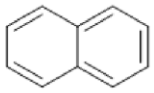
52nd IChO 2020
International Chemistry Olympiad
Istanbul, Turkey
CHEMISTRY FOR A BETTER TOMORROW

# 9-masala:

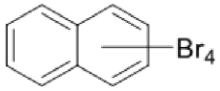
## YMR, simmetriya va strukturaviy analiz.

### Naftalin galogenidlari: keng qo`llaniluvchi muhim birikmalar

Benzoldan tashqari naftalin ham mashhur aromatik birikma hisoblanadi. Shu sababli naftalinning (**1**) kimyosi keng o`rganiladi va uning ko`plab hosilalari sintez qilingan. Naftalinning galogenli birikmalari ko`plab reaksiyalarda ishlatiladi. Shuning uchun ham adabiyotlarda uning barcha galogenli hosilalari haqida ma`lumotlar mavjud. Simmetrik birikmalarning ham $^{1}H$, ham $^{13}C$ YMR spektrlari o`ziga xos bo`lib, strukturaviy analizda nosimmetrik strukturalarni inkor qilishda rosa qo`l keladi. Keling naftalin tetrabromidi (**2**) izomerlarini ko`rib chiqamiz.



**1**
Naphthalene




**2**
Naphthalene tetrabromides

1. $^{13}C$ YMR spektrda 3 ta signal va $^{1}H$ YMR spektrda 1 ta signal (singlet) ga ega bo`lgan barcha naftalin tetrabromidlarining strukturalarini chizing.

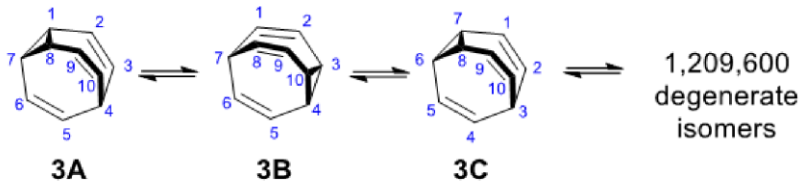
2. $^{13}C$ YMR spektrda 5 ta signalga ega bo`lgan barcha naftalin tetrabromidlarining strukturalarini chizing.

3. $^{13}C$ YMR spektrda 6 ta signal va $^{1}H$ YMR spektrda dubletga ($J$ = 8-9 Hz) ega bo`lgan barcha naftalin tetrabromidlarining strukturalarini chizing.

4. $^{13}C$ YMR spektrda 6 ta signal va $^{1}H$ YMR spektrda dubletga ($J$ = 1.5-2.0 Hz) ega bo`lgan barcha naftalin tetrabromidlarining strukturalarini chizing.

### Dinamik YMR: tautomerlarning tezkor o`zaro transformatsiyasi va YMR dagi bir xil yadrolar

Bulvalen (**3**) degenerativ Koup qaytaguruhlanishiga rosa moyil modda. Enantiomerlarni hisobga olmaganda bulvalenning o`nta turli pozitsiyalardagi valent tautomerlari soni 10!/3 = 1 209 600 ta. Ushbu tezkor qaytaguruhlanishlar tufayli YMR ning vaqt shkalasida barcha uglerod va vodorod atomlari bir xil bo`lib qoladi. Yetarlicha baland haroratda ham $^{1}H$ YMR, ham $^{13}C$ YMR spektrlarida bulvalen yagona keng pikka ega bo`ladi. Biroq -60°C da Koup qaytaguruhlanishi amalga osholmaydi va olefinik vodorodlar bilan alifatik vodorodlar alohida-alohida signal hosil qiladi.

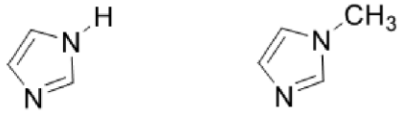



3A 3B 3C

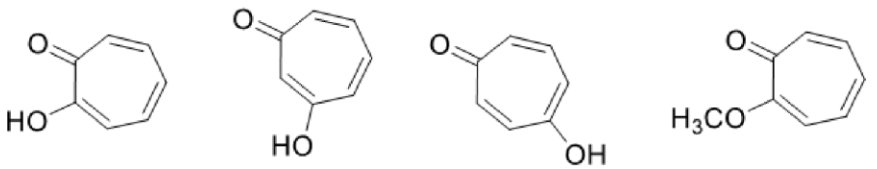
Bullvalene

**5.** Koup qaytaguruhlanishi amalga oshmasligini inobatga olib, past haroratda bulvalenning $^{13}C$ YMR spektrida nechta signal bo`ladi? Uning strukturasida bir xil uglerod atomlarini **a**, **b**, **c** ... harflari bilan belgilang.

**6.** Tezkor tautomerlanish tufayli ba`zi molekulalar spektrda yanayam simmetrikroq bo`lib ko`rinadi. Buni hisobga olib, quyidagi moddalarning $^{13}C$ YMR spektrlarida nechtadan signal bo`ladi?

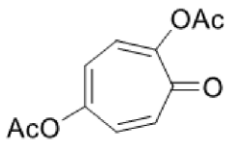


1*H*-imidazole 1-methyl-1*H*-imidazole



α-tropolone β-tropolone χ-tropolone 2-methoxtropone

**7.** Adabiyotlarda keltirilishicha tropolon diasetatining hosilasi (**4**) $^{13}C$ YMR spektrda kutilganidan kamroq signallarga ega. Ushbu simmetriyaga sabab bo`layotgan rezonans strukturalar yoki o`zgarishlarni chizing. $^{13}C$ YMR spektrda ushbu molekula nechta signal namoyon etadi?

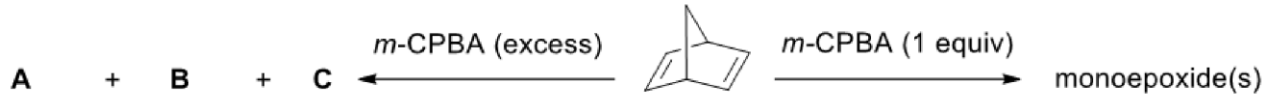


**4**

**Bisiklik alkenlarning epoksidlanish reaksiyasi stereokimyosi**

**8.** Quyida berilgan ma`lumotlardan foydalanib, hosil bo`layotgan stereoizmoerlarning barcha maqbul strukturalarini chizing.

**Diqqat**: $^{13}C$ YMR spektrda **A** va **B** izomerlar 3 ta, **C** izomer esa 4 ta signalga ega.

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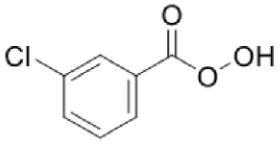
*m*-CPBA = *m*-Chloroperoxybenzoic acid




**9.** Quyidagi sharoitlarda hosil bo`layotgan stereoizomerlarning strukturalarini chizing. Epoksid mahsulotlarning $^{13}C$ YMR spektrlarida nechtadan signal bo`ladi?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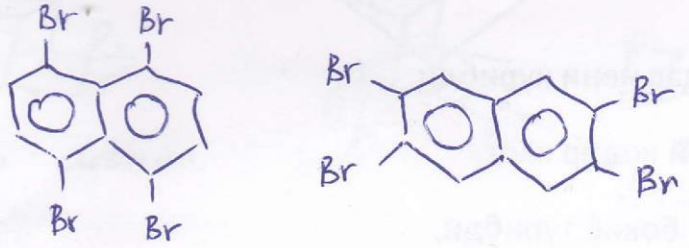
# 9-masala

1)



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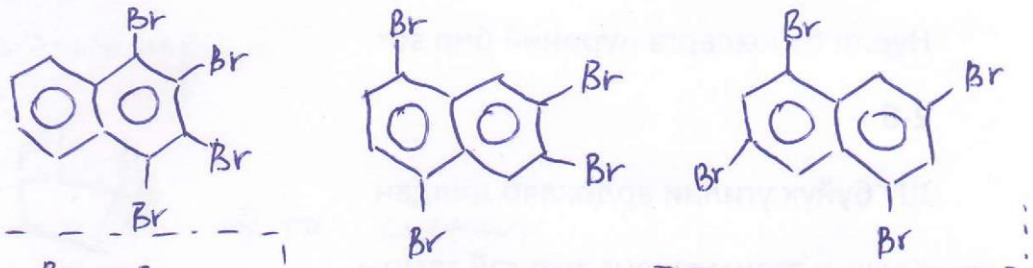

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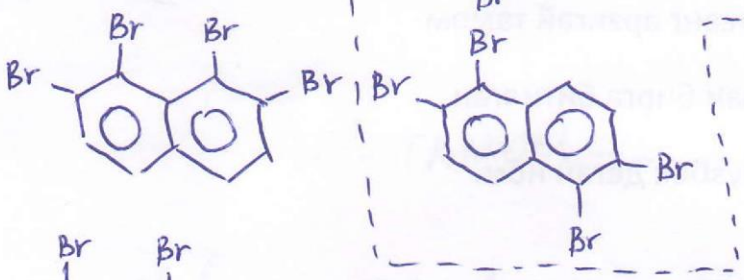

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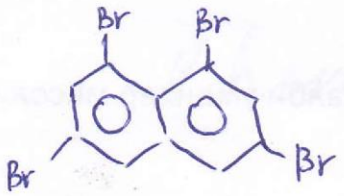
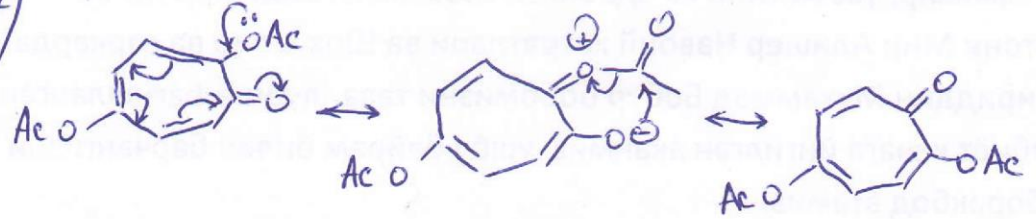


5)

4 ta signal.

6) 2, 3, 4, 4, 4, 5

7)



8 ta signal.

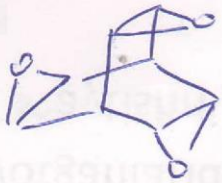
8)

A va B

C

три эпоксидлар:

4 та сигнал



2 та сигнал

моноэпоксид:

4 та сигнал

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