

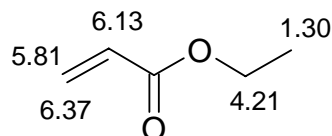
Valikvõistluse ülesannete lahendused

7. aprill 2003, Tartu

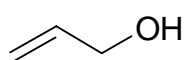
Lahendused.

1. a). ^1H TMR spektri kvartett ja triplett vastavad etüülrühmale. Signaalid piirkonnas 5.8-6.4 ppm vastavad kaksiksidemele, mis annab kokku 3H ja vinüülrühma. IR spekter viitab nii kaksiksidemele (1638) kui ka karbonüülrühmale (1728). Brutovalemist jääb järele veel üks hapnik. Sellega on ühend **A** – ester, etüülakrülaat. $\text{CH}_2=\text{CHCOOC}_2\text{H}_5$.

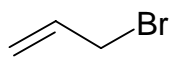
b). 1.30 – CH_3 (etüül); 4.21 – CH_2 (etüül); 5.81-6.37 - vinüülrühm.



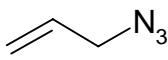
c).



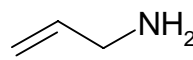
B



C

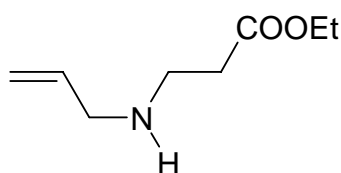


D

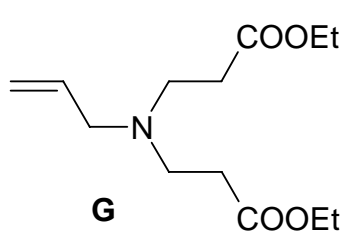


E

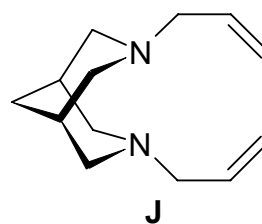
d).



F

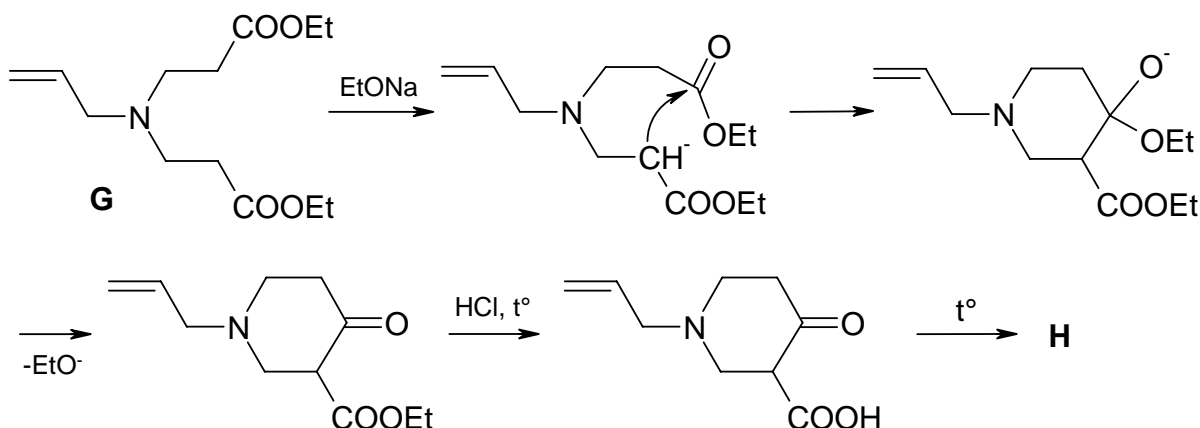


G

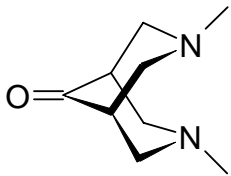


J

e).

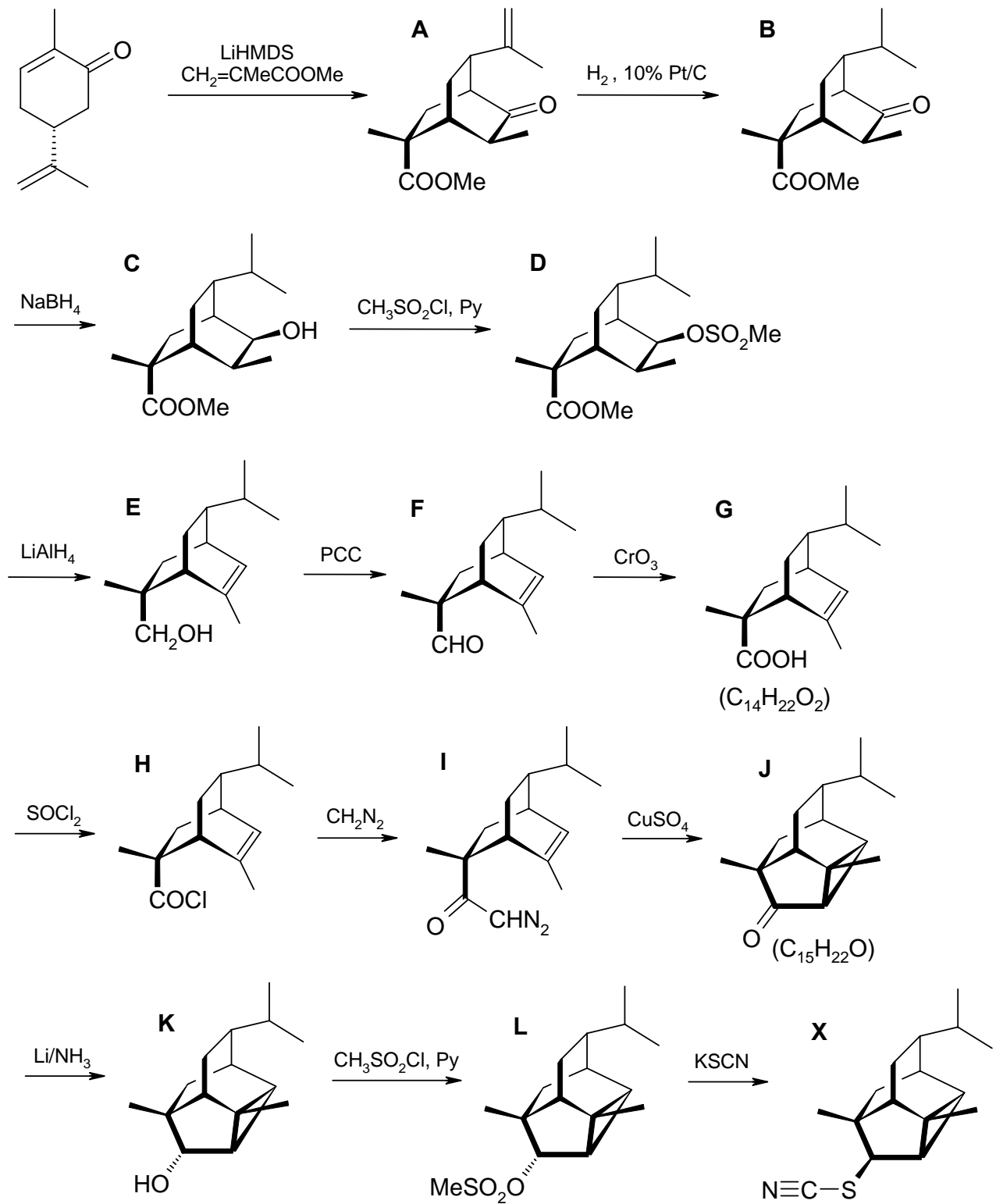


f). Puhta analoogia põhjal – ühendi **I** saamisel lähtuti aineist **H**, mis sisaldas ühte allüülrühma ning reagentist **E**, mis sisaldas samuti ühte allüülrühma. Produktis **I** oli seega kaks allüülrühma. Kuna küsimuse 6. lähteaine sisaldab allüülrühma asemel metüüli ning reagentiks on ka metüülamiin, siis on vastav produkt selline:

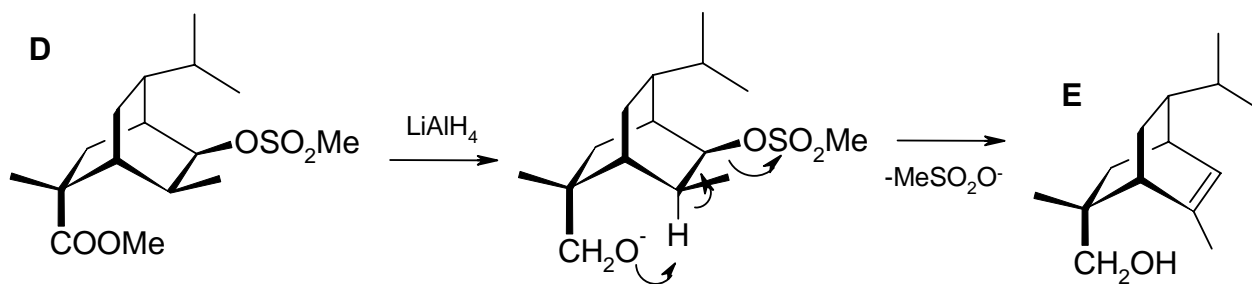


2. LAHENDUS

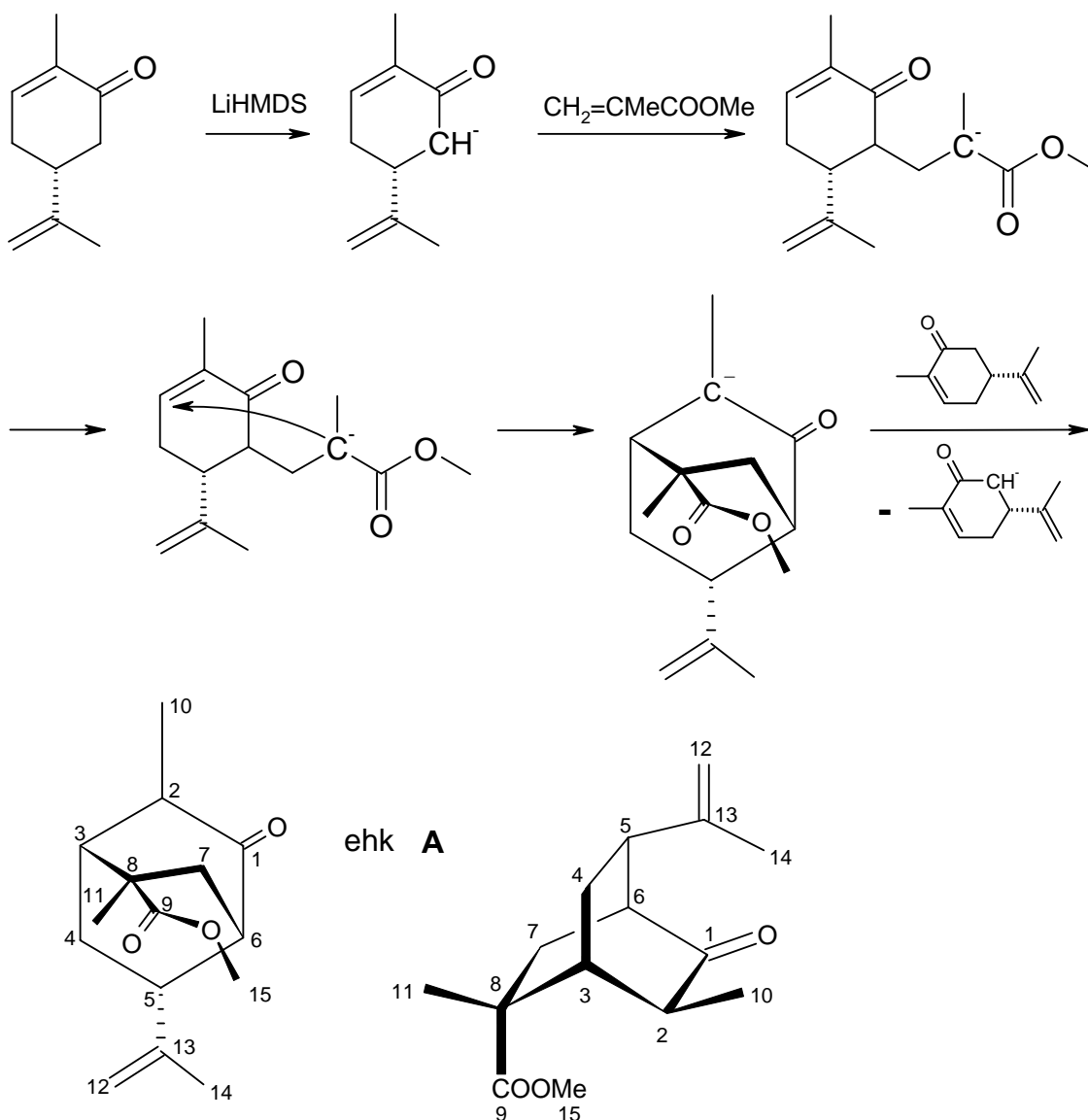
a).



b).



c).



Esimeses etapis toimub deprotoneerimine, siis tekkinud anioon liitub küllastamata estri $\text{CH}_2=\text{CHMeCOOMe}$ kaksiksidemele (Michaeli reaktsioon). Tekib uus anioon, mis liitub sisemolekulaarselt järelejäänud kaksiksidemele (Michaeli reaktsioon). Tekkinud osake deprotoneerib lähteainet ja muutub neutraalseks. Süsiniku aatomid on nummerdatud, et paremini näha ühendi **A** moodustumist.

3. LAHENDUS

a).

CH₃J (liias), siis Ag₂O/H₂O

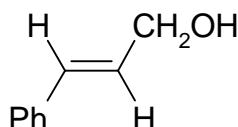
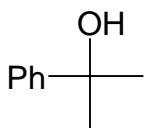
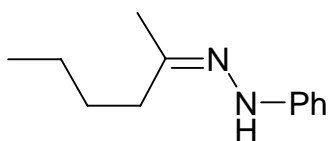
KCN

EtMgl

PBr₃

H₂, Pd/C/BaSO₄

b).



4. LAHENDUS

$$1. \quad \bar{x} = \frac{V_2}{V_3} = \frac{k_2 \cdot [\text{monomeer}] \cdot [\text{polümeerne katioon}]}{k_3 \cdot [\text{polümeerne katioon}]} = \frac{k_2}{k_3} \cdot [\text{monomeer}]$$

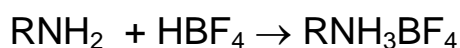
$$\bar{x} = \frac{10^6 \cdot 2}{5 \cdot 10^3} = 4 \cdot 10^2$$

2. Monomeeri M = 104

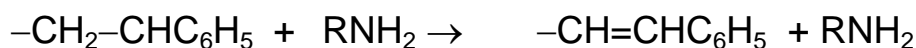
$$\bar{M} = \bar{x} \cdot M = 500 \cdot 104 = 5,2 \cdot 10^4$$

3. Kuna katalüsaator on nagunii happeline, siis fenooli (nõrk hape) lisamine reaktsiooni kiirust ei muuda.

4. Amiini lisamine vähendab reaktsiooni kiirust, sest amiin reageerib nii katalüsaatoriga (tõkestab initsieerimist):



nii ka polümeerse katiooniga (takistab ahela kasvu):



5. Reaktsioonikeskkonna dielektrilise konstandi suurendamine suurendab reaktsiooni kiirust (soodustab ionide tekkimist)

5. LAHENDUS

a) $\Delta G^0 = \Delta H^0 - T\Delta S^0$

$$\Delta G^0 = 192\,800 - 332,4 \cdot 104,6 = 158031 \text{ J}$$

$$\ln K_p = -\frac{\Delta G^0}{RT} = -\frac{158031}{8,31 \cdot 332,4} = -57,18$$

$$K_p = 1,48 \cdot 10^{-25}$$

b) $p(\text{Br}) = \sqrt{K_p}$

$$p(\text{Br}) = 3,85 \cdot 10^{-13} \text{ bar}$$

c) $n = \frac{PV}{RT}$

$$n(\text{Br}) = \frac{3,85 \cdot 10^{-13} \cdot 1}{0,0831 \cdot 332,4} = 1,39 \cdot 10^{-14}$$

$$N(\text{Br}) = 6,02 \cdot 10^{23} \cdot 1,39 \cdot 10^{-14} = 8,37 \cdot 10^9$$

$$N(\text{Br}_2) = 6,02 \cdot 10^{23} \cdot \frac{1,0 \cdot 1,0}{0,0831 \cdot 332,4} = 2,18 \cdot 10^{22}$$

$$\alpha = \frac{0,5 \cdot 8,37 \cdot 10^9}{2,18 \cdot 10^{22}} \cdot 10^2 = 1,92 \cdot 10^{-11} \%$$

d) $\ln \frac{1,0}{0,132} = \frac{\Delta H_a}{8,31} \left(\frac{1}{282,5} - \frac{1}{332,4} \right)$

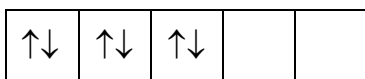
$$\Delta H_a = 31710 \text{ J/mol}$$

6. LAHENDUS

a) $\text{K}_4[\text{Fe}(\text{CN})_6]$ kaaliumheksatsüanoferraat (II)

$\text{K}_3[\text{Fe}(\text{CN})_6]$ kaaliumheksatsüanoferraat (III)

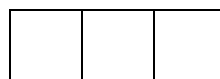
b) **A:** Fe^{2+} kompleks:



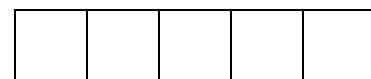
3d



4s

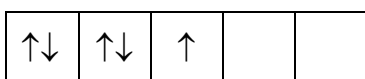


4p



4d

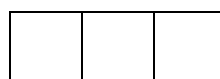
B: Fe^{3+} kompleks:



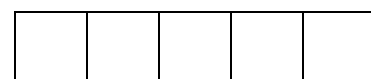
3d



4s



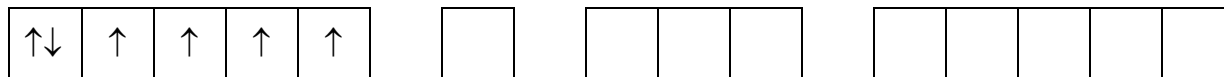
4p



4d

- c) **A:** $\Delta > p$, madalaspinniline, diamagneetiline.
B: $\Delta > p$, madalaspinniline, paramagneetiline.

d) Fe^{2+} vaba ioon:



- e) **A:** Fe^{2+} kompleksis: 3d, 4s ja 4p orbitaale, d^2sp^3 -hübridisatsioon
B: Fe^{3+} kompleksis: 3d, 4s ja 4p orbitaale, d^2sp^3 -hübridisatsioon

