Selected Papers on
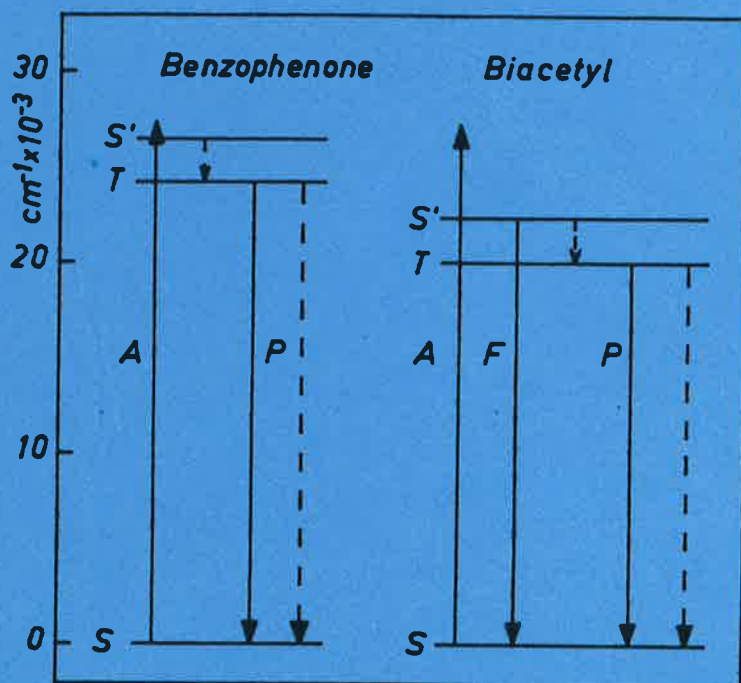# Photochemistry

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Introduction

Photochemistry is the study of chemical reactions initiated by light and is as broad as science itself. It encompasses everything from the theoretical developments of wave mechanics, to studies of the conversion of carbon dioxide to carbohydrates in plants, to the patents that led to xerography and the Polaroid camera. The word *radiation* stems from the name of the Egyptian sun god, Aton Ra. The Persians had a sun god too. The Greeks had the legend of Idelios, and in England and Brittany stand the ruins of the Druid temples to the sun. To early man, the sun stood for strength and warmth, and he was awed by it. The medicinal effects of the sun were also recognized early in human history. From ancient Indian medical lore we find lepers being treated with photosensitizing plant pigments, and furocoumarins have been used since antiquity to dye the skin of albinos in middle Eastern countries.

The effects of light on pure substances were probably discovered by Scheele, the discoverer of chlorine (1775), who noticed that silver halide salts blackened in sunlight. The Grotthaus-Draper law articulated what these effects were due to. Grotthaus in 1820[1] and Draper in 1843 (p. 3) recognized that for a chemical reaction to be catalyzed by "actinic rays," the rays had to be absorbed by the reacting chemical substance. John Draper was a professor of chemistry at New York University and the first president of the American Chemical Society.[2] In the 1840s he published a series of short papers on the reactions of H_2 with Cl_2. The little note chosen for reprinting, from the *Philosophical Journal of Dublin, Edinburgh, and London*, appeared in the same year as Justus Liebig's long article on animal fats in the same journal. It was the latter that impressed English wool growers to the point that they established a chemical research laboratory in London, and A. W. von Hoffmann, a Liebig student, was chosen as its head. "For photochemistry to occur, indigo or blue light must be absorbed by the system," said Draper.

The first artificial light source, a mercury resonance lamp, was reported in a patent published in the *London Times* on August 3, 1860.

Section One: Theoretical Foundations

Photochemistry and spectroscopy are, have been, and must always be delicately interwoven at the interface of all major research areas in chemistry, biology, and physics. In fact, the history of chemistry itself winds around photochemistry and spectroscopy, for it was at this interface that the nature of the chemical bond was discovered.

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[1] Th. V. Grotthaus, "Physikalische Chemische Forschungen," Bl. 1 Nürnberg, *Ostwald's Klassiker der exakten Wissenschaften*, Nr. 152 (1820). I've been looking for a copy of this paper for years but haven't found one; maybe by mentioning it here, somebody will send me a copy.

[2] The American Chemical Society published a bit about Draper in *Chemical and Engineering News* during its centennial in 1976.

The theory of photochemistry must start with Planck's law "that the energy of a monochromatic resonator was not continuous but was divided into smaller and smaller discontinuous but unique energy packets." As Planck read the paper at the October 19, 1900, sitting of the Deutschen Physikalischen Gesellschaft in Berlin: "Meine Herren: I have had the honor of directing your attention to a new rule for several weeks. This rule, to me, expresses the law of distribution of radiative energy in all regions of the normal spectrum. Based upon the formula that I have already demonstrated, it not only gives apparent good agreement of little numbers ... but also gives the dependence of the entropy of radiating monochromatic rapid resonators (of some vibrational energy) a very simple logarithmic relationship .... We regard, however, and this is the essential point of the whole argument, E as the combination of all determined numbers of finite equal parts, and we determine the natural constant $h = 6.55 \times 10^{-27}$ erg/ sec. This constant times the frequency of the resonator, n, give the energy in ergs ...." The original Planck's law paper is reprinted (p. 4), along with his brief paper read on October 19, 1900 (p. 9).

Quantum theory began as this "atomic theory of energy." An oscillator could acquire energy in discrete units, or *quanta*, the magnitude of which were not fixed by nor depended on the frequency n of the oscillator. Planck's constant had the dimensions of time and energy and requires that oscillators acquire energy in whole integral amounts: $hn, 2hn, ... nhn$.

Einstein, publishing in the same time period, was living in Bern, where he was a patent officer 3rd class.[3] As Clark portrays it,[4] Einstein claims he took the job in the patent office because he could spend just 8 hours a day doing it, and the remainder of the time he could spend on physics. The work for which he won the Nobel prize in physics in 1921 was on the photoelectric effect (p. 11). Applying the quantum postulate to black body radiation, he said,

> It seems to me that the observations of black body radiation, photoluminescence, the production of cathode rays from UV light and other radiation changes in the group which could be called "light productions" are better understood if we take the point of view that the energy of light is divided into discontinuities in space. If we take this point of view it leads to the prediction that light emanating from a point is not continuous but is divided into larger + larger packets in space, eventually described by an endless num-

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[3] There are many biographies of Einstein; that by Clark[4] is the one I've used most frequently. Einstein lived in Bern until 1908, when he was appointed professor at the "Sudetan" University in Prague. The stories about how he was unable to get a position as assistant at the ETH after completing his Ph.D. there are likely true. Nevertheless, after the publication of three papers in *Annalen der Physik* in 1905 (of which that on the photoelectric effect is reprinted here, p. 11), he was eventually appointed professor of theoretical physics at Zürich in 1911 by Robert Gnehm, an organic dye chemist who synthesized, among other things, Rose Bengal for the first time. Einstein stayed at Zürich for only two years, being appointed professor of theoretical physics at the Kaiser Wilhelm Institute in Berlin in 1914. The story of Planck's efforts, and those of Walther Nernst, to convince Einstein to return to Germany are probably oversensationalized, but nevertheless they certainly seem true enough as Clark presents them. Regarding Robert Gnehm, this editor has written rather extensively on Gnehm, whose original synthesis of Rose Bengal (p. 246) remains in his laboratory notebooks, which are part of the ETH library archives. Gnehm's original letter of appointment to Einstein is also there.

[4] R. Clark, *Einstein: The Life & Times*, World Publishing Co., New York (1971).

ber of ... localized energy quanta which themselves travel, without being divided, and which can be produced or absorbed as a whole.

But how did light interact with matter? Stark (pp. 20, 26), using Einstein's 1905 paper, related the quantum hypothesis to the absorption of kinetic energy in molecules (liberally translated and paraphrased by an organic chemist): " ... absorbed light can be changed to the kinetic energy of molecules through collision. This process is the ... kernel of the experimental studies of the transformation of the kinetic energy of atomic rays into light quanta .... It is easier to understand that the absorption of ... ultraviolet light by organic molecules, such as acetone, involves a change in the valence electrons ...." Thus, as early as 1908 and some eight years before G. N. Lewis published his first paper on the nature of the covalent bond, Stark had recognized in at least rudimentary form that light was converted to kinetic energy by absorptions that caused electronic transitions in molecules.

Einstein's 1912 papers (pp. 33, 37) state the law of photochemical equivalence:

> In the following, the relationship of Wien's[5] radiation law and the law of photochemical equivalence will be derived. I state the photochemical equivalence law as this: the decomposition of a gram equivalent requires a photochemical energy absorption process of nhn, where n = the number of molecules in a gram-mol, h = the known constant in the Planck radiation law, and n = the frequency of the active rays. The law is essentially the consequence of the assumption that the number of active molecules per unit time is proportional to the thickness of active radiation; it is emphasized that the thermodynamic relationship and the radiation law do not replace one another.

In a subsequent paper Einstein says,

> In the preceding article, it was demonstrated from a thermodynamic viewpoint ... that the photochemical decomposition of gas molecules occurred through the absorption of radiation of frequency n_0 and of energy hn_0. The relationship was based on the consideration that only an infinitely smaller frequency region has the power to affect photochemistry on a gas .... Molecular photodecomposition occurs from ... absorbed energy of a specific frequency.

From these papers and the two or three that follow come the word *photon* and the concept of the quantum yield, denoted by ϕ.

Experimental measures of the quantum yield of a photochemical process are attributed mostly to Warburg. In a series of papers published from 1911 to 1924, he outlined the quantum experimental foundation of modern photochemistry. The concepts are summarized in the paper beginning on p. 39:

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[5] This refers to physicist Willi Wien.

It is an experimental fact that the photochemical effects are caused and are proportional only to absorbed radiation, and it is a characteristic of every case of photolysis that characteristic chemical effects are caused only by the units of radiative energy absorbed. I have designated the quantity which expresses this photochemical effect in mols per absorbed gram-calories through the symbol φ. It can be measured either from the quantity of products produced or from the quantity of reactants consumed.

I next include the paper by G.N. Lewis on the nature of the covalent bond (p. 45). Although not directly related to photochemistry, its concepts are so important to all thoughts about chemical changes in organic molecules that I thought it properly included: "We may go further and give a complete formula for each compound using the symbol of the kernel ... and by adjoining to each symbol a number of dots corresponding to the number of electrons in the atomic shell ...."

Stern and Volmer's 1919 paper, "Über die Abklingungszeit der Fluorescence" (p. 57), begins to deal with questions that are still with us regarding the duration of excited states. In this paper they deal with the duration of intensity as a function of pressure in an iodine lamp. The second Stern-Volmer paper (p. 63) deals with elementary photochemical decomposition processes and states, I believe for the first time, that photochemical reactions don't occur directly after light absorption but result from an excited state that acts as an intermediate.

In a paper from 1923, Cario and Franck (p. 70) report a theoretical interpretation of sensitized fluorescence in gases that is essentially still in use today.

The fundamental papers that led to the Franck-Condon principle are printed next. Franck's paper, in translation (p. 76), builds on the work of Warburg and Einstein and starts with the assumption that the law of photochemical equivalence holds. He asks the question, Can a photochemical dissocation occur in one elementary act? That is, can it occur without the intervention of the excited state? Condon extends Franck's notion that, in the main, photochemical processes occur through the intervention of an excited state and that chemical reaction occurs as a result of collisions (p. 80). The essential part of the Franck-Condon argument is that the only change occurring when light is absorbed is in kinetic energy. The relative position of the atoms in a diatomic oscillator, for example, are unchanged. The paper by Morse developing the notion of the Morse curve follows next (p. 90).

In the literature at this point, attention seems to turn to what happens to a molecule after it has absorbed radiation. Although, strictly speaking, the Paneth-Hofeditz paper on the free methyl radical doesn't fit, it's so important to the general process of photochemical change that we have included it next (p. 94). We follow it with the paper by Jabloński from *Zeitschrift für Physik* on the mechanism of photoluminescence in colored phosphors (p. 101). The original Jabloński diagram is Figure 1.

Singlet energy transfer is dealt with in the paper by West and Miller, "Photosensitization and fluorescence by aromatic hydrocarbons" (p. 106). The benzene and naphthalene sensitized decomposition of alkyl halides is described.

The development of the energy transfer involving excited states of complicated, polyatomic molecules, based on the foundation of Planck and Einstein, was phenomenological. The explanation of absorption and emission phenomena in colored phosphors to include the notion of singlet and triplet states began with Jabloński's 1935 paper. G. N. Lewis's work, with Kasha, Magel, and Lipkin, on the nature of the long-lived emissions of fluorescein in boric acid glass definitively identified the triplet state, and denoted it with biradical character. Three Lewis papers from this era[6] are reprinted here (pp. 118, 132, 151). Terenin[7] had begun to consider energy transfer in a 1943 paper (p. 161) on photochemical processes of aromatic molecules. Some 10 years later, Terenin and Ermolaev (p. 177) gave simple evidence for sensitized emission, later to be known as *energy transfer*, in work in which the phosphorescence of naphthalene was observed, formed from benzophenone by triplet transfer in a glass. This paper was followed almost immediately by the work of Bäckström[8] and Sandros (pp. 186, 193), who found energy transfer from benzophenone to biacetyl in fluid solution.

We end this section with Hammond's work on energy transfer in fluid solution. In a 1961 communication to the editor of the *Journal of the American Chemical Society* (p. 204), Hammond, with Leermakers and Turro, reports first on the photochemical reactions of piperylene sensitized by aromatic ketones: "It probably is safe to assume that energy transfer will not occur if the diene triplet lies much above the triplet state of the sensitizer." Hammond had already shown that benzophenone was photoreduced in a reaction exclusively assigned to its triplet. In two immediately subsequent papers in the *Journal of Physical Chemistry* (pp. 205, 209), the Hammond group deals with the exothermic transfer of energy from the aromatic carbonyl compound triplet to olefins and dienes, and the quenching of the excited state of the carbonyl compound. This section is concluded with Hammond's long, definitive work on the subject of energy transfer to dienes published in the *Journal of the American Chemical Society* in 1964 (p. 212).

Section Two: Papers with Impact on Generations of Experimental Photochemists

This may seem an unusual heading for the next series of papers, but the reprints I have chosen for this section are those that forced the direction of research. Theory mixes with experiment in many of the latter among them.

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[6] Lewis's work over the course of his career ranged over many subjects. The nature of emitting states of Fluorescein was one of the last areas of work carried on in his laboratories at Berkeley.

[7] Terenin was a professor at and the first director of the Soviet Academy's Institute of Biochemistry in Moscow.

[8] Bäckström was a professor of chemistry and head of the Chemistry Department at Chalmers Technical School in Göteborg, Sweden.

The earliest papers, however, are on organic reactions, the first of which is Fritzsche's work on anthracene dimers (p. 235).

The next reprints, on the synthesis of dyes, are from the laboratory of Adolf Baeyer, who at the time was in Strassborg. The first describes the synthesis of fluorescein and other xanthenes (p. 241), the second is on the synthesis of phenolphthalein (p. 243), and the third discusses the history of eosin (p. 245). From Gnehm's laboratory notebook we copy the instructions for what is the first synthesis of Rose Bengal (p. 246), and Ciamician and Silber's original paper on the photoreduction of benzophenone follows next (p. 247). The work for all of these was done in the 19th century, yet the chemistry of fluorescein and eosin is still with us today, as is the photoreduction of benzophenone.

Next is Ciamician's speech given before the International Congress of Applied Chemistry in New York and reprinted in *Science* in 1912 (p. 249). Ciamician, who at this time was near retirement,[9] argues for solar energy as a replacement for fossil fuel. The next paper in this series is the critical work of Hans Stobbe on the photodimerization of cinnamic acid (p. 259), and the last paper in this group, by Oskar Süs (p. 263), first disclosed the chemistry of diazo ketones and the subsequent Wolff rearrangement of the carbene. This work, and the follow up papers of Leopold Horner and his students, led to the development of positive photoresists.

Several things happened in the early 1920s that had a major influence. The first was the appearance of several books on photochemistry. Plotnikov's was first in 1920,[10] followed by the first edition of Ellis and Wells in the United States in 1925.[11] Stiles's *Photosynthesis--The Assimilation of Carbon by Green Plants* and Kistiakowsky's *Photochemical Processes* appeared in 1928 and were also important publications of the time. A book by W. F. Hess, *Rickets, Osteomalaci, and Tetany*, told the story of vitamin D, the sunshine vitamin, in the detail known at the time.

Related to all of the above, and important for many reasons, were the studies on singlet oxygen, including Kautsky's original paper (p. 276), Schenck and Ziegler's synthesis of ascaridol (p. 277), and one paper by Corey and Taylor (p. 278) and two others by Foote and Wexler (pp. 280, 282) in which singlet oxygen was formed by electrical discharge in one case and chemically in the other case, and the reaction products were compared with those of sensitized oxygenation. Foote's work on the quenching of singlet oxygen by β-carotene (p. 283) was greatly significant in the biochemical community.

The final papers in this section deal with two standbys of the photochemist's repertoire, benzophenone and stilbene. The photoreduction of benzophenone

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[9] Two histories of Giacomo Ciamician, who was a professor at Bologna, have appeared. N. Heindel, M. A. Pfau, *Journal of Chemical Education* 42, 383 (1965), and M. Pfau, N. Heindel, *Ann. Chem.* 10, 187 (1965).

[10] The oldest photochemistry book that the editor has been able to find is by Plotnikov, *Alegemeine Photochemie*, published by de Gruyter in Berlin in 1920. A second edition was published in 1936.

[11] Albert Wells died in Bowling Green, Ohio, in 1967 and is buried in a cemetery that abuts the Bowling Green campus. The second edition of Ellis and Wells, published in 1941, is a veritable compendium of all the photochemical processes known at that time.

was discovered by Ciamician and Silber but was studied in detail first by Cohen (p. 285) and later by Weizmann, Bergmann, and Hirshberg (p. 304). The chemical mechanism was really put in place by Pitts and Letsinger in 1959 (p. 307). Hammond's group identified the reactive intermediate as the triplet state of benzophenone (p. 317); this was followed by a long, detailed experimental paper that essentially outlined the methodology for physical organic photochemistry (p. 318). The comparison of the chemical reactivity of the benzophenone triplet state to an alkoxy radical is due to Walling (p. 324), and this concept significantly assisted organic chemists in mechanistic interpretations of organic photochemical processes. The final paper in this group is the remote oxidation paper by Breslow and Winnik (p. 328). These workers used the benzophenone triplet to selectively functionalize aliphatic side chains at specific positions.

Section Three: Intermediates in Photochemical Processes

This is the one section of this collection of reprints that could be almost infinite in length because of the development of laser flash photolysis and transient intermediate spectroscopy. It is the area of mechanistic photochemistry that has grown the most over the past 15 years or so. We follow, in this section, the development of experimental methods that produce actual observations of reactive intermediates in photochemical processes. The first paper is the flash photolysis paper from Norrish labs, but it is followed by experimental efforts that have been used successfully to trace reaction intermediates in the photochemical reactions of benzophenone and its derivatives.

The first papers on flash photolysis came from the work of R.G.W. Norrish and George Porter in 1949 (p. 333), for which they shared the Nobel prize in 1967. Bell and Linschitz (p. 334) used flash photolysis to identify benzophenone triplet as the reactive intermediate in the reduction of benzophenone in an experiment that followed almost immediately on the heels of the Hammond work. A most recent collaborative paper from the labs of Neckers and Rodgers (p. 339) uses laser flash photolysis to identify all of the preradical intermediates in the photochemical decomposition of p-benzoyl-tert-butyl perbenzoate, a system in which the benzophenone triplet is remotely coupled to a para positioned, weak functionality. In this work the lifetime of the benzophenone triplet is measured as a few nanoseconds. A troublesome fact in the photoreduction of benzophenone had been the appearance of a yellow intermediate. The structure of this intermediate was assigned by Filipescu and Minn by absorption spectroscopy in 1968 (p. 342). Chemically induced dynamic nuclear polarization (CIDNP), first observed by Ward and Lawler (p. 346) as well as by Fischer and his group (p. 348), was used by Closs and Closs (p. 352) to prove that benzophenone abstractions from hydrocarbons produced triplet radical pairs. Electron spin resonance (ESR) was used by Schenck and his group (p. 354) to study the diphenylhydroxymethyl radicals produced in benzophenone photoreduction. The Hatchard-Parker paper on a ferrioxalate actinometer is included in this section as well (p. 357). We put it here because we know it's important and it has to go somewhere, but we didn't know exactly where.

Section Four: Photochemistry of Aliphatic Ketones

If there's a veritable truth about photochemistry, it is that the best kind of photochemical reactions to study are those that occur with high quantum yield. Unnecessary to state, perhaps, but if a reaction does not occur efficiently, studying it is a waste of time.

The photochemistry of ketones was important for two reasons: ketones undergo facile, high quantum yield changes when irradiated with relatively long wavelength light. They absorb in the mid-range UV. Aldehydes undergo other changes; specifically, they lose a hydrogen atom and form acyl radicals.

Aliphatic ketones undergo two different chemical processes. The first is a simple split into radicals (as, for instance, in the case of aldehydes), which results in the loss of carbon monoxide and the decarbonylated product. We now refer to this as the Norrish type I reaction. The second is a rearrangement elimination referred to as the Norrish type II process, in which the part lost is an olefin. The two reactions are compared below with t-butyl cyclopentanone.
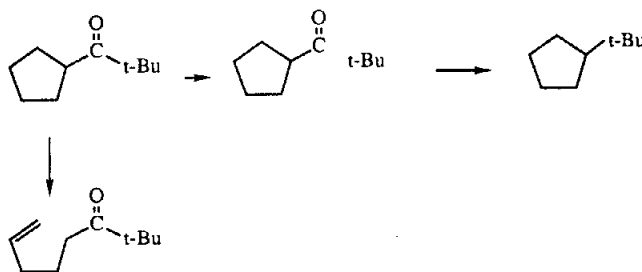
The first example of the Norrish II reaction is the paper by Norrish and Appleyard (p. 377). Although photochemists tend to forget the work of Kharasch and his students at the University of Chicago,[12] this group studied a number of processes involving free radical intermediates in solution. The addition of aldehydes to olefins (p. 382) is one of these reactions. The first reaction of aldehydes and ketones with olefins that resulted in an oxetane, or cycloaddition product, was reported by Paternò and Chieffi (p. 387) and studied in detail first by Büchi and his students (p. 398), who looked at the reaction of 2-methyl pentene with simple aldehydes. N.C. Yang was the first to call the reaction the Paternò-Büchi reaction, a name that has stuck. Corey and his students worked out the regiochemistry as part of a first step in the synthesis of caryophyllene (p. 403). Intramolecular hydrogen abstractions, i.e., the Norrish type II reaction, were not the only pathways open to aliphatic ketones. Yang's early work in the field identified hydrogen abstraction/coupling products, as well as cyclobutanol formation (p. 417). A particularly important contribution of Yang was on the reaction of ortho-alkylbenzophenone (p. 418). He cleverly isolated the enol as a Diels-Alder adduct. Like many photochemical processes discovered in the 1950s and 60s, this reaction became very important because it was applied to impart light stability to poly-

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[12] Kharasch had some sort of complaint with the editors of the *Journal of the American Chemical Society*, so he initiated a new journal for organic chemists, the *Journal of Organic Chemistry*. Until Fred Greene retired a few years ago, J. Org. Chem. had never had an editor who was not, nominally at least, of the Kharasch school—i.e., a free radical chemist.

mers. The mechanism of the Norrish type II reaction was worked out by Peter Wagner, working in Hammond's laboratories (p. 419). In a little known paper, Starr and Eastman illustrated some of the mechanistic principles of the Norrish type II reaction in what was essentially a synthetic paper (p. 421). This was followed by definitive mechanistic work by Yang and Feit on methyl t-butyl ketone (p. 431).

Section Five: Natural Products

We include just five papers in this section, among which are a paper from Havinga's lab on vitamin D and two papers from Chapman's laboratories, the first on colchicine and the other on the tropones.

Havinga's work on vitamin D (p. 435) concluded nearly 30 years of attention to the chemistry of a series of derivatives of ergosterol that had antirachitic properties. After the exhaustive pioneering work of Windaus and his many coworkers on the steroids,[13] and Dimroth,[14] the paper we have included represents a summary of Havinga's efforts, conducted in conjunction with a group at Philips in Weesp, The Netherlands, that manufactured vitamin D for European markets.

No group of papers on natural products chemistry would be complete without some contributions from one of the many groups who have worked on the photochemistry of the dienes. The paper from Dauben's group (p. 442) is representative.

Colchicine, an important natural product used for generations to treat gout, produces at least three products in sunlight. The structure of α-lumicolchicine was particularly difficult to solve by classical methods and eventually took NMR methods to confirm. Therefore, this structure was not firmed up until Chapman's work on tropones in the late 50s and early 60s, after NMR spectrometers became commercially available. Two Chapman papers are included. The first is on the basic photochemistry of simple tropones (p. 450); the second is on the structure of α-lumicolchicine (p. 457).

Finally, in this section we include one other historical paper of general interest. This is a paper, in his own hand, by J. M. Bijvoet, the Dutch crystallographer who first solved the absolute stereochemistry of the sodium, rubidium salts of the optical antipodes of tartaric acid. It was this work (p. 459) that solved, once and for all, the three-dimensional structure of D(+)-glucose.

Section Six: Synthetic Challenges Solved by Photochemical Processes

In the first edition of Cram and Hammond,[15] on the inside front and back covers were drawn the structures of a number of simple compounds that had

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[13] A. Windaus, E. Auhagen, Z. Physiol. Chem. 196, 108 (1931).

[14] K. Dimroth, Chemische Berichte 215, 183 (1937).

[15] D. J. Cram, G. S. Hammond, Organic Chemistry, McGraw-Hill, New York (1958).

yet to be synthesized: cyclobutadiene, cyclopropanone, cyclooctatetraene, vinyl alcohol, etc. The achievement of photochemical processes to synthesize simple molecules that had previously defied synthesis was probably aided by the advent of new techniques to confirm their structures, but it is impressive nevertheless.

The first paper we include here is van Tamelen's synthesis of two examples of Dewar benzene, the first from 1,2,5-tributylbenzene (p. 467) and the second the synthesis of Dewar benzene itself (p. 469). Eaton's two first papers on the cubane system (pp. 471, 473) completed the synthesis of this highly symmetrical simple hydrocarbon. Low temperature methods, pioneered by Chapman, allowed the synthesis of cyclobutadiene (p. 475) and benzene (p. 478). According to Chapman, cyclobutadiene had been the target of synthetic chemists since Kekule's time,[16] and the success of his group was due to a combination of low temperature photochemistry with infrared spectroscopy, which was used for its detection.

Cyclopropanone was finally achieved by Turro shortly after he was appointed an assistant professor at Columbia. He followed a method developed, but never published, by Kende in his Ph.D. dissertation at Harvard--the addition of diazomethane to ketene (p. 480). Prior to this, Turro had discovered that cyclobutadiones decarbonylate one step at a time (the principle is illustrated in the paper on their mass spectra, p. 481; mass spectral decompositions tend to belie photochemical pathways). Finally, in this series we include two paper from Barton's many on synthetic methodology using photochemical reactivity, and a synthesis of aldersterone acetate using this methodology. Barton's notion was that activation of non-reactive C-H centers might be achieved by photochemical routes. For this he investigated a number of nitrite photolyses and remote activation reactions involving them. The first paper in this series is reprinted (p. 485), and his synthesis of aldersterone acetate follows (p. 486).

Section Seven: Critical Papers and Some Curiosities

Sometimes it's hard to recognize the difference between a critical paper and a mere curiosity. The Freeman/Klemperer paper on the dipole moment of the excited state of formaldehyde generated a great deal of interest among organic chemists. It helped them explain that the excited states of certain ketones likely were less polarized than might have been expected from ground state analogy. The Freeman/Klemperer paper (p. 489) was both a curiosity and a crucial paper. There's no question whatsoever about the next paper--this is the first Woodward-Hoffmann communication (p. 491). Howard Zimmerman's enormously important contributions on dienones are represented by his first communication (p. 494) and by a salient paper Professor Zimmerman gave at an organic chemistry symposium in 1961 (p. 496). Setlow's paper in Science (p. 502) suggested that the crosslinking of nucleic acids was responsible for the damaging effects of ultraviolet radiation on DNA and the damage UV causes to cells and viruses. And, finally, a couple of curiosities as much as critical

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[16] A. Kekule, Annalen Chemie 162, 77 (1872).

papers: ours on the synthesis of Polymer Rose Bengal (p. 510) and another from our laboratory on the organic chemistry of Rose Bengal (p. 512).

Section Eight: Patents

The development of photochemistry is almost inextricably linked to the development of industries in the photochemical sciences, included among which are some of the most important in the western world. Photography and xerography worldwide, for example, account for something in excess of $50 billion a year in sales.

When I was considering this collection of reprints on the fundamentals of photochemistry, I decided I must include some of the patents that made a difference; the question was, which patents and how many of them. Major developments such as photocopy machines don't result from a single inspiration of genius patented by the wizard inventor and protected for commercial development forever. Major developments are exactly that--developments--and the patents that describe them are numerous, complex, and difficult. Chester Carlson, for instance, published more than 20 patents in the early 1940s before there was even a working prototype of a Xerox machine.

What I decided to do was ask colleagues working for the companies in question, many of whom were engrossed in current day activities still resulting from the original inventions, which patents they thought were most important to Polaroid, in the development of xerography, in photoresist technologies, in photopolymer printing and lithography. In the development of the laser the situation was even more convoluted and complicated, so I asked some attorney friends and read a couple of books on the subject. The patents included here came from Polaroid, Xerox, Du Pont, and Kodak, while the laser patents were assembled from the information found in many books on its development.

Xerography

Robert Marchessault, NSERC-Xerox Professor of Chemistry at McGill University in Montreal, Quebec, used to be director of research at Xerox of Canada. He wrote the following story for *The Spectrum*, the quarterly newsletter of Bowling Green University's Center for Photochemical Sciences, on the occasion of the 50th anniversary of the discovery of xerography.[17]

> [10-22-38 Astoria] This humble statement marks the beginning of xerography. This technology, created in makeshift laboratory in Astoria, Long Island, New York, by Chester Carlson and originally named *electrophotography*, has swept the world and revolutionized the manner of information transfer. In its own right, xerography is as significant an invention as the telephone or telegraph.
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> Carlson, born in Seattle on February 8, 1906, was the only child of an itinerant barber who had settled his family in San Bernardino,

California. At the age of 14, Carlson was working after school and on weekends as the chief support of his family. His father was crippled with arthritis and his mother died of tuberculosis when he was 17.

Even as a boy, Carlson had the curious mind of the inventor and always asked questions about the how and why of things. He was fascinated with the graphic arts and with chemistry--two disciplines he would eventually explore and use with remarkable results. After attending a junior college where he majored in chemistry, Carlson majored in physics at Cal Tech and graduated in 1930.

He entered the job market during the Depression. After applying to 82 firms, he finally landed a $35/week job as a research engineer at Bell Telephone Laboratories in New York City. Unfortunately, this did not last long and he secured a new position at the electronics firm of P. R. Mallory and Co. While there he studied law at night, earned a law degree from a New York law school, and eventually became manager of Mallory's law department.

As he worked at his job, Carlson noted that there never seemed to be enough copies of patent documents. Furthermore, he frequently had to send for expensive photographs of documents on the outside. It occurred to him that offices might benefit from a device that could make copies of documents at the push of a button.

Beginning in 1934, Carlson spent many evenings in the New York Public Library reading all he could about imaging processes. He was convinced he did not want to follow conventional photographic technology where light is an agent to cause chemical change. He wanted to avoid the use of chemicals and especially to come up with a novel idea which had not been exhaustively explored by research laboratories in large companies. Finally, he decided to focus on two physical principles: photoconductivity and electrostatics.

Photoconductive materials are insulators in the dark and conductors in light. Clearly they had the potential to capture an image as a pattern of charges. The pattern could be developed with a powder which would electrostatically neutralize the latent image. The steps involved in the key experiments undertaken by Carlson and his young physicist colleague, Otto Kornei, culminating on the fateful date in October, 1938, with the world's first xerographic copies, are outlined in many patents.

Carlson obtained the first of many patents in 1940 and spent the next four years trying to find someone who would develop and market his invention. Finally, in 1944 the Battelle Memorial Institute in Columbus, Ohio, agreed to undertake development. In 1947, Haloid Corporation, a small firm in Rochester, New York (later to become Xerox), obtained the commercial rights to xerography and 11 years later introduced the first paper copier.

Chester Carlson died on September, 19, 1968, on the eve of the rapid expansion of computer technology that would usher in the kind of information storage he foresaw.

Today, in its 50th year, xerography is the foundation stone of the worldwide copying industry.

To Carlson, who had endured and struggled for so long, came fame, wealth, and honor, all of which he accepted with grace and modesty, in keeping with his shy, quiet personality. He personally benefitted from his invention to the extent of $150 million. Some $100 million of his fortune he gave away during his lifetime anonymously.

There are many stories about the Carlson discovery, some apocryphal, others true. Many industrial scientists at companies around the country tell of looking at the Carlson patents in the 1940s and seeing little of commercial value in them. But Carlson persisted, and with the help of Joseph Wilson, electrophotography became xerography and the Xerox machine was born.

Try your hand at it. Would you recognize the potential of electrophotography from the Carlson patent of October 6, 1942 (p. 525)?

Polaroid

E. H. Land, the inventor of the Polaroid camera, died in 1991. I remember the first Polaroid Land camera I saw--at a basketball game in Mayville, New York, in the winter of 1953. A Chautauqua (New York) High School proud mother was taking instant black and white photographs of the Chautauqua cheerleaders. The critical Land patents are the so-called "pod patents," the rupturable container patents filed in 1948 and issued in 1951. The one issued to Land on February 27, 1951 (p. 535), is the patent from which Polaroid black and white instant photography was built.

A Harvard dropout, Land developed the Polaroid concept and for 40 years dominated the Polaroid Corporation he founded in Cambridge, on the edge of MIT. An incredibly intense man, he would devote himself and the efforts of scientists in his employ for projects that interested him until the project was solved, and then he would move on to something else. A *Polaroid Update* on the life of Edwin Land is included (p. 565).

Howard Rogers, an early associate of Land, developed instant color photography, or Polacolor (p. 571). Senior Polaroid scientists to this day will tell you that many distinguished scientists and academic savants said it couldn't be done. But Rogers, who like Land was a Harvard student who didn't finish his degree, did it anyway.

Negative Photoresists

Minsk at Kodak provided the patent basis for what eventually became "negative photoresists." The Minsk systems were based on the dimerization reaction that occurs between cinnamic acid residues. The Minsk contribution was the

synthesis and application of polyvinyl cinnamate to the "photomechanical resist problem." The first Minsk patent, dated September 9, 1952, is included (p. 590).

Louis Plambeck's work at Du Pont, along with that of Abraham Cohen, was responsible for the preparation of relief images from polyolacrylate monomers. These chemistries formed the basis of what became photolithography and what is now becoming stereolithography. Many of the applications are in the proofing and printing industries. One of Plambeck's many patents, dated August 28, 1956, is included (p. 596).

Lasers

The development of the laser occurred in the late 1950s and was a matter of some contention later. I first saw a laser as a postdoctoral fellow at Harvard in 1963 when someone (who, I don't remember; perhaps a salesman) brought a ruby laser to Paul Bartlett's laboratory and we shined its red beam on the biological sciences building across the parking lot from Converse Laboratories. I've included three patents here: one dated March 24, 1959, to Charles Townes (p. 610), who at the time was a professor of physics at Columbia, and two to Gordon Gould, a former student of Townes (June 11, 1968, p. 617, and June 22, 1971, p. 646). The first Gould patent is on a device for generating continuous wave light amplified emission and the other is on a pulsed system. It was on December 10, 1981, that Arthur Schalow, then a professor of physics at Stanford but originally on the staff at Bell Laboratories, received the Nobel Prize in physics. Schalow and Townes held the first patent on the maser.

As in every section of this book, we had a hard time selecting these patents. Others would have chosen differently, but these were our choices; we hope the readers find them interesting.

Epilogue

As scientific research heads into the 21st century, photochemistry promises to play an expanding role. Its commercial implications in the imaging sciences are well known and promise to expand. The possible implications of the optical computer as well as simple, cheap, more powerful lasers portend applications still unenvisioned.

We've tried to trace the history of a field of intellectual endeavor through a series of papers in this Milestone volume. As was said in the preface, anyone else tracing the history of this field would have chosen a different set of papers and a completely different emphasis. Our emphasis was first on the theoretical foundations and then some experimental examples illustrating how these foundations were built upon to synthesize a rational outcome.

The synthetic achievements of photochemistry are more than curiosities--they represent pinning nature down to the point that it produces what the experimenter wants it to.

The patents we have chosen are just those that occurred to us and are based on our own consulting experience over nearly 30 years in photoscience. Doubt-

less there are others that illustrate the point that science itself is a possible *raison d'etre*, but it always helps if one can point to some practical implications and commercial successes--particularly when seeking funding for future basic scientific studies.

This project has been a lot of fun. I've conversed at length with George Hammond and Günther Schenck about the papers I should include. I've also had discussions with N.C. Yang, with David Schuster, with Heinz Roth, and with several other practicing photochemists about this project. Some of the materials I have gathered personally--for example, the papers from the ETH Library on Robert Gnehm; for this I thank Dr. Gregor Graf from Ciba-Geigy, Basel, for extensive assistance. The papers from Professor J. M. Bijvoet I obtained nearly 15 years ago, just prior to his death in Winterswijk, The Netherlands, at age 85. I discovered that Albert Wells is buried in the cemetery that sits in the middle of the Bowling Green campus about 10 years ago when his son-in-law took a class I offered at the university.

Finally, I thank all of the photochemists who have sent me papers for consideration. There are many areas I've left out. I make no apology for that. I couldn't include everything. As always, comments from those reading this effort will be greatly appreciated.

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