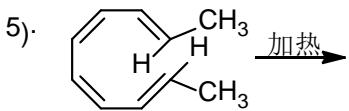
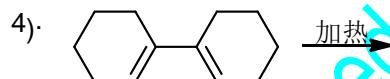
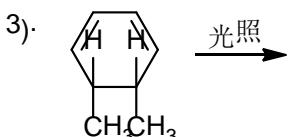
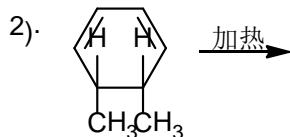
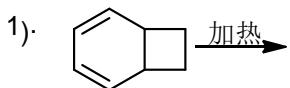
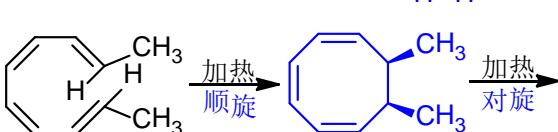
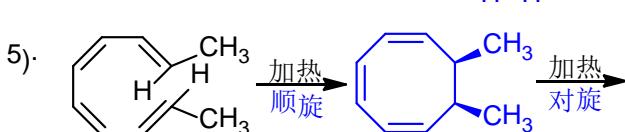
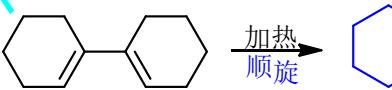
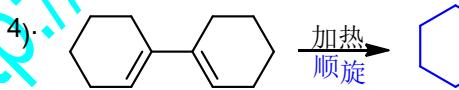
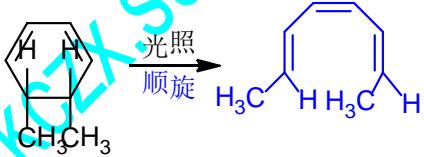
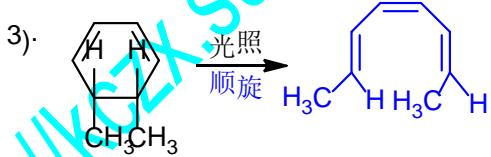
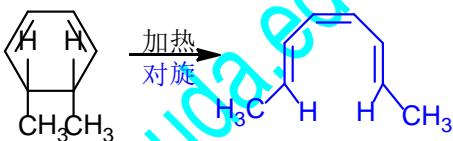
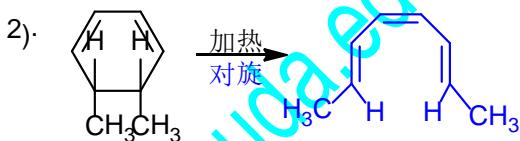
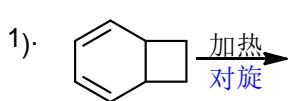


第十七章 周环反应

1. 推测下列化合物电环化时产物的结构:

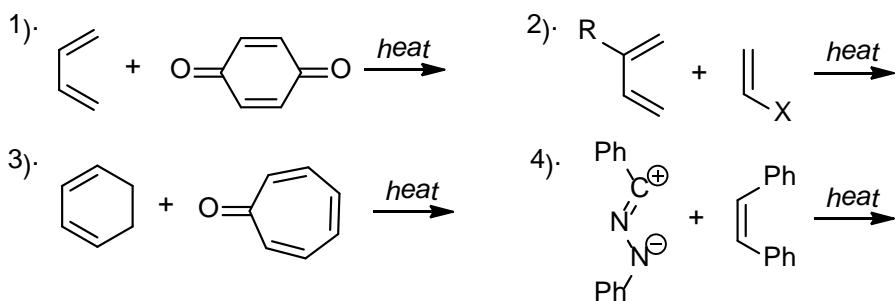


解答:

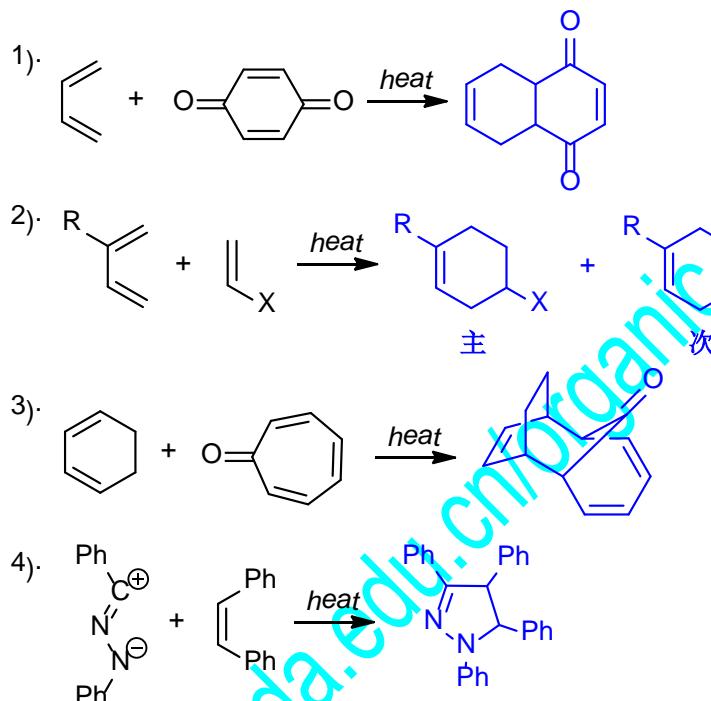


加热 对旋

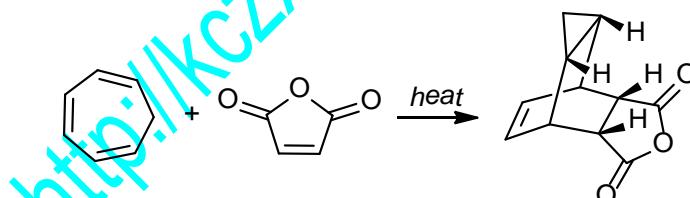
2. 推测下列化合物环加成化时产物的结构:



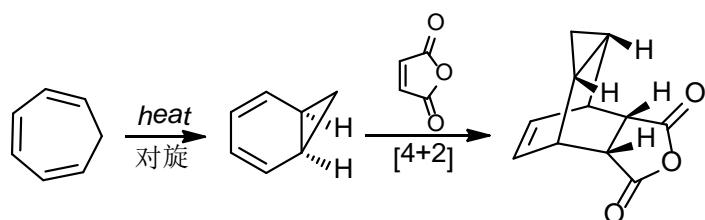
解答:



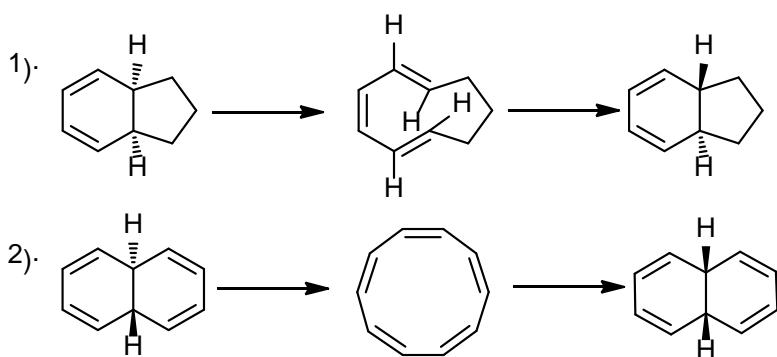
3. 马来酸和环庚三烯反应的产物如下，请说明这个产物的合理性。



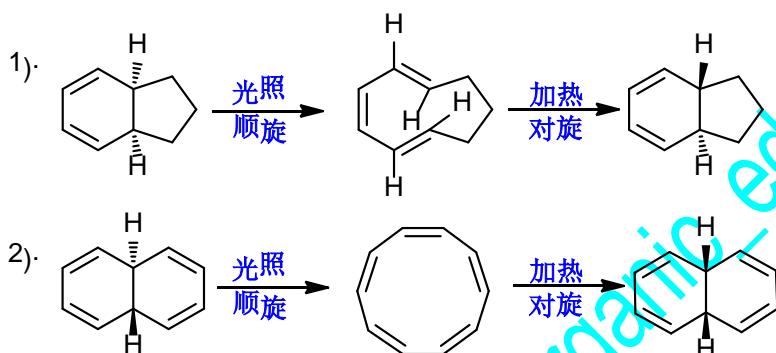
解答:



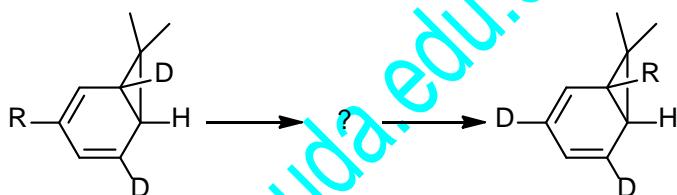
4. 指出下列反应过程所需的条件:



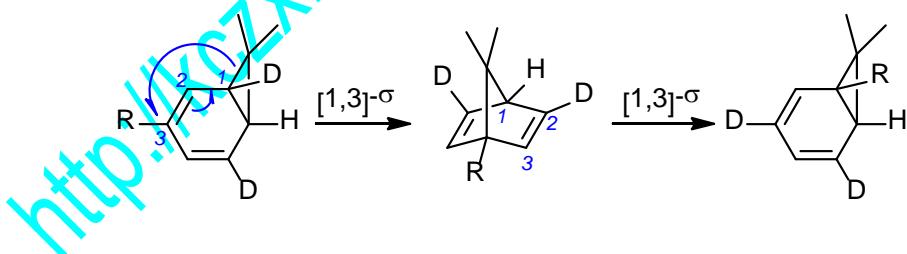
解答:



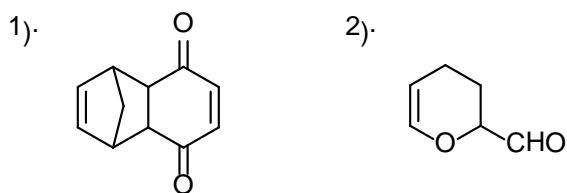
5. 说明下列反应从反应物到产物的过程:



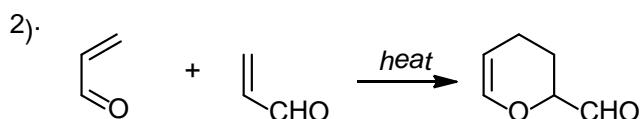
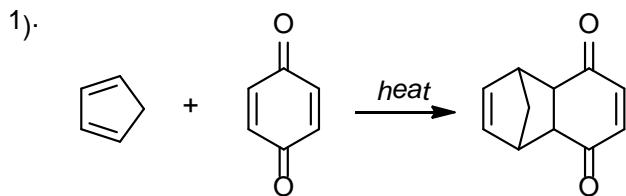
解答:



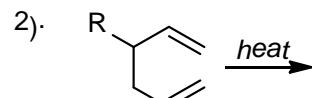
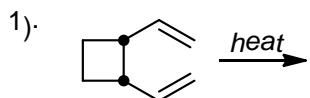
6. 自选原料通过环加成反应合成下列化合物:



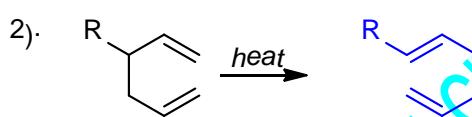
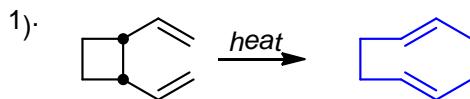
解答:



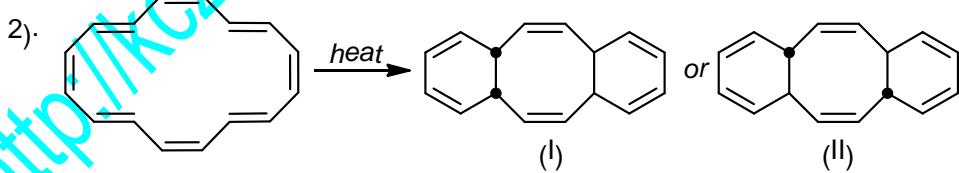
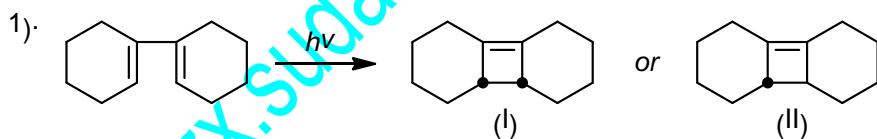
7. 加热下列化合物会发生什么样的变化:



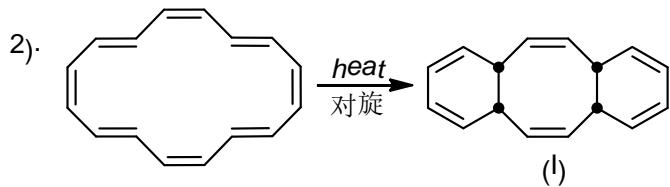
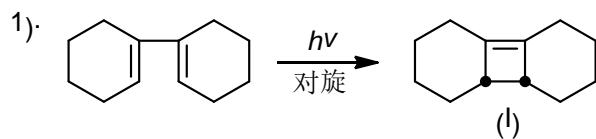
解答:



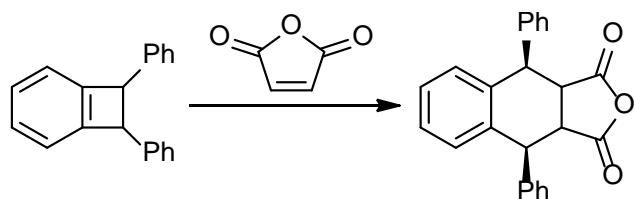
8. 下列的反应按光化学进行时, 反应产物可得到哪一种.



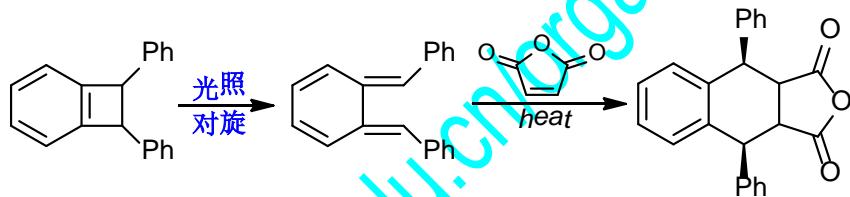
解答:



9. 通过怎样的过程和条件，下列反应能得到给出的结果：



解答：



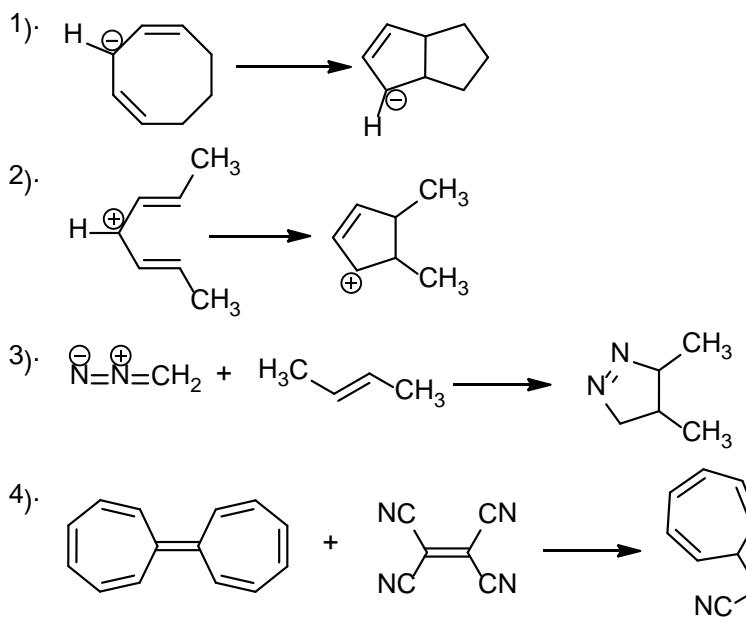
10. 通过什么办法把反-9,10-二氢萘转化为顺-9,10-二氢萘：



解答：

同第四题第二小题。

11. 确定下列反应在加热反应时所涉及的电子数：

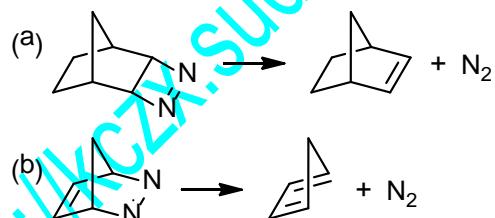


解答:

1). 6e; 2). 4e; 3). 6e; 4). 16e.

12. 解释下列现象:

- 1). 在荻尔斯-阿尔德反应中, 2-叔丁基-1,3-丁二烯的反应速率比 1,3-丁二烯快得多。
- 2). 在-78°C 时, 下边的反应(b)比反应(a)快 10^{22} 倍。



- 3). 化合物  重排成甲苯时放出大量的热, 但它本身却相当稳定。

解答:

- 1). 在荻尔斯-阿尔德反应中, 1,3-丁二烯为双烯体。研究表明, 双烯体上连接给电子取代基时, 可以提高其 HOMO 轨道的能量, 从而使 HOMO 轨道与亲双烯体的 LUMO 能量更加接近, 反应速率加快。
- 2). 反应(a)属于环加成[2+2]的逆反应, 而反应(b)属于环加成[4+2]环加成的逆反应。根据前线轨道理论, [2+2]环加成的热反应是禁阻的, 而[4+2]

环加成的热反应是允许的。因此，(b)的反应速率要比反应(a)的快很多。

3). 化合物为线性共轭多烯，不具有芳香性，分子的能量水平要比芳香分子甲苯的高，因此它重排成甲苯时会释放大量的热量。另一方面，该烯烃重排成甲苯时，主要通过分子内[1,3]或[1,7]- σ 迁移反应来实现的。根据 σ 迁移反应的轨道对称性原理，[1,3]或[1,7]- σ 同面迁移属于禁阻反应，异面迁移则会受到分子的环状结构的限制，因此，该重排反应的活化能很高，所以化合物本身相当稳定。

http://kczx.suda.edu.cn/organic_edu.html