Simple and efficient assembly for preparative photochemistry

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ABSTRACT. A simplified and efficient assembly for the preparative photochemistry is described. The apparatus was tested in some classical organic photochemical reactions such as photobleaching of riboflavin, and photo reduction of the benzophenone, as well as in some organometallic reactions: photodimerization of pentacarbonyliron and in inorganic reactions: photo reduction of silver and platinum salts or complexes. Two new protocols were described: the photo reduction of copper (II) chloride and the first photochemical synthesis of ferricenium tetrachloroferrate. We demonstrated that the assembly may be useful in organic, inorganic and organometallic preparative photochemistry.

Key words: photochemistry (assembly for), photo-reactor, photochemistry (reactions).

RESUMO. Um aparelho simples para fotoquímica preparativa. Uma aparelhagem laboratorial eficiente e simplificada para fotoquímica preparativa é descrita. O aparelho foi testado em algumas reações clássicas de Química Orgânica, como o foto-branqueamento de riboflavina e a fotoredução de benzofenona, bem como em algumas reações organometálicas: fotodimerização de ferro pentacarbonilo e em reações inorgânicas: fotorredução de sais ou complexos de prata e platina. Dois novos protocolos, fotoredução de cloreto de cobre (II) e a primeira síntese fotoquímica de tetracloroferrato de ferricínio, são descritos. Demonstramos, assim, que o aparelho pode ser útil em fotoquímica preparativa orgânica, inorgânica e organometálica.

Palavras-chave: fotoquímica (aparelho para), foto-reator, fotoquímica (reações).

Introduction

In the last two decades, some unusual techniques: sonochemistry (Federman Neto *et al.*, 1997; Mason, 1997; Coins *et al.*, 1998; Naffrechoux *et al.*, 2000; Magdolen *et al.*, 2001; Meciarova *et al.*, 2001); microwave irradiation (Abramovitch, 1991; Strauss and Trainor, 1995; Loupy *et al.*, 1998; Puciová *et al.*, 1998; Seiyas *et al.*, 1999; Eynde *et al.*, 2001), photochemistry (Naffrechoux *et al.*, 2000) have been employed for the synthesis of some compounds, which are, otherwise, difficult to obtain by other methods. In recent years, photochemistry was combined with ultrasound irradiation (Gaplovsky *et al.*, 2000; Toma *et al.*, 2001).

Photochemistry is now extensively used in chemistry. Some recent and interesting applications includes: organic synthesis of cycloaddition compounds (Hoffmann *et al.*, 2002), toxic residues degradation in water (Sakkas *et al.*, 2002), food sterilization (Bintsis *et al.*, 2000), as well as in many applications in material's science and manufacture of high technology products: diamond films (Strother *et al.*, 2002), organosilicon polymers (Uhlig, 2002), nanotechnology materials (Khomutov *et al.*, 2002), biopolymers (Fisher *et al.*, 2001).

In the laboratory, preparative photochemistry is generally carried out in commercial, expensive photo-reactors, built in quartz (transparent to UV) glassware (Ex. Normag Photo-reactor). The classical assemblies were revised by Kopeck and Liska (1978).

Some simple and cheap devices (De Paoli and Rodrigues, 1978; De Paoli and Jorge, 1980) were later developed, but they have only moderate efficiency. Togniolo *et al.*, 2001, used a very simple device, with the reaction mixture
direct irradiation (in a open porcelain dish) with UV light, but the reaction mixture cooling, as well as the complete air exclusion, were difficult.

Material and methods

The photochemical device was built as shown in Figure 1.

Ferrocene (Aldrich, 98%) was purified by recrystalization from 95% ethanol. $PtCl_2$ (Aldrich), $PtCl_4$ (Aldrich), K_2PtCl_4 (Johnson Matthey), pentacarbonyliron (Aldrich) and other reagents and solvents were used as received.

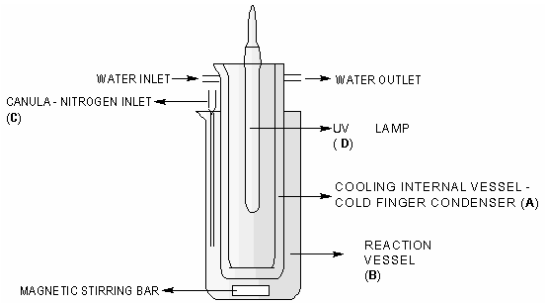


Figure 1. Assembly for Preparative Photochemistry

The apple-green color $Ni(OH)_2$ and the rose color $Co(OH)_2$ were prepared (Brauer *et al.*, 1965) through reaction between the corresponding chlorides and NaOH in aqueous solution. Silver(I) chloride was prepared (Vogel, 1974) through reaction between aqueous silver(I) nitrate and HCl, in quantitative yield. Sodium chloride may be used, but the yield may be lower, due to soluble dichloro argentates (Kleppa and Meschel, 1965) formation.

A) Photo reduction of Silver(I) Chloride:

Silver (I) chloride (1.4 g, 10 mmol) was suspended in 42 mL of isopropanol, and photolysed with stirring, for 1 h. A light violet compound was formed (silver sub-chloride). The photolysis was continued for more 8-10 h. The reaction mixture was evaporated in vacuum to 3-5ml of solvent, and filtered. The black sponge (metallic silver) obtained was washed with water and air-dried. Yields: 97%. This product gives a clear solution when dissolved in concentrated nitric acid, and the addition of HCl 1:1 gives a white AgCl precipitate. These properties demonstrate that this solid is metallic silver.

B) Photo reduction of Platinum Compounds:

The platinum salts: $PtCl_2$, $PtCl_4$ or K_2PtCl_4 (0.15 g) were dissolved or suspended in 42mL of isopropanol and photolysed as described in A. After 30 min. of irradiation, a dark violet colloidal suspension was obtained, changing to a brown colloid (1 h. of irradiation) and to black colloid (3 h. of irradiation). After 10 h. of irradiation, the reaction mixture was treated as described in A, giving metallic platinum, in form of small bright, metallic, crystalline lozenges. The yields: 96% using $PtCl_2$, 99% using $PtCl_4$ and 82% using K_2PtCl_4.

C) Copper(I) chloride:

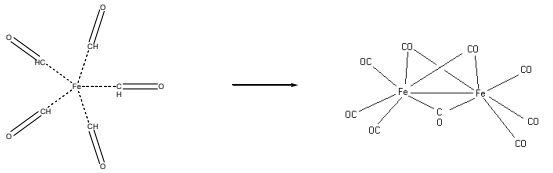
A solution of $CuCl_2.2H_2O$ (2,6 g, 20 mmol) in 42 ml of isopropanol, was irradiated, with stirring and bubbling N_2 into the reaction mixture (see Figure 1). The irradiation was continued for 36 h. The reaction mixture was transferred to an Erlenmeyer flask, purged with N_2 and closed. The solvent was removed with a cannula, the solid was washed four times with degassed water and dried over a strong N_2 stream. The manipulations were carried out according to the previously published simplified method for synthesis in inert atmosphere (Federman Neto *et al.*, 1998).

When exposed to air, the compound quickly changed its color to light green (formation of copper oxychloride).

D) Di-iron-eneacarbonyl:

An iron pentacarbonyl solution (5,89 g, 3,9 mL, 30 mmol) in 42 mL of glacial acetic acid was irradiated, with stirring, with a very slow N_2 stream, bubbled into the reaction mixture, to provide an inert atmosphere and to split off the carbon monoxide. The entire assembly (Figure 1) was immersed in an ice bath and the irradiation was continued for 18 h. The reaction mixture was filtered off and the solid washed with a few mL of glacial acetic acid and, finally, with ethyl ether. $Fe_2(CO)_9$ (Yields: 82%) was obtained, in the form of dark yellow orange platelets, mp. 102°C (dec.) (lit. (Braye *et al.*, 1966) 100 - 120°C dec.).

IR (KBr disc, cm^{-1}) - 2000 - 2070 (terminal CO stretching); 1800 CO stretching). This agrees with the literature (Sheline and Pitzer, 1950; Sheline, 1951) and suggests a structure with D_{3h} symmetry (Nakamoto, 1984), showed in Scheme 1.



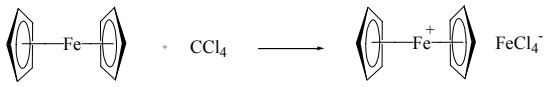
Scheme 1. Pentacarbonyliron photo dimerization

This compound spectrum was found in the AIST International Catalog of Standards (NIST, 2002, SDBS number 27402), but in addition to the expected bands, the catalog spectrum shows bands at 3500, 1600, 900 cm^{-1}. This suggests that the sample used for measuring the catalogue spectrum was not pure, maybe contaminated with iron(II) acetate.

E) Ferricenium Tetrachloroferrate:

Ferrocene (1.86 g., 10 mmol) was dissolved in 42 ml of carbon tetrachloride and irradiated for 36 h. The precipitated ferricenium tetrachloroferrate (Scheme 2) was filtered off, washed with the same solvent, dried in air and took the form of very dark blue, almost black, microcrystalline powder. The yield was low: 2 %, even when the irradiation time was prolonged to 3 days. m.p. > 300ºC (lit. (Neuse *et al.*, 1985) > 300ºC).

IR (KBr disk, cm^{-1}) 3100 (CH stretching); 1100 and 1010 ("ferrocene bands" (Federman Neto *et al.*, 1986, 1997, 2002; Federman Neto and Lanchote, 1998), demonstrating that the compound contains unsubstituted cyclopentadienyl rings); 880, 860 (CH, aromatic); 430 (Fe-Cp ring stretching); 380 (tetrahedral $FeCl_4^-$ anion, Nakamoto, 1984). The spectrum agrees with the literature (Nesmeyanov *et al.*, 1960; Pavlik and Klikorka, 1965; Spilners, 1968; Neuse *et al.*, 1985; Federman Neto, 1986) and the properties and spectrum were compared with an authentic sample, prepared by Nesmeyanov *et al.* (1960) and Spilners (1968), method.



Scheme 2. Ferricenium tetrachloroferrate formation through ferrocene photolysis

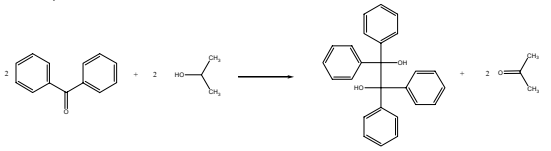
F) Benzopinacol:

Benzophenone (3.6 g, 20 mmol) was dissolved in 42 mL of isopropanol and 1 drop of acetic acid, and photolysed as described in A, but bubbled with N_2, as in C, for a 48-h total period. The solvent was removed in vacuum; the solid was filtered off and purified from the acetic acid solution through precipitation with water. Benzopinacol (yield: 78 %) was obtained (Scheme 3) in form of white crystals, m.p. 184 ºC (lit. (Hawley and Garcia-Ramos, 1975) 185-186 ºC).

IR (KBr disk, cm^{-1}): 3600 (OH stretching); 3000 (CH stretching, aromatic rings); 1620 (C-C stretching, aromatic); 1490 (C (aromatic) - C (aliphatic) stretching), 1150 (C-O stretching).

NMR ($CDCl_3$, δ ppm): 7.25 (m, 20 H, phenyl ring hydrogen's); 3.10 (s, 2 H, OH hydrogen's).

The spectra agreed with the AIST International Catalog of Standards (NIST, 2002, SDBS number 7707).



Scheme 3. Benzopinacol photochemical synthesis

G) Catalytic Hydrogenation of Styrene, catalyzed by metallic Platinum:

A brown colloidal platinum suspension was prepared, through the method described in B, and the photolysis was interrupted. To the slurry, styrene (2.2 g, 2.3 mL, 20 mmol) (previously distillated under reduced pressure, in order to remove the inhibitor) was added, and the solution was hydrogenated at 60 psig, in a Parr apparatus. The solvent was evaporated in vacuum and ethyl benzene was isolated from the residue, through fractional distillation at atmospheric pressure. b.p. 135-136ºC (lit. (Hawley and Garcia-Ramos, 1975) 136.187ºC). Yield: 37%.

H) Other Reactions:

Solutions of anhydrous or hydrated cobalt(II) or nickel(II) chlorides, or suspensions of cobalt(II) hydroxide or nickel(II) hydroxide in isopropanol cannot suffer photo reduction in the conditions employed.

Results and discussion

The construction of a simplified, inexpensive, easy-handling and efficient apparatus for preparative photochemistry may be interesting.

During our current studies on organic and organometallic synthesis, we developed a very simple and efficient apparatus for preparative photochemistry, first tested for riboflavin (Moore *et al.*, 1963) photobleaching, as an experiment in medicinal chemistry, and now routinely used in our laboratory for many preparative photochemical reactions.

The assembly was constructed in borosilicate glass (Pyrex), transparent (Kinkead *et al.*, 1994) to the UVA spectrum, between 400 to 315 nm, but absorbing the UVB (315-280 nm) and UVC (280-200 nm) spectra.

It consists in a cylindrical reactor with a magnetic stirring bar. A double wall cold finger condenser (**A**) is immersed into the cylinder (**B**). Water, circulating in it, cools the lamp and the reaction mixture. The cylinder itself is the reaction vessel. If necessary, inert atmosphere is provided by bubbling gaseous N_2 directly into the reaction mixture *via* cannula (**C**) When the double wall condenser (**A**) is immersed in the cylinder (**B**) containing the reaction mixture, the liquid level raises up, providing a thick layer of dilute solution, easily transversed by the UV light.

The irradiation lamp (**D**) is a relatively cheap, high pressure mercury vapour lamp (750 W, 220 V) of the type used in public illumination, electrically wired to its suitable pulse transformer (reactor) (De

Paoli and Rodrigues, 1978; De Paoli and Jorge, 1980, Togniolo *et al.*, 2001).

When additional cooling is necessary, the entire assembly may be immersed in an ice bath. The complete apparatus is shown in Figure 1.

The majority of reactions were carried out in isopropanol as solvent. Other solvents (acetic acid, carbon tetrachloride) were used when necessary. Large volumes of solvent are needed, because only dilute solutions are easily photolysed, but the solvent may be recycled through distillation.

In inorganic photochemistry, primary alcohols (ethanol) are generally used (Vorobyova *et al.*, 1987; Park *et al.*, 1991) as solvents, but it is well known in organic photochemistry that the secondary alcohols (isopropanol) are more efficient (Hashiguchi *et al.*, 1995, 1997; Mizushima *et al.*, 1999).

We tested the apparatus in organic preparative photochemistry in the classical photo-reduction of benzophenone (Scheme 3) (Moore *et al.*, 1982; Gaplovsky *et al.*, 2000; Toma *et al.*, 2001) with good results.

The apparatus was also applied in some organometallic photochemical reactions:

a) Di-iron eneacarbonyl, $Fe_2(CO)_9$, an iron carbonyl reactive form for the synthesis of many (olefin) carbonyl complexes (Chen *et al.*, 1993; Squizani *et al.*, 1996; Barmann *et al.*, 2000; Chen and Ellis, 2000) and many other compounds. It is prepared through photochemical dimerization (Sheline and Pitzer, 1950, Sheline, 1951; Brauer and Stecken, 1965; Braye *et al.*, 1966, King, 1965; Ellis and Beck, 1995; Mocelin *et al.*, 1996; Jibril and Abu-Ninreh, 1996;) of iron pentacarbonyl, pure or diluted in acetic acid, with UV light or sunlight. Sometimes, acetic anhydride (Gigg *et al.*, 1968) or diethyl ether (Sheline, 1951) were used as solvents or co-solvents. We carried out the $Fe(CO)_5$ irradiation in acetic acid solution (Scheme 1).

This reaction is very sensitive (King, 1965; Braye *et al.*, 1966) to the temperature, the light nature and the irradiation conditions. For this, the yields may be used as an efficiency relative "measure" of the irradiation apparatus. We obtained good yields, 82%, which suggests that our assembly is efficient. The main reason for our apparatus efficiency may be the low thickness of the irradiated solution layer (Figure 1), easily transversed by UV light.

b) In addition to more common chemical methods (Darin *et al.*, 1999), it was reported that acetyl ferrocene may be reduced to the corresponding alcohol by isopropanol (as hydrogen donor) and a ruthenium (II) catalyst (Hashiguchi *et al.*, 1995, 1997) under chemical, (not photochemical) conditions. Related reductions are known (Mizushima *et al.*, 1999). In a preliminary experiment, an acetyl ferrocene solution irradiation in isopropanol was unsuccessful. Only decomplexation occurs and we obtained dicyclopentadiene and iron (III) oxide as products. In fact it is known (Abd-El-Aziz *et al.*, 1998; Federman Neto *et al.*, 1986, 1997, 2002; Federman Neto and Landhote, 1998) that light may decompose organometallic compounds (see below).

c) When the irradiation of ferrocene in carbon tetrachloride was carried out, ferricenium tetrachloroferrate was formed, in low yields (2%) (Scheme 3). In fact, it was reported for the first time by Collinson *et al.* (1961), that ferrocenes are oxidized by light in the presence of chlorinated solvents. We (Federman Neto *et al.*, 1986, 1997; Federman Neto and Landhote, 1998; Darin *et al.*, 1999) and several other researchers (ex.: Nesmeyanov *et al.*, 1960; Collinson *et al.*, 1961; Brauer and Stecker, 1965; King, 1965; Abd-El-Aziz *et al.*, 1998; Cotton *et al.*, 1999; Galow *et al.*, 1999; Sato *et al.*, 1999) have observed, since the fifties, that many transition metal organometallic compounds are decomposed by light. More recently, this type of reaction was studied in detail, for physical-chemical purposes (Phan and Hoggard, 1998) but, in spite of the low yield, this is the first report of this kind of reaction for preparative uses.

We also tested our assembly in some inorganic reactions:

a) A silver chloride suspension irradiation in isopropanol. After 1 h. a light violet compound was formed. This compound is widely known (Beltzer, 1911) and called "silver sub-chloride", Ag_2Cl, and, in photography early times, this salt was supposed a pure compound (Monckhoven, 1889). Now, it is known (Usman *et al.*, 2000) that it is an inclusion compound of metallic silver with silver (I) chloride (Ag.AgCl). Continuing the irradiation for 8 h., metallic silver was obtained, in the form of a sponge or a black solid. The formation of colloidal silver (Fabrikanos *et al.*, 1963) is possible, but was not observed in the conditions employed.

b) The photo-reduction of some platinum compounds: $PtCl_2$, $PtCl_4$ and K_2PtCl_4, dissolved or suspended in isopropanol. After 30 minutes of irradiation, a violet colloid was formed, which turned to a brown colloidal suspension (1 h. of irradiation), then a black colloidal suspension (3 h. of irradiation) and finally, into metallic platinum bright crystals.

The colloidal suspensions of silver and platinum are known (Monckhoven, 1889; Beltzer, 1911) from

old. They may be obtained by photolysis, chemical reduction (with formaldehyde, glucose, etc.) or through electric arch process, under water ("electric metal colloids", Boutonnet *et al.*, 1882). The colloid color depends of the particles (Ganeev *et al.*, 2001) size. Metallic colloids may also be prepared though modern methods: metal salts reduction with strong reductors: metallic sodium or potassium, sodium naphthalide, some chemically reduced metals ("Rieke active metals") (Rieke, 1989, 2000; Lee *et al.*, 2000), alkali metal borohydrides (Darin *et al.*, 1999; Chen *et al.* 1993; Chen and Ellis, 2000), metallic zinc (Sakai *et al.*, 1968). Less strong reductors, such as hydrazinium salts, usually reduce the metal salt to a lower valence salt (Togniolo *et al.*, 1999; Brauer and Stocker, 1965; Kaufmann *et al.*, 1963), but it was reported (You *et al.*, 1993) that hydrazine hydrate reduces nickel(II) hydroxide to metallic nickel. In the conditions employed, nickel (II) or cobalt(II) hydroxides or chlorides were not photochemically reduced.

In addition to silver (Sato *et al.*, 1999) and platinum, the photochemical reduction of other metal salts to the metal or to the low valence salts is known: Ex.: cerium(IV) (Vorobyova *et al.*, 1987), uranium (VI) (Park *et al.*, 1991) etc., generally carried out in ethanolic solution.

The employ of our photochemical procedure gives a more pure colloid than chemical processes, and it's easier to carry out than other methods, including some of the modern ones.

Nickel and platinum metals (Dragutan *et al.*, 2000) are important in catalysis. For example, in the beginning of catalytic hydrogenation, developed by Sabatier (Roberts, 2000) and improved by Roger Adams (Kaufmann, 1989), PtO_2 ("Adams catalyst") and Raney nickel were used. Now, all the platinum group metals (palladium, rhodium, ruthenium, osmium, etc.) are used (Roessler, 1996; Kozub *et al.*, 2000), generally anchored over carbon (Auer *et al.*, 1998).

The efficiency of the photochemically prepared colloidal platinum in catalytic hydrogenation was tested. Styrene was added to the brown colloidal platinum, prepared through a $PtCl_4$ solution irradiation in isopropanol, and the reaction mixture was hydrogenated in a Parr apparatus. Ethyl benzene was formed in moderate yields (37%), but the reaction conditions were not optimized. It was used only to demonstrate the colloidal platinum catalytic activity.

c) Application of photochemical apparatus to Cu_2Cl_2 preparation (new method), through a $CuCl_2.2H_2O$ solution irradiation in isopropanol. We obtained a white precipitate, insoluble in water. It has the organoleptic and characteristic properties of the Cu_2Cl_2, copper(I) chloride (Gmelin's Handbuch, 1959). Copper (I) chloride is usually prepared through the reaction of copper (II) chloride or copper (II) sulfate in the presence of sodium chloride, with metallic copper, sodium sulphite (Furniss *et al.*, 1979) or hydroxylamine salts (Bragger *et al.*, 1997). The main advantage of our method is that all the manipulations may be carried out with a minimum exposure to air (see Experimental) and, therefore, the Cu_2Cl_2 was obtained in white and pure form, not mixed with impurities (Cotton *et al.*, 1999; Greewood and Earnshawn, 1997) of the green oxychloride, $Cu_2Cl_2.CuO.3H_2O$ or the brown $Cu.CuCl_2$.

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