



52<sup>nd</sup> IChO 2020  
International Chemistry Olympiad

Istanbul, Turkey

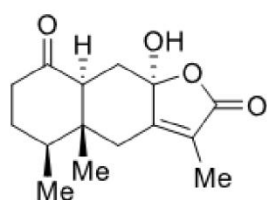
CHEMISTRY FOR A BETTER TOMORROW

## 2-masala:

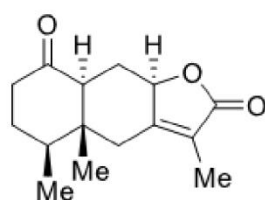
### Istanbulinlar va ularga yaqin boʻlgan Seskviterpen tabiiy birikmalar.



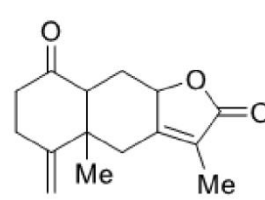
Baʼzi bir elementlar dunyoning turli joylari nomi bilan atalgan. Bu borada Shvetsiyaning Itterbiy qishlogʻiga hech qaysi joy teng kelolmaydi, 4 ta element uning nomi bilan atalgan: itterbiy (Yb), ittriy (Y), erbiy (Er) va terbiy (Tb). Biroq turli joylarning nomlari faqatgina elementlarning ismida oʻz aksini topibgina qolmaydi. Shunday qiziq hodisalardan biri Istanbul shahri nomi bilan atalgan **istanbulin A-E** tabiiy birikmalar sinfidir. Ushbu sinfning dastlabki ikki aʼzosi, istanbulin A va B, birinchi boʻlib 1971-yilda Prof. Dr. Ayhan Ulubelen va uning jamoasi tomonidan *Smyrniium olusatrum* oʻsimligidan ajratib olingan. Sinfning boshqa vakillari, istanbulin C-E lar, 1979 va 1982-yillarda Ulubelen va uning jamoasi tomonidan ajratib olindi.



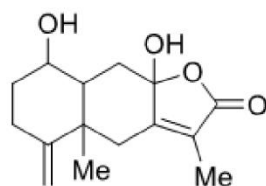
Istanbulin A



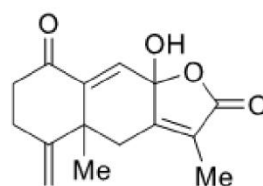
Istanbulin B



Istanbulin C



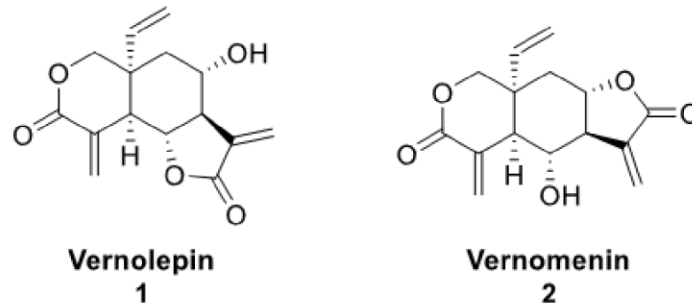
Istanbulin D



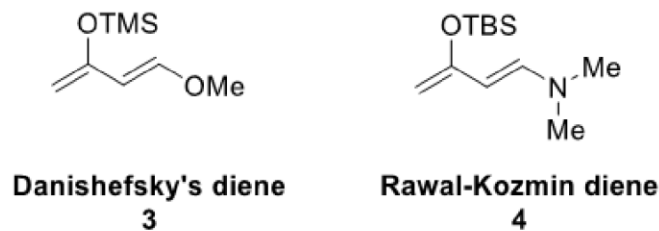
Istanbulin E

Istanbulinlar seskviterpenlar deb nomlanuvchi tabiiy birikmalar oilasining vakillari hisoblanishadi. Seskviterpenlarning muhim ikki vakili o`xshash 6-6-5 kondensirlangan sikllardan iborat vernolepin (1) va vernomenin (2) lar hisoblanishadi. 1976-yilda Danishefskiy va uning jamoasi Danishefskiy dienini Dils-Alder reaksiyasi kiritirish orqali ushbu ikki tabiiy birikmani to`liq sintez qilishga muvaffaq bo`lishganligini e`lon qilishdi.

Ushbu masalada keltirilgan barcha xiral molekularlar rasemik aralashma sifatida qaralsin.

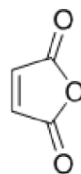


Quyida organik sintezda keng qo`llaniluvchi ikkita elektronga boy bo`lgan dienlar, Danishefskiy dieni (3) va Raval-Kozmin dieni (4), keltirilgan.



TMS: trimethylsilyl; TBS: *tert*-butyldimethylsilyl

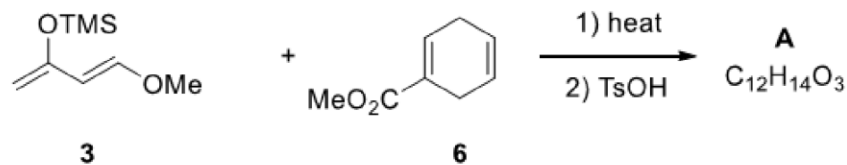
- 3 va 4 dienlarning asosiy rezonans strukturalarini chizing. Har bir dienda yuqori elektron zichlikka ega bo`lgan uglerod atomlarini belgilang.
- 3 va 4 birikmalar Dils-Alder reaksiyalarida dien sifatida juda ko`p qo`llaniladi. 3 va 4 larning Dils-Alder reaksiyasiga kirisha oladigan konformatsiyalarini chizing. Qaysi dien malein anhidridi (5) bilan Dils-Alder reaksiyasiga kirishishga moyilroq ekanini bashorat qiling.



maleic anhydride  
5

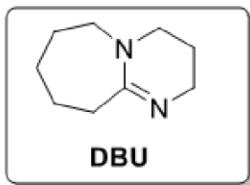
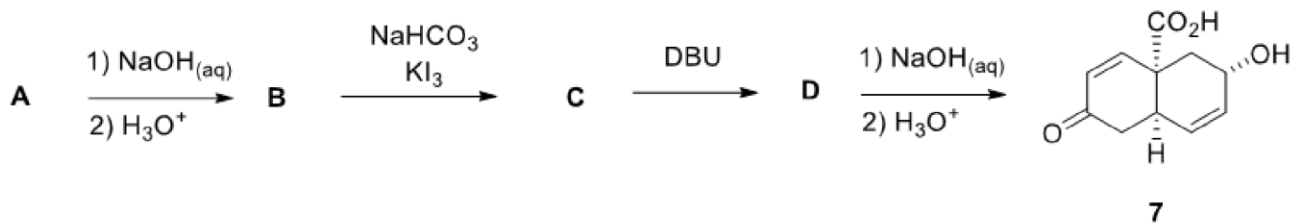
- Danishefskiy dieni (3) va 6 birikma aralashmasi qizdirilganida va ketidan kislota (TsOH, *p*-toluolsulfonat kislota) bilan ishlov berilganda asosiy mahsulot sifatida A birikma hosil bo`ladi. 3 va 6 o`rtasidagi Dils-Alder reaksiyasidan hosil bo`lishi mumkin bo`lgan C<sub>12</sub>H<sub>14</sub>O<sub>3</sub>

formulali barcha moddalarning strukturalarini chizing. Agar enantiomerlar juftligi paydo bo'lsa, ulardan faqat bittasini chizing.

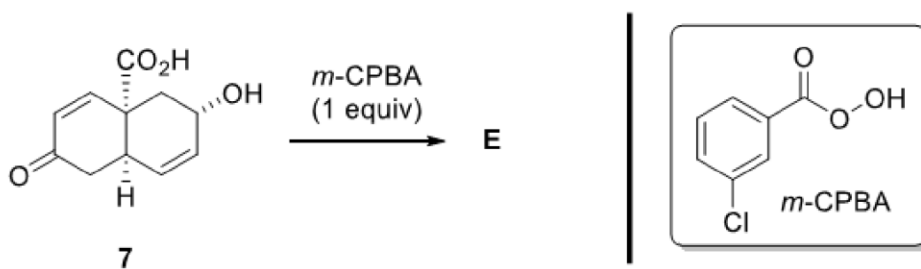


4. Asosiy mahsulot **A** ning strukturasini aniqang.

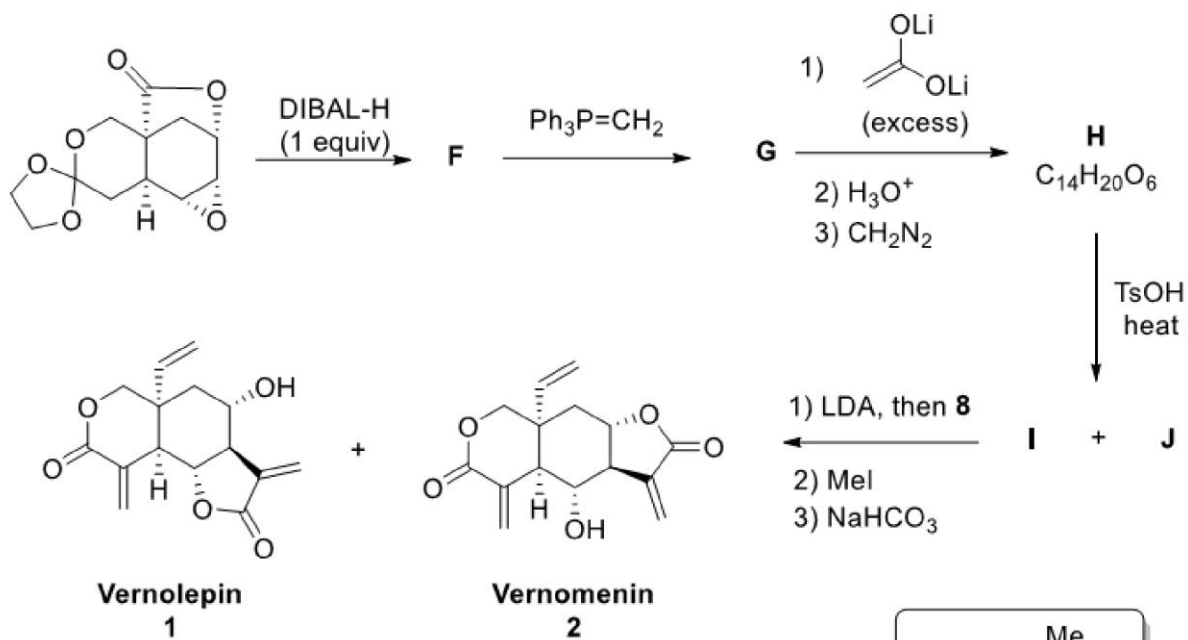
5. Dils-Alder addukti **A** quyida keltirilgan 4 ta bosqichda **7** birikmaga aylantirildi. **B** ning kislotali qobiliyati ma'lum. **B-D** strukturalarini chizing.



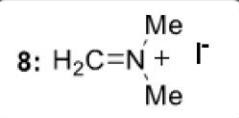
6. **7** birikma 1 ekvivalent *m*-CPBA bilan reaksiyaga kirishsa, asosiy mahsulot sifatida **E** hosil bo'ladi. *m*-CPBA bilan selektiv reaksiyaga kirishuvchi funksional guruhni ko'rsating va **E** ning strukturasini chizing.



7. Vernolepin (**1**) va vernomenin (**2**) larning sintezi quyidagicha yakunlangan. **F-J** birikmalarning strukturalarini chizing. Oxirgi bosqichda **I** modda **1** ning prekursori hisoblanadi.

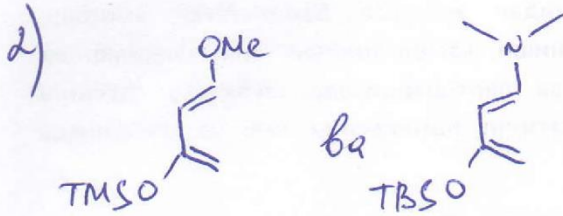
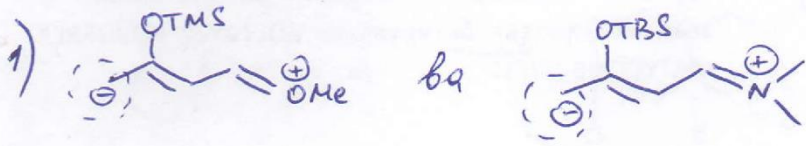


DIBAL-H: Diisobutylaluminum hydride :  $[(\text{CH}_3)_2\text{CHCH}_2]_2\text{AlH}$   
 LDA: Lithium diisopropylamide :  $[(\text{CH}_3)_2\text{CH}]_2\text{NLi}$

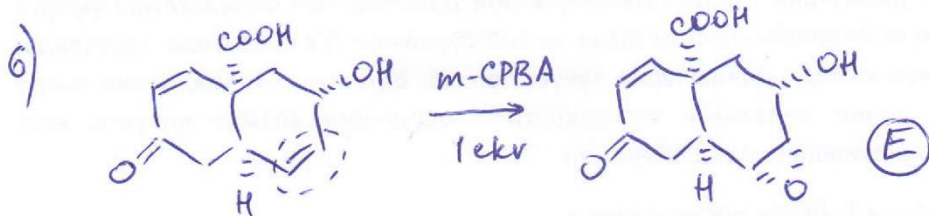
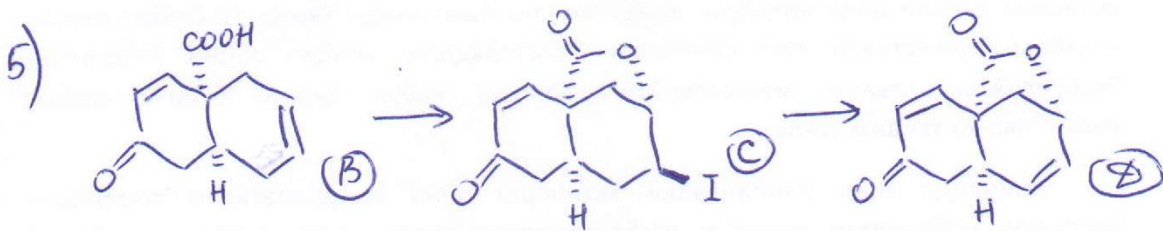
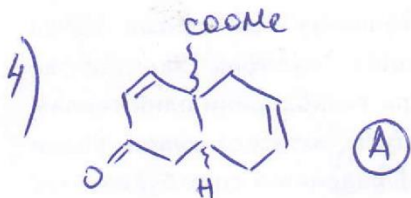
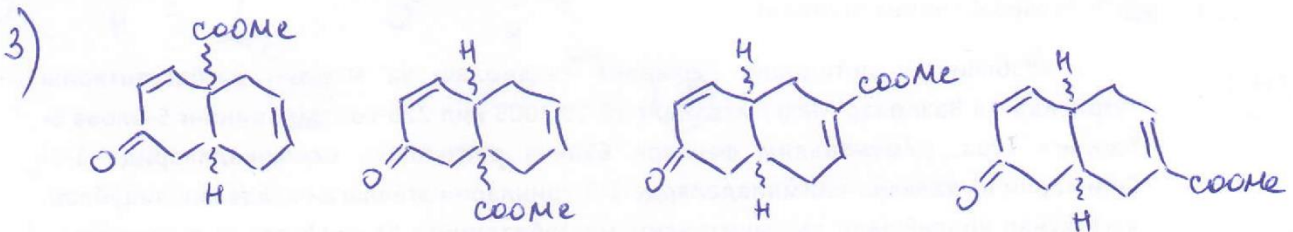


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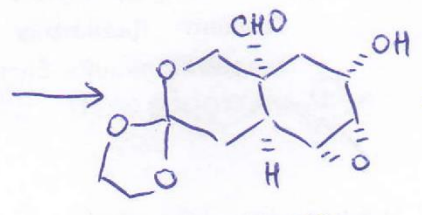
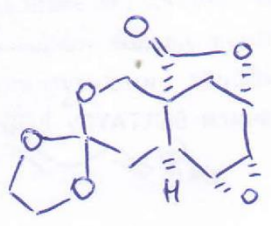
## 2-масала



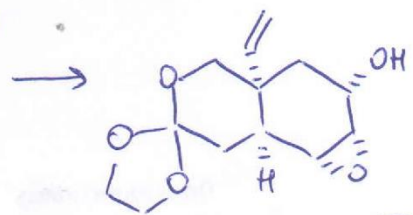
Равел-Козмин диени. Себеби: унинг электрон  
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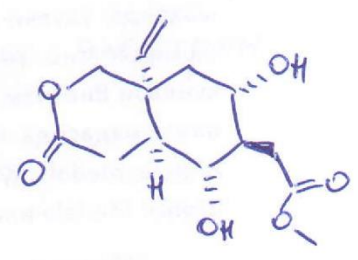
7)



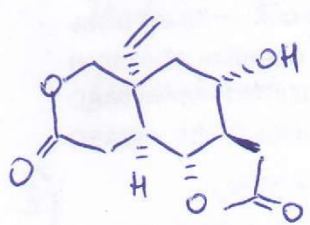
(F)



(G)

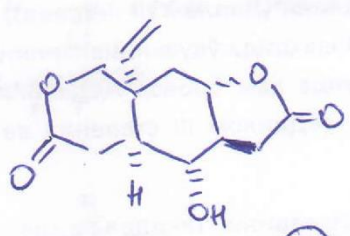


(H)



(I)

+



(J)

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