



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

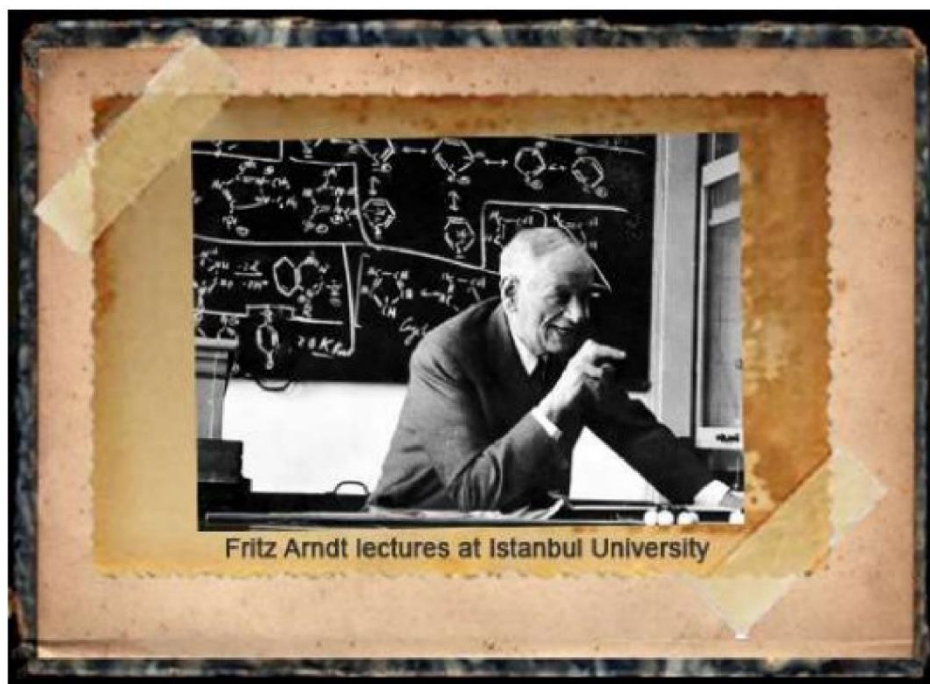
Istanbul, Turkey

CHEMISTRY FOR A BETTER TOMORROW

## 5-masala:

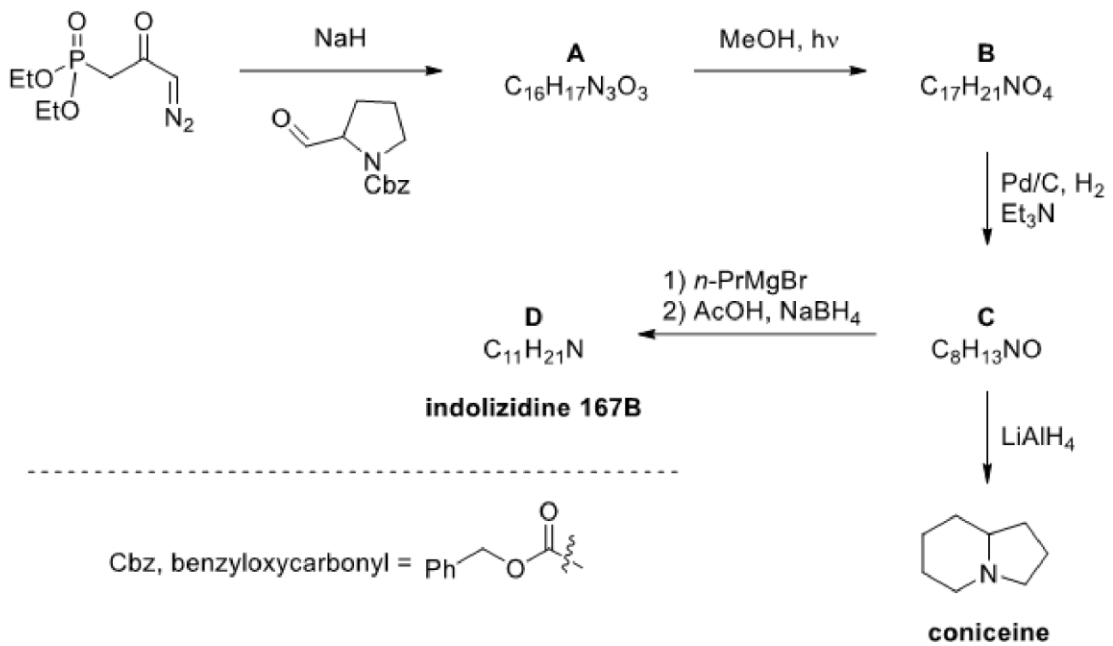
### Arndt-Eystert gomologlanishi.

Fritz Georg Arndt (6-iyul, 1885 – 8-dekabr, 1969) Turkiyada kimyoning taraqqiy topishiga ulkan hissa qo`shgan buyuk nemis kimyogari edi. U ikki xil davrda o`z kasbiy faoliyatining qariyb 20 yilini Istanbul Universitetida o`tkazdi. U Bernd Eystert bilan birgalikda Arndt-Eystert sintezini ishlab chiqdi. Arndt-Eystert sintezi karbon kislotadan bitta uglerodga ko`p gomolog karbon kislotalarni olish ( $\text{RCO}_2\text{H}$  ni  $\text{RCH}_2\text{CO}_2\text{H}$  ga aylantirish) usuli bo`lib, gomologlanish jarayoni deb nomlanadi. Arndt-Eystert gomologlanishining asosiy bosqichi termik, fotokimyoviy yoki kumush (I) ishtirokida diazoketonning ketenga Volf qaytaguruhlanishi hisoblanadi. Reaksiya suv, spirt yoki amin kabi nukleofillar ishtirokida kechib, yakunda keten inetrmediati mos ravishda karbon kislota, efir yoki amidga aylanadi. Ushbu masalada indolizidin alkaloidlarining sintezi o`rganiladi.



1. Quyidagi sxemada aks ettirilgani kabi indolizidin 167B va koniseinni  $\beta,\gamma$ -to`yinmagan efir **B** orqali sintez qilish ham oson, ham tez. Asosiy bosqich (**A**  $\rightarrow$  **B**) Volf qaytaguruhlanishidir. **C** birikma laktam bo`lib, ko`priklardan biri azot atomi bo`lgan bisiklik geterosikl hisoblanadi hamda unda olti a`zoli sikl to`yingan besh a`zoli siklga kondensirlangan.

Stereokimyoviy detallarsiz **A-D** moddalarning strukturalarini chizing.



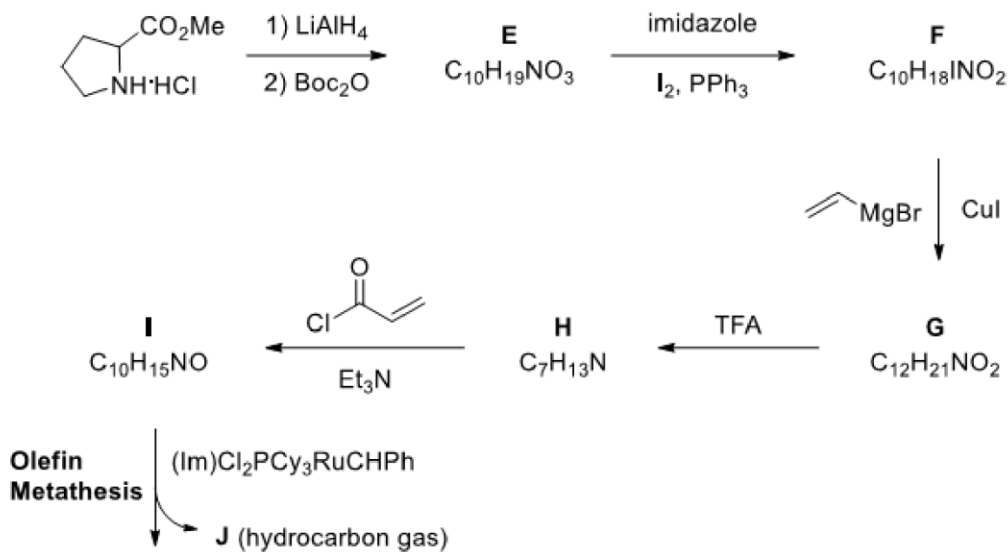
2. Arndt-Eystert gomologlanish reaksiyasida fotokimyoviy Volf qaytaguruhlanishi vaqtida  $\alpha$ -diazoketon azotni chiqarib yuborib,  $\alpha$ -ketokarbenni hosil qiladi. Ushbu intermediat 1,2-alkil migratsiyasiga uchraydi va ketenga aylanadi.

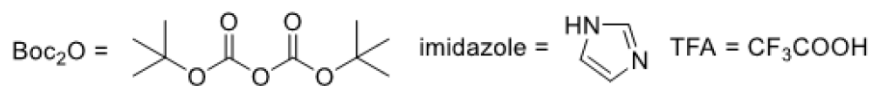
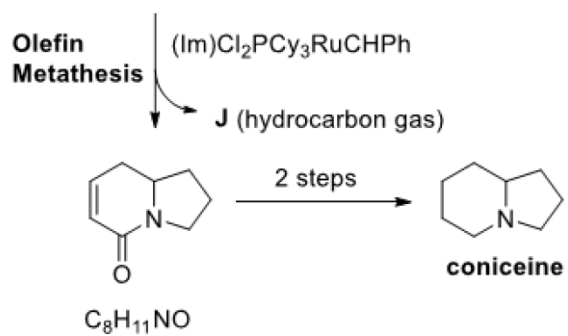
Ikkinchi bosqichdagi (**A**  $\rightarrow$  **B**) intermediatlar  $\alpha$ -ketokarben va ketening strukturalarini chizing.

3. **C** birikmaga propilmagniy bromidi qo`shib, ketidan AcOH/NaBH<sub>4</sub> bilan ishlov berish indolizidin 167B sintezining oxirgi bosqichi hisoblanadi.

To`rtinchi bosqichdagi (**C**  $\rightarrow$  **D**) intermediatning ( $\text{C}_{11}\text{H}_{20}\text{N}^+$ ) strukturasini chizing.

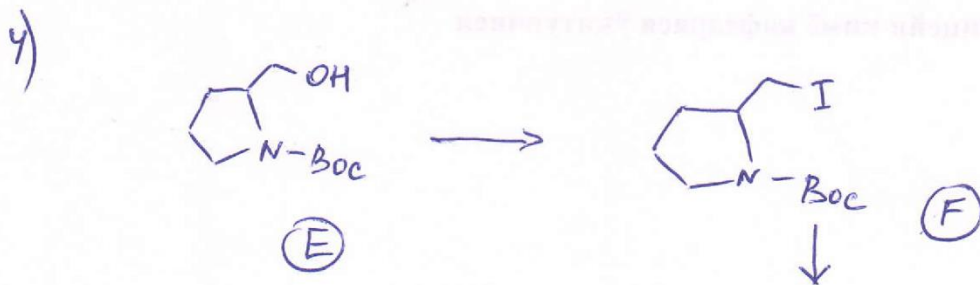
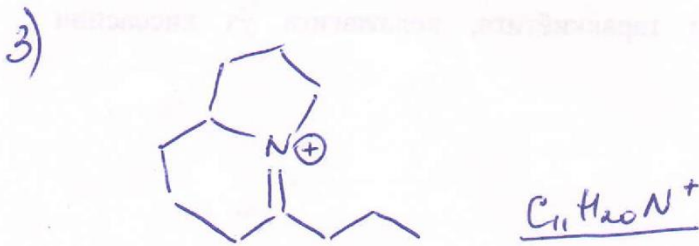
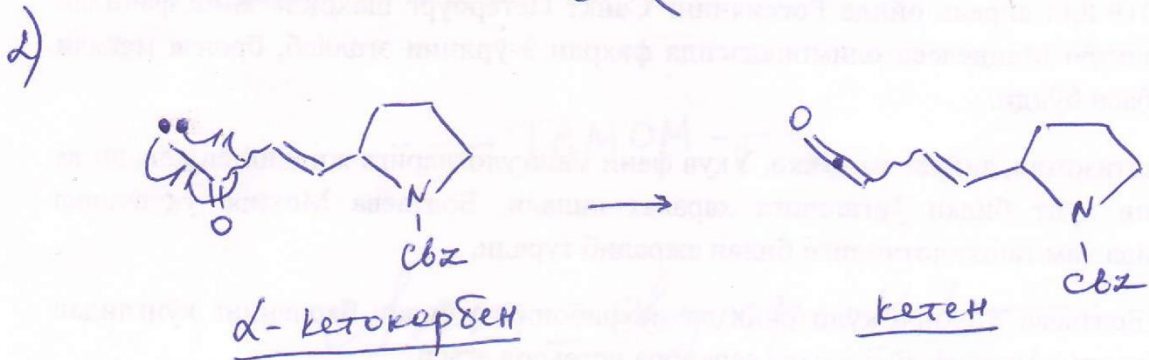
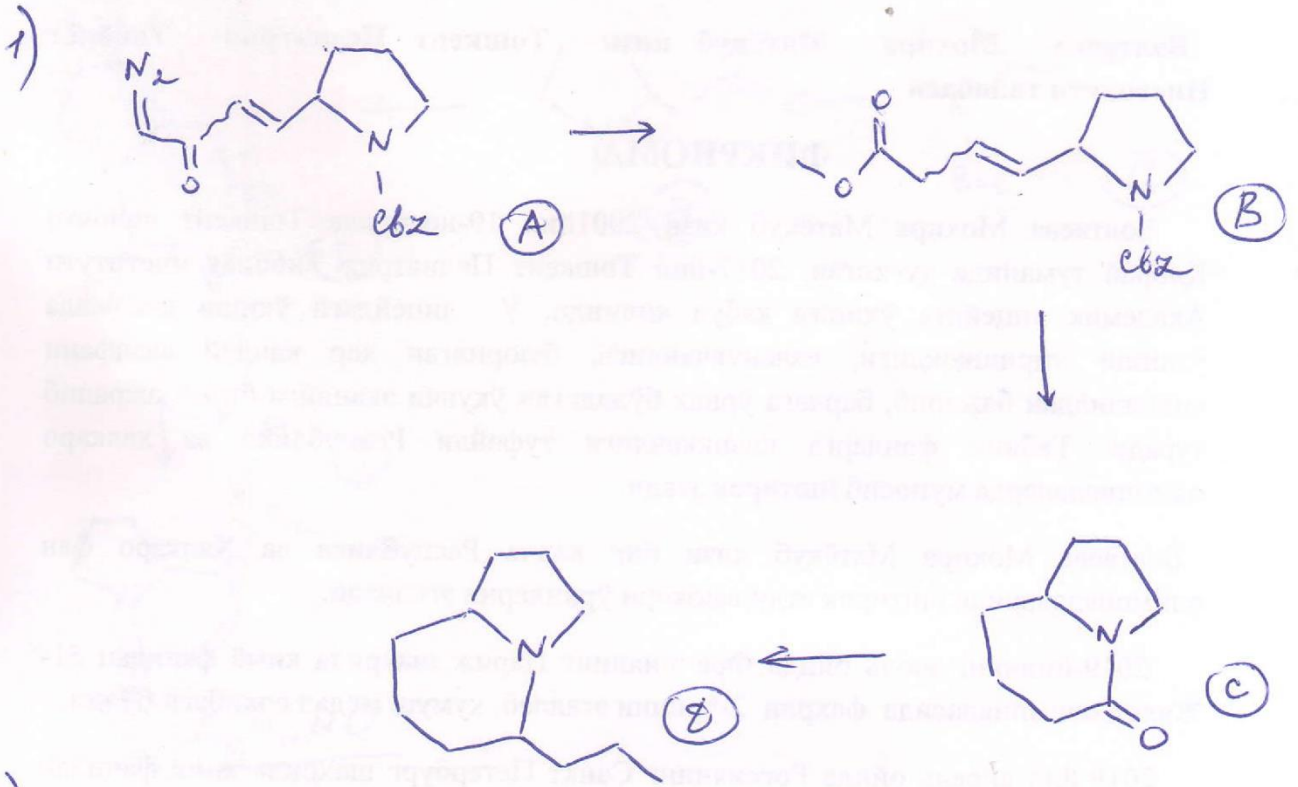
4. Koniseinning alternativ sintezi quyida ko`rsatilgan. **E-J** larning strukturalarini chizing.

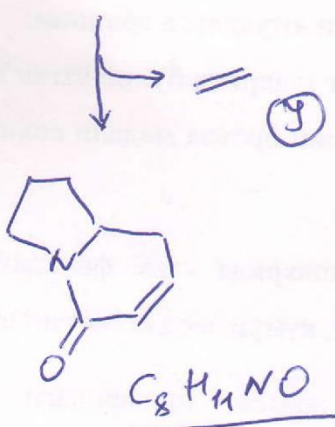
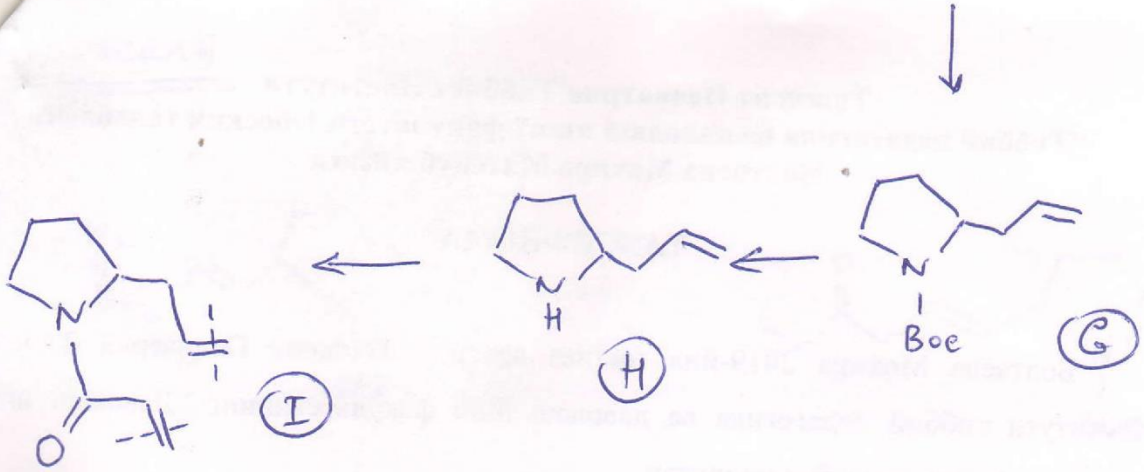




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5- масала





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