POP QUIZ!

Match wits with the high school students who take the IChO EXAM

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THE INTERNATIONAL Chemistry Olympiad (IChO) exam is no piece of cake, even for chemists who are considerably older than the high school students who take it.

"Graduate students might be able to answer most of the questions, but not all of them, and certainly not within the period of time that's expected," says Michael P. Doyle, chair of the chemistry and biochemistry department at the University of Maryland, College Park, which will host the olympiad on July 21–30. Even established scientists would find it hard to answer a number of the questions, he adds. But it's not impossible; at last year's IChO in Ankara, Turkey, a student from the Czech Republic earned a perfect score on the theoretical part of the exam. (The other part of the exam is a lab practical.)

Despite the challenge, chemistry olympians don't seem to regard the experience as an ordeal. "It would destroy me," Doyle admits, but "students come into this with a visible sign of relaxation and enthusiasm."

They gain their confidence in part from intensive preparation ahead of IChO. That advance work includes practice with a large number of preparatory problems, says Doyle, who along with his departmental colleague Andrei N. Vedernikov chaired the 15-member volunteer committee that wrote this year's preparatory and exam problems.

IChO guidelines specify the length of the exam as well as the topics that can be considered fair game for questions. Exam writers can also throw in a few questions from outside those areas as long as the topics are introduced in the preparatory questions.

The exam, which is translated by mentors from each of the student teams' countries, is presented to the students in a paper booklet, with a second booklet in which they write their answers. Answers are numerical or structural to avoid errors in translation during grading.

The questions tend to be lengthy and have multiple parts. Here's a sampling of some of the briefer questions from previous years' exams.

IChO Theoretical Problems

Name ______________________

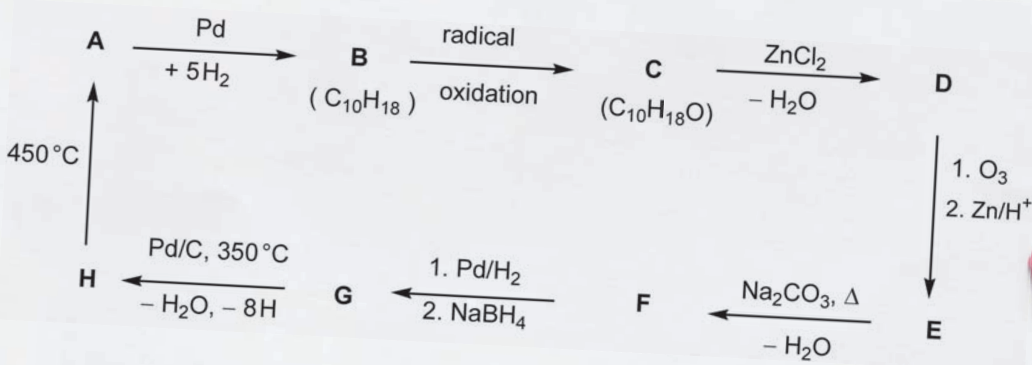
1. A proposed mechanism for the reaction between NO and H_2 is given below:

$$2NO(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2(g)$$

$$N_2O_2(g) + H_2(g) \xrightarrow{k_2} N_2O(g) + H_2O(g)$$

Derive the rate law for the formation of N_2O from the proposed mechanism using the steady-state approximation for the intermediate.

2. Determine the structure of the compounds **A-H** (stereochemistry is not expected), based on the information given in the following reaction scheme:



Hints:

- **A** is a well-known aromatic hydrocarbon.
- A hexane solution of **C** reacts with sodium (gas evolution can be observed), but **C** does not react with chromic acid.
- ^{13}C NMR spectroscopy shows that **D** and **E** contain only two kinds of CH_2 groups.
- When a solution of **E** is heated with sodium carbonate an unstable intermediate forms at first, which gives **F** on dehydration.

3.

A fuel cell is made up of three segments sandwiched together: the anode, the electrolyte, and the cathode. Hydrogen is used as fuel and oxygen as oxidant. Two chemical reactions occur at the interfaces of the three different segments.

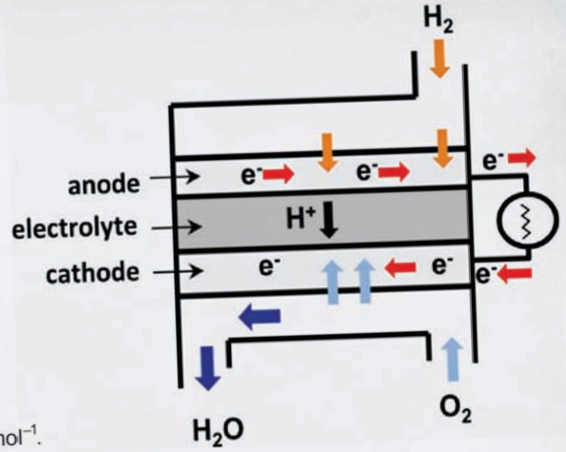
$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

$H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^-$

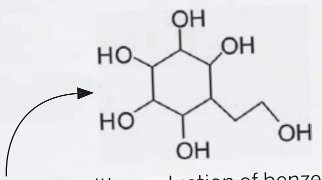
The net result of the two reactions is

$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

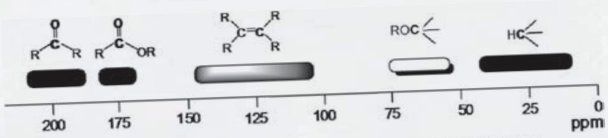
The hydrogen for the fuel cell is supplied from the hydrolysis of sodium borohydride. Calculate the standard potential for the cathode half reaction if the standard reduction potential for the anode half reaction is –0.83 V and $\Delta_f G°$ ($H_2O(l)$) is –237 kJ·mol^{-1}.



4.

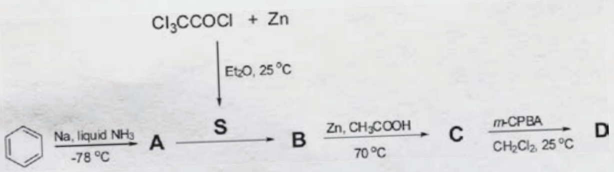


The total synthesis of **1** starts with a reduction of benzene by sodium in liquid ammonia to give **A.** The ^{13}C NMR spectrum of **A** consists of two signals at 124.0 and 26.0 ppm.



^{13}C-NMR chemical shift ranges of typical functional groups

Trichloroacetyl chloride in the presence of Zn gives a reactive species **S.** One equivalent of **S** undergoes [2+2] cycloaddition with **A** to form a racemic product **B.** The reaction of **B** with Zn in acetic acid gives **C.** Compound **C** contains only carbon, hydrogen and oxygen. The ^{13}C NMR spectrum of **C** exhibits three sp^2 carbon signals at 210.0, 126.5, and 125.3 ppm.

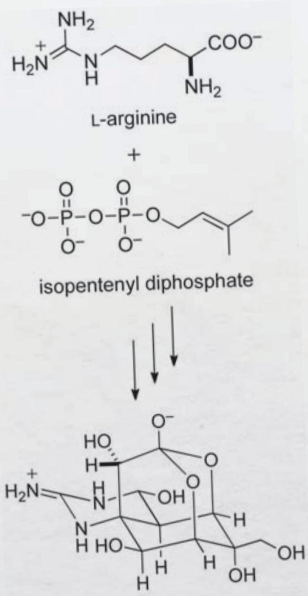


The reaction of **C** with one equivalent of *m*-chloroperbenzoic acid (*m*-CPBA) in methylene chloride gives **D** as a major product. The ^{13}C NMR spectrum of **D** also exhibits three signals in the sp^2 region at 177.0, 125.8, and 124.0 ppm.

Draw the structures of **A, B, C, D,** and the intermediate **S.**

5.

Certain varieties of puffer fish, Fugu in Japanese, are highly prized as foods in Japan. Since the viscera (especially ovaries and livers) of the fish contain a potent toxin (tetrodotoxin), food poisoning often results from its ingestion. Studies on tetrodotoxin have been performed from the beginning of the 20th century; its chemical structure was elucidated in 1964. Although biosynthesis of tetrodotoxin still remains to be clarified, it is proposed that tetrodotoxin may be biologically synthesized from L-arginine and isopentenyl diphosphate. Among the carbons included in tetrodotoxin, circle all the carbons that are expected to be of L-arginine origin.



& MORE ONLINE Stumped? Find the answers to these quiz questions at http://cenm.ag/popquiz.

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Derive the rate law for the formation of N_2O from the proposed mechanism using the steady-state approximation for the intermediate.

$$\frac{\Delta P_{N_2O}}{\Delta t} = k_2(P_{N_2O_2})(P_{H_2})$$

steady-state approximation for N_2O_2

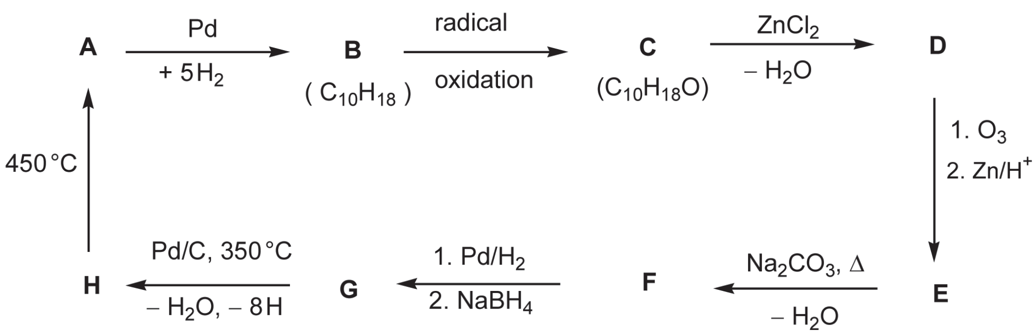
$$\frac{\Delta P_{N_2O_2}}{\Delta t} = 0 = k_1(P_{NO})^2 - k_{-1}P_{N_2O_2} - k_2P_{N_2O_2}P_{H_2} = 0$$

$$P_{N_2O_2} = \frac{k_1(P_{NO})^2}{k_{-1} + k_2P_{H_2}}$$

$$\frac{\Delta P_{N_2O}}{\Delta t} = k_2P_{H_2}\frac{k_1(P_{NO})^2}{k_{-1} + k_2P_{H_2}}$$

$$\text{Rate} = \frac{\Delta P_{N_2O}}{\Delta t} = k_1.k_2\frac{(P_{NO})^2P_{H_2}}{k_{-1} + k_2P_{H_2}}$$

2. Determine the structure of the compounds **A-H** (stereochemistry is not expected), based on the information given in the following reaction scheme:



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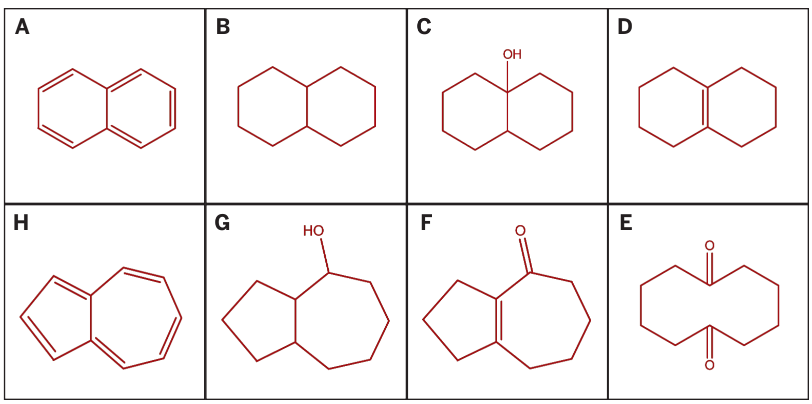

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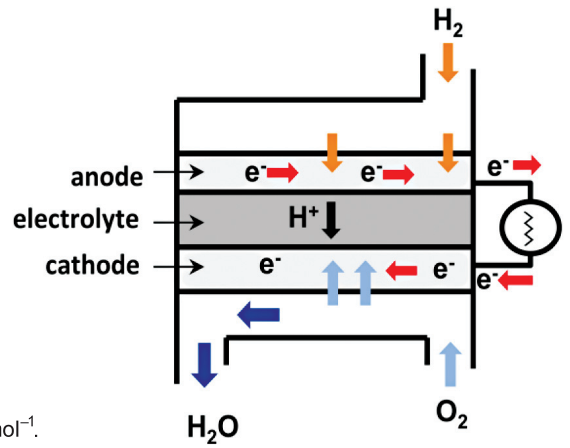

Since $\Delta G° = -nFE°$

$2(-2.37\times10^5) = -4\times96{,}485\times E°_{cell}$ $\quad E°_{cell} = +1.23$ V

$1.23 \text{ V} = E°_{cathode} - (-0.83)$ $\quad E°_{cathode} = +0.40$ V

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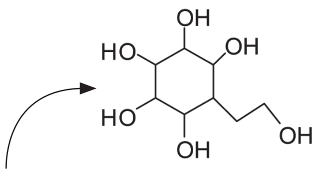

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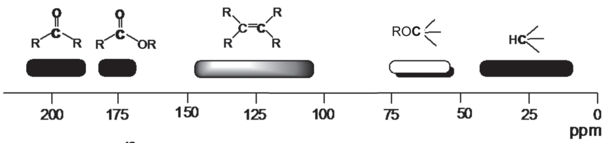

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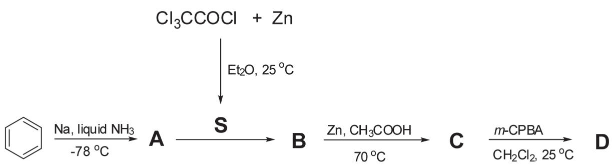

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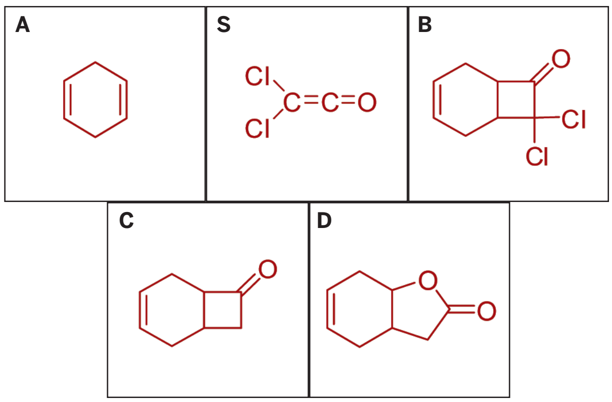

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