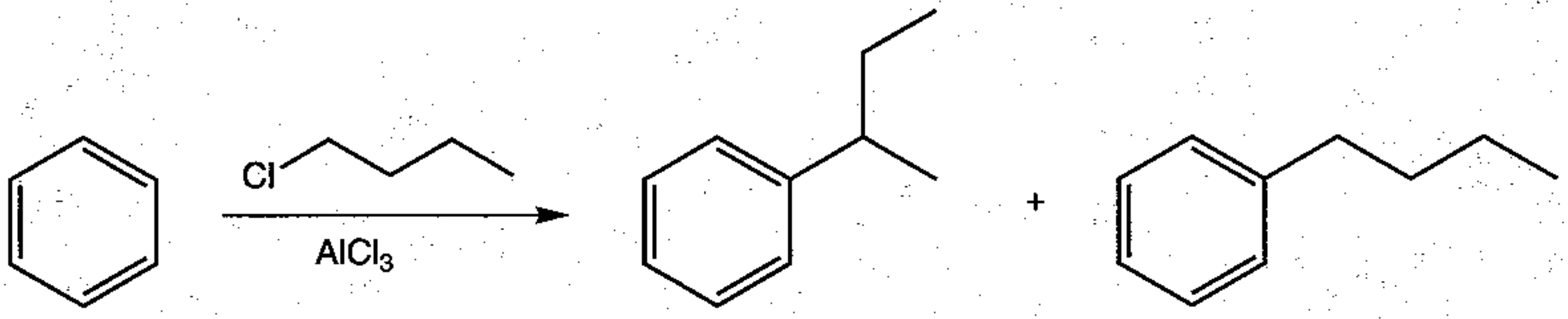
These are Friedel–Crafts alkylations. There is potential for polysubstitution in each case. If benzene is used as the solvent, the monosubstituted aromatic ring will be the major product.

(a) This reaction gives 2-phenylbutane.



2-Phenylbutane

(b) This time there will be rearrangement. We don't know which product will be major, but it is likely to be 2-phenylbutane.

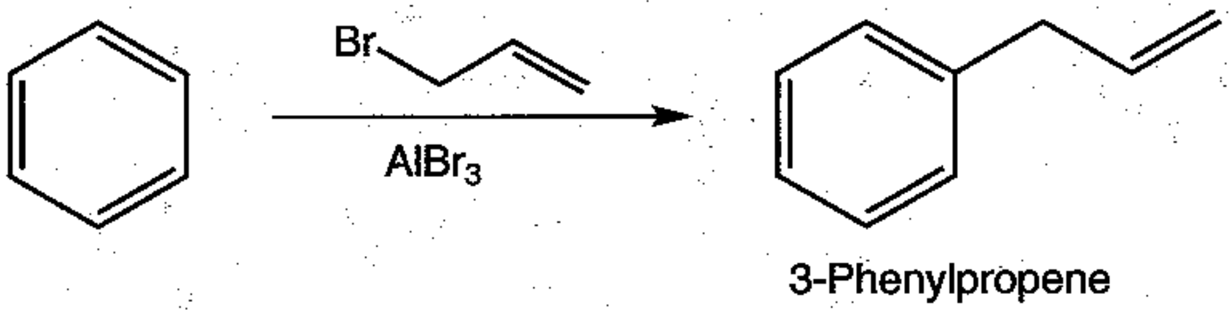


2-Phenylbutane 1-Phenylbutane

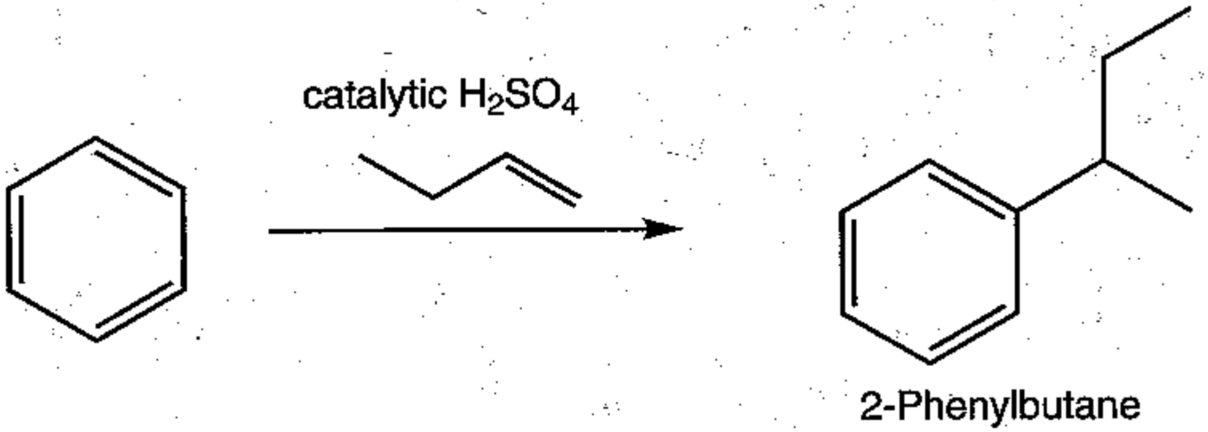
解答

7. 次の反応生成物は何か

(c) Alkyl bromides can also be used in Friedel–Crafts alkylations. The major product would be 3-phenylpropene. If benzene is not the solvent, polypropylene might be the major product.



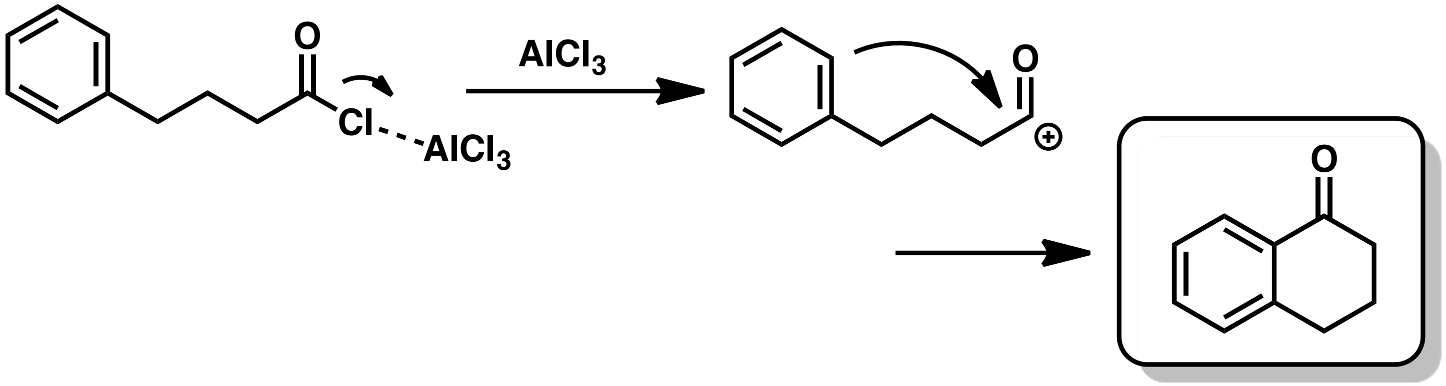
(d) This reaction also gives 2-phenylbutane. The alkene would react with the acid (Chapter 3) to give the *sec*-butyl cation, which would react with the benzene solvent. If benzene is not the solvent, then polybutylene would likely be the major product.



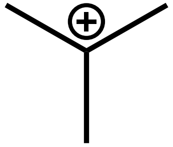
解答

8. 次の反応生成物は何か

(a)



(b)　付加反応の時と同様の反応が起こり、中間体として



が発生、ベンゼンとの間で芳香族求電子置換反応