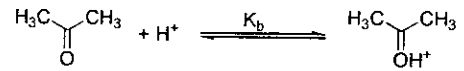
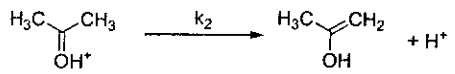
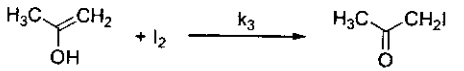


(1) (rapidly)



(2) (rate-limiting stage)



(3) (rapidly)

The rate of the entire process is determined by that of enol formation (2).

Use the above scheme to derive the theoretical kinetic equation of dimethyl ketone iodination (show dimethyl ketone as A).

**9.** Write down the condition when the derived equation coincides with the experimental kinetic equation $w = k'[A][H^+]$ that you had to obtain doing when the experimental parts.

**10.** Iodination of dimethyl ketone can be also carried out in an acid-free medium, the initial rate being considerably lower in this case than in an acidic medium. Draw the kinetic curves in the acid-containing and acid-free media.

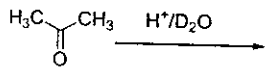
**11.** Compare the rate constants of bromination and iodination of dimethyl ketone with $Br_2$ and $I_2$ under the conditions of your experiment (encircle one of the following):

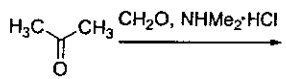
a) $k_{Br} < k_I$; b) $k_{Br} > k_I$; c) $k_{Br} \cong k_I$; d) $k_{Br} >> k_I$

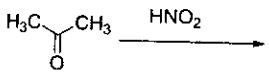
**12.** Messinger's method is another procedure for dimethyl ketone determination. The method involves addition of an excess of iodine to the alkaline aqueous solution of dimethyl ketone with subsequent titrimetric determination of the unreacted iodine after acidification of the mixture. Write down the equation of the reaction occurring upon iodine addition to dimethyl ketone.

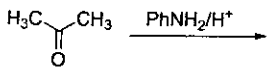
**13.** Is the Messinger's method selective towards dimethyl ketone? Write down the reaction supporting your answer.

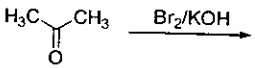
**14.** Write down the structures of the products of the following reactions.

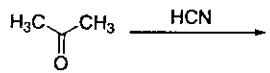














# The 42nd Mendeleev Olympiad (2008)

## Identification of organic compounds

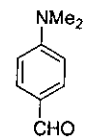
**(author Beklemishev M.K.)**

The task consist of two parts: identification of organic compounds, some of which are common medicines, and quantitation of analgin in tablets.

**Reagents, labware and equipment**

| *Item* | *Quantity* | *Label* |
|---|---|---|
| ***For each student*** | | |
| Laboratory stand with clamp and ring | 1 pc. | |
| 250 mL Erlenmeier flask, for titration | 3 pcs. | |
| 100 mL volumetric flask, for the sample | 1 pc. | |
| 25 mL burette | 1 pc. | |
| 10 mL pipette | 3 pcs. | |
| Pipette filler | 1 pc. | |
| 100 mL beaker | 1 pc. | |
| 50 mL measuring cylinder | 1 pc. | |
| Spatula | 3 pcs. | |
| Glass rod | 3 pcs. | |
| Eyedropper | 6 шт. | |
| Paper towels | 1 pack | |
| Distilled water in wash bottle | 0.5 L | $H_2O$ |
| *p*-Nitrophenol (for analysis, in a vial) | 1 g | One of **A-G** |
| Benzoic acid (for analysis, in a vial) | 1 g | One of **A-G** |
| Salicylic acid (for analysis, in a vial) | 1 g | One of **A-G** |
| Acetylsalicylic acid (for analysis, in a vial) | 1 g | One of **A-G** |
| Paracetamol (for analysis, in a vial) | 1 g | One of **A-G** |
| Streptocide White (for analysis, in a vial) | 1 g | One of **A-G** |
| Analgin (for analysis, in a vial) | 1 g | One of **A-G** |
| Analgin (for determination, in a beaker) | weighed amount | **H** |
| Potassium permanganate, 0.04 M aqueous solution | 15 mL | $KMnO_4$ |
| Iron(III) chloride, 0.01 M aqueous solution | 15 mL | $FeCl_3$ |
| Sodium nitrite, 0.1 M aqueous solution | 15 mL | $NaNO_2$ |

| | | |
|---|---|---|
| Hydrochloric acid, 1 M aqueous solution | 15 mL | HCl |
| Sodium hydroxide, 3 M aqueous solution | 15 mL | NaOH |
| *p*-Dimethylaminobenzaldehyde, 0.06 M solution in 50 % ethanol containing 1.4 M HCl | 15 mL | *p*-DMABA |

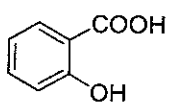



*p*-DMABA

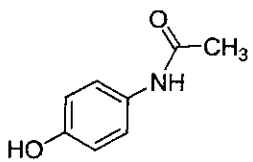
## Part 1.

## Identification of organic compounds

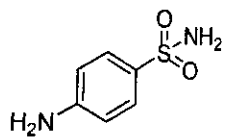
Each participant is supplied with containers labeled **A** – **G**, each containing an individual compound from 7 listed below: *p*-nitrophenol, benzoic acid, salicylic acid, acetylsalicylic acid, paracetamol, streptocide, and analgin:



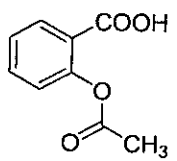

*Salicylic acid*



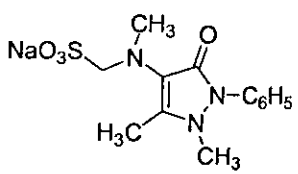

*Paracetamol*




*Streptocide White*




*Acetylsalicylic acid*




*Analgin*

Identify the compounds using the reagents provided (decipher the compound in each vial). Identification is based on the ability of compounds to give more or less intensely colored products as a result of interaction with the corresponding reagents.

*Tips:*

1. Perform qualitative reactions in the 96-well plate (fig. 1/2008).

2. The unknown compounds can be subjected to analysis in the solid form. Transfer small amounts of compounds into the wells on spatula tip. Carefully wipe the spatula with paper towels.



3. Do not remove the vial stoppers; only pull out the pipettes from the stoppers. Do not pour high amount of the solutions into the wells (1-2 drops of a reagent are sufficient).

4. Follow both intensity of a product color as well as the time of its appearance.

5. Oxidation of the compounds by permanganate should be tested in neutral and alkaline media.

Fig. 1/2008. 96-well plate for qualitative reactions.

6. One of the unknown compounds (that with aromatic ring most enriched with electrons) promptly reacts with nitrous acid at room temperature yielding a yellow nitro-derivative.

7. *p*-DMABA reacts with amines under acidic conditions affording Schiff bases. Most intensely colored products are formed with the compounds containing a primary amino group:

$$Ar'–CHO + H_2N–Ar'' \rightarrow Ar'–CH=N–Ar'' + H_2O.$$

8. Many phenols interact with iron(III) ions, the coloration being most intense in the case of chelate formation.

9. The sample of acetylsalicylic acid may contain salicylic acid as an impurity.

## Procedure

**a)** ***Identification of the unknown compounds***

Place a small amount of the substance from vial **A** into each of the six wells of the 96-well plate. Add the alkali solution to the first well, neutral $KMnO_4$ solution to the second well, $KMnO_4$ and alkali solutions to the third well, $FeCl_3$ solution to the forth well, $NaNO_2$ and hydrochloric acid solutions to the fifth well, and *p*-DMABA solution to the sixth well. Repeat the same for the substances from vials **B – G**. Write down the observations in Table 1/2008.

**Table 1/2008. A sample protocol for recording the observations.**

| Vial Code | The reagents added | | | | | | |
|---|---|---|---|---|---|---|---|
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Based on the study, identify the compounds in vials **A – G** (fill in the Table):

| *Compound* | *n*-Nitrophenol | Benzoic acid | Salicylic acid | Acetylsalicylic acid | Paracetomol | Streptocide White | Analgin |
|---|---|---|---|---|---|---|---|
| *Vial Code* | | | | | | | |



**b)** ***Confirmation of the identification results***

Aromatic amines react with sodium nitrite in acidic medium affording diazonium salts (diazotization reaction), which, in turn, interact with electron enriched aromatic compounds with formation of intensely colored products (azo coupling reaction). The reaction takes place in weakly acidic or weakly alkaline medium; the deprotonated forms of the products usually possess the strongest coloration.

**Questions and assignments**

**1.** Write down the equation of a diazotization reaction, denoting the aromatic moiety as Ar.

**2.** Write down the equation of an azo coupling reaction, denoting the aromatic moiety as Ar'.

To confirm the identification you have accomplished, study the possibility of diazotization of one of the compounds **A – G** followed by azo coupling with another compound from the same list (**A – G**). Remember that an intensely colored product is formed. Complete the Table (only one colored product is scored).

| Compound selected for diazotization (vial code) | Compound used for azo coupling (vial code) | Color of the product |
|---|---|---|
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |