II. Literature Search and Report for Your Substituted Benzophenone. (CH 463/H 2016) (excerpted from lab manual)

Your first task is to find secondary and primary references and prepare a research proposal after a search of the primary literature. Your proposal should cover all information and pertinent data that has been published on your assigned substituted benzophenone using your assigned chemical reagents and method. The first week, particular emphasis is to be placed on information about the synthesis, work up, isolation, and purification of the compound, and in following weeks your job is to locate as much information as possible on the electronic spectroscopy and photochemical reactivity for your compound. You should pay special attention to the physical properties of significance to you in this experiment, e.g., melting points, solubility and solvents suitable for recrystallization, boiling points at various pressures, etc. Has anyone synthesized your compound by the same method you are going to use or by a closely related method? What were the conditions, methods of working up the reaction mixture, yields, etc.? Previous literature reports on the absorption spectra (UV, IR, Raman), NMR, phosphorescence behavior, photochemical reduction, and properties of the photoreduction product, benzopinacol, are also important.

The two most useful secondary reference sources that are locators for the primary literature are the scientific search engines: SciFinder (Chemical Abstracts), and Reaxsys (the German Beilstein's Handbuch der Organischen Chemie and Gmelin). The first day you will use these search engines to search for primary references for the synthesis and characterization of your assigned compound. These user interfaces have been installed on the computers in the lab and you can also register to use these programs on your own laptops - see the Valley Library web page for electronic databases. You may still need to go to Valley Library to retrieve paper copies of primary literature sources from the stacks and/or request electronic copies using InterLibrary Loan for any journals that OSU does not have access to. The librarians at the Valley Library Science-Technology desk are also available to help you. The reference indexes (in print), Chem Abstracts System Source Index (CASSI, QD1.A532) is a useful guide to find the standard abbreviations for journals and this information can often be found online as well. There are several helpful links on the CH 463 web page (Supplemental Materials).

Beilstein is a major structure and factual database of organic chemistry and is comprised of abstracts written from a critical review of the primary literature (this is different than just listing references). Some abstracts written after 1959 are unreviewed organic substance records (registry numbers, structures, formula and weight, chemical name, general chemical data including preparation and property data). Citations to Beilstein and Gmelin are common in the Handbook of Chemistry and Physics (CRC), Lange's Handbook, and the Aldrich catalog/handbook, for example.

Examples of additional secondary references:

1. SDBS data base online at course web page- supplementals
2. NIST web \book availab on line at course web page- supplementals
3. Chemical Vendor web sites, e.g., Sigma Aldrich and TCI web sites
4. CRC Atlas of Spectral Data and Physical Constants of Organic Compounds, 2nd Ed. Vol. II (QD291/A8(ref));
5. Atlas of Absorption Spectra, L. Láng (QC437.L27);
6. Phillips, Freedman, Craig, Organic Electronic Spectral Data (QD 95.O7, V. 6), G. Olah, Friedel-Crafts and Related Reactions, 4 Vols. (QD501.O6); etc.

The secondary reference sources will direct you to the original primary journal articles. Your job is to use these secondary references to locate the primary articles. The original papers may well be in German, French, Italian, or Russian - but don't worry! Scientific/chemical dictionaries and your instructors will assist you in reading these if you bring a legible copy (note: please treat old journals with care - they are not easily replaced). There are some on-line scientific dictionaries for translation purposes as well (see course web page).

Before starting your synthetic work the second week, you are required to turn in your research proposal and detailed draft of your proposed synthetic work and receive approval from the main course instructors (Pastorek or Firpo). This proposal should be 1-2 pages of written text (see class handout for more directions) and you should give specific details based on what you found in the literature explaining on how you plan to carry out the synthesis, work up, isolation, purification and characterization for your assigned compound.

Tips on Searching the Scientific Literature for Benzophenone Project.

For the first part of the project you are looking for information and details on the synthesis and characterization of your assigned compound. Clues are often found in unlikely places, such as in figures and tables in published articles, and information that you are looking for may not be the main emphasis of the publication, or your compound may appear in a table in a paper reporting a systematic study of many substituted benzophenones that all have a common preparation scheme.

Usually one clue leads to another, and eventually you will find enough published information (presumably reviewed by reputable scientists) to design your synthesis. Often it pays to follow up on secondary leads by consulting the reference list at the end of promising journal articles and search for those sources. A good place to start is by searching the secondary references such as handbooks,

catalogs and databases that lead you to the primary journal articles. The goal is to find the original published reviewed journal articles that have the information that you need. The following is a flow chart of sorts on how to start your search.

1. Find the Chemical Abstracts Registry number (CAS) or Registry Number (RN) for your compound. This is a unique identifier and can be a useful tag to search on instead of using a chemical name. The RN/CAS's can be found for example in the Aldrich Catalog/Handbook and in the MSDS. For example the RN/CAS for unsubstituted benzophenone is: [119-61-9]. [Note square brackets are used to designate the CAS].

2. Locate a few proper chemical names for your compound. For example, **benzophenone is a parent name but in IUPAC language it also known as diphenyl methanone**. Symmetrically substituted benzophenones are named either as *bis* (phenyl) methanone, e.g., *bis* (4-iodophenyl) methanone, or as 4,4-di(substituent)benzophenone, e.g., 4,4'-diiodobenzophenone. For non-symmetrically substituted benzophenones, for example, 4-iodophenyl-4-nitrophenyl methanone is the same as 4-iodo-4'-nitrobenzophenone.

3. OSU currently has unlimited user licenses for the entire campus (~$200K/yr) for Scifinder Scholar and Reaxsys. You can access these through the OSU Library site an setup a login using your onid email. The search results you locate depend on how you search and which database is searched (there are several databases that are part of SciFinder, such as, Registry, CAReacts, etc.). Success also depends on the date the journal article was published. For example, it is usually more efficient to search using the chemical name or the CAS number as a RESEARCH TOPIC rather than searching the compound using a structure search - try both methods. Searching the structure should at a minimum lead to the CAS number if you can't find it somewhere else. If you get a lot of hits after entering a search string, refine your search by searching the first hit list with another TOPIC such as synthesis of , preparation of , spectroscopy of, etc. to narrow down the choices. Once you have a hit list of references, you can check the box next to the likely candidates to view the abstract and often download a pdf of the full text of the paper through an interface called CAS Port. If OSU owns a license for the electronic version of a particular journal, you can download a pdf file of the actual article. If OSU owns a hardcopy license, you can take the list of references and go to Valley Library and retrieve the paper journal from the stacks. If OSU does not own rights to the journal you can request a copy of the article by InterLibrary Loan (ILL) on line. This means that if a library in the consortium of University libraries that OSU belongs to has the journal, they will email you a pdf within a few days to a few weeks. To request ILL, use the electronic form on the Valley web page.

4. You might have to physically go to the stacks at Valley Library on the first floor. Occasionally but rarely, the abstracts are detailed enough so you can design your synthesis without the physical copy of the primary article.

5. Don't get discouraged, there are often false trails. Keep on trying and check with your Instructors frequently!

6. Check the Valley Library Catalog and Orbis, a consortium of university libraries that share resources. See the link on Valley library web page.

7. Check your organic text book and other organic text books for Friedel -Crafts acylation using aluminum chloride catalyst and Pd catalyzed cross coupling reactions using boronic acids. Also consult the references cited in your text book.

8. If you can't find ANYTHING on your compound, try searching for information on a similar benzophenone and adapt that procedure after discussion with one of your instructors. For example, if you are assigned 4-chloro-4'-propylbenzophenone and can't find ANYTHING, try looking up a preparation for a more simple but similar benzophenone, e.g., 4-chlorobenzophenone or 4-chloro-4'-methylbenzophenone or 4-propylbenzophenone and design your own synthesis (the Instructors are available to help). Method 2 in the lab manual can be useful as a general guide in these cases.

Key words to watch for in your search

Part A of Project - Synthesis and characterization

- Friedel-Crafts acylation synthesis
- Aluminum Chloride catalyst; $AlCl_3$; carbon disulfide (solvent), CS_2
- Pd catalyzed cross coupling reactions using phenyl boronic acid (for Suzuki type rxn)
- melting point
- boiling point (at what pressure?)
- solubility in various solvents - sometimes this shows up in published work on the spectroscopy, or is listed along with melting points
- IR, NMR, Raman spectra for main peaks.

Keep your eyes open for references for the physical chemistry/analytical study for the Part B of Project: Photophysics and Photochemistry and note pertinent references so you can retrieve and read these later:

- UV absorption spectrum; solvent?
- molar absorptivity, extinction coefficient
- lambda max
- emission wavelength; solvent?
- excitation wavelength; solvent?
- integrated absorption coefficient
- Singlet (S_1) and Triplet (T_1) UV transitions; $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions

- emission lifetime, phosphorescence lifetime; solvent?
- phosphorescence quantum efficiency; solvent?
- photochemical reduction by sun light or UV light to the benzopinacol
- photochemical reduction efficiency
- mp, IR, NMR for your reduced ethanediol (i.e., benzopinacol).