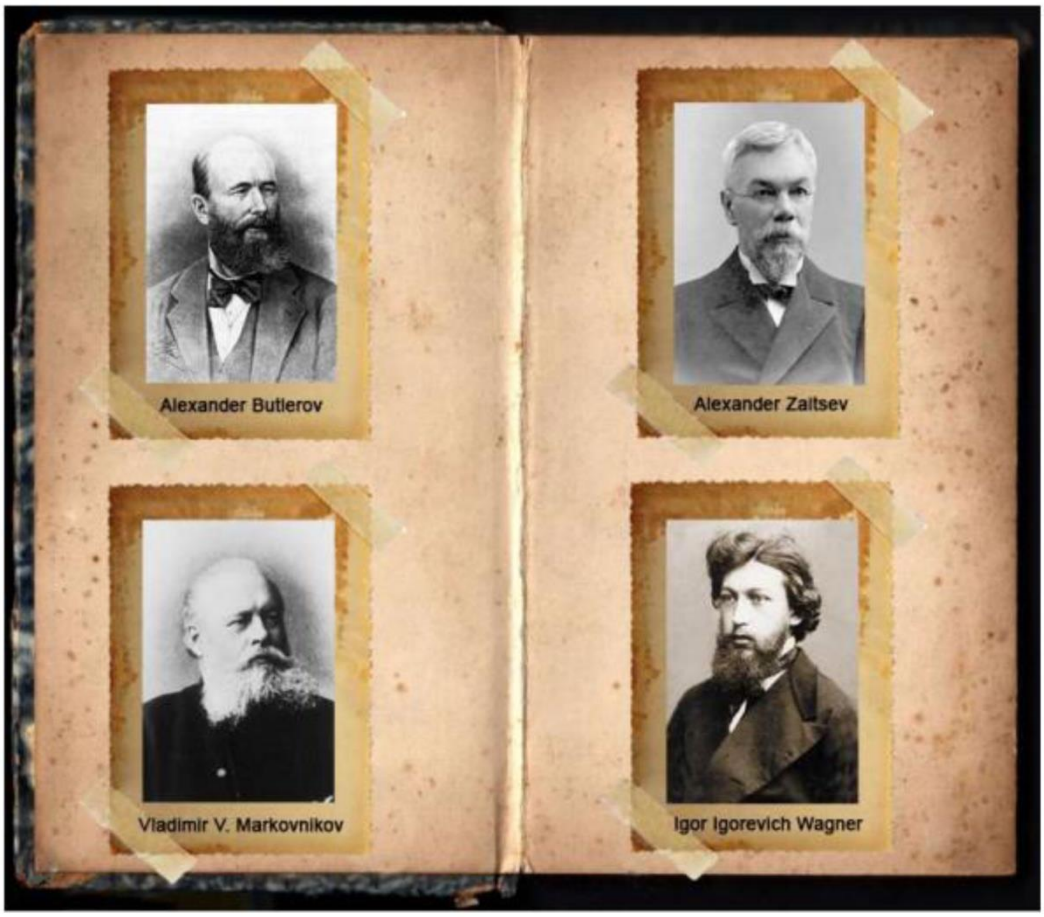
52nd IChO 2020
International Chemistry Olympiad
Istanbul, Turkey
CHEMISTRY FOR A BETTER TOMORROW

4-masala:

Dastlabki rus organik kimyogarlari va Markovnikov qoidasi.

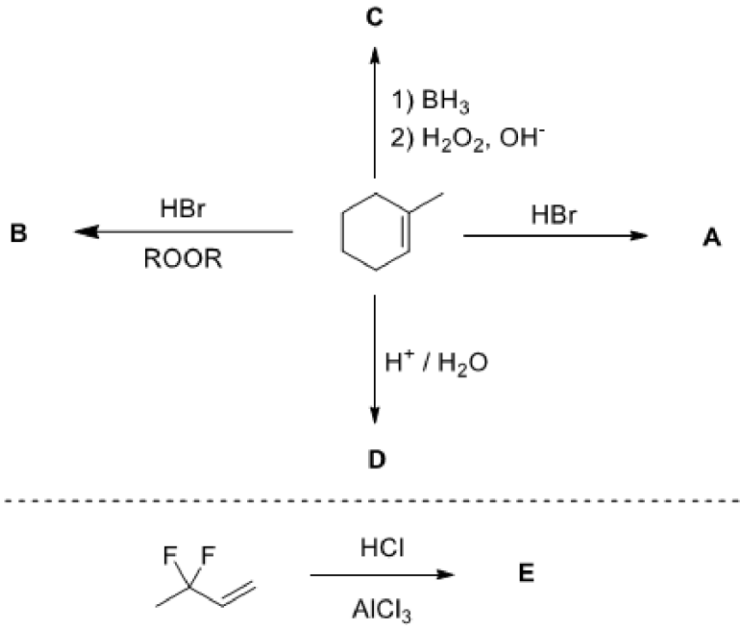


O`tgan yili 1869-yilda Vladimir Markovnikov tomonidan aniqlangan Markovnikov qoidasining 150-yillik yubileyi nishonlandi. Markovnikov mashhur rus olimi Aleksander Butlerovning PhD shogirdi edi. 1869-yil Markovnikov PhD himoyasida bugun barcha organik kimyo kitoblarida tilga olinadigan o`sha mashhur qoidani kashf etdi. Markovnikov qoidasiga ko`ra, nosimmetrik alken yoki alkin vodorod galogenidi (vodorod xloridi, vodorod bromidi yoki vodorod yodidi) bilan ta`sirlashganida HX dagi vodorod atomi eng ko`p vodorod atomlarini saqlagan uglerod atomiga borib birikadi. Biroq ba`zida reagent yoki substratga qarab, teskari birikish ham kuzatilishi mumkin va bunday turdagi reaksiyalar *anti*-Markovnikov birikishi deb nomlanadi. Markovnikov qoidasi faqatgina vodorod galogenidlarining alken yoki alkinlarga birikishi uchungina tegishli bo`lishiga qaramasdan, boshqa birikish reaksiyalarida ham regioselektivlikni ifodalash uchun Markovnikov yoki *anti*-Markovnikov atamalaridan foydalanishadi.

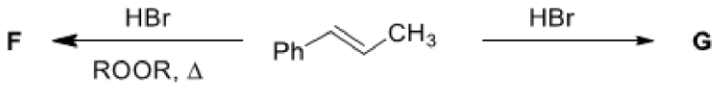
Bugungi kunda qoidaning mukammal jaranglashi quyidagicha: "*qo`shbog` yoki uchbog`ga birikish eng barqaror intermediatlar orqali amalga oshadi*". Turli holatlarda elektron yoki fazoviy effektlar ta`siri ostida Markovnikov yoki *anti*-Markovnikov birikish mahsulotlari hosil bo`ladi.

Ushbu masala yanayam mashhur organik kimyogar olim Aleksander Butlerov va uning Qozon Universitetidagi (Tatariston, Rossiya) hamkasblari va shogirdlarining kashfiyotlariga bag`ishlanadi.

1. Asosiy mahsulotlar **A-E** larni tegishli stereokimyoviy ma`lumotlarni (optik izomerlarni chizish shart emas) ko`rsatgan holatda chizing.



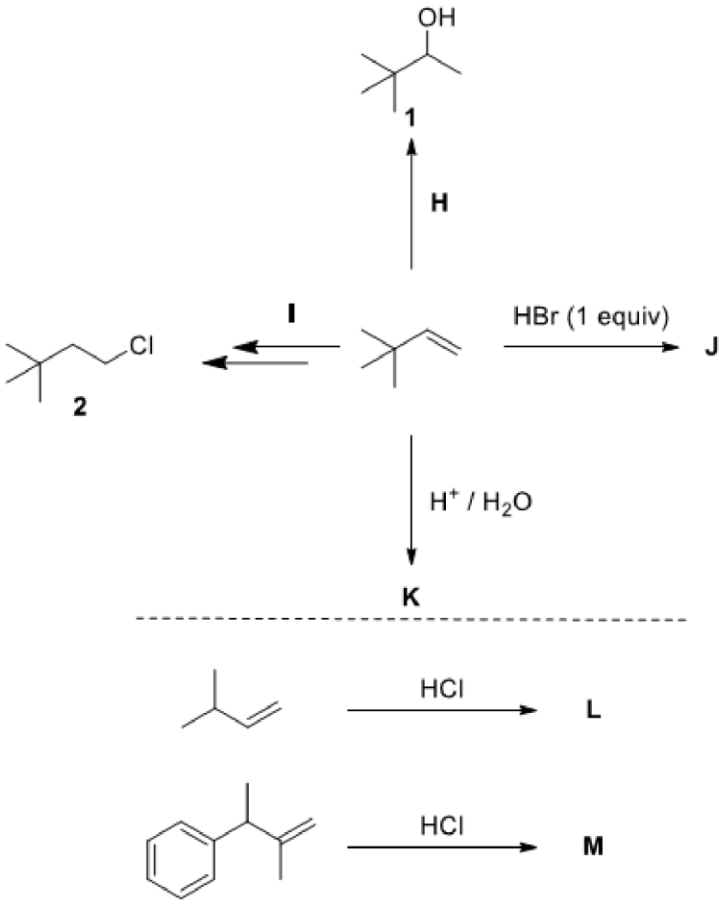
2. Quyidagi reaksiyalarning asosiy mahsulotlari **F** va **G** ning strukturalarini chizing.



Vagner-Merveyn qaytaguruhlanishi

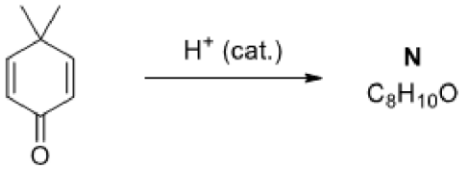
Vagner Qozon universitetida Butlerov va Markovnikov bilan bir vaqtda ishlagan yana bir mashhur olim. Vagner bornil xloridi ichki qaytaguruhlanish orqali pinenga aylanadi deb taklif qildi. Merveyn ushbu turdagi qayta guruhlanishni boshqa birikmalarda ham o`rganib, uni umumlashtirdi. Shu sababli bunday tipdagi reaksiyalar Vagner-Merveyn qaytaguruhlanishi deb nomlanadi. Ushbu reaksiyalar karbokation hosil bo`lgandagina amalga oshadi. Karbokation imkoni bo`lsa, qo`shni guruhlarning migratsiyasi orqali yanayam barqarorroq bo`lgan karbokationga aylanadi. Agar reaksiya karbokation yoki chegaraviy karbokation intermediatlari orqali amalga oshmasa, qaytaguruhlanish ham bo`lmaydi.

3. Har bir reaksiyada intermediatlar hosil bo`lishini inobatga olib, **H** va **I** reagentlar va **J-M** asosiy mahsulotlarning strukturalarini chizing.



Kislota-katalizli Vagner-Merveyn qaytaguruhlanishi

4,4-dimetilsiklogeksa-2,5-dien-1-onning kislota-katalizli reaksiyasi natijasida YMR ma`lumotlari aniqlangan quyidagi modda hosil bo`ladi.



For **N**; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.95 (d, *J* = 8.0 Hz, 1H), 6.61 (d, *J* = 2.8 Hz, 1H), 6.57 (dd, *J* = 8.0, 2.8 Hz, 1H), 5.39 (bs, 1H), 2.16 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.4, 137.9, 130.4, 128.6, 116.6, 112.3, 19.8, 18.7.

4. **N** mahsulotning strukturasini toping va haqqoniy mexanizmni taklif eting.

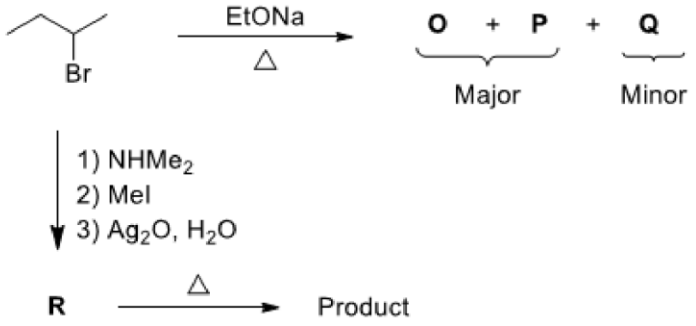
5. YMR idishida turgan eritmaga D_2O qo`shilsa, $^{1}$H YMR spektrda qanday o`zgarish bo`ladi?

Zaytsev qoidasi

Butlerovning yana bir PhD shogirdi Zaytsev ham o`z ismi bilan ataluvchi qoidani kashf etdi. Zaytsev qoidasi eliminatsiya reaksiyalarida hosil bo`luvchi asosiy alkenni aniqlovchi empirik qoida hisoblanadi. Aleksander Zaytsev Qozon Universitetida ko`plab eliminatsiya reaksiyalarini o`rgandi va ularda hosil bo`layotgan alkenlardagi umumiy jihatni ilg`ay oldi. Unga ko`ra eliminatsiya

reaksiyalarida qo`shbog`ida eng ko`p o`rinbosar tutgan alken hosil bo`ladi. Quyidagi savollar Zaytsev qoidasiga bag`ishlanadi.

6. **R** birikmani va eliminatsiya mahsulotlari **O-Q** larni aniqlang. Quyidagi sxemada **R** ning termik parchalanishi natijasida qanday mahsulot hosil bo`ladi?



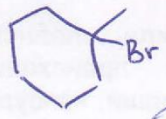
7. Qaysi asoslar EtONa ga nisbatan mahsulotlar ichida **Q** ning ulushini ko`paytira oladi?

- ☐ NaOMe
- ☐ KOMe
- ☐ *i*-PrOK
- ☐ *t*-BuOK
- ☐ NH_3
- ☐ DBU
- ☐ *i*-Pr_2NEt

- - - TAMOM - - -

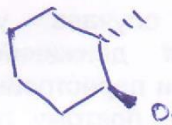
4-Задача

1)

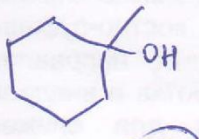


A

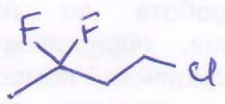
B



C

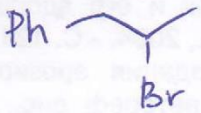


D

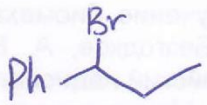


E

2)



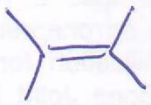
F



G

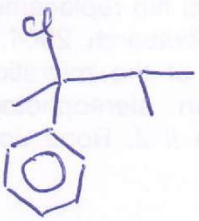
3) H – 1) $Hg(OAc)_2$ 2) $NaBH_4$ I – 1) B_2H_6 2) $NaOCl$

J



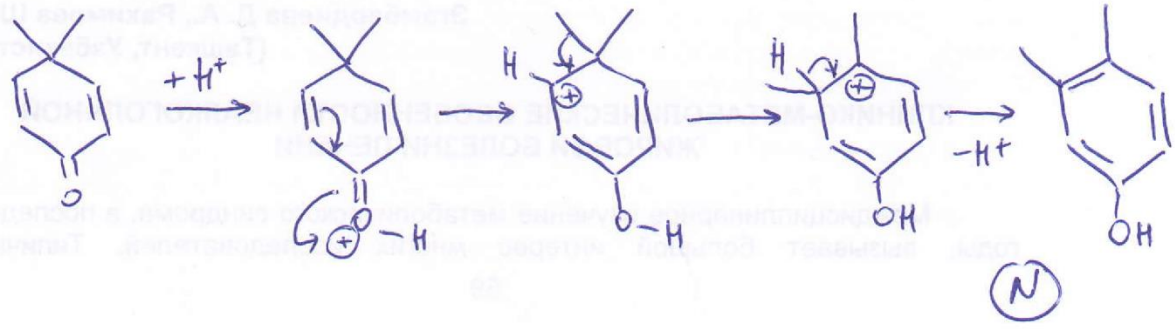
K

L

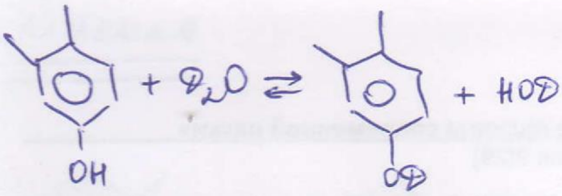


M

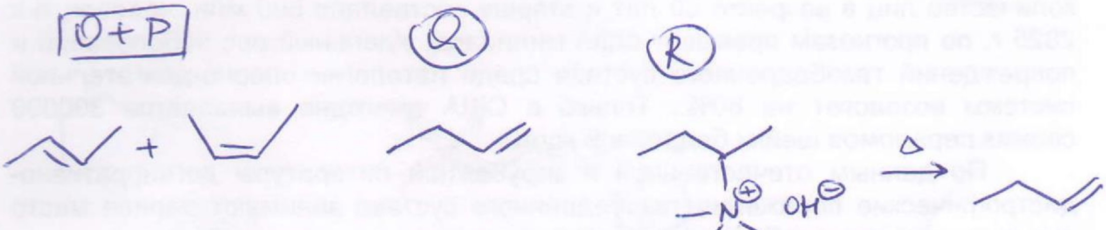
4)



N

5) 

5,39 ppm даги кенг синглет йўқолади.

6) 

7) 3,4,6,7

— — — TAMOM — —