

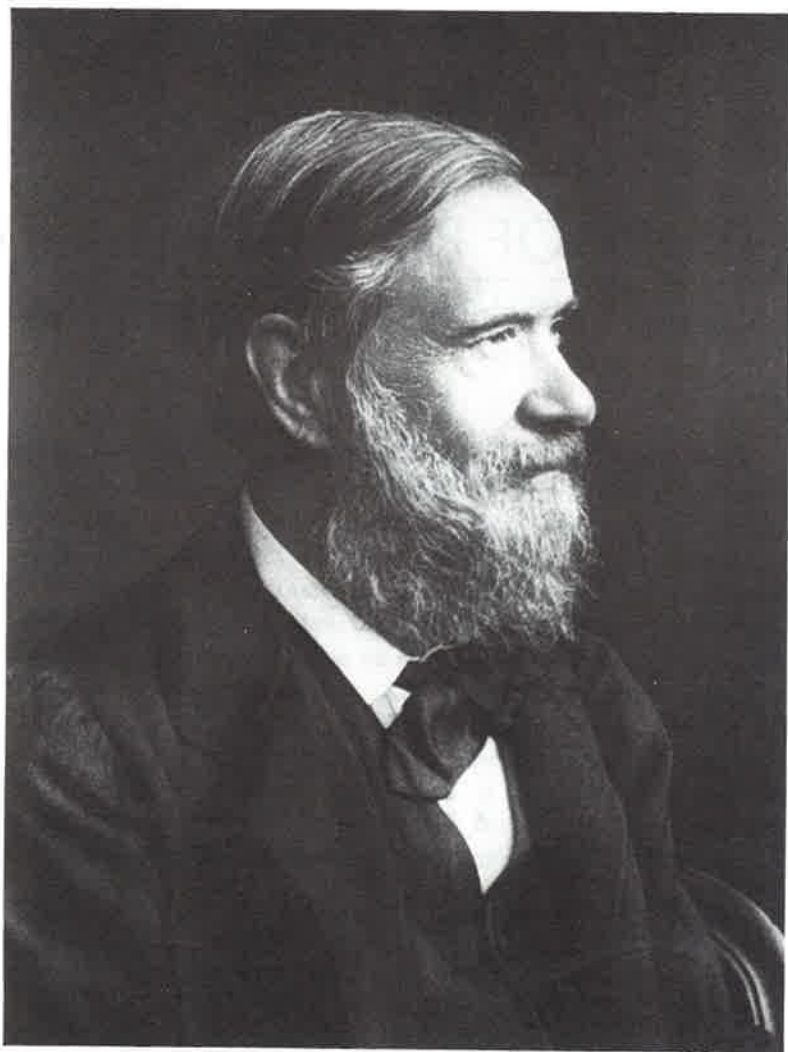
# HISTORY OF PHOTOCHEMISTRY

## Organic Photochemistry One Hundred Years Ago

In 1988 (the) Università degli Studi di Bologna will celebrate the nine hundredth anniversary of its foundation. To help commemorate this occasion, photochemists from around the world will congregate at (the) Istituto Chimica di Giacomo Ciamician for the XII IUPAC Symposium on Photochemistry. This institute is named after, and a living memorial to a pioneer in photochemistry, who had studied in Vienna, received a doctorate in Giessen, Germany, was an assistant of Stanislao Cannizzaro in Roma, taught briefly in Padova, and accepted a professorship in Bologna in 1889, coincidentally almost one hundred years ago. To commemorate the anniversaries of the Università and of one of its most distinguished professors, it is appropriate to review the status of photochemistry one hundred years ago, particularly the new reactions observed and the new insights gained in the years 1880 to 1895.

Had the European Photochemical Association existed one hundred years ago, a listing of laboratories involved in some aspects of photochemical research would have included the following:

<b>Germany</b>	Technische Hochschule Berlin C. T. Liebermann Universität Bonn H. Klinger
<b>Italy</b>	Università di Roma S. Cannizzaro Università di Pisa F. Sestini
<b>Poland</b>	Uniwersytet Lwowski J. Schramm



**Stanislao Cannizzaro** (1826 - 1910), known for the base induced "disproportionation" reaction of benzaldehyde named after him and for the elegant treatise on molecular theory which he presented at the 1860 Karlsruhe Congress, studied the structures of santonin and two of its photoproducts, photosantonin acid and iso-photosantonin acid. In his laboratory Giacomo Ciamician first became acquainted with photochemical experiments (Courtesy of E. F. Smith Memorial Collection, The Beckman Center for the History of Chemistry, University of Pennsylvania).

In these laboratories light-induced chemical reactions were carried out as a matter of routine. Other scientists used light occasionally: Bertram and Kürsten, Engler and Dorant, Orndorff and Cameron, W. H. Perkin, and J. Wislicenus published a single paper on the subject; Ciamician published two preliminary accounts and Silber joined him in one investigation; and C. Jannasch observed a photoreaction when he attempted to use sunlight as a source of heat, a time honored procedure that dates back at least to 1653,<sup>1</sup> but probably is much older. To some of these pioneers, the role of light in promoting chemical reactions came as a complete surprise whereas others were fully aware of this possibility and exploited its unique features. Among the organic reactions that were recognized as induced by sunlight, we mention the formation of several dimers and of the unique reaction products derived from santonin. The photochemistry of the latter posed particularly vexing problems that were actively pursued a century ago in at least two laboratories in Italy. This is the starting point of our excursion.

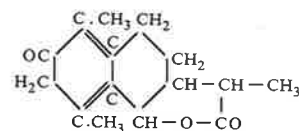
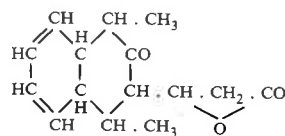
#### **Fausto Sestini and Stanislao Cannizzaro**

There is little doubt that Fausto Sestini (1839-1904) provided the decisive stimulus for Italian photochemistry with his pioneering studies of the solution photochemistry of santonin. He began his studies<sup>2</sup> in 1866 and continued to probe the structures of santonin and its photoproducts until his retirement.<sup>3-6</sup> Sestini irradiated santonin in 65% aqueous ethanol and obtained "photosantonin," which he later recognized as a diethyl ester that could be converted to a lactone/acid, photosantonin acid. The latter was prepared directly by irradiation of santonin in 80% acetic acid.

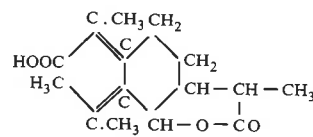
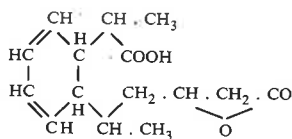
The event in Sestini's career, that was to become most significant for Italian photochemistry, was a four year appointment as director of the agricultural station in Rome, 1872-1876. During this time he met Stanislao Cannizzaro (1826-1910) and roused his interest in the photosantonin problem. They jointly published one paper<sup>3</sup> and in the following years pursued the challenging problem independently, as Sestini accepted a call to the University of Pisa to head the institute for agricultural chemistry.

Cannizzaro and his coworkers confirmed the formation of photosantonin acid and discovered a new photoproduct, which they called isophotosantonin acid.<sup>7-10</sup> These products were well characterized by their composition, crystal properties,<sup>11</sup> solubilities, optical rotations,<sup>12</sup> and by the properties of their salts.<sup>5</sup> Based on these data Cannizzaro recognized the relation of the santonin skeleton to that of naphthalene. However, the correct position of the functional groups in this skeleton eluded Cannizzaro<sup>13</sup> and Sestini. We illustrate the difficulty of this assignment by the structures proposed by Cannizzaro and Fabris<sup>10</sup> in 1886 and by Gucci and Grassi-Cristaldi<sup>14</sup> in 1891.

Santonin



Photosantonin Acid

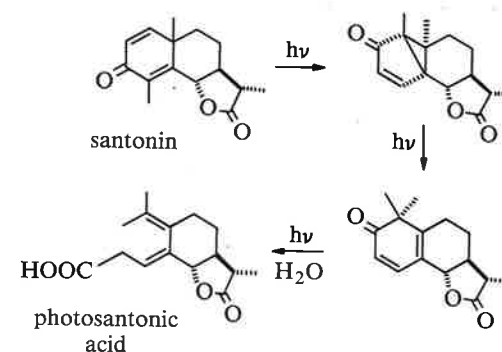


Cannizzaro, Fabris, 1886

Gucci, Grassi-Cristaldi, 1891

Aside from the unusual stereochemistry of the lactone ring, the latter authors assigned a large segment of the structure correctly and only failed to recognize one five-carbon fragment. However, their proposal did not enjoy a better reception than any of the alternative formulations, which deviate more substantially from the correct structure.

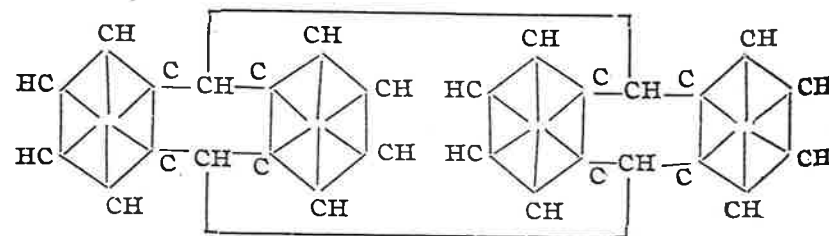
Organic chemistry simply had not matured to a level that would have allowed an unambiguous assignment. The structural and stereochemical complexity of santonin and the intriguing nature of its photoreactions would continue to puzzle chemists long after the period considered here. The structure of photosantonin acid was elucidated only in 1957 and the intermediates in its formation were not identified until 1963.



### Photodimers

In contrast to santonin and photosantonin acid the structures of several photodimers were recognized during the years discussed here. The earliest photodimerization achieved in the laboratory was that of anthracene observed by Fritzsche in Petersburg in 1867. Fritzsche established that the product was formed only upon irradiation but apparently did not recognize it as a dimer. He referred to it as the "para body".<sup>15</sup>

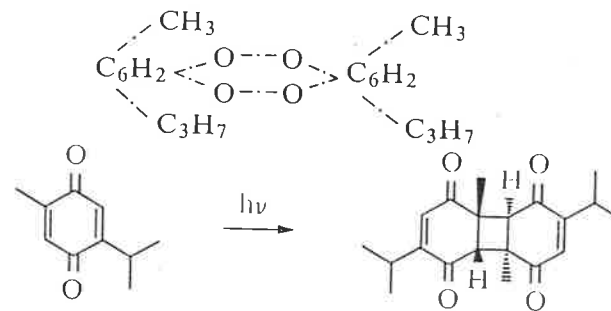
Twenty five years after the discovery Elbs recognized the photoproduct as a dimer<sup>16</sup> based on a molecular weight determination by freezing point depression, a method that had been developed in the 1880s. Subsequently, Linebarger<sup>17</sup> as well as Omdorff and Cameron<sup>18</sup> proposed the actual structure. They understood anthracene as a molecule in which two benzene groups are linked to a C<sub>2</sub>H<sub>2</sub> group, and "paranthracene" as a dimer in which each central carbon of one monomer is linked to one central carbon of the second monomer.





Carl Theodor Liebermann (1842 - 1914), who elucidated the chemistry of many naphthalene and anthracene derivatives and had a major role in the first synthesis of alizarine as well as its industrial fabrication, carried out a greater variety of photochemical reactions than any other nineteenth century chemist (Courtesy of the E. F. Smith Memorial Collection, The Beckman Center for the History of Chemistry, University of Pennsylvania).

Another dimerization reaction was discovered in 1877 by Liebermann in Berlin. He was familiar with the work of Fritzsche; thus, the thought that light might cause chemical changes was not foreign to him. He observed that under the influence of sunlight the yellow crystals of thymoquinone turned into a white, porcelain-like mass. He established the conversion as a photoreaction, the first organic [2+2]cycloaddition.<sup>19</sup> Liebermann considered the compound a "polymer", a term which would have included dimers or trimers. He noted that the photoproduct was cleaved under reducing conditions, and concluded that the quinone molecules were linked through the oxygen atoms, as shown below.<sup>20</sup> However, this assignment ignored the fact that the "polymer" could be converted to a "polydioxime," a result which clearly excludes the carbonyl groups as possible connecting links.



Only one year after Liebermann's publication Breuer and Zincke reported the formation of a quinone,  $C_{16}H_{10}O_2$ , which upon exposure to sunlight gave two different "polymeric" materials. They did not understand the structure of the quinone, nor the nature of the photoproducts. However, they noted that one of the products readily regenerated the parent quinone upon heating, whereas the second product proved to be more stable.<sup>21,22</sup> The quinone was later recognized as 2-phenylnaphthoquinone; the dimers are likely to have cyclobutane structures. The different reactivities are those expected for a head-to-head dimer (more readily cleaved) and a head-to-tail one.

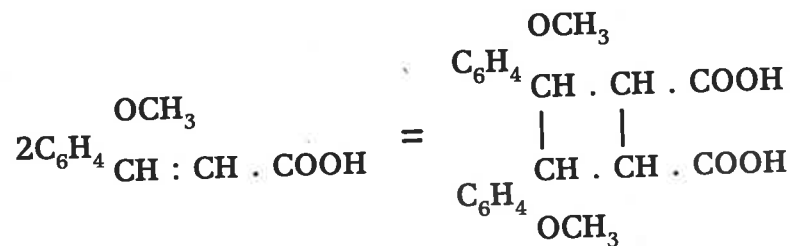
Liebermann also observed the photodimerization of styrene derivatives. In 1895, he referred to a photochemically generated "polycinnamate." Also, he found that exposure of cinnamylidenemalonic acid to sunlight converted the yellow substance to a white crystalline product. He ruled out that this reaction was "simply a stereoisomeric conversion" (vide infra) but failed to recognize the product.<sup>24,25</sup>

However, the credit for the first dimerization of a styrene derivative clearly belongs to Bertram and Kürsten, two industrial chemists in Leipzig.<sup>26</sup> Their work not only precedes that of Liebermann (though by a narrow margin), but it is also further reaching in its understanding and more definitive in its conclusions. Bertram and Kürsten were working on the constituents of cassia oil, when they noted that  $\beta$ -methylcoumaric acid slowly "polymerized" when exposed to diffuse daylight. Based upon the molecular weight they identified the product as a dimer and also recognized its structure: "this union is likely to occur by mutual saturation of the double bonds." Their publication in *Journal für praktische Chemie* concludes:

Unter dem Einfluss des Lichts haben sich also zwei Moleküle der  $\beta$ -Methylcumarsäure zu einem Molekül der neuen Säure zusammengelagert.

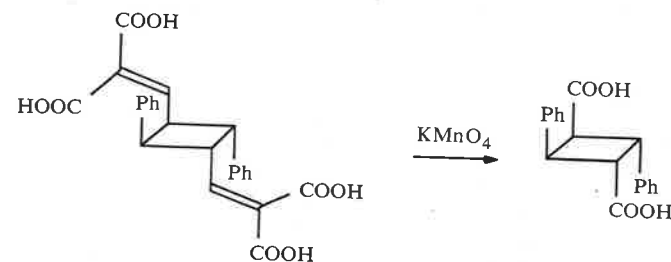
Diese Vereinigung wird wahrscheinlich unter Aufhebung der Doppelbindungen durch gegenseitige Sättigung stattgefunden haben, denn die polymere Säure wird nach dem Behandeln mit Brom, oder nach Einwirkung von Natriumamalgam zum grössten Theile unverändert wieder gewonnen.

Der Vorgang ist also folgendermaassen zu formuliren:



They extended their investigation to cinnamic acid and obtained an acid of mp 274°, to which they assigned the structure of  $\alpha$ -truxillic acid. It is remarkable that these chemists recognized the nature of the dimer, whereas Liebermann did not recognize the identity of his "polycinnamate," in spite of his familiarity with truxinic and truxillic acids.

The true nature of the photoproduct derived from cinnamylidenemalonic acid was recognized several years later by Riiber, who reinvestigated this reaction with Liebermann's consent and encouragement. He determined that the product had twice the molecular weight of the diolefin diacid and established its structure as a head-to-tail dimer involving the styrenic double bonds. Permanganate oxidation of the product gave rise to  $\alpha$ -truxillic acid, establishing structure and stereochemistry of the dimer.<sup>27,28</sup>



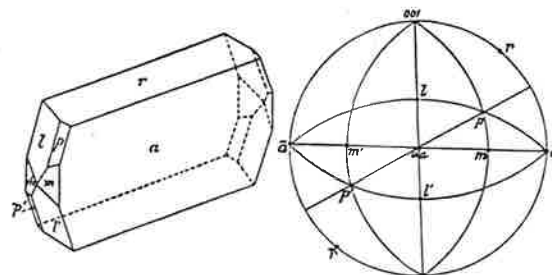
### Geometric Isomerization of Olefins

Geometric isomerization is one of the simplest and most general photoreactions of olefins. The credit for the first observation of this kind, in 1881, belongs to W. H. Perkin. He was investigating 2-alkoxycinnamic acids obtained from coumarin and observed the conversion of several " $\alpha$ -acids" into their " $\beta$ -isomers" upon exposure to sunlight.<sup>29</sup> Perkin's paper is distinguished by the thorough characterization of these compounds; it contains mp and bp, solubility data, specific gravity at two temperatures, magneto-optical rotation data, refractive indices, and a detailed crystallographic description. Some of the crystal data for the o-methoxycinnamic acid isomers are shown below.

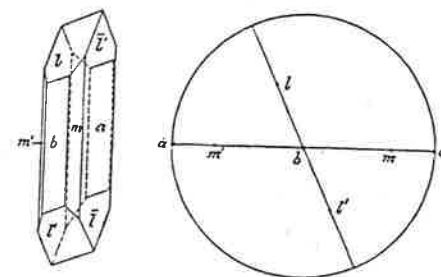


William Henry Perkin (1838 - 1907), a pioneer of the synthetic dyestuff industry, was the first to observe and recognize a light-induced *cis-trans* isomerization.

$\alpha$ -METHYLORTHOXYPHENYLACRYLIC ACID



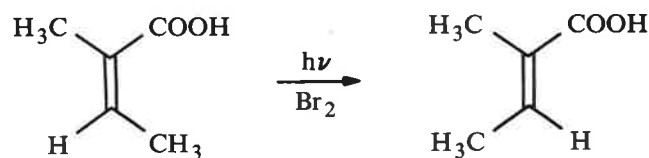
$\beta$ -METHYLORTHOXYPHENYLACRYLIC ACID



This is the first reference to magneto-optical rotation, which Perkin soon developed into an important tool for assigning structures.<sup>30,31</sup> He also studied the wavelength dependence of this photoreaction "to see which rays of light caused the change." He used "variously coloured solutions" as filters, of which he identified "sulphate of quinine" and "ammoniacal sulphate of copper." He concluded that "the alteration is due to the action of the violet and ultraviolet rays." Perkin obviously was familiar with the principles of absorption spectroscopy and used it as an analytical tool, *e.g.* to characterize synthetic dyes.

About ten years later Liebermann observed similar photoinduced cis-to-trans rearrangements for cinnamic and several other unsaturated acids.<sup>32</sup> In the course of these studies one of his coworkers tried the "rearrangement with iodine...so characteristic for isocinnamic acid." This lead to greatly accelerated interconversions. A benzene solution of "allo"-cinnamic acid required five months of exposure to sunlight to produce a 40% precipitation of cinnamic acid, whereas a solution containing iodine required only 12 days for 70% precipitation, a more than ten-fold increase in rate. "Allo"-furfuracrylic acid reacted much faster, but the most rapid rearrangement was observed for "allo"-cinnamylideneacetic acid ( $\delta$ -phenylpentadienoic acid), which in the presence of iodine required only one minute of exposure to sunlight to produce a precipitation of the more stable isomer. Liebermann considered the iodine assisted photoinduced isomerization a "general group reaction of the aromatic allo-acids" and recommended the most rapid conversion for a classroom demonstration.<sup>32</sup>

Liebermann was unsuccessful in his attempts to extend the iodine assisted photoisomerization reaction to non-aromatic unsaturated acids. However, Wislicenus achieved this interconversion. Irradiation in the presence of aqueous bromine converted isocrotonic to crotonic acid, angelic to tiglic acid, and, most rapidly, maleic to fumaric acid.<sup>33</sup>



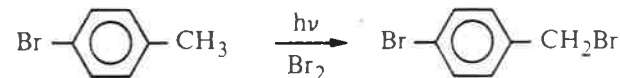
Wislicenus (1835-1902) is best known for his thorough understanding of structural and stereochemical problems. Even before the publications by van't Hoff and LeBel he had concluded: "if molecules can be structurally identical, yet possess dissimilar properties, the difference can be explained only by a different arrangement of the atoms in space." In his involvement in photochemistry he showed the same clarity of thought and the skillful diligence that characterize his entire work. For example, he recognized that the halogen assisted reactions do not lead to a complete

conversion to the more stable isomer, but that the reverse reaction could also occur. In essence, the result is an equilibrium mixture.<sup>33</sup>

### Photoinduced Halogenations

In connection with the halogen induced geometric isomerizations of olefins it is of interest to mention briefly the light induced halogenation of aromatic hydrocarbons. These reactions were investigated between 1884 and 1888 by Julian Schramm in Lemberg (Lvov, the center of eastern Galicia, then a Polish province) in the institute of B. Radziszewski. Most of these results were reported before the *Krakauer Akademie der Wissenschaften* and either reprinted or published in *Berichte*.<sup>34-37</sup>

At the time it was recognized that the halogenation products of aromatic hydrocarbons varied with the reaction temperature. Thus, bromination of toluene yielded o- and p-bromotoluene in the cold, whereas benzyl bromide was obtained at elevated temperatures. Schramm systematically studied the light induced brominations of alkylbenzenes with normal and branched sidechains. In the words of a contemporary reviewer he showed that "light and darkness work in the same way as elevated and low temperatures, respectively." Schramm found that direct sunlight and even diffuse daylight caused side chain bromination (and chlorination) even at low temperatures. He realized that substituents in the para position accelerate the reaction, whereas meta substituents slow it down. He found, for example, that the side chain bromination of m-xylene was sluggish whereas that of mesitylene did not occur at all.

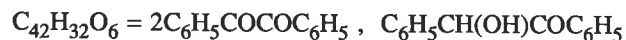


Schramm apparently had a good knowledge of the chemical literature (which was a somewhat easier task in the 1880's than in the 1980's). He realized that p-bromobenzyl bromide had been isolated, though not recognized, as early as 1874 in the light induced bromination of toluene.<sup>37</sup> Paul Jannasch, in Fittig's laboratory in Göttingen, had tried to improve the poor yield of a dibromo derivative obtained from toluene.<sup>38</sup> Accordingly, he had carried out the bromination "at summer temperatures under

simultaneous exposure to direct sunlight." In one of these experiments he had obtained crystals of mp 63°. Schramm recognized this material as p-bromobenzyl bromide. Schramm also foresaw the commercial potential of photohalogenations. He voiced the hope that "this method would be suitable for the industrial preparation of these products."

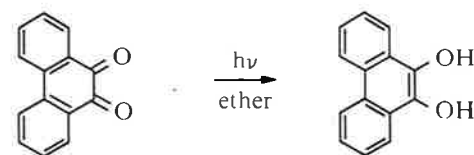
### Heinrich Klinger and the Photoreduction of Carbonyl Compounds

Aside from the dimerization of quinones, which is observed mainly in the solid state, photoreductions must be considered the principal light-induced reactions of quinones in solution. The credit for having observed and investigated the first reactions of this type belongs to Heinrich Klinger, who originated his work in Kekule's institute in Bonn. He was interested in an assumed isomer of benzil and, toward that end, prepared solutions of that diketone in ether. On several occasions, seemingly at random, he obtained a solid product. Among the pioneers of photochemistry, Klinger is the only one who relates the puzzled frustration of an experimental chemist dealing with an unknown variable and faced with seemingly irreproducible results. After "many time-consuming experiments" he finally noticed that "some of the tubes were exposed to direct sunlight *in the morning hours*." He identified the crystals as a molecular complex of two moles of benzil with one mole of benzoin

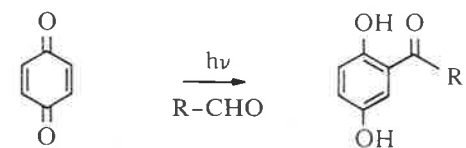
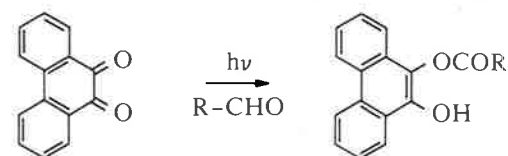


and concluded that "sunlight causes a partial reduction of benzil dissolved in wet ether."

Having recognized the reducing action of sunlight on benzil, Klinger carried out analogous experiments with phenanthrenequinone and began to investigate the role of the solvents. He also carried out preliminary experiments with benzoin, nitro compounds, several quinones, fuchsones, etc. Klinger first reported these results in preliminary form in *Sitzungsberichte der niederrheinischen Gesellschaft für Natur- und Heilkunde* in 1883 and 1885;<sup>38</sup> he formally published them in a *Berichte* article in 1886.<sup>39</sup> There is very little doubt that Klinger had priority over Ciamician (*vide infra*), albeit by a narrow margin.



Two years later he used acetaldehyde as the reaction medium and observed a "strange synthetic effect,...with precedent only in the living plant;...as the two compounds are joined to form one, in which the quinone appears reduced but the acetaldehyde oxidized." The product observed in this light-induced reaction, monoacetylphenanthrenehydroquinone was indeed a new type of photoproduct.<sup>41</sup> Klinger extended the reaction to a series of aldehydes and ketones and also investigated alternative quinones. The reaction of benzoquinone with benzaldehyde proved to be particularly interesting. The product isolated in this reaction, 2-benzoylhydroquinone (or 2,5-dihydroxybenzophenone), established an interesting variation of the phenanthrenequinone derived product.<sup>42</sup>



Klinger referred to these reactions as "Synthesen durch Sonnenlicht" (syntheses by sunlight); he must be considered the first to have exploited photochemical methods for synthetic purposes.<sup>43,44</sup> He perceived these reactions as similar to the photosynthesis of the living plant.

To probe this similarity further he investigated the wavelength dependence by using aqueous solutions of inorganic ions as filters, including cuprous ammonium sulfate and potassium dichromate solutions. He noted that the photochemical response of the quinones was most

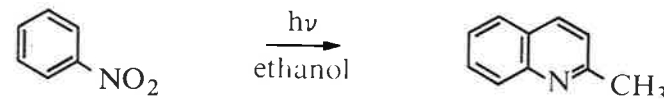
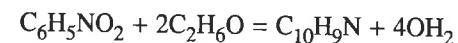




pronounced in the blue, whereas green plants showed optimum response in the red region of the spectrum.

### Ciamician and Silber - An Early Episode

It was in Cannizzaro's Istituto Chimico della Regia Università in Rome that Ciamician and Silber were first introduced to photochemical reactions. It would have been hard to overlook an effort involving... "one kilogram of santonin dissolved in 52 liters of acetic acid...exposed to sunlight in several bottles...."<sup>10</sup> Nevertheless, their interest was aroused only slowly. When they joined Cannizzaro's group in 1881, they first focussed their attention on pyrrole chemistry. They produced a sizeable body of work, which earned Ciamician the Award of the Regia Accademia dei Lincei in 1887. In the summer of 1885 Ciamician began some photochemical experiments and the following year Silber joined in the investigations. Ciamician "insolated" (exposed to sunlight) alcoholic solutions of benzoquinone. After five month's exposure he observed conversion to hydroquinone and acetaldehyde.<sup>45,46</sup> The following year Silber carried out the analogous experiment with nitrobenzene.<sup>47</sup> This reaction produced aniline and acetaldehyde, but the exceptionally skilled Silber also found evidence for the formation of 2-methylquinoline (quinaldine), which they rationalized tentatively as follows:



These were interesting and promising results and the two investigators must have had every intention to follow up these early findings. However, their first engagement in photochemical research was not destined to be of extended duration. The limitation of their initial efforts had its roots in the custom of nineteenth century chemistry that allowed a researcher to "reserve" a field for continued investigation. Most respectable scientists would honor such a claim (chemistry has indeed come a long way in the last one hundred years).

After reporting his first results in the *Rendi conti della Regia Accademia dei Lincei* on January 3, 1886,<sup>45</sup> Ciamician became aware of Liebermann's 1885 publication.<sup>20</sup> He must have been satisfied that his work was sufficiently different from Liebermann's, for he rushed his work to publication in the *Gazzetta Chimica* "to ensure the unencumbered continuation of my research."<sup>46</sup>

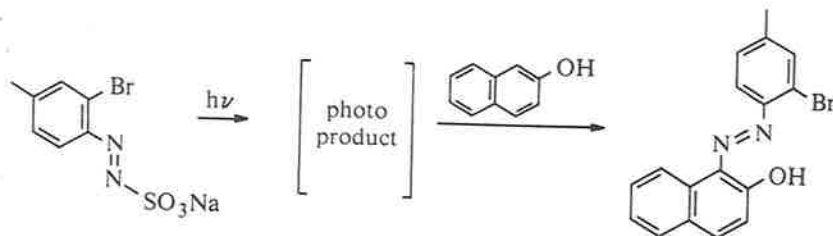
He took this step even though he had not yet proven that the observed redox reaction was indeed a photoreaction ("That the conversion is indeed caused by light will be ensured by repeating the experiment in the dark"). However, before Ciamician's *Gazzetta* paper was reviewed in the *Berichte*, Klinger's work on the reaction of phenanthrenequinone appeared, in which Klinger claimed this area of research for himself, including specifically the photoreduction of nitrobenzene.<sup>40</sup>

There is very little doubt that Ciamician's experiments in Rome were carried out independently of Klinger's studies in Bonn. The *Rendi conti* publication could not have been more than a few months later than Klinger's *Sitzungsbericht* of 1885. Nevertheless Ciamician and Silber honored Klinger's claim graciously. They sent a brief summary of their preliminary work to *Berichte*; it contained the previously missing control experiment for the benzoquinone photo-reduction and a brief account of the nitrobenzene reduction.<sup>47</sup> They announced that, for the time being, they would concede the field to Klinger and not pursue the subject any further. In conclusion, they expressed that they were "looking forward with great interest to the results of the further experiments delineated by Klinger."

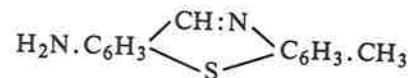
### Photochemistry of Diazo and Diazonium Compounds

Because of their practical importance in photoresist materials and their significance as precursors for divalent-carbon species, it appears appropriate to discuss briefly the photoreactions of diazo compounds and of the somewhat related diazonium salts. This class of compounds became accessible through the pioneering studies of Peter Griess beginning in 1858.<sup>48</sup> Although it is not clear when their sensitivity to light was first noticed, attempts to utilize them for the purpose of imaging are documented as early as 1889. Adolf Feer noticed that irradiation of

diazonium sulfonates,  $R-N=N-SO_3Na$ , in the presence of phenolates or aryl amines led to the formation of azo dyes, presumably via the free diazonium ion.<sup>49</sup> After a film containing these reagents was exposed, unreacted diazonium sulfonate could be removed by washing, leaving a colored negative.



Only a year later, Green, Cross and Bevan received a patent for a process generating a positive image.<sup>50</sup> Their process was based on the fact that irradiating converts the diazo compounds of "dehydrothioutilidine" (primulin) into products incapable of coupling.



After exposure, an image could be "developed" by converting the unreacted diazonium compound to an azo dye with an appropriate reagent.

It is indicative of the progress of photochemistry that in 1890 Green and colleagues no longer considered mere light sensitivity noteworthy, but were concerned with the practical exploitation of this property.

### Conclusion

One hundred years ago photochemistry was but a modest facet of the exciting and rapidly expanding science of chemistry. The principal contributors studied photochemical problems only as an aside to the work for which they were (and are) best known. Only a limited number of reactions were known and the sun was virtually the exclusive light source. Moreover, in almost all cases sunlight was used unfocussed and unfiltered. Only Liebermann experimented with alternative light sources, particularly with an arc lamp, a gas burner with a metal oxide mantle, and a

magnesium flame; his results were far from promising. Perkin and Klinger studied the wavelength dependence of photoconversion, by using filter solutions; Perkin also mentions an experiment in which "light was concentrated on..." a sample.

On the other hand, several of the general reaction types known today had been encountered. When Liebermann discovered the iodine mediated photoisomerization of olefins, he subjected a representative cross section of then known photoreactions to the newly found reaction conditions. He surveyed three dimerizations and one rearrangement, but did not refer to abstraction or transfer reactions, such as those studied by Klinger. Experiments were under way to utilize organic photoreactions for the purpose of imaging, and Klinger and Schramm had pointed out, respectively, the preparative and even industrial prospects of photochemistry. All these facts suggest that the time was ripe for an outstanding scientist, who would devote a major effort to organic photochemistry and establish it as a major scientific discipline. It appears that Ciamician's priority dispute with Klinger delayed the advent of photochemistry by more than a decade.

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