

THE POTENTIAL OF PHOTOCHEMICAL TRANSITION METAL REACTIONS IN PREBIOTIC ORGANIC SYNTHESIS. I. OBSERVED CONVERSION OF METHANOL INTO ETHYLENE GLYCOL AS POSSIBLE PROTOTYPE FOR SUGAR ALCOHOL FORMATION

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Abstract. Photochemical processes involving redox reactions between metal ions and organic substrates possess the versatile potential for having harnessed solar energy for prebiotic organic synthesis. The present study in our Laboratory has shown that ultraviolet irradiation of transition metal ions such as of Ni, Co, Fe, Cu and Ti dissolved in primary or secondary alcohols causes photoreduction of the metal ions with the concomitant oxidation of the alcohol to aldehyde or ketone. An observed accompaniment of this novel 'light' reaction has been the known 'dark' pinacol reaction, whereby the carbonyl derivative underwent bimolecular coupling to the diol by the photogenerated reduced transition metal reagent. These tandem 'light-dark' processes possess the potential for the stepwise synthesis of dimeric 1,2-diols from simpler alcohols under conditions that might have prevailed on the prebiotic earth. Experiments reported here have demonstrated that such a tandem 'light-dark' conversion of methanol into ethylene glycol, via formaldehyde, does in fact occur, when nickel(II) acetylacetonate solutions in methanol undergo prolonged irradiation at 185–254 nm. Since ethylene glycol can be considered as the simplest sugar alcohol, these findings may provide novel insight into the prebiotic oligomerization of formaldehyde into higher sugar alcohols or even sugars.

Keywords: formaldehyde oligomerization, metal- and light-mediated redox reactions, prebiotic synthesis of sugars and sugar alcohols, photochemical oxidation, transition metal reductions of carbonyl derivatives

1. Introduction

Cosmological theories on the chemical origins of life on earth have ranged from the ancient Greek view of the generation of all matter from the four elements of fire, air, water and earth, as espoused by Empedocles (490–430 B.C.), to the current view that all essential biomolecules evolved from a prebiotic pool of simple organic molecules in an aqueous environment and in contact with a source of nitrogen. In the latter case, the chemical evolution of the requisite amino acids, sugar, fats and the essential nitrogen bases of RNA and DNA becomes to the modern chemist a challenge for organic synthesis in such environments. Initially at least, the question



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TABLE I
The four Empedoclean elements and their modern counterparts

Empedoclean element	Modern term
Fire	Energy source (heat, light, spark)
Air	O ₂ N ₂ CO ₂
Water	Water (redox reactions)
Earth	Metal salts, carbides

to be answered is not whether life has probably emerged from such a prebiotic pool, but whether life could possibly emerge from abiotic organic reactions.

In assessing the possibility of this route to life, the modern organic chemist can utilize the Empedoclean approach if the four elements of the ancients be given an expanded connotation (Table I). If fire is understood also to include photochemical and electrical discharge as sources of energy and if then water is recognized as inducing photochemical redox processes leading to oxidation or reduction, then the debate on whether the primordial earth possessed a reducing or oxidizing atmosphere becomes irrelevant. The body of evidence on the photolysis of water supports the formation of hydrogen atoms and OH radicals at all wavelengths (Calvert *et al.*, 1966). Furthermore, transition metals have long been shown capable of catalyzing a wide range of thermal and photochemical redox reactions of inorganic and organic compounds in aqueous media (Borowska *et al.*, 1987; Chanon *et al.*, 1989; Mauzerall, 1992, 1995; Bernstein *et al.*, 1999) In the search for possible transformations of simple organic molecules into essential biomolecules, therefore, transition metal-catalyzed processes, both thermal and photochemical, have great appeal in possible prebiotic organic chemistry.

In medieval alchemy, achieving the union of the four Empedoclean elements in the proportions proper to a substance was thought to require a fifth element or *quinta essentia* (a forerunner of 'vital force', Paracelsus, 1493–1541 A.D.). The corresponding *quintessence* required of the modern organic chemist in devising possible prebiotic pathways for uniting the four modern elements is an unbounded *chemical imagination*.

2. A Primordial RNA World and the Oligomerization of Formaldehyde

An important hypothesis greatly assisting the formulation of prebiotic organic reactions is that of a primordial RNA world. As expressed by G.F. Joyce in the monograph, 'The Rise and Fall of the RNA World':

It is generally believed that there was a time in the early history of life on earth when RNA served as both the genetic (bioinformational) material and

the agent of catalytic function (Woese, 1967; Crick, 1968; Orgel, 1968; Sharp, 1985; Pace and Marsh, 1985; Lewin, 1986; Gilbert, 1986; Cech, 1986). The DNA/protein-based life form that is common to all known terrestrial biology is thought to have descended from an RNA-based life form approximately 4 billion years ago. (Joyce, 1991)

In this line with this approach, the formulation of prebiotic chemistry would then focus on the feasible synthesis of the RNA components, D-ribose, the four pyrimidine or purine bases and phosphoric acid and their selective assembly into first a ribonucleotide and then into an appropriate sequence of an RNA.

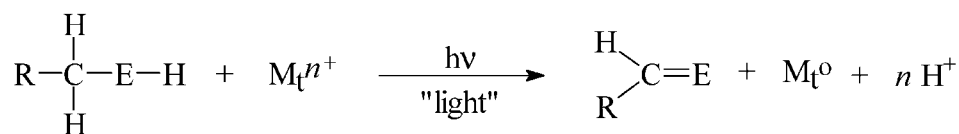
Now the prebiotic generation of phosphates from volcanic sources of phosphides and of purine or pyrimidine bases from the oligomerization of HCN can be demonstrated by actual laboratory simulation of conditions attainable on the primordial earth (Miller *et al.*, 1974). Accordingly, their availability for the prebiotic synthesis of RNA can be reasonably supposed. But the major problem in such an RNA synthesis has been and remains the availability of D-ribose.* This sugar presents a twofold problem, one of synthesis and one of persistence. D-ribose can be viewed as a pentamer of formaldehyde and in fact, can be generated from this simple aldehyde by the action of aqueous $\text{Ca}(\text{OH})_2$ (Butlerov reaction, 1861). Unfortunately, the whole array of straight-chain and branched oligomers of $(\text{CH}_2\text{O})_n$ are obtained where $n = 2,3,4,5,6\dots$ and the content of DL-ribose in such a mixture is maximally 2%. Furthermore, the sugars formed can arise not only as *racemic* but also as diastereomeric isomers. Thus the Butlerov reaction can be judged as a very unlikely prebiotic source of even *racemic* ribose.

A second serious problem is the estimated lability of ribose in the primordial ocean. As modeled on aqueous solutions between 40 °C and 120 °C and at pH of 4 to 8, the half-life of ribose to degradation has proved to be hours to days ($t_{1/2} = 73$ min. at 100 °C and pH of 8) (Larralde *et al.*, 1995). As a result, even if generated in a practical aqueous concentration, ribose would not persist sufficiently long to combine with the nitrogen base and phosphoric acid to form the ribonucleotide.

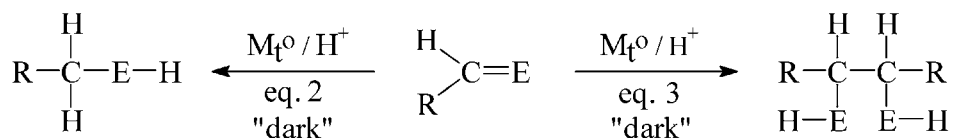
Because of these imposing difficulties with the availability of ribose via the Butlerov reaction, we have sought to devise an alternative, feasible and stereoselective source of ribose and to generate it as a chemical derivative which would have been much more stable to degradation in the primordial ocean. In the next section we present our general hypothesis for the prebiotic photochemical generation of ribose and other biomolecules necessary for the emergence of life on earth. A detailed

* If alternatively in the hypothesis of Eschenmoser and coworkers (Schöning *et al.*, 2000) one proposes a TNA world [(L)- α -threofuranosyl oligonucleotides] as forerunner to the present DNA world, a possible prebiotic synthesis of tetroses and specifically L-threose still must be put forward. Even for this possibility the present 'light-dark' redox reactions should offer some appeal.

The prebiotic PNA world [peptide nucleic acids] proposed by Miller (1997) would still require some possible prebiotic synthesis of its ethylenediamine component. It is not farfetched to suggest a 'light-dark' redox reaction on methylamine as a route to ethylenediamine, an exact parallel to the process of converting methanol into ethylene glycol, as observed in the present study.



Equation 1.



Equations 2-3.

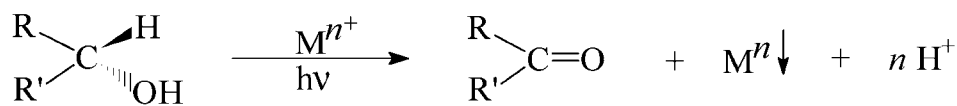
experimental testing of this ramified hypothesis will be the subject of the present and succeeding publications of our Laboratory.

3. Photochemical Transition Metal-Mediated Approach to Sugars and Other Prebiotic Compounds

Ultraviolet light has long been recognized as the most abundant energy source on the prebiotic earth for organic synthesis (McLaren *et al.*, 1964; Miller *et al.*, 1974; Pinto *et al.*, 1980; Gaustad *et al.*, 1982; Mauzerall, 1990, 1992, 1995; Ramamurthy, 1991). Photochemical processes involving redox reactions of transition metals such as Ti, Cu, Ni, Co and Fe possess the selective and versatile potential for having harnessed solar energy for useful prebiotic synthesis (Chanon *et al.*, 1989). Such irradiation can be captured by the photoreduction of the metal ions with the concomitant oxidation of simple alcohols, amines or even alkanes (Equation 1).

The stored chemical energy in M_t^0 from Equation 1 can be released in dark reactions (Equations 2 and 3), whereby new and useful C-H and C-C bonds would be formed. A cycle of these light and dark reactions, catalyzed by transition metals, could convert simple organics, such as CH_3OH , CH_3NH_2 and CH_3CH_3 , into longer carbon chain derivatives, e.g. vicinal glycols, diamines, diimines and amino alcohols, which are appealing prebiotic precursors, especially for the generation of sugars, amino acids and the hydrocarbon skeletons of fats.

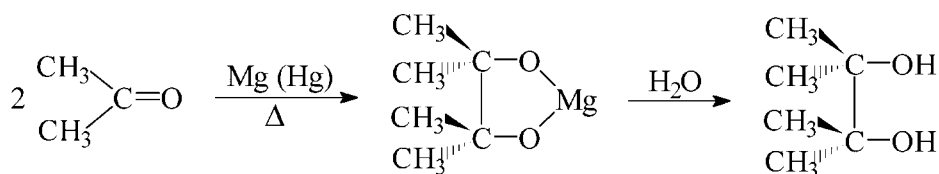
Recent precedent exists both for the photochemical oxidation of alcohols and simultaneous reduction of metal ions (eq. 4, Eisch *et al.*, 1992; 1994, 1995, 1997, 1998, Eisch, 2001), as well as for the thermal bimolecular reduction of carbonyl derivatives by metal(0) reagents (Equation 5, Fittig, 1859). It is noteworthy that the more active transition metals, such as $\text{M}_t = \text{Ni}, \text{Co}$, and the less active main group



R,R' = H, CH₃, CH₃CH₂, CH₃CH₂CH₂, C₆H₅

Mⁿ⁺ = Cu(II), Ni(II), Co(II), Pd(II), Pt(II), Ag(I), Zn(II)

Equation 4.



Equation 5.

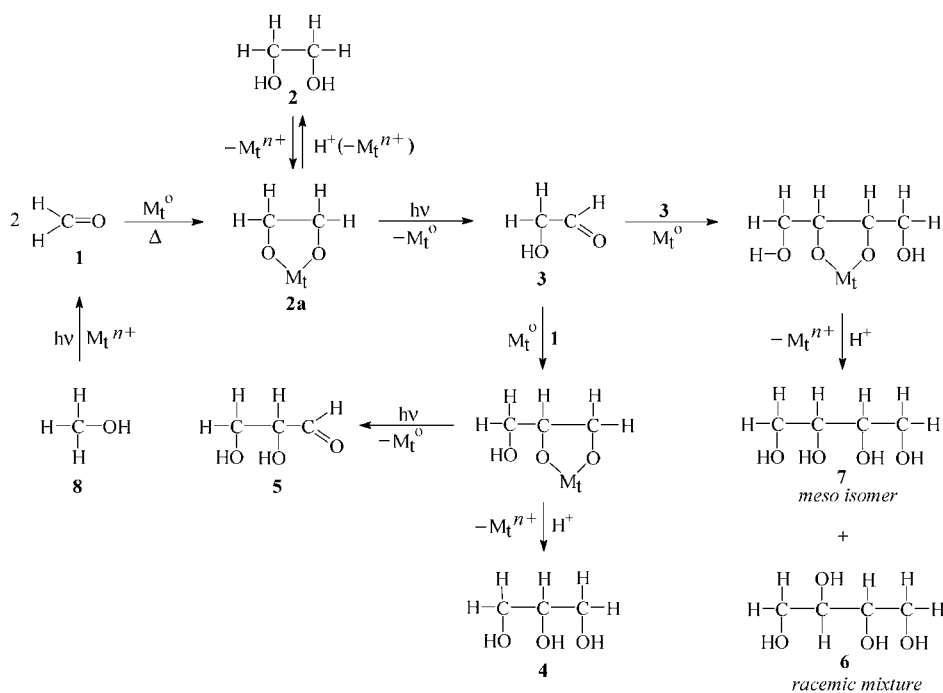
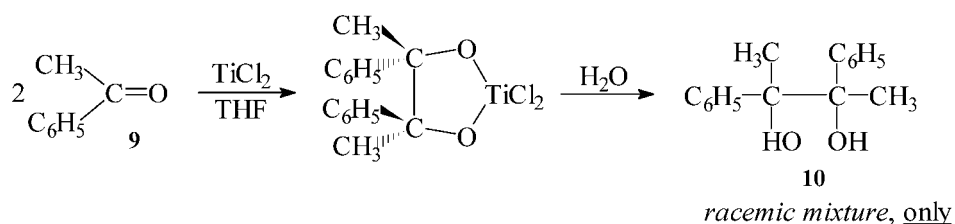
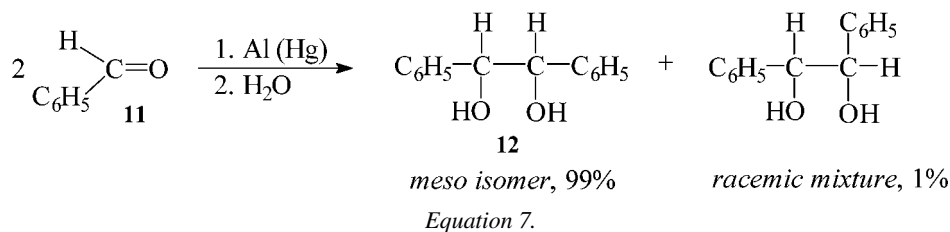


Figure 1. Proposed 'light-dark' redox reactions involved in the transition metal-catalyzed oligomerizations of formaldehyde (1). Source of H⁺ in equations could be from water, alcohols, solvents etc.



Equation 6.



Equation 7.

metals, such as $M_m = \text{Zn}$, are able to undergo both the thermal oxidation (eq. 2 or 3) and the photoreduction reaction (Equation 1). Such transition metal-catalyzed reactions, operating in tandem, could for example convert formaldehyde (**1**) into ethylene glycol (**2**) or glycolaldehyde (**3**), nominally the simplest sugar (Figure 1). A cross-reductive coupling of **1** and **3** could thereupon lead to glycerol (**4**) and thence after photochemical oxidation to *racemic* glyceraldehyde (**5**). In the homo-reductive coupling of **3** a pair of diastereomeric tetraols, **6** as *racemic mixture* and *meso* **7**, could now arise and the selectivity in such coupling would be important to the overall efficiency in producing ribose and its more chemically stable precursor, ribitol, by these 'light-dark' coupled reactions.

This stereochemical aspect of a practical prebiotic synthesis of ribose (via ribitol) will be explored in section 5.* But here we should note that the observed stereochemistry of such reductive coupling, so-called, pinacol coupling, depends upon the specific metal reductant and experimental conditions employed. The following couplings of acetophenone (**9**) to produce only **10** as *racemic mixture* and of benzaldehyde (**11**) to yield almost only *meso* **12** are exemplary (eqs. 6 and 7). These known stereoselectivities raise the prospects for attaining selective pinacol couplings in the prebiotic oligomerization of formaldehyde that would favor the production of the carbon-carbon chain of ribitol.

In the following sections it remains the principal goal of this article to present evidence for the feasibility of producing formaldehyde (**1**) through the photooxidation of methanol (**8**) by transition metal ions and thereafter the reductive coupling

* In this discussion of pinacol coupling, the terms, *stereochemistry* and *stereoselectivity*, refer to the formation of either the *meso isomer*, having a plane of symmetry (as in **7**), or the *racemic mixture* of enantiomers, isomers which are nonsuperimposable mirror images of each other (as in **6**). Neither *isomer* **7** nor *racemic mixture* **6** show any chirality or optical activity.

of **1** by the transition metal(0) produced to generate ethylene glycol (**2**) via **2a** (Figure 1). These transformations are the primary ‘light-dark’ reactions fundamental to converting formaldehyde into higher sugars and sugar alcohols.

4. Experimental Section

4.1. MODEL FOR PREBIOTIC ORGANIC SYNTHESIS

The generally accepted reaction site postulated for prebiotic chemistry has been a tidal basin or lagoon, in which the dissolved reactants could become concentrated by evaporation and react under a reducing or at least nonoxidizing atmosphere. Due to the absence of atmospheric oxygen and ozone in the prebiotic era, far UV-radiation (< 300 nm) would have been able to penetrate to the earth’s surface in much larger intensity than at present (Cleaves *et al.*, 1998). In the present proposal, moreover, the dissolved transition metal salt leached from the surrounding earthen crust would act in concert with the sunlight (> 250 nm) absorbed by the thin surface layer of the aqueous pool to effect transformation of simple compounds, such as methane, methanol, formaldehyde, hydrogen cyanide or carbon dioxide into the requisite bimolecules for DNA and amino acid synthesis (Cleaves *et al.*, 1998). This thin surface of any aqueous pool might actually have been a separate hydrocarbon phase, less dense than water, in which the photochemical oxidation of dissolved organic substrates could most readily have occurred. The prebiotic source of such basic chemicals could variously have been the hydrolysis of metal carbides or carbonate, Miller-Urey lightening-discharge syntheses, thermal Fischer-Tropsch reactions or meteorites (Miller *et al.*, 1976). The transition metals most likely available for reaction, as judged by their total abundance would have been: Fe (39.8%), Ni (3.2), Co (0.3), Cr (0.2) and Mn (0.1). Other metals, such as copper and zinc, might have occurred in certain areas because of their separation and selective concentration.

In the present study, where we attempt to test the feasibility of the primary ‘light’ and ‘dark’ redox reactions proposed in Equations 1–3, we found it advantageous to work in nonaqueous media, such as solvents of low polarity, so that any metal deposition, such as given in Equation 1, would be observed and measured. In aqueous media, such active metals would not be deposited but would react immediately with water with the release of hydrogen gas. Furthermore, our test reactions were conducted anaerobically, under an atmosphere of nitrogen or argon, to avoid the complexities that dioxygen would add to such ‘light’ and ‘dark’ reactions. Finally, the model photochemical reactions were conducted with UV light of 185–254 nm-wavelength (a good simulation of the wavelength but not necessarily the intensity of prebiotic sunlight) and were promoted with known photosensitizers, such as benzophenone, benzopinacole, benzalaniline or N,N’,1,2-tetraphenylethylene diamine (*meso-isomer* or *racemic-mixture* of isomers). These

promoters were chosen for their known efficiency and availability. In the prebiotic setting, any number of simple organic compounds, such as biacetyl or acetylacetone, might have acted as the photosensitizer. From our present uncertainty concerning the intensity of UV irradiation reaching the earth in the prebiotic era, it might have been that photosensitizers would not have been necessary for these metal-alcohol redox processes. We have observed, for example, that $\text{Ti}(\text{OMe})_4$ or $\text{Ni}(\text{acac})_2$ solutions in methanol produce $\text{Ti}(\text{OMe})_2$ or nickel metal, respectively, when irradiated with a medium-pressure mercury lamp without any added sensitizer (Eisch and Gitua, 2002).

4.2. PROTOTYPICAL 'LIGHT' REACTION: COPPER METAL DEPOSITION (EISCH *et al.*, 1996)

The reaction solution for photochemical copper deposition was prepared by placing 50.0 ml of a saturated solution of copper(II) acetylacetonate (1.00 g) in dry, oxygen-free methanol into a quartz tube containing 0.01 g of *meso*-N,N',1,2-tetra-phenylethylenediamine as a photosensitizer under a protecting atmosphere of dry nitrogen. The reactor-tube was briefly connected to vacuum, refilled with nitrogen, closed and then placed into the UV-chamber. The UV-chamber contained eight ultraviolet lamps (8 watts each) disposed in a cylindrical array. The contents of the reactor-tube were irradiated at 185–254 nm for 18 hours. After 18 hours the reactor tube was removed from the UV-chamber. The inner wall of the tube was coated with a copper metal film.

At the end of this period, the residual solution was decanted, the surface containing the film was washed with acetone, the deposited copper film was dissolved in 30% nitric acid, and the resulting solution was titrated with ethylenediaminetetraacetic acid solution to determine the copper deposited on the tube in percentage weight of copper metal based on the copper present in the copper(II) acetylacetonate employed. In this manner it was found that 33% of the available copper was deposited. This photodeposition was evidently attenuated progressively as the copper deposit on the phototube's wall curtailed the irradiation of the solution. Some of the final, filtered photolysate solution was treated with an aqueous solution of 5,5-dimethyl-1,3-cyclohexanedione to precipitate the dimedone derivative of formaldehyde, mp. 176–178 °C, which was obtained in 60% yield of the amount expected from the copper deposition obtained.

Similar individual photolyses were carried out according to the foregoing procedure, except that the dry methanol was replaced by an equivalent amount of these alcohols: 1) ethanol; 2) propanol; and 3) isopropyl alcohol. In each case, a comparable copper film was deposited on the phototube and the filtered photolysate was then treated with an acidified solution of 2,4-dinitrophenylhydrazine in methanol. The corresponding 2,4-dinitrophenylhydrazones of acetaldehyde, propionaldehyde and acetone were obtained from runs 1, 2 and 3, respectively. Yields of the individual 2,4-dinitrophenylhydrazones ranged from 25% to 40% of the

copper available. The individual 2,4-dinitrophenylhydrazone was identified by the undepressed mixtures m.p. with an authentic sample.

The foregoing experimental results are an amplification of a novel photochemical metal deposition process patented in 1992 (Eisch *et al.*, 1992, 1994).

4.3. ANALOGOUS 'LIGHT' REACTIONS LEADING TO METAL DEPOSITION

Individual photolyses of the following metal salts according to the foregoing prototypical photochemical reaction led to the deposition of a metal film: cobalt(II) acetylacetonate, nickel(II) acetylacetonate, platinum(II) acetylacetonate, palladium(II) acetylacetonate, silver(I) acetylacetonate, copper(I) chloride, copper(II) bromide and zinc(II) acetylacetonate.

4.4. PROTOTYPICAL 'DARK' REACTIONS: METAL OR SUBVALENT METAL REDUCTIVE COUPLING OF CARBONYL DERIVATIVES

Although it might be ideal to demonstrate directly the efficient reductive coupling of formaldehyde to ethylene glycol as a prototypical dark reaction, formaldehyde may pursue a complex network of reactions (Cannizzaro, Butlerov and other transformations) in aqueous media with metal bases. In ongoing studies we have demonstrated the reductive coupling of formaldehyde to ethylene glycol in a stoichiometric reaction with bis(cyclooctadiene)nickel(0) in THF solution. Instead of this current research, we offer model dimerizations of aldehydes and ketones effected by TiCl_2 and Ni(0) complexes, respectively.

4.5. BENZALDEHYDE (**11**) AND TITANIUM(II) CHLORIDE

In an argon atmosphere freshly distilled benzaldehyde (530 mg, 0.51 ml, 5 mmol) was treated with $\text{TiCl}_2 \cdot 2\text{THF}$ (10 mmol) in THF at room temperature for 30 hr. to give, upon hydrolytic workup, a yellow crystalline product, which was purified by recrystallization from 95% ethanol to give only the *racemic*-1,2-diphenyl-1,2-ethanediol (262 mg, 49% yield) as colorless crystals, mp. 134–135 °C.

4.6. ACETOPHENONE (**9**) AND TITANIUM(II) CHLORIDE (EISCH *et al.*, 1995)

Acetophenone (601 mg, 5 mmol) was allowed to react with $\text{TiCl}_2 \cdot 2\text{THF}$ (10 mmol) in THF at room temperature for 40 hr. to give a light yellow liquid which, upon hydrolytic workup, crystallized upon standing. The crude product was purified by recrystallization from 95% ethanol to give only the *racemic*-2,3-diphenyl-2,3-butanediol (325 mg, 54% yield) as colorless crystals, mp 123–124 °C.

4.7. 9-FLUORENONE (**13**) AND BIS(CYCLOOCTADIENE)NICKEL(0) (EISCH *et al.*, 1996)

Under argon the purple solution resulting from admixing bis(cyclooctadiene)nickel (530 mg, 1.55 mmol) with 2,2'-bipyridine (240 mg, 1.55 mmol) in 30 ml THF was treated with 280 mg 9-fluorenone (1.55 mmol). The solution, which became deep green immediately, was allowed to stir at 25 ° for 30 min and then was brought to reflux for 15 h before quenching with degassed 6N-HCl under argon. The products, 9,9'-dihydroxy-9,9'-bifluorenyl (70 mg, 25%), and 9-fluorenyl (70 mg, 30%) were isolated by means of flash column chromatography (ethyl acetate; hexanes, 1:3).

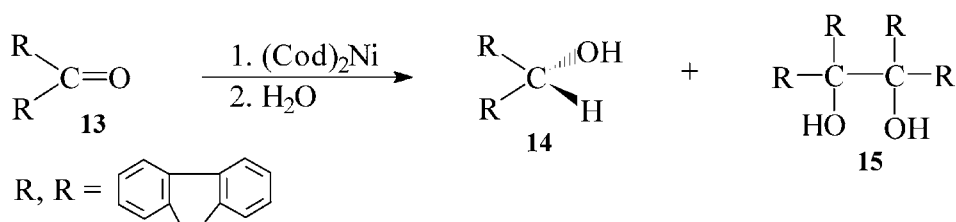
4.8. PROTOTYPICAL TANDEM 'LIGHT-DARK' REACTION OF METHANOL WITH NICKEL(II) ACETYLACETONATE

In the irradiation of methanolic solutions of nickel(II) acetylacetonate it was observed that the nickel film deposited during irradiation redissolved to a great extent when the phototube stood in the dark for a number of hours. This observation suggested that the nickel metal had reacted with the methanol to evolve H₂ or with formaldehyde to form ethylene glycol (**2**) or its nickel salt (Figure 1). In the hope of observing the one-vessel conversion of methanol to ethylene glycol, the following prolonged irradiation was undertaken.

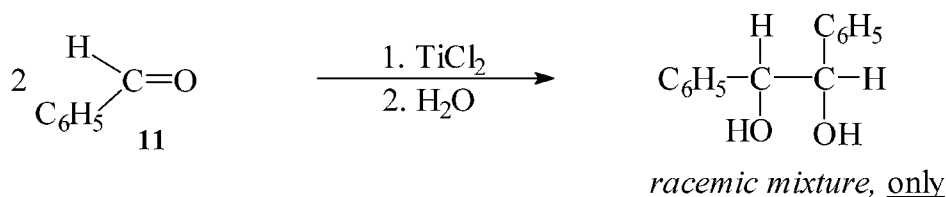
In the foregoing described photoreactor a quartz tube under argon was charged with 810 mg of nickel(II) acetylacetonate, 30 mg of benzophenone as photosensitizer and 40 ml of a 1:3 methanol-THF mixture as solvent. The solution was irradiated for 144 h, during which time the photolysate faded somewhat from its initial green color and black specks (Ni) appeared. Volatiles were evaporated from the filtered photolysate, which was dissolved in chloroform and extracted with aqueous 3N HCl to remove nickel salts. The chloroform layer was dried and evaporated. The NMR spectra of the residue displayed a prominent ¹H peak at 5.04 (OH) and 3.80 (CH₂) ppm and a ¹³C peak at 65.6 ppm. Adding a small amount of authentic ethylene glycol gave enhanced ¹H and ¹³C peaks coincident with the foregoing peaks, confirming the formation of ethylene glycol in this reaction. From the ¹H NMR spectrum of the reaction product the signal intensity of the CH₂ group of the ethylene glycol was estimated from the intensity of the methyl groups of the acetylacetonate (initially present as 6.0 mmol of Ni(acac)₂). This calculation gives the yield of ethylene glycol as at least 7% of the Ni(acac)₂ or 0.42 mmol.

5. Results and Discussions

The foregoing experimental findings give abundant support to the conclusion that a wide variety of main-group and transition metal salts undergo photochemical reduction to the metal with wavelengths of ultraviolet radiation most probably present in prebiotic sunlight penetrating to the earth's surface. The concomitant

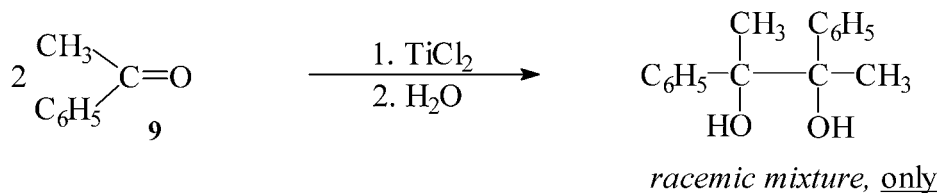


Equation 8.



Equation 9.

oxidation step or 'light' reaction of such a photo-redox process is capable of oxidizing primary and secondary alcohols to the corresponding aldehydes or ketone, as is evident in such photolyses, where variously methanol, ethanol, propanol or isopropyl alcohol served as the substrate. With this corroborating evidence, the primary 'light' process expressed generally in Equations 1 and 4 can be considered as feasible and wholly possible as a prebiotic reaction. The thermal 'dark' metal-mediated pinacol coupling generalized in Equation 3 already has a large degree of feasibility as a prebiotic reaction because of the many well-known examples (Equations 5, 6 and 7). However, further experimental observations are offered here, which demonstrate the actual occurrence of competitive monomolecular (**14**) and bimolecular reduction (**15**) of a carbonyl derivative such as 9-fluorenone (**13**) (Equation 8), as proposed in Equations 2 and 3 and the stereoselectivity possible as reflected in the reductive coupling of benzaldehyde (**11**) (Equation 9) and of acetophenone (**9**) (Equation 10).



Equation 10.

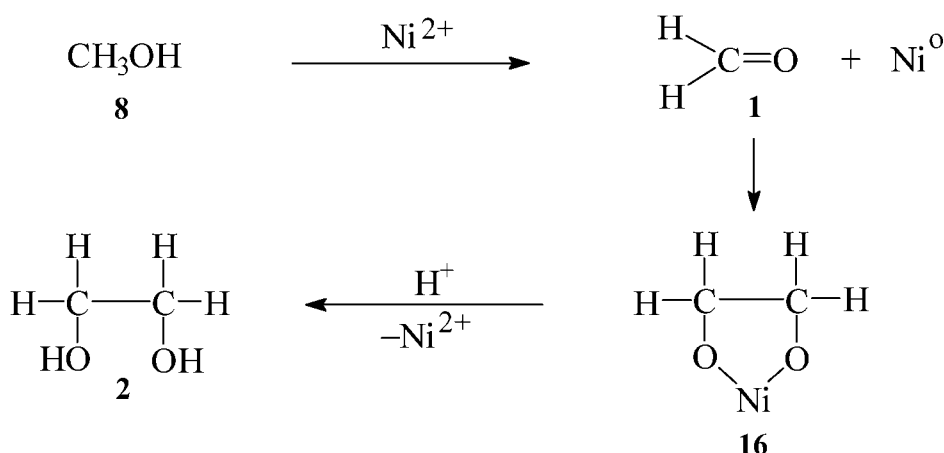


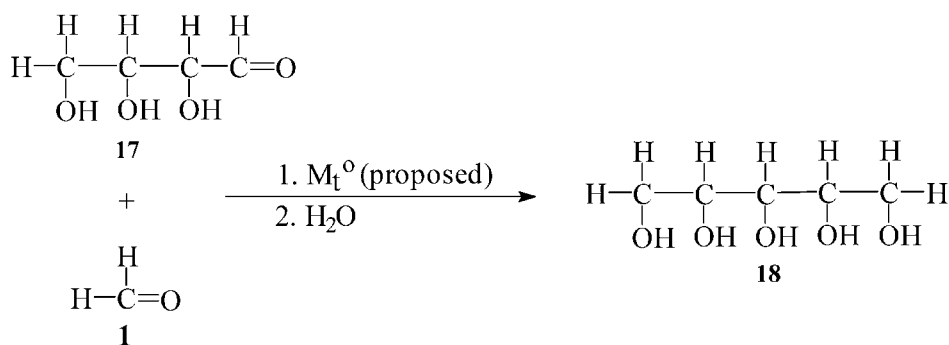
Figure 2. Tandem 'light-dark' reactions converting methanol to ethylene glycol.

Here again, it can be concluded that the primary dark process is a feasible prebiotic reaction and has the potential of providing stereoselectivity in the growth of the carbon chain involved in the oligomerization of formaldehyde.

The final process investigated in this initial report is the possibility of tandem 'light-dark' reactions occurring during irradiation. We have now established that irradiating a methanolic solution of nickel(II) acetylacetonate leads to the formation of ethylene glycol, assumed to be formed via **16** (Figure 2). This observation is consonant with the view that the formaldehyde and nickel metal formed in the 'light' reaction combine by pinacol coupling in an accompanying 'dark' reaction. Although the yield of ethylene glycol, $\sim 7\%$ of the nickel salt employed, is low, two factors are readily identified as determining such a small yield. First of all, the formaldehyde generated in low concentration in the methanol must encounter the nickel surface in a second-order reaction, $[\text{H}_2\text{CO}]^2$, for dimerization: a condition leading to a very slow rate of glycol formation. Secondly, any photogenerated formaldehyde could react with nickel alkoxide salts and thus be consumed in other reactions, such as Butlerov, Cannizzaro and Tishchenko processes.

6. Conclusions

The primary 'light' and 'dark' reactions necessary for the transition metal-catalyzed photodimerization of formaldehyde initially to ethylene glycol (Equations 1 and 3 and Figure 1) have been shown to be feasible under simulated prebiotic conditions. The way is now open for the further testing of the oligomerizations of formaldehyde, as in the conversion of ethylene glycol (**2**) into the tetraols **6** and **7** depicted in Fig. 1. The photooxidation of **7** to erythrose (**17**) and its stereocontrolled pinacol



Equation 11.

coupling with formaldehyde (**1**) could lead to ribitol (**18**), a relatively stable source of DL-ribose (Equation 11).

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