A GREEN CHEMISTRY LAB COURSE

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Abstract. The traditional course content of chemistry classes must change to achieve better awareness of the important issues of sustainability in chemistry within the next generation of professional chemists. To provide the necessary material for the organic chemistry teaching lab course, which is part of almost all study programs in chemistry, material was developed and collected (http://www.oc-praktikum.de) that allows students and teachers to assess reactions beyond the experimental set up, reaction mechanism and chemical yield. Additional parameters like atom economy of chemical transformations, energy efficiency, and questions of waste, renewable feed stocks, toxicity and ecotoxicity, as well as the safety measures for the chemicals used are discussed.

Keywords: basic organic teaching laboratory, Internet-based learning, green chemistry, sustainable chemistry.

1. Introduction

The right education of future professionals in the field of chemistry is the key achieving a more sustainable development [1, 2]. Taking on this challenge for the area of basic practical organic chemistry in higher education, a collaborative project of six German universities has created a collection of lab experiments that is accompanied by background information on sustainable development, classical and new laboratory techniques and the evaluation of chemical substances and reactions. The material is freely accessible on the internet in English (http://www.oc-praktikum.de) among other languages. The NOP acronym is derived from the German title "*Nachhaltigkeit im Organisch Chemischen Praktikum*" (sustainability in the organic chemistry lab course) [3, 4].

A.M. Bahadir and G. Duca (eds.), *The Role of Ecological Chemistry in Pollution Research and Sustainable Development*,

Organic teaching labs are a typical element in university education in chemistry, biochemistry, biology, pharmacy, physics, medicine and even some areas of environmental and civil engineering. However, most curricula are still based on traditional lab classes in chemistry. They focus on teaching basic experimental techniques for synthesis and analysis, and how to handle hazardous chemicals. The efficiency of a chemical transformation is usually measured by the chemical yield of the product obtained. Students do not learn how to get a more complete picture of a reaction, by using indicators of its sustainability, and they are not provided with tools to increase its overall efficiency and sustainability. However, aspects of overall efficiency and sustainability of a reaction must be added to the content of teaching lab courses in organic chemistry to prepare future generations of chemists. Toxicological and ecotoxicological knowledge and data have to be integrated in a way that it becomes a natural part of the discussion of an experiment. Within this considerably wider scope (Fig. 1.1) students learn how to plan, set up and analyze organic reactions taking their effect on the environment and human beings into account. Sustainability starts with the conceptual planning of a chemical transformation.

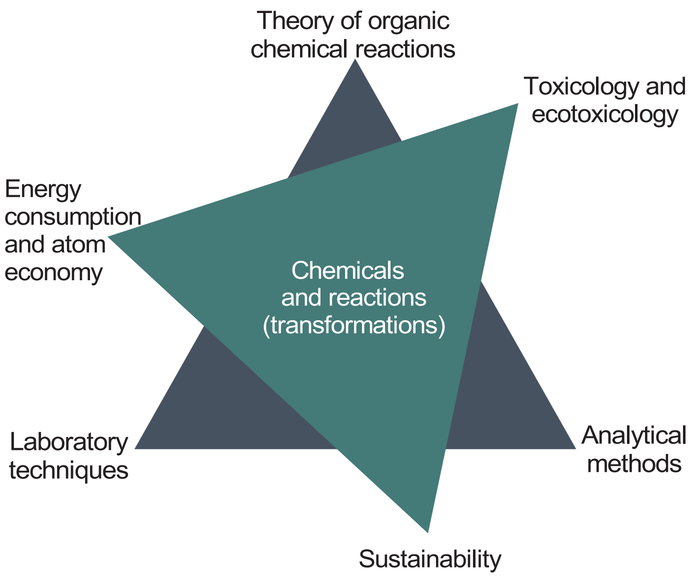

Fig. 1.1. The classical elements of organic chemistry education (black triangle) are extended by topics assessing sustainability of chemical reactions and compounds (green triangle).

We introduce in this chapter the NOP internet database, which provides a wealth of material, covering experimental procedures, toxicity data, alternative reaction procedures, some data about energy efficiency and more to assess a chemical reaction in a wider sense. The provided information can be individually adapted to classes at various levels of University education.

Education in chemistry has a very long history. For a long time the most important goal of a chemist was to make a compound in suitable amounts and high purity from available starting materials. This biased the chemical education, which had a strong focus on practical lab techniques and methods for compound purification. The question of how much energy is needed for a reaction and how much waste is produced was raised for industrial processes only. Although the goal for synthetic organic chemist is still the same, to make a compound in good yield and high purity, additional parameters must be considered in the development of new processes today. The last 20 years in which much more attention was paid on the effect of chemical production and chemical compounds on human health and the environment have taught us one clear lesson: It is much better, easier and less expensive to develop processes and compounds that are sustainable from scratch than to optimize an existing poorly developed chemical process or to remove dangerous chemicals from the environment in order to reduce potential hazards and pollution. For these purposes, chemists, biochemists, engineers, scientists working in drug development or constructing new materials must think in terms of long-term sustainability when transforming their ideas into products and processes. This calls for a different chemical education which teaches more than reaction mechanisms and experimental techniques. Students must learn to judge the suitability of a chemical transformation or the use of a chemical compound within a matrix of many parameters. It is not only the yield of the reaction that counts. Which starting materials are needed? Can they be made from renewable resources? Do we get toxic by-products and how can they be avoided? How much waste is generated by the process and is it energy efficient? Are we terminating the reaction at the earliest possible time? Asking these questions at the beginning of chemical research and technology development will lead to a more efficient and sustainable use of chemistry. Asking these questions in the teaching lab course will clearly change the way students conceive a chemical reaction and prepare them much better for their professional career.

2. Laboratory experiments of NOP

In contrast to alternative chemistry lab course experiments developed by Hutchinson and other groups [5] it was not tried to exclusively select "green" experiments, i.e., with an especially low hazard potential of the involved substances. The approach of the NOP project is rather based on the idea that we will always need chemists that are trained in handling hazardous substances in a responsible manner. However, in order to foster the conscience of the overall greenness of an experiment in organic chemistry, a classification of the experiments in three groups was developed, which are intuitively visualized by green, yellow and red traffic lights (Fig. 2.1).

	1001	**Nitration of toluene to 4-nitrotoluene, 2-nitrotoluene and 2,4-dinitrotoluene**	nitroaromatics, aromatics	electrophilic substitution of aromatics, nitration of aromatics	distilling under reduced pressure, adding dropwise with an addition funnel, working with wash bottles, extracting, shaking out, recrystallizing, filtering, evaporating with rotary evaporator, stirring with magnetic stir bar, draining of gases, use of a cooling bath, heating with oil bath	Difficult
	5026	**Oxidation of anthracene to anthraquinone**	aromatics, quinone	oxidation	mechanochemical reaction, grinding with a planet ball mill, filtering, evaporating with rotary evaporator	Easy
	3021	**Oxidation of anthracene to anthraquinone**	aromatics, quinone	oxidation	stirring with magnetic stir bar, evaporating with rotary evaporator, filtering, recrystallizing	Easy
	1021	**Isolation of trimyristin from nutmeg**	carboxylic acid ester, triglyceride, natural product	isolation of natural products	extracting with Soxhlet extractor, evaporating with rotary evaporator, recrystallizing, filtering, heating under reflux, heating with oil bath, stirring with magnetic stir bar	Easy
	5019	**Isolation of trimyristin from nutmeg**	carboxylic acid ester, triglyceride, natural product	isolation of natural products	microwave-assisted extraction, recrystallizing, filtering, evaporating with rotary evaporator	Medium

Fig. 2.1. Evaluated experiments of the NOP database.

Some experiments have been developed using two alternative techniques, i.e., conventional heating under reflux and conducting in a microwave apparatus [6] (*not* a household microwave system!). This allows a comparisons of different experimental techniques.

The red traffic lights are not intended to express that such reactions should not be carried out in the laboratory. They merely visualize that a high level of care is needed when conducting those experiments, and that there is an especially large potential for optimization of the reaction in terms of sustainability. The green light is given for experiments that are especially favourable regarding their substance and energy efficiency, as well as their treatment/avoidance of hazardous substances. The yellow light is attributed to experiments that do bear risks for men and/or environment, and that should be carried out with considerable caution.

From the 75 experiments currently available in the NOP database, only 13 have undergone a complete evaluation at present (October 2008). For the remainder of the experiments, a traffic light with a question mark is shown. These experiments meet the criteria for inclusion concerning quality and reproducibility, and a standardized set of background information is given as well. This set includes an assessment of data availability for every substance, its risk and safety phrases according to the EU directive 67/548/EEC and its amendments on the classification and labelling of dangerous substances, as well as an assignment of effect factors according to the German Hazardous Substance Regulation (TRGS 440). An operating scheme visualizing the experimental procedure is given for each experiment (Fig. 2.2) and substantial information is provided on how the final product can be checked for its identity, purity and side products. The concise experimental instructions for each experiment are available as a PDF file in a standardized way.

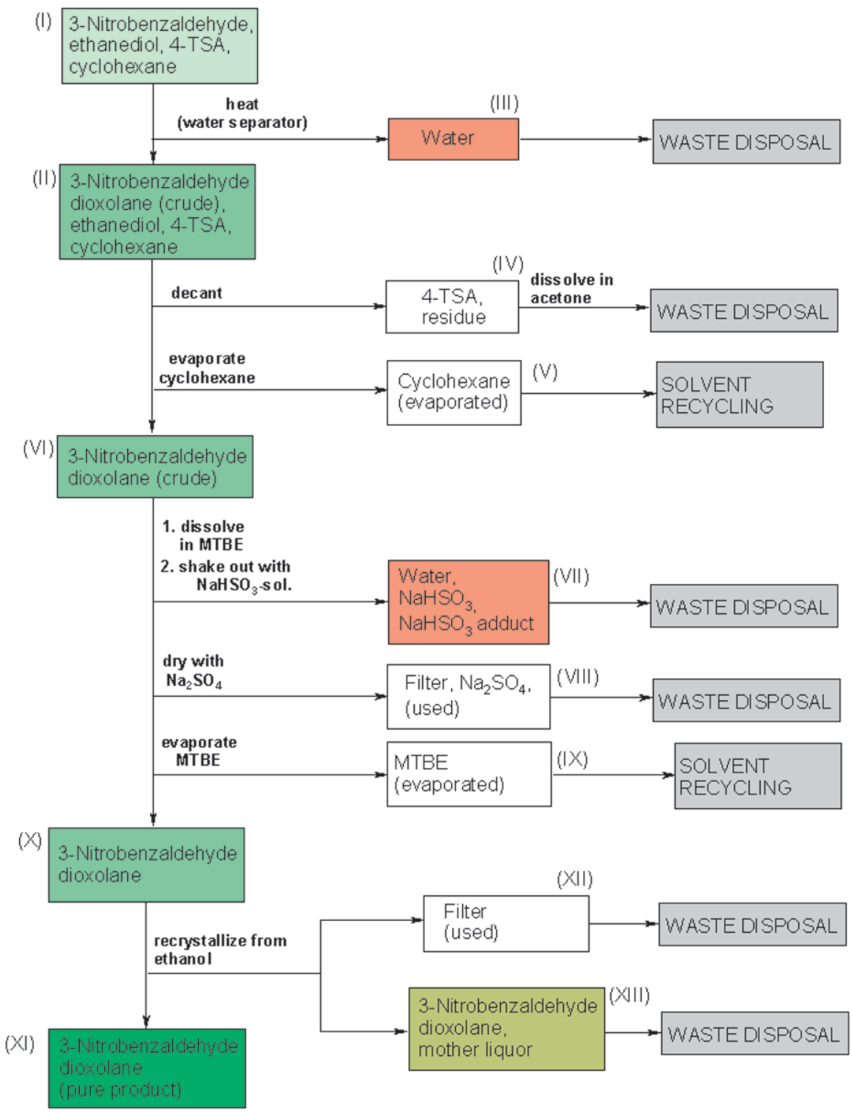

Fig. 2.2. Example of a flow chart ("Operating Scheme") for an experiment in the NOP database.

The "Globally Harmonized System of Classification and Labelling of Chemicals" (GHS) is currently being established providing a unified way of communicating hazard potentials. While this is still under way, the substance specific hazard information in the NOP is largely based on the system of the European Union, consisting of a system of 10 hazard symbols and a large number of various risk (R) and safety (S) phrases. For each experiment, the website provides a substance overview, listing amount, name, hazard symbols, R and S phrases for any substance and auxiliary material used in the reaction (Fig. 2.3).

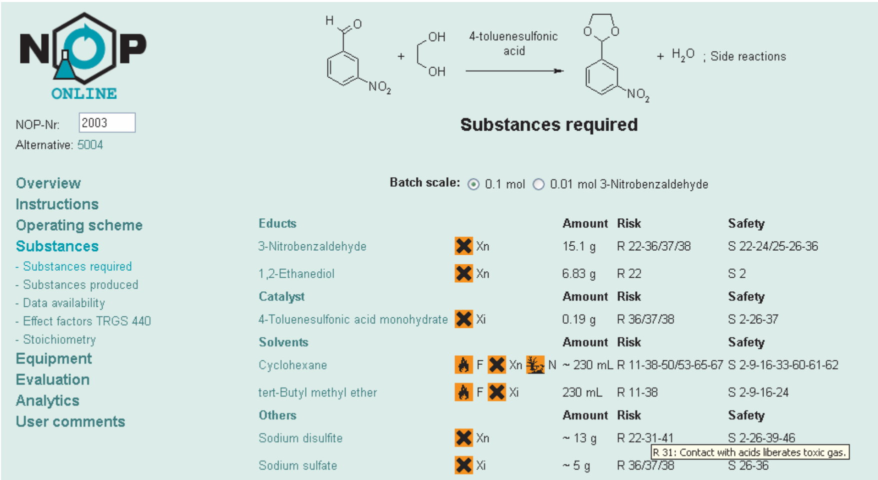

Fig. 2.3. Overview of required substances together with quantities, risks and safety information.

Based on the risk and safety phrases, the German Technical Directive for Hazardous Substances TRGS 440 defines effect factors ranging from zero to 50,000, which is an indicator for the level of workplace risk caused by a particular substance. Effect factors have been determined for all substances in the NOP substance database. These effect factors are visualized for each experiment, using a colour scale from white (effect factor 0) to dark orange (effect factor 50,000). An example is given in Fig. 2.4.

For the experiments that have already been fully evaluated, a comprehensive search on physical–chemical properties, toxicological and ecotoxicological data has been conducted and the most important results are available on the NOP website, together with a source attribution for all data.

An important aspect is the provision of a comprehensive set of data for the characterization of the experiments and all chemicals used by means of instrumental analyses (GC, HPLC, MS, coupled systems) of raw and purified substances as well as spectral information (FT-IR, NMR ($^{1}H/^{13}C$) etc.) that enables the teachers and students to use for advanced instrumental analytical and spectroscopic courses without having these instruments and/or substances at their own institutes.

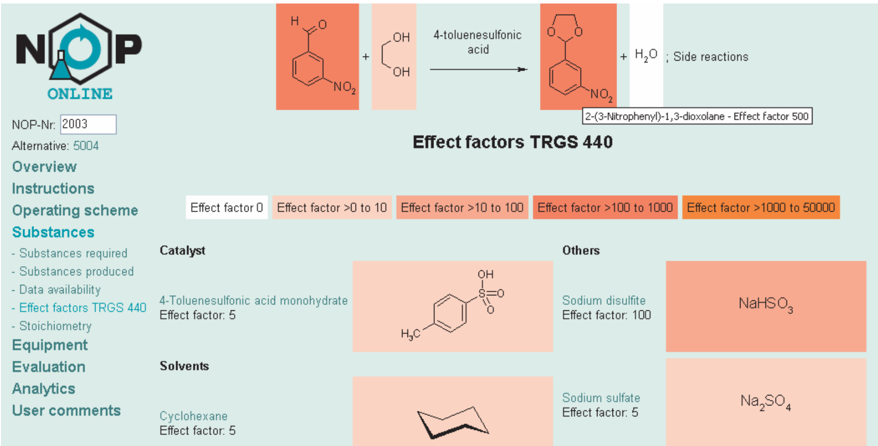

Fig. 2.4. Effect factors of an experiment from the NOP database.

3. NOP material in teaching

The NOP website is not a ready-to-use class. The material has to be adapted to the specific needs of a teaching unit by the instructor. The 75 experimental instructions may find use in the basic organic teaching lab of degree courses in chemistry, biology, biochemistry, but also for students of medicine or engineering. The instructor can select and extract the experiments that are suitable for the course using the NOP database. However, the material does also provide the basis for a specialized class in environmental chemistry or ecotoxicology, one may teach safety regulations using the material or discuss the examples in a class covering spectroscopic identification of organic compounds or HLPC and GC techniques. Team tasks are another option: Starting from one of the given procedures the challenge is to increase its efficiency by finding the minimal reaction time for saving energy, the optimal reaction temperature or the best work up conditions. Reactions are run in parallel by the team members using different conditions and monitoring the conversion. The individual lab training remains, but only all the results together will give a full picture of the reaction and answer the question. The team task can be designed from very simple, e.g., varying temperature or reaction time, to complex, e.g., energy consumption or choice of solvent.

4. National versions of NOP

The NOP platform allows including versions in different languages. So far, the NOP is available in German, English and Italian. Translations into Russian, Indonesian, Arabic, Turkish and Greek have been completed and will be available on-line soon. The translation into Portuguese is in progress. The national versions are coordinated by a national editor, who is responsible for the content, the translations and the continuous improvement of the database. The benefits of NOP as teaching material is particularly accepted by universities of emerging countries since this material is freely accessible via the internet and the translation into their own languages allows the use of this material also for students who are not familiar with the English language. The NOP project team welcomes national editors from any country, who would like to translate and adapt the NOP material for their national higher education system.

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