



52nd IChO 2020
International Chemistry Olympiad

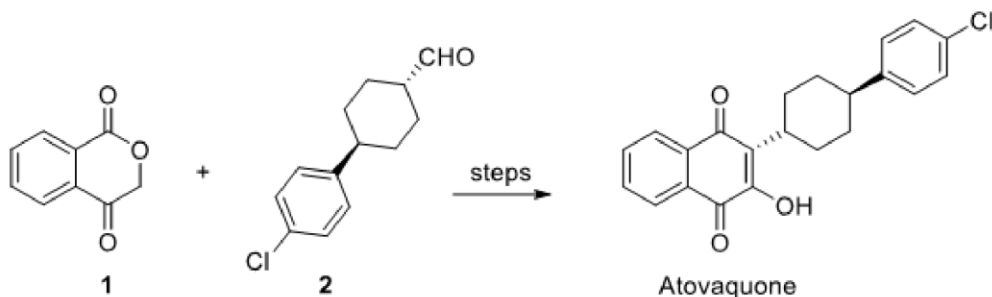
Istanbul, Turkey

CHEMISTRY FOR A BETTER TOMORROW

6-masala:

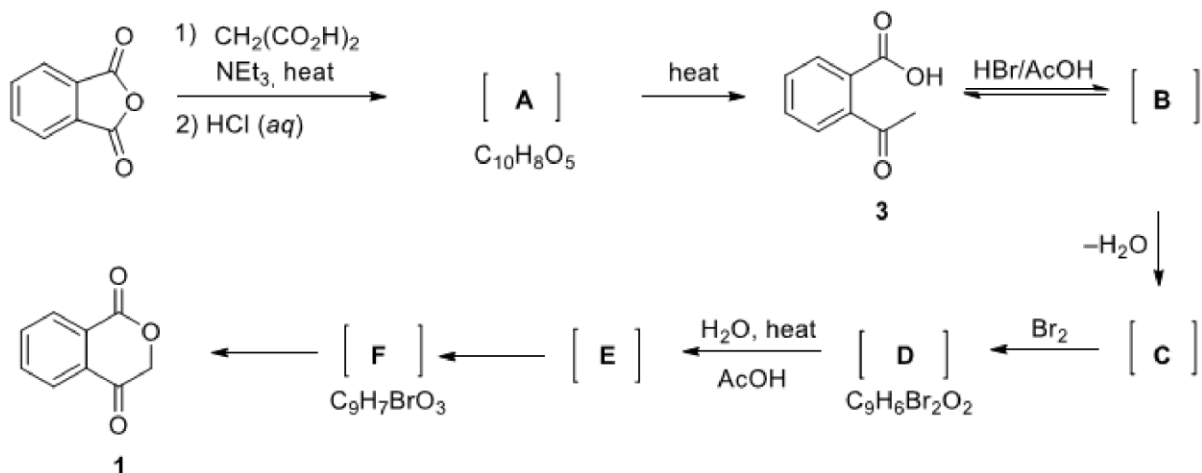
Atovakvon.

Atovakvon pnevmosistli pnevmoniya va bezgakni davolash uchun tavsiya etiladigan dori hisoblanadi. Ketoefir **1** va aldegid **2** atovakvon sintezida asosiy moddalar bo'lib hisoblanishadi.



1. Quyida ketoefir **1** ning sintez sxemasi keltirilgan. Ftal anhidridi va Et_3N aralashmasiga dikislota bilan ishlov beriladi. Bunda gaz ajralishini kuzatish mumkin. Reaksiyon aralashmaga HCl eritmasi bilan ishlov berilganda ikkita karboksil guruhga ega bo'lgan **A** inetrmediat orqali kislota **3** hosil bo'ladi. Kislota **3** o'ziga izomer bo'lgan va yarimasetal hamda efir guruhlarini tutuvchi **B** intermediatga aylanadi, **B** degidratatsiyalanib alken **C** ga, **C** esa kislotali sharoitda bromlanib **D** ga aylanadi. Dibromid **D** $\text{H}_2\text{O}/\text{AcOH}$ qaynoq aralashmasida solvolizga uchratilib uchlamchi karbokation intermediat **E** hosil bo'ladi, **E** o'z navbatida suv bilan ta'sirlashib yarimasetal **F** intermediatini hosil qiladi. So'ngida yarimasetal **F** intermediat qaytaguruhlanib ketoefir **1** ga aylanadi.

Diqqat: to'rtburchak qavs mahsulot ajratib olinmasdan, shu idishning o'zida keyingi reagentlar bilan ta'sirlashtirilayotganligini bildiradi. 3 ning 1 ga aylanishi bitta idishda amalga oshuvchi ko'p bosqichli, lekin bir etapda bajariluvchi reaksiyadir.

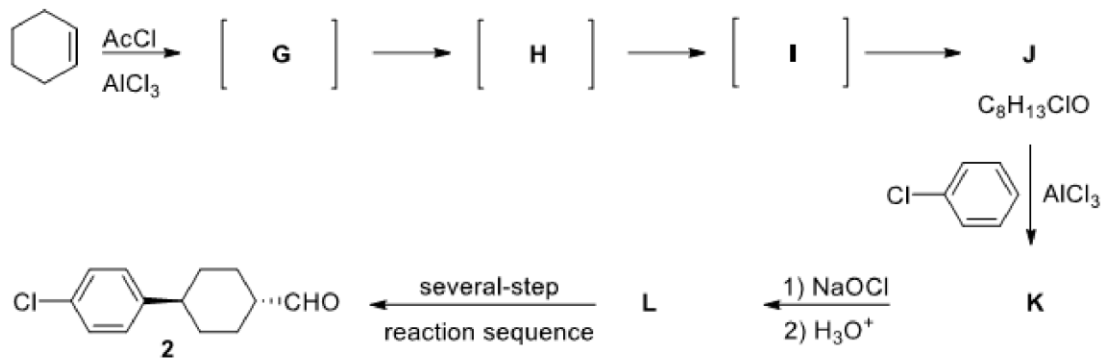


Spectroscopic data for intermediates **B** and **C**: **B**: $^1\text{H NMR } \delta = 7.86\text{--}7.52$ (4H), 4.13 (bs, 1H, exchangeable with D_2O), 1.97 (s, 3H). **C**: $^1\text{H NMR } \delta = 7.92\text{--}7.58$ (4H), 5.24 (m, 2H); $^{13}\text{C NMR } \delta = 166.8, 151.8, 139.0, 134.4, 130.4, 125.3, 125.1, 120.6, 91.3$; MS $m/z = 146.0$

1 ning sintezidagi **A-F** intermedialarning strukturalarini chizing.

2. Aldegid **2** ning sintezi siklogeksendan boshlanib, Fridel-Krafts asillanishi, galoform va oksidlanish-qaytarilish reaksiyalari bosqichlarini bosib o'tadi. Siklogeksenning asetil xlorid bilan Fridel-Krafts bo'yicha asillanishi xlorosiklogeksil-metil-ketonga olib keladi. Siklogeksenning asetil xlorid bilan reaksiyasida dastlab karbokation **G** hosil bo'ladi, keyin u ketma-ket ikki marotaba Vagner-Merveyn bo'yicha gidrid migratsiyasiga uchrab izomer bo'lgan **H** va **I** inetrmedialarga aylanadi. Karbokation **I** xlorid ioni bilan birikib **J** ni hosil qiladi, **J** esa xlorbenzol bilan Fridel-Krafts reaksiyasiga kirishib **K** ga aylanadi. Metilketon **K** ning natriy gipoxloridi (NaOCl) bilan galoform reaksiyasidan kislota **L** hosil bo'ladi. Kislota **L** bir necha bosqichda aldegid **2** ga aylantiriladi.

Izomer karbokation **G-I** larning strukturalarini chizing.



3. Quyidagi karbokationlar xiralmi?

G	<input type="checkbox"/> Yes
	<input type="checkbox"/> No
H	<input type="checkbox"/> Yes
	<input type="checkbox"/> No
I	<input type="checkbox"/> Yes
	<input type="checkbox"/> No

4. **J-L** larning strukturalarini chizing.

5. **L** ga tegishli to'g'ri fikrlarni tanlang.

- L** has 4 stereoisomers.
- L** is a chiral compound.
- L** is an achiral compound.

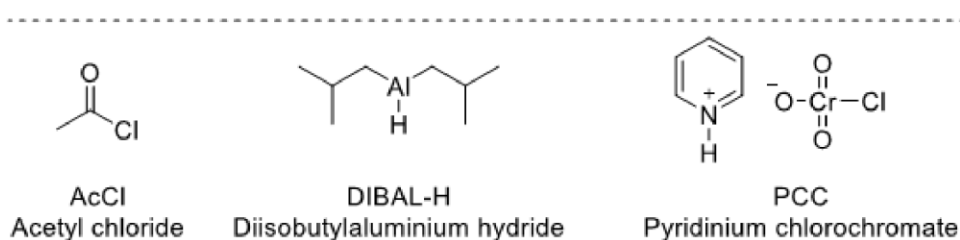
- L** is a meso compound.
- L** has 2 stereoisomers.
- Stereoisomers of **L** are diastereomers of each other.
- Stereoisomers of **L** are enantiomers of each other.

6. **K** ning galoform reaksiyasidan quyidagi moddalardan qaysi biri hosil bo`ladi?

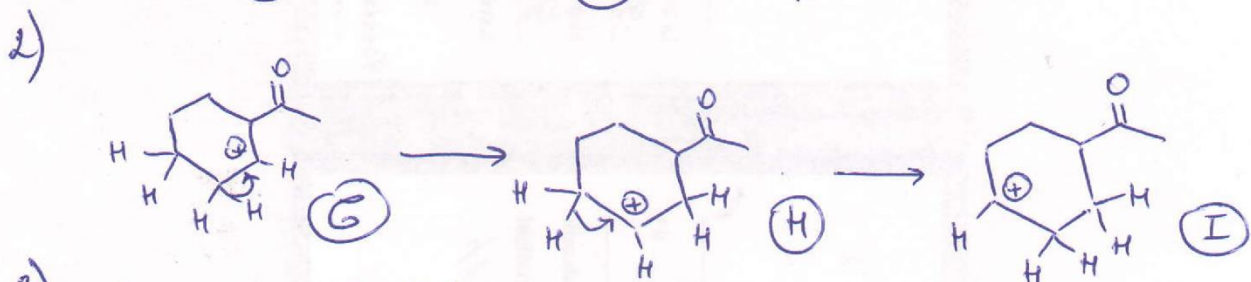
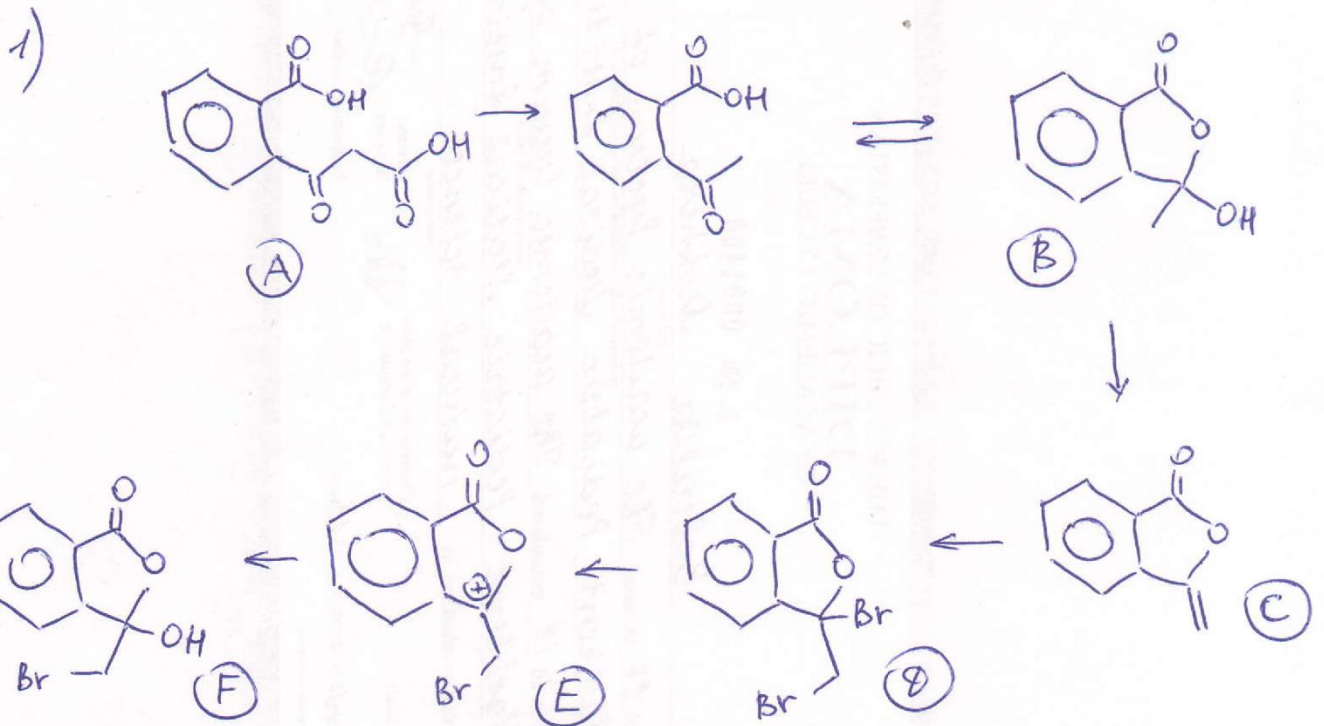
- CH₂Cl₂
- CH₃Cl
- CHCl₃
- CCl₄

7. **L** dan aldegid **2** ni olish uchun quyidagi reaksiyalardan qaysilarini ishlatish mumkin?

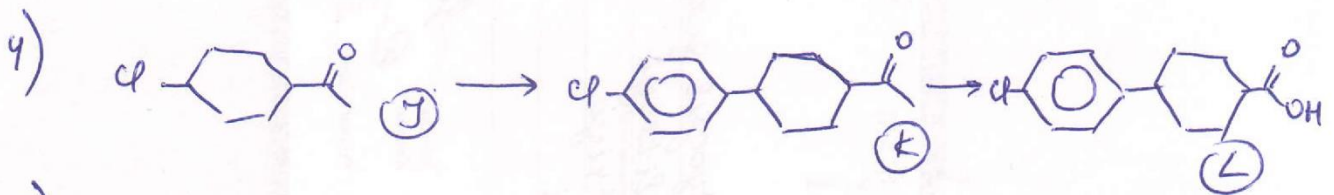
- L** $\xrightarrow[2) (\text{COCl})_2, \text{DMSO}, \text{NEt}_3]{1) \text{ a) LiAlH}_4 \text{ b) H}_3\text{O}^+}$ **2**
- L** $\xrightarrow[2) \text{ a) DIBAL-H (1 equiv), } -78 \text{ }^\circ\text{C b) H}_3\text{O}^+]{1) \text{ CH}_3\text{OH/H}^+}$ **2**
- L** $\xrightarrow[2) \text{ CrO}_3/\text{H}_3\text{O}^+]{1) \text{ NaBH}_4/\text{EtOH}}$ **2**
- L** $\xrightarrow[3) \text{ DIBAL-H (1 equiv), } -78 \text{ }^\circ\text{C b) H}_3\text{O}^+]{1) \text{ SOCl}_2, 2) \text{ HONHMe} \cdot \text{HCl}, \text{NEt}_3}$ **2**
- L** $\xrightarrow[2) \text{ CrO}_3/\text{H}_3\text{O}^+]{1) \text{ EtOCOCl}, \text{NEt}_3}$ **2**
- L** $\xrightarrow[3) \text{ PCC}]{1) \text{ EtOCOCl}, \text{NEt}_3, 2) \text{ NaBH}_4/\text{EtOH}}$ **2**
- L** $\xrightarrow[2) \text{ DIBAL-H (1 equiv), } -78 \text{ }^\circ\text{C b) H}_3\text{O}^+]{1) \text{ EtOCOCl}, \text{NEt}_3}$ **2**



6-маселя



3) G, H - ха; I - урк.



5) 3, 5, 6

6) 3

7) 1, 2, 4, 6, 7

--- ТАМОМ ---