THE PHOTOCHEMISTRY OF THE FUTURE (1912)

GIACOMO CIAMICIAN (1857-1922)

(Translation supplied by the author)

Modern civilization is the daughter of coal for this offers to mankind the solar energy in its most concentrated form: that is in a form in which it has been accumulated in a long series of centuries. Modern man uses it with increasing eagerness and thoughtless prodigality for the conquest of the world and, like the mythical gold of the Rhine, coal is to-day the greatest source of energy and wealth.

The earth still holds enormous quantities of it, but coal is not inexhaustible. The problem of the future begins to interest us and a proof of this may be seen in the fact that the subject was treated last year almost at the same time by Sir William Ramsay before the British Association for the Advancement of Science at Portsmouth and by Prof. Carl Engler before the Versammlung deutscher Naturforscher und Aerzte at Karlsruhe. According to the calculations of Prof. Engler Europe possesses today about 700 billion tons of coal and America about as much; to this must be added the coal of the unknown parts of Asia. The supply is enormous but, with increasing consumption, the mining of coal becomes more expensive on account of the greater depth to which it is necessary to go. It must therefore be remembered that in some regions the deposits of coal may become practically useless long before their exhaustion.

Is *fossil* solar energy the only one that may be used in modern life and civilization? That is the question.

Sir William Ramsay has made a very careful study of the problem from the English point of view. He has considered the various sources of energy such as the tides, the internal heat of the earth, the heat of the sun, water power, the forests and even atomic disintegration, and has come to the conclusion that none can be practically used in England on account of her special contour and climate.

Though the internal energy of the earth may produce terrible disasters through volcanic eruptions and earthquakes, it can hardly be used by man. The energy derived from the rotation of the earth (tides) can hardly be counted upon on account of the enormous quantities of water that would have to be handled. Atomic disintegration has recently been treated in a brilliant lecture by Frederick Soddy, with special reference to the enormous energy changes which are involved. If man ever succeeds in availing himself of the internal energy of the atoms, his power will surpass by far the limits assigned to it today. At present he is limited to the use of solar energy. Let us see however whether the *actual* energy may not supplant that stored up in fossil fuel. Assuming that the solar constant is three small calories a minute per square centimeter, that is thirty large calories a minute per square meter or about 1800 large calories an hour. We may compare this quantity of heat with that produced by the complete combustion of a kilogram of coal, which is 8000 calories. Assuming for the tropics a day of only six hours sunshine we should have, for the day, an amount of heat equivalent to that furnished by 1.35 kg. of coal, or one kilogram in round numbers. For a square kilometer we should have a quantity of heat equivalent to that produced by the complete combustion of 1000 tons of coal. A surface of only 10,000 square kilometers receives in a year, calculating a day of only six hours, a quantity of heat that corresponds to that produced by the burning of 3650 million tons of coal, in round numbers three billion tons. The quantity of coal produced annually (1909) in the mines of Europe and America is calculated at about 925 million tons and, adding to this 175 million tons of lignite, we reach 1100 million tons or a little over one billion. Even making allowances for the absorption of heat on the part of the atmosphere and for other circumstances, we see that the solar energy that reaches a small tropical county – say of the size of Latium – is equal annually to the energy produced by the entire amount of coal mined in the world! The desert of Sahara with its six million square kilometers receives daily solar energy equivalent to six billion tons of coal!

This enormous quantity of energy that the earth receives from the sun, in comparison with which the part which has been stored up by the plants in the geological periods is almost negligible, is largely wasted. It is utilized in waterfalls (white coal) and by plants. Several times its utilization in a direct form through mirrors has been tried, and now some very promising experiments are being made in Egypt and in Peru; but this side of the problem is beyond my power to discuss and I do not propose to treat it here.

The energy produced by water power during the period of one year is equal to that produced by 70 billion tons of coal according to the data given in Professor Engler's lecture. It is however very small, as might be expected, in comparison with the total energy that the sun sends to the earth every year. Let us now see what quantity of solar energy is stored by the plants: on the total surface of the various continents, which is 128 million square kilometers, there is a yearly production of 32 billion tons of vegetable matter, which, if burnt, would give the quantity of heat that corresponds to the total combustion of 18 billion tons of coal. It is not much but even this is 17 times as much as the total present production of coal and of lignite.

I

Now let us consider the first part-of our subject. Is it possible or, rather, is it conceivable that this production of organic matter may be increased in general and intensified in special places, and that the cultivation of plants may be so regulated as to make them produce abundantly such substances as can become sources of energy or be otherwise useful to civilization? I believe that this is possible. It is not proposed to replace coal by organic substances produced by plants; but it is conceivable that this organic matter may be utilized more satisfactorily than is now the case.

It has frequently been said even by persons of authority that some day the transformation of coal into bread may become not only possible but economically desirable. According to these people the ideal of the future should be to produce through synthesis from coal all substances necessary for the alimentation of man: such substances as starch, sugar and fat, also proteins and perhaps cellulose; in other words to abolish agriculture altogether and to transform the world in to a garden of useless flowers. Never was a greater fallacy thought or expressed: the real problem is just the reverse of this. My friend Professor Angeli wisely called to my attention that, while the externals of life have been changed greatly by the progress of industry so as to use all our technical knowledge to increase our comfort, the quality and quantity of human alimentation have hardly changed at all; nay, a new science has come into existence (bromatology) to see that no artificial product of industry enters harmfully into our alimentation. At the time of Napoleon III an attempt was made to substitute gelatine for meat; but it was seen very soon – and now the reason for it is known by all – that this substitute could not be sufficient to maintain life. With the relatively small reserves of coal that the past geological epoch have stored for us, it will never be desirable to produce from coal what nature generously offers us through solar energy. It is on the other hand a work worthy of praise to attempt to make plants produce the fundamental substances in larger quantity. Modern agriculture tries to do this by intensive cultivation; but it is also desirable to make the plants store up solar energy and transform it into mechanical energy.

A well-known instance of this occurred when the development of the daily press in all civilized countries made it imperative to provide wood pulp in a sufficient quantity and at low prices. Trees, better adapted to the purpose, were soon found and they were those which, on account of their rapid growth, could furnish the necessary cellulose sooner. For the problem we are now considering the quality of the plants is of secondary importance; they may be herbs or trees; they may grow in swamps or dry places, on the sea coast or even in the sea; the essential point is that they grow fast or that their growth may be intensified. It would be like realizing the desire of Faust:

“Und Bäume die sich täglich neu begriüen!”

Mephistopheles did not consider a similar task impossible:

“Ein solcher Auftrag schreckt mich nicht,
Mit solchen Schätzen kann ich dienen.”

Should we consider the task impossible, naturally in a more limited sphere, after so many centuries of culture? I do not believe so. The above estimate of the total production of organic matter over all the solid surface of the earth, that is of 32 billion tons a year, has for its basis the old calculation of Liebig of 2.5 tons per hectare. This may be considered even to-day the average production for all the earth. According to A. Mayer, through instenified culture the production may be increased to 10 tons per hectare and in tropical climates it may reach 15 tons. On a square kilometer it would be 1500 tons, corresponding to 840 tons of coal, while the solar energy received in a year by a square kilometer would be equivalent to about 300,000 tons of coal, the part of the total energy stored up by the plants being about 1/300. A great deal remains to be done, but if we consider that since Liebig, largely by adopting the methods proposed by him, the production has been at least quadrupled, we may hope to do much more in the future, especially if we are spurred on by necessity or even by convenience.

By increasing the concentration of carbon dioxide up to an optimum value (1 to 10% according to Kreusler) and by using catalyzers, it seems quite possible that the production of organic matter may be largely increased, making use, of course, of suitable mineral fertilizers and selecting localities adapted to the purpose owing to the climate or the condition of the soil. The harvest, dried by the sun, ought to be converted, in the most economical way, entirely into gaseous fuel, taking care during this operation to fix the ammonia (by the Mond process for instance) which should be returned to the soil as nitrogenous fertilizer together with all the mineral substances contained in the ashes. We should thus get a complete cycle for the inorganic fertilizing substances, the only waste being that common to all industrial processes. The gas so obtained should be burnt entirely on the spot in gas engines and the mechanical energy thus generated should be transmitted elsewhere or utilized in any way that seems advisable. We need not go into details. The carbon dioxide, resulting from the combustion, should not be wasted but should be returned to the fields. Thus the solar energy, obtained by rational methods of cultivation, might furnish low-priced mechanical energy, perhaps better than through the systems based on mirrors, because the plants would be the accumulators of the energy received by the earth.

But the problem of the utilization of plants in competition with coal has another and more interesting side. First of all we must remember the industries which have their basis in agriculture: the cotton and other textile industries, the starch industry, the production of alcohol and of all fats, the distillation of wood, the extraction of sugar, the production of tanning substances and other minor industries. All these industries are susceptible of improvement not only by the introduction of more advantageous technical devices in the treatment of the raw materials but also by a largely increased production of the raw materials. Let us think for an example of the progress made in the production of beet sugar.

The plants are unsurpassed masters of – or marvellous workshops for – photochemical synthesis of the fundamental substances, building up from carbon dioxide with the help of solar energy. They also produce the so-called secondary substances with the greatest ease. These latter are usually found in the plants in small quantity and are of value for special reasons. The alkaloids, glucosides, essences, camphor, rubber, coloring substances and others are of even greater interest to the public than the fundamental substances on account of their high commercial value. In this field a battle is raging between chemical industry and nature, a battle which does honor to human genius. Up to now the products prepared from coal tar have almost always been triumphant. I do not need to remind you of the various victories; but it is possible that these may prove to have been Pyrrhic victories. A great authority on organic industries considered recently what would happen in case, for any reason, there were a rapid increase in the price of coal tar and consequently of the substances contained in it. He pointed out the inevitable effect of this on the coal tar industries. We all remember with admiration the story of the great difficulties that had to be met in the choice of the raw material for the production of indigo. It was necessary finally to use naphthalene because toluene could not be obtained in sufficient quantity. But it is not merely through a rise in the price of the raw materials that an industry may suffer; it may be brought to a standstill by a diminished interest and activity in a certain field of scientific study. It has been thoroughly established that modern industry is affiliated very intimately with pure science; the progress of one determines necessarily that of the other. Now the chemistry of benzene and its derivatives does not constitute the favorite field of research as it did during the second half of the last century. The centre of interest is now to be found in the matters and problems connected with biology. Modern interest is concentrated on the study of the organic chemistry of organisms. This new direction in the field of pure science is bound to have its effect on the technical world and to mark out new paths for the industries to follow in the future.

It is a fact that lately several organic industries have been successfully developed, outside of the field of benzene and coal tar. There are flourishing industries in essences and perfumes and in some alkaloids, like coca. In these industries products, which plants produce in relatively large amounts, are converted into products of higher commercial value. For instance everybody knows that essence of violet is now made from citral contained in lemon oil. This is a line along which we ought to follow because we are certain of making progress. It is to be hoped that in the future we may obtain rubber commercially in some such way.

The question has still another side, which I believe deserves your attention; it concerns certain experiments recently made by myself together with Professor Ravenna at Bologna. It is not because we have arrived at any practical results that I refer to these experiments; but because they show definitely that we can modify to a certain extent the chemical processes that take place during the life of the plants. In a series of experiments made in an effort to determine the physiological function of the glucosides, we have succeeded in obtaining them from plants that usually do not produce them. We have been able, through suitable inoculations, to force maize to synthesize salicine. More recently, while studying the function of the alkaloids in the plants, we have succeeded in modifying the production of nicotine in the tobacco plant, so as to obtain a large increase or a decrease in the quantity of this alkaloid. This is only a beginning, but does it not seem to you that, with well-adapted systems of cultivation and timely intervention, we may succeed in causing plants to produce, in quantities much larger than the normal ones, the substances which are useful to our modern life and which we now obtain with great difficulty and low yield from coal tar? There is no danger at all of using for industrial purposes land which should be devoted to raising foodstuffs. An approximate calculation shows that on the earth there is plenty of land for both purposes, especially when the various cultivations are properly intensified and rationally adapted to the conditions of the soil and the climate.

This development is the real problem of the future.

II

Technical organic industry may yet expect great help from photochemistry understood in the sense above expressed and the competition between this and the chemistry of coal tar will be a great incentive for new progress. It is also true that human genius will always tend to proceed along lines selected by itself, and there is no question but that the great development in the coal tar industry has been due in part to this splendid spirit of independence. It may be asked whether there are not other methods of production which may rival the photochemical processes of the plants. The answer will be given by the future development of photochemistry as applied to the industries and on this I have a few ideas to express. The photochemical processes have not had so far any extensive practical application outside of the field of photography. From its very beginning photography has aroused a great deal of interest; it was taken up technically and, as usually happens in similar cases, it had a rapid and brilliant success. But notwithstanding the many applications photography represents only a small part of photochemistry. So far, photochemistry has only been developed to a very slight extent, perhaps because chemists have been attracted by problems which seemed more urgent. So it happens that while thermochemistry and electrochemistry have already reached a high degree of development, photochemistry is still in its infancy. Now, however, we notice a certain awakening due to a series of studies concerning general problems and special processes, especially in the organic field, in which my friend Dr. Paul Silber and myself have taken an active part. Two recent publications, one by Plotnikow and the other by Benrath bear witness to this. But much remains to be done both in theoretical and general photochemistry as well as in the special branches. The photochemical reactions follow the fundamental laws of affinity, but have a special character. They are especially notable for the small temperature coefficient and are, however, comparable – a fact which is not without technical importance – to the reactions which take place at very high temperatures. According to a brilliant idea of Plotnikow, luminous radiations produce a different ionization from that due to electrolytic dissociation; the separation of an ion requires a quantity of light which is determined by the theory of Planck and Einstein. The question is therefore related to the most recent and profound speculations of mathematical physics.

For our purposes the fundamental problem from the technical point of view is how to fix the solar energy through suitable photochemical reactions. To do this it would be sufficient to be able to imitate the assimilating processes of plants. As is well known, plants transform the carbon dioxide of the atmosphere into starch, setting free oxygen. They reverse the ordinary process of combustion. It has always seemed probable that formaldehyde was the first product of the assimilation; and Curtius has at last demonstrated its presence in the leaves of the beech trees. The artificial reproduction of a similar process by means of ultraviolet rays has already been obtained by D. Berthelot. With convenient modifications could not this now actually be done on the tropical highlands? Yet the true solution consists in utilizing the radiations that pass through the entire atmosphere and reach the surface of the earth in large amounts. That a way of accomplishing this exists is proved by the plants themselves. By using suitable catalyzers, it should be possible to transform the mixture of water and carbon dioxide into oxygen and methane, or to cause other endo-energetic processes. The desert regions of the tropics, where the conditions of the soil and of the climate make it impossible to grow any ordinary crops would be made to utilize the solar energy which they receive in so large a measure all the year, that the energy derived from them would be equal to that of billions of tons of coal.

Besides this process, which would give new value to the waste products of combustion, several others are known, which are caused by ultraviolet radiations and which might eventually take place under the influence of ordinary radiations, provided suitable sensitizers were discovered. The synthesis of ozone, of sulphur trioxide, of ammonia, of the oxides of nitrogen, as well as many other syntheses, might become the object of industrial photochemical processes.

It is conceivable that we might make photoelectrical batteries or batteries based on photochemical processes, as, for instance, in the experiments of C. Winther.

Passing to the field of organic chemistry, the reactions caused by light are so many that it should not be difficult to find some which are of practical value. The action of light is especially favorable to processes of reciprocal oxidation and reduction which give rise to or are associated with phenomena of condensation. Since the common condensation is that of the aldolic type there is much hope for the future, the aldolic condensation being the fundamental reaction of organic synthesis. Some experiments recently made by my friend Silber and by myself may serve here as an illustration. The simplest case is that of the action of light on a mixture of acetone and methyl, alcohol in which

$$\begin{array}{lcl} CH_3 & & CH_3 \\ | & & | \\ CO + CH_3\,OH & = & COH - CH_2\,OH \\ | & & | \\ CH_3 & & CH_3 \end{array}$$

isobutylene glycol is produced. But this condensation which may be considered as a simultaneous process of oxidation and reduction, is accompanied by the reduction of the ketone to isopropyl alcohol and by the oxidation of the methyl alcohol to formaldehyde, which latter, however, does not remain as a product which can be isolated because it reacts with the remaining methyl alcohol and is transformed into ethylene glycol:

$$\begin{array}{lcll}
CH_3 & & CH_3 & \\
| & & | & CH_2\,OH \\
CO + 2\,CH_3\,OH & \rightarrow & CHOH + & | \\
| & & | & CH_2\,OH \\
CH_3 & & CH_3 &
\end{array}$$

Applying the same photochemical reaction to the mixture of acetone and ethyl alcohol we have analogous products: trime-thylethylene glycol; and along with this isopropyl alcohol and dimethylethylene glycol:

$$\begin{array}{lclcl}
CH_3 & & & & CH_3 \\
| & & & & | \\
| & & & & CHOH \\
| & & & & | \\
C\,.\,OH & — & CH\,.\,OH & e & CHOH \\
| & & | & & | \\
CH_3 & & CH_3 & & CH_3
\end{array}$$

With acetone and isopropyl alcohol, as could be expected, there is formed only pinacone:

$$\begin{array}{lclclcl}
CH_3 & & CH_3 & & CH_3 & & CH_3 \\
| & & | & & | & & \\
CO & + & CHOH & = & C\,.\,OH & — & COH\,. \\
| & & | & & | & & | \\
CH_3 & & CH_3 & & CH_3 & & CH_3
\end{array}$$

In the aromatic series benzophenone and benzyl alcohol give triphenylethylene glycol, together with other products:

$$\begin{array}{lclclcl}
C_6\,H_5 & & & & C_6\,H_5 & & \\
| & & & & | & & \\
CO & + & CH_2\,OH & = & COH & — & CHOH \\
| & & | & & | & & | \\
C_6\,H_5 & & C_6\,H_5 & & C_6\,H_5 & & C_6\,H_5
\end{array}$$

This was the first case in which this condensation has been observed; others were afterwards studied by Paternò, who replaced the benzyl alcohol by several other aromatic substances. The observations of Klinger showed that the aldehydes also underwent condensations and this has since been confirmed by Benrath.

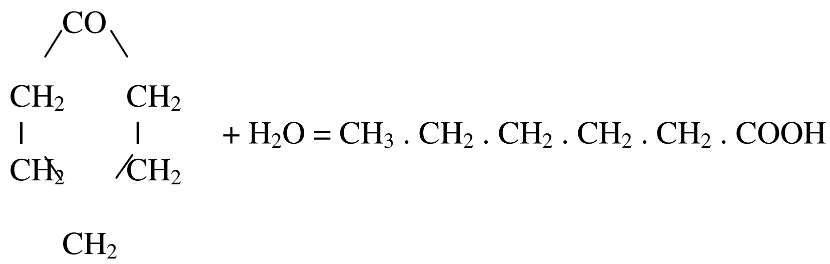
To get an idea of the variety of photochemical reactions we may confine ourselves to a systematic study of the ketones and alcohols. In ordinary organic chemistry the reactions often take place in some definite way; but the photochemical reactions often furnish surprises and proceed along quite different lines. From the very first experiments we knew that benzophenone did not form addition products with ethyl alcohol, but was converted into pinacone at the expense of the alcohol, which was oxidized to aldehyde. Proceeding with the study of aliphatic ketones, similar to acetone, we have this year discovered a remarkable fact. Methylethylketone condenses with itself and forms the paradiketone, reducing itself at the same time to secondary butyl alcohol:

$$
\begin{array}{ccccccc}
CH_3 & & CH_3 & & CH_3 & & CH_3 \\
| & & | & & | & & | \\
3CH_2 & & CH_2 & & CH & — & CH \\
| & = & | & + & | & & | \\
CO & & CHOH & & CO & & CO \\
| & & | & & | & & | \\
CH_3 & & CH_3 & & CH_3 & & CH_3
\end{array}
$$

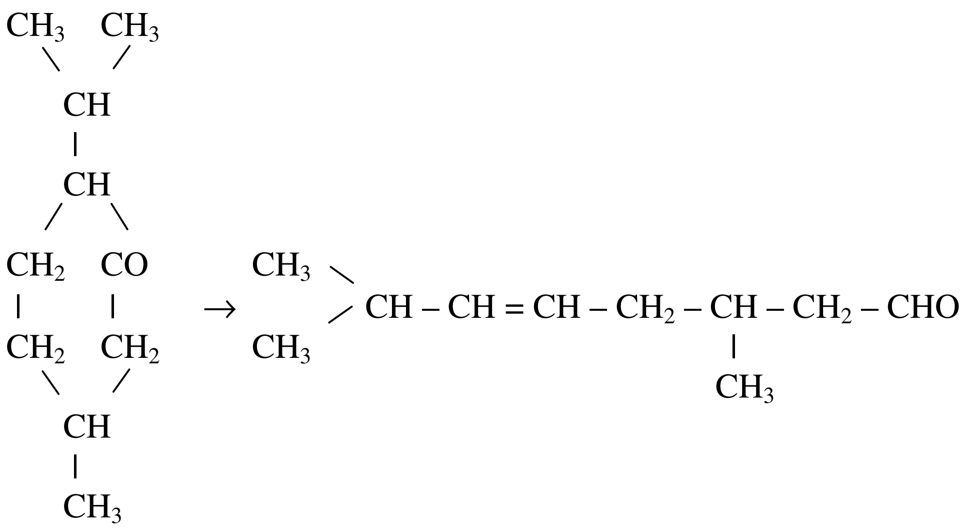
Of course the synthesis of diketones by light could not be an isolated reaction; we had previously noticed the formation of diacetyl: acetonylacetone is found, as we now know, among the products of acetone in solution in ethyl alcohol and it is also possible that the metadiketones, such as acetylacetone for instance, may be prepared photochemically. These reactions have a special importance on account of the special character of the diketones and their tendency to change in all sorts of ways. From them derivatives of benzene can be obtained as well as of pyrrazol and isoxazol, of quinoline, of furfurol, of thiophene and of pyrrol. In regard to this last change I wish to remind you that tetramethylpyrrol corresponds to the paradiketone previously referred to. If I dare to be reckless, as you may see I am at this moment, contrary to my custom, but perhaps urged thereto unconsciously by the American genius which heeds no obstacles, I may refer to the relations between the polysubstituted pyrrols with alcohol radicals and chlorophyll, and I may see in these reactions the possibility of the synthesis of this fundamental substance by means of an artificial photochemical process. Its formation in plants, like its function, is due to a photochemical process; we do not know, however, whether and in what measure light enters into all the synthetic plant reactions, from which originate the various substances which we find in plants. The research should proceed together in the two fields; phytochemistry and photochemistry will be of great help one to another. Industrially this co-operation might have a great future: the raw materials obtained from the plants might be refined through artificial photochemical processes.

Lately we have been interested intensely by the changes that some substances of the group of the terpenes and of the camphors undergo when exposed to light, especially through hydrolytic processes. So far, indeed, our experiments have taught us that light can spoil rather than improve essences.

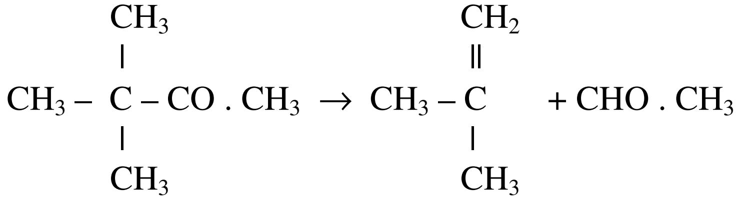
The cycloketones, for instance, are hydrolized and give the corresponding fatty acids; the cycloesanone gives capronic acid and menthone gives decylic acid.



In photochemistry, however, one reaction does not exclude the other; the reactions may be reversed as some recent experiments with ultraviolet rays demonstrate; for the ultraviolet rays sometimes reverse reactions caused by less refrangible radiations. It is important to find suitable sensitizers and catalyzers. We can see what the future has in store for us from such reactions as the photolysis of the ketones, which often accompanies the hydrolysis, and by means of which we prepare isocitronellal, for instance from menthone,



or the transformation of camphor into an unsaturated cycloketone, etc. The analogous breaking down of pinacoline into butylene and acetic aldehyde



is remarkable because it demonstrates what violent decompositions light may cause. It may be an enemy, but just on account of that it is necessary to be familiar with the weapons of the adversaries in order to be able to conquer them and to avail ourselves of their strength.

I do not believe, however, that the industries should wait any longer before taking advantage of the chemical effects produced by light. The polymerizations, the isomeric changes, the reductions and oxidations with organic and inorganic substances, and the autoxidations which light causes so easily should already find profitable applications' in some industries if researches were carried out carefully with this in mind. The action of light on nitric and nitrosilicic compounds, as we know it from experience, is one that ought to be utilized profitably. Our own transformation of orthonitrobenzoic aldehyde into nitrosobenzoic acid has recently has been studied by various chemists, and has been made use of by Pfeiffer, who prepared a nitrophenylisatogen from chlorodinitrostilbene. This reminds us of the not less known transformation of benzylidene orthonitroacetophenone into indigo by Engler and Dorant and makes us foresee a new field in the photochemical production of artificial colors and dye-stuffs. The scope of studies on this subject ought not to be limited to preserving colors from fading, bleaching and all changes produced by light. The photochemistry of colors and dye-stuffs ought to furnish new methods of preparation and of dyeing. Very encouraging experiments have already been made with diazoic compounds and mention should be made of the recent observation of Baudisch that α-nitrosonaphthylhydroxylamine is changed on the fibre to azoxynaphthalene when exposed to light. The autoxidation of leuco compounds by light is an old practice of which the ancients availed themselves for preparing purple; now the process is explained, thanks to the familiar researches of Friedlander, but it is clear that a great deal remains to be learned in this field.

Phototropic substances, which often assume very intense colors in the light, and afterwards return in the darkness to their primitive color, might be used very effectively. Such substances might well attract the attention of fashion rather than fluorescent materials which give the impression of changing colors. The dress of a lady, so prepared, would change its color according to the intensity of light. Passing from darkness to light the colors would brighten up, thus conforming automatically to the environment: the last word of fashion for the future.

Solar energy is not evenly distributed over the surface of the earth; there are privileged regions, and others that are less favored by the climate. The former ones would be the prosperous ones if we should become able to utilize the energy of the sun in the way which I have described. The tropical countries would thus be conquered by civilization which would in this manner return to its birth-place. Even now the strongest nations rival each other in the conquest of the lands of the sun, as though unconsciously foreseeing the future.

Where vegetation is rich, photochemistry may be left to the plants and by rational cultivation, as I have already explained, solar radiation may be used for industrial purposes. In the desert regions, unadapted to any kind of cultivation, photochemistry will artificially put their solar energy to practical uses.

On the arid lands there will spring up industrial colonies without smoke and without smokestacks; forests of glass tubes will extend over the plains and glass buildings will rise everywhere; inside of these will take place the photochemical processes that hitherto have been the guarded secret of the plants, but that will have been mastered by human industry which will know how to make them bear even more abundant fruit than nature, for nature is not in a hurry and mankind is. And if in a distant future the supply of coal becomes completely exhausted, civilization will not be checked by that, for life and civilization will continue as long as the sun shines! If our black and nervous civilization, based on coal, shall be followed by a quieter civilization based on the utilization of solar energy, that will not be harmful to progress and to human happiness.

The photochemistry of the future should not however be postponed to such distant times; I believe that industry will do well in using from this very day all the energies that nature puts at its disposal. So far, human civilization has made use almost exclusively of fossil solar energy. Would it not be advantageous to make better use of radiant energy?