

A Computational Study of a Prebiotic Synthesis of the Steroid Progesterone (C and D Rings)

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Abstract: - The magnesium ion metalloporphyrin complex is shown to bind the ligands propyne (p) and ethyne (e) on the metal or nitrogen pyrrole sites as a two site catalyst in their copolymerization. The order of addition of the monomers is (pepee). The steroid ring D (pep) is formed first from the propyne adduct bound to the metal site and the but-diene adduct bound to the N-site. The optimal orientation of these adducts determines the β -orientation of the 17-substituent. Further reaction with hydroxyl radicals allows this to be a 17 β -acetyl substituent. Further addition of two ethyne monomers forms an N-diene cyclopentene derivative able to cyclise to form the steroid ring C (pee) with a trans conformation and a 13- β methyl substituent. The reactions have been shown to be feasible from the overall enthalpy changes in the ZKE approximation at the HF and MP2 /6-31G* level, and with acceptable activation energies.

Key-Words: - Prebiotic photochemical synthesis, progesterone (C & D rings), propyne, ethyne, Mg.porphin.

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1 Introduction

Progesterone, pregn-4-ene-3,20-dione [1], a progestational hormone [2] which binds to a specific receptor [3] is a derivative of the saturated tetracyclic hydrocarbon, perhydrocyclopentane phenanthrene [4]. This has six centres of asymmetry [4] arising from the fusion of the four rings where the numbering and designation are standard [1]. This steroid is closely related to the terpenes [5] constructed of multiples of the five-carbon hydrocarbon isoprene (2-methyl-1,3-butadiene). The biosynthesis of progesterone is from the steroid cholesterol [4], which in turn is derived from the steroid lanosterol [4] formed from the isoprene units of squalene (a dihydrotriterpene) consisting of consecutive isoprene units [4].

From a prebiotic perspective [6] it is desirable if the reactant molecules formed spontaneously from a supposed prebiotic atmosphere to be inevitably present. It has often been held that the atmosphere of the Earth was originally mildly reducing [4,7] implying the presence of concentrations of carbon monoxide, ammonia, water and hydrogen. It is

also supposed that ethyne (e) and propyne (p) were present as found in interstellar space [8,9] and present on Titan, a moon of Saturn. It has also been demonstrated that porphin may act as a catalyst for the formation of sugars [10] and terpenes [11].

This paper proposes a model for the catalytic photochemically activated copolymerization of these gases to form progesterone where the order of polymerization is pepee on the catalyst magnesium porphin, and involves some hydroxylation and hydrogenation.

The reactions described have been deduced as kinetically and thermodynamically viable, but photochemical excitation is required.

2 Problem Formulation

This proposed computational study of a plausible synthesis of the steroid progesterone involves the calculation of the enthalpy changes for reaction intermediates in the ZKE approximation and the calculation of activation energies at the HF level. These activation energies

may all be accessible as the catalyst may absorb appreciable photochemical activation (0.21 h). The computations tabulated in this paper used the GAUSSIAN03 [12] commercial package. The standard calculations at the HF and MP2 levels including zero-point energy corrections at the Hartree Fock level [13], together with scaling [14], using the same basis set, 6-31G*. are as previously published [6]. Enthalpy changes at the MP2 level not including scaled zero point energies are designated as $\Delta H_{(MP2)}$. The charge transfer complexes are less stable when calculated at the Hartree Fock level [13], and activation energies calculated at the HF level without scaling are less accurate..

If the combined energy of the products is less than the combined energy of the reactants it may show that the reaction is also likely to be spontaneous at higher temperatures. This paper uses the atomic unit of energy, the hartree [12].

1h = 627.5095 kcal.mol⁻¹. 1h = 4.3597482 x 10⁻¹⁸ J
 Charges are in units of the electronic charge.

3 Problem Solution

3.1 Total Energies (hartrees)

The steroid is described as being formed as a copolymerization of the gases ethyne and propyne on the two site catalyst Mg.porphin. References prefaced by steroid refer to the standard steroid numbering as shown, Fig.1 [1].

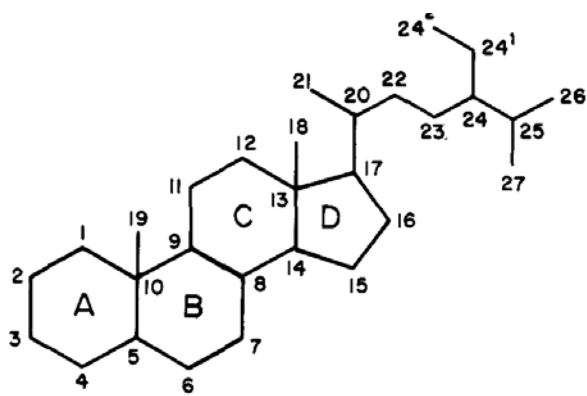
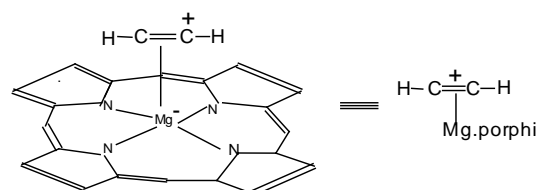
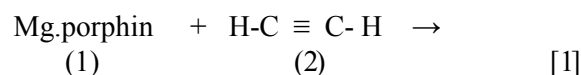


Fig.1. Standard steroid substituent numbering.[1]

The gas ethyne may form two adducts with the catalyst on the metal and N-pyrrole sites as follows:

The enthalpy of formation of the van der Waals complex is small but it appears stable.

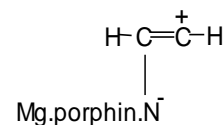
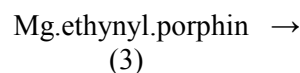
Mg.porphin is a powerful catalyst able to form charge transfer complexes with a number of different kinds of molecules [15-16]. With ethyne the ligand is positively charged (0.08) and the porphin has a negative charge [17]. The acetylene sets as ligand with a linear H-C ≡ C-H structure as shown.



Mg.1,ethynyl .porphin (3)

$$\Delta H = -0.01421 \text{ h}$$

The Mg.ethynyl.porphin may be photochemically excited for the ethyne to migrate to bond with a pyrrole unit as a higher energy ethyne adduct [10], as shown,



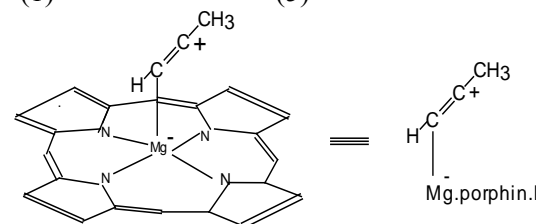
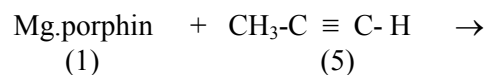
Mg.1,porphin.ethynyl (4)

[2]

$$\Delta H = 0.01353 \text{ h}$$

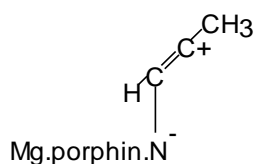
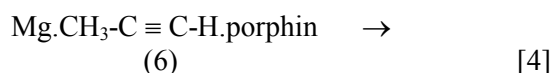
The gas propyne may also form two adducts with the catalyst on the metal and N-pyrrole sites ,as follows:

The enthalpy of formation of the van der Waals complex is small but it appears stable.



Mg.1,CH₃-C ≡ C-H.porphin (6) [3]

$$\Delta H = -0.00209 \text{ h}$$



$$\Delta H = 0.01862 \text{ h}$$

The first of these complexes on the metal site is lower in energy than the corresponding complex on the N-pyrrole site.

These complexes are integral reactants in the proposed synthesis. The energies of the stable complexes are shown in Table 1.

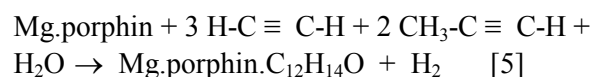
Table 1

MP2 /6-31G* total energies and zero point energies (hartrees) for the respective equilibrium geometries

Molecule	MP2 hartree	ZPE (HF) hartree
Mg.porphin (1)	-1185.12250	0.29262
ethyne (2)	77.06679	0.02945
Mg.1.ethynyl.porphin (3)	-1262.19985	0.31797
Mg.porphin.ethynyl (4)	-1262.18547	0.31701
propyne (5)	116.24181	0.02945
Mg.propyne.porphin (6)	-1301.36738	0.35382
Mg.porphin.propyne (7)	-1301.34810	0.35308
Mg.porphin.des-A,B-11,12,15,16-tetrahydroprogesterone (8). Fig.5.	-1723.91254	0.53557
Mg.1.ethynyl.porphin.propynyl (9)	-1378.45514	0.37898
Mg.1,4-dehydro-pent-1,3-dien-1yl.porphin (10)	-1378.35213	0.37787
Mg.1.porphin.4-dehydro-pent-1,3-dien-N1-yl (11)	-1378.35468	0.38400
Mg.1.propynyl. porphin.4-dehydro-pent-1,3-dien-N1-yl (12)	-1494.61860	0.44550
Mg.1,3-(ethen-N2-yl)-4-didehydro-2-methyl-pentenyl). porphin. (13)	-1494.70161	0.45015
Mg.1,3-(ethen-N2-yl)-4,4'-dihydroxy-2-methyl-pentenyl). porphin (14)	-1646.02060	0.48900
Mg.1,3-(ethen-N2-yl)-2-methyl-4-oxo-penten-1yl). porphin (15)	-1569.75654	0.46511
Mg.1,4-acetyl-5-dehydro-5-methyl cyclopent-2-en-1-yl.porphin (16)	-1569.757754	0.45045
Mg.1.porphin. 4-acetyl-5-dehydro-5-methyl-cyclopent-2-en-N1-yl (17)	-1569.74604	0.45605
Mg.1.ethynyl.porphin. 4-acetyl-5-dehydro-5-methyl-cyclopent-2-en-N1-yl (18)	-1647.01437	0.48899
Mg.1,2-(5-acetyl-2-dehydro-1-methyl- cyclopent-3-en-1yl)- ethen-1yl.porphin (19)	-1646.97223	0.49579
Mg.1.porphin.2-(5-acetyl-2-dehydro-1-methyl-cyclopenten-3-en-1yl)- ethen-N1-yl.porphin. (20)	-1646.93081	0.48996
Mg.1.ethynyl.porphin. 2-(5-acetyl-2-dehydro-1-methyl cyclopent-3-en-1yl)- ethen-N1-yl (21)	-1724.05510	0.52665
Mg.1,4-(5-acetyl-2-dehydro-1-methyl cyclopent-3-en-1yl)- but-1,3-dien-1yl.porphin (22)	-1724.10298	0.52846
Mg.1.porphin.4-(5-acetyl-2-dehydro-1-methyl cyclopent-3-en-1yl)-but-1,3-dien-N1-yl (23)	-1724.13701	0.53222
Mg.1.porphin.4-(5-acetyl-2-dehydro-1-methyl cyclopent-3-en-1yl)-but-1,3-dien-N1-yl (cis) (24)	-1724.11743	0.53026
Mg.1.porphin.4-(5-acetyl-2-dehydro-1-methyl cyclopent-3-en-1yl)-but-1,3-dien-N1-yl (gauche) (25)	-1724.12050	0.53134
Mg.1.porphin.9H-1-acetyl-8-methyl-inden-N4-yl (26)	-1723.91254	0.53557
OH·	-75.52257	0.00911
OH·	-75.51314	0.00885
H ₂ O	-76.19685	0.02298
H ₂	-1.14414	0.01059

3.2 The overall stoichiometry for the formation of the steroid: progesterone (C&D Rings).

Although Mg.porphin is here taken as the catalyst for the reaction, the overall stoichiometry to form the progesterone (C & D rings) is as follows,



Mg.porphin.des-A,B-11,12,15.16-tetra-dehydroprogesterone (8)
(C&D rings) Fig.5.

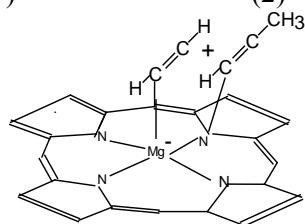
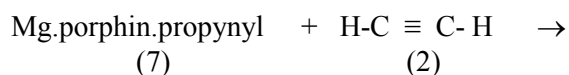
$$\Delta H = -0.03374 \text{ h}$$

The enthalpy change is negative indicating that this may be the energetically favourable route to the initial formation of the steroid. The

intermediates by which these stoichiometric reactions may have occurred are as follows:

3.3 The formation of Mg.1, ethynyl.porphin.propynyl

The ethyne may form a weak charge transfer complex with Mg.porphin.propynyl as,



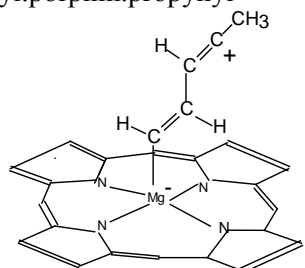
Mg.1, ethynyl.porphin.propynyl (9) [6]

$$\Delta H = -0.04341 \text{ h}$$

The adduct charges are: ethyne, 0.08, propyne 0.00.

3.4 The formation of Mg.1, 4-dehydro-pent-1,3-diynyl. porphin

The Mg.1, ethynyl.porphin.propynyl adducts may coalesce to form a stable complex where some activation energy is required, as



Mg.1, 4-dehydro-pent-1,3-dien-1-yl.porphin (10) [7]

$$\Delta H = 0.10203 \text{ h}$$

The charge on the adduct is 0.28.

The form of the potential energy surface at HF accuracy showing the excitation required is shown in Fig.2.

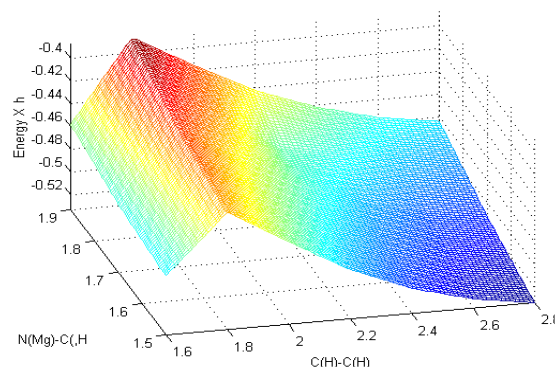
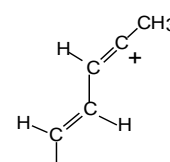
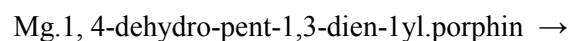


Fig.2. Potential energy surface for the coalescing of adducts ethyne and propyne. The abscissae is the C-C stretch, the ordinate the N-C stretch. The energy is $-1374 + X \text{ h}$. The saddle point is at (1.8,1.5). The Mg.1,ethynyl.porphin.propynyl is at (2.8,1.5), the Mg.1,4-dehydro-pent-1,3-dien-1-yl.porphin at (1.6,1.9).

The activation energy to form the adduct was 0.125 h, that to dissociate it 0.037 h.

3.5 The formation of Mg.1,porphin.4-dehydro-pent-1,3-dien-1-yl

The Mg.1,4-dehydro-pent-1,3-dien-1-yl.porphin may be excited by radiation to the higher energy state, as shown,



Mg.porphin.N⁻

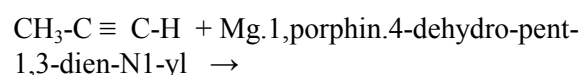
Mg.1,porphin.4-dehydro-pent-1,3-dien-N1-yl (11) [8]

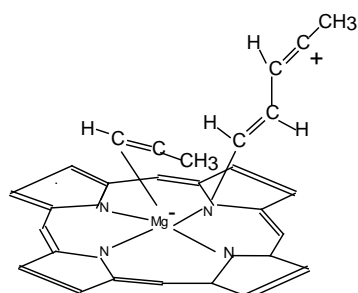
$$\Delta H = 0.00290 \text{ h}$$

The activation energy to form the adduct was the same as the enthalpy change. Adduct charge = -0.35

3.6 The formation of Mg.1, propynyl.porphin.4-dehydro-pent-1,3-dien-N1-yl

Mg.1,porphin.4-dehydro-pent-1,3-dien-N1-yl may add a further propyne adduct on the free metal coordination site as,





Mg.1, propynyl. porphin.4-dehydro-pent-1,3-dien-N1-yl (12) [9]

$$\Delta H = -0.02087 \text{ h}$$

Adduct charges were: propyne, 0.06, pent-1,3-diene entity, 0.19. This di-adduct has a preferred conformation as shown in Fig.3.

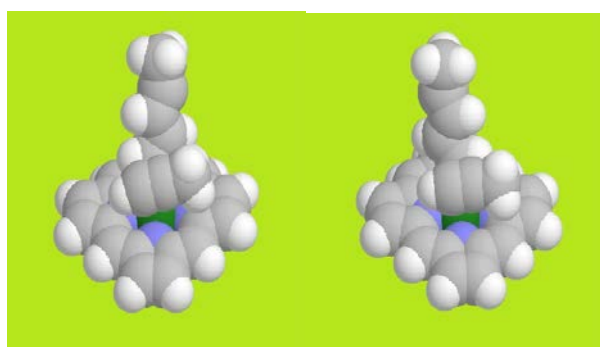
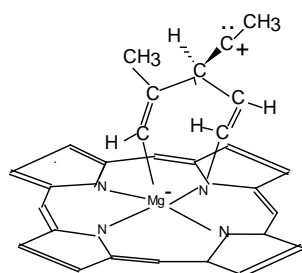


Fig.3. The preferred conformation (left) and non-preferred conformation (right) of Mg.1, propynyl. porphin.4-dehydro-pent-1,3-dien-N1-yl.

It is the first conformation, Fig.3 (left) which ultimately determines the β conformation of steroid 17-substituents in the steroid structures. It is calculated at the HF level as 0.371 kcal.mol⁻¹ more favourable.

3.7 The formation of Mg.1, 3-(ethen-N2-yl)-4-didehydro-2-methyl-pentenyl). porphin

The two adducts may coalesce when excited to form a diradical, as,
Mg.1, propynyl. porphin.4-dehydro-pent-1,3-dien-N1-yl \rightarrow



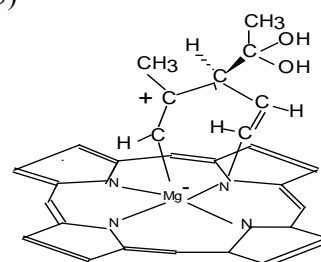
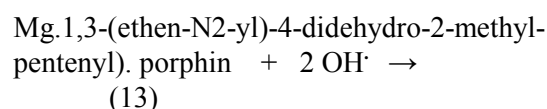
Mg.1,3-(ethen-N2-yl)-4-didehydro-2-methyl-pentenyl). porphin. (13) [10]

$$\Delta H = -0.07887 \text{ h}$$

The activation energy to form the bond was 0.073 h whilst that to open it was 0.128 h. The adduct charge was calculated as 0.08.

3.8 The formation of Mg.1, 3-(ethen-N2-yl)-4,4'-dihydroxy-2-methyl-pentenyl). porphin

The Mg.1,3-(ethen-N2-yl)-4-didehydro-2-methyl-pentenyl). porphin diradical is liable to reaction with hydroxyl free radicals formed from the photolysis of water [18], as



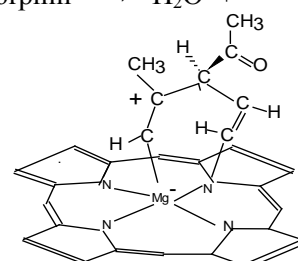
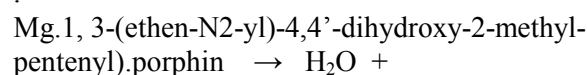
Mg.1,3-(ethen-N2-yl)-4,4'-dihydroxy-2-methyl-pentenyl). porphin (14) [11]

$$\Delta H = -0.25548 \text{ h}$$

The activation energy for the hydroxyl radicals to react with the diradical adduct was zero. The charge on the adduct was -0.14.

3.9 The formation of Mg.1, 3-(ethen-N2-yl)-2-methyl-4-oxo-penten-1yl). porphin

The Mg.1,3-(ethen-N2-yl)-4,4'-dihydroxy-2-methyl-pentenyl). porphin with gem hydroxyl groups is liable to lose water, represented here as an acid base catalyzed reaction, as



Mg.1,3-(ethen-N2-yl)-2-methyl-4-oxo-penten-1yl). porphin (15) [12]

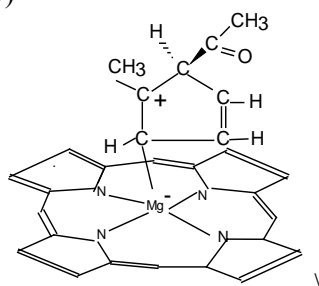
$$\Delta H = 0.06640 \text{ h}$$

No significant activation energies were recorded for these acid-base catalyzed reactions. The charge on the adduct was, 0.61.

3.10 The formation of Mg.1, 4-acetyl-5-dehydro-5-methyl cyclopent-2-en-1-yl.porphin.

The Mg.1,3-(ethen-N2-yl)-2-methyl-4-oxo-penten-1yl). porphin may reduce its energy by cyclisation as,

Mg.1,3-(ethen-N2-yl)-2-methyl-4-oxo-penten-1yl). porphin (15) →



Mg.1,4-acetyl-5-dehydro-5-methyl cyclopent-2-en-1-yl.porphin (16) [13]

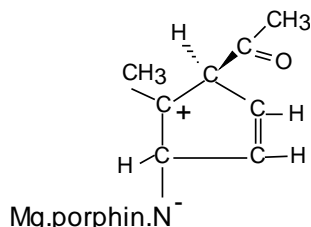
$$\Delta H = -0.01426 \text{ h}$$

The activation energy for the cyclisation was found to be 0.105 h, whilst the activation energy for the reverse reaction was 0.141. h. The charge on the adduct was 0.19.

3.11 The formation of Mg.1, porphin. 4-acetyl-5-methyl-5-dehydro- cyclopent-2-en-N1-yl.porphin

The Mg.1, 4-acetyl-5-dehydro-5-methyl cyclopent-2-en-1-yl.porphin may be excited to a higher energy state where it is bonded to the nitrogen atom of a pyrrole unit, as

Mg.1,4-acetyl-5-dehydro-5-methyl cyclopent-2-en-1-yl.porphin →



Mg.1,porphin. 4-acetyl-5-dehydro-5-methyl-cyclopent-2-en-N1-yl. (17) [14]

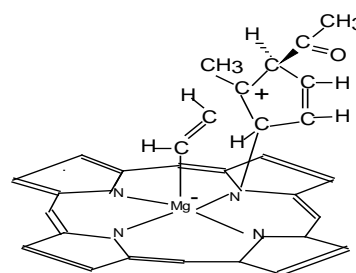
$$\Delta H = 0.01669 \text{ h}$$

The activation energy for the transformation was found to be 0.029 h, whilst the activation energy for the reverse reaction was 0.007 h. The adduct charge was 0.21.

3.12 The formation of Mg.1, ethynyl.porphin. 4-acetyl-5-dehydro-5-methyl-cyclopent-2-en-N1-yl.

The Mg.1,porphin. 4-acetyl-5-dehydro-5-methyl cyclopent-2-en-1-yl may add a further ethyne adduct on the free metal site, as

Mg.1,porphin. 4-acetyl-5-dehydro-5-methyl cyclopent-2-en-1-yl + ethyne → (17)



Mg.1,ethynyl.porphin.4-acetyl-5-dehydro-5-methyl-cyclopent-2-en-N1-yl (18) [15]

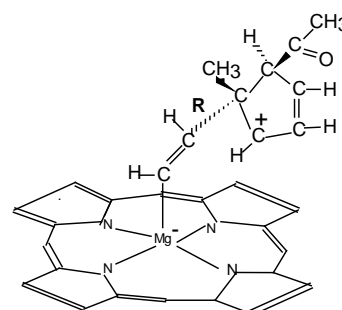
$$\Delta H = -0.19843 \text{ h}$$

The charges on the adducts were: ethyne 0.02, cyclopentene entity, 0.04.

3.13 The formation of Mg.1, 2-(5-acetyl-2-dehydro-1-methyl- cyclopent-3-en-1-yl) ethen-1-yl.porphin

Bonding of the Mg.1,ethynyl.porphin. 4-acetyl-2-dehydro-5-methyl- cyclopent-2-en-N1-yl.porphin may occur as,

Mg.1,ethynyl.porphin.4-acetyl-2-dehydro-5-methyl- cyclopent-2-en-1yl →



Mg.1,2-(5-acetyl-2-dehydro-1-methyl- cyclopent-3-en-1-yl)- ethen-1-yl.porphin (19) [16]

$$\Delta H = 0.04820 \text{ h}$$

The activation energy to bond the two adducts was calculated as 0.112 h, whilst that to sever the bond was 0.140 h. A further activation energy of 0.052 was required to sever the C-N bond. The potential energy surface for this bonding is shown in Fig.4.

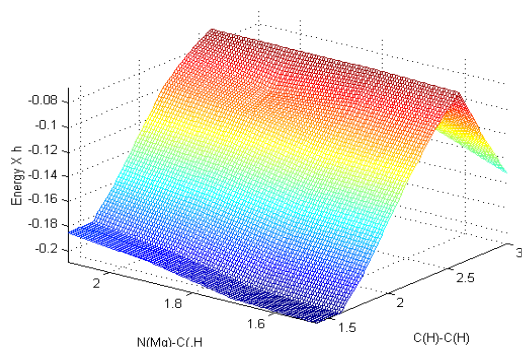


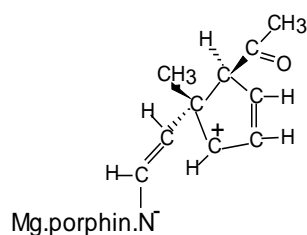
Fig.4. The form of the potential energy surface for the bonding of the ethyne and 4-acetyl-2-dehydro-5-methyl cyclopent-2-en-1-yl adducts on the surface of the catalyst Mg.porphin. The initial reactant is near (3.0,1.6), the product at (1.4,2.1). The saddle point at (2.6,1.5) The energy is $-1642 + X$ h.

The charge on the adduct was -0.13. However, at the transition state, $R=2.03$, the charges are ethyne,-0.37, cyclopentene entity, 0.19, respectively. These charges orient the adducts to bond as shown with the magnetic field of the radiation being perpendicular to the plane of the porphin and directed towards the observer. Steric affects also assist the orientation..

3.14 The formation of Mg.1, porphin. 2-(5-acetyl-2-dehydro-1-methyl cyclopent-3-en) ethen-N1-yl

Ultra violet light may promote the adduct to a higher energy state where bonding is to a pyrrole nitrogen atom, as

Mg.1,2-(5-acetyl-2-dehydro-1-methyl- cyclopent-1yl) ethen-1yl.porphin (19) \rightarrow



Mg.1,porphin.2-(5-acetyl-2-dehydro-1-methyl cyclopent-3-en-1yl) ethen-N1-yl (20) [17]

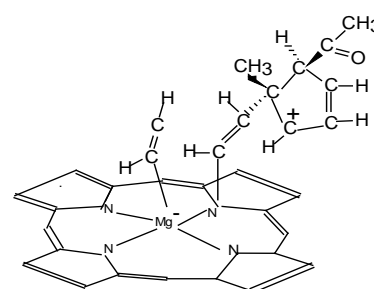
$$\Delta H = 0.03623 \text{ h}$$

The activation energy was calculated the same as the enthalpy change. The adduct charge was -0.34.

3.15 The formation of Mg.1, ethynyl. porphin. 2-(5-acetyl-2-dehydro-1-methyl cyclopent-3-en-1yl) ethen-N1-yl

The Mg.1,porphin. 2-(5-acetyl-2-dehydro-1-methyl cyclopent-3-en-1yl)- ethen-N1-yl may incorporate another ethyne adduct on the free metal site as,

ethyne + Mg.1, porphin. 2-(5-acetyl-2-dehydro-1-methyl cyclopent-3-en-1-yl) ethen-N1-yl \rightarrow



Mg.1, ethynyl.porphin.2-(5-acetyl-2-dehydro-1-methyl cyclopent-3-en-1yl) ethen-N1-yl (21) [18]

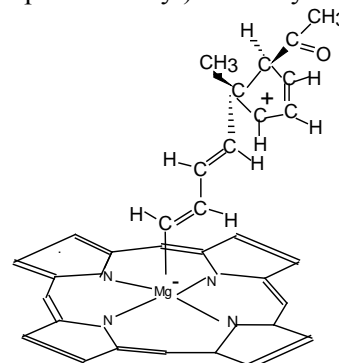
$$\Delta H = -0.05106 \text{ h}$$

Adduct charges: ethyne 0.06, cyclopentene entity 0.41.

3.16 The formation of Mg.1,4-(5-acetyl-2-dehydro-1-methyl cyclopent-3-en-1yl) but-1,3-dien-1yl.porphin

The Mg.1,ethynyl.porphin.2-(5-acetyl-2-dehydro-1-methyl cyclopent-3-en-1yl)-ethen-N1-yl and ethyne adducts may bond to form a metal bound adduct, as,

Mg.1,ethynyl.porphin. 2-(5-acetyl-2-dehydro-1-methyl cyclopent-3-en-1yl)-ethen-1yl \rightarrow



Mg.1,4-(5-acetyl-2-dehydro-1-methyl cyclopent-3-en-1yl)-but-1,3-dien-1yl.porphin (22) [19]

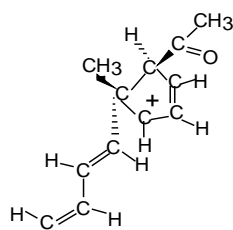
$$\Delta H = -0.04626 \text{ h}$$

This molecule may exist in an all trans conformation where a 3-membered ring is not formed with the cyclopentene entity. The activation energy to bond was calculated as 0.1 h whilst that to dissociate the bond was 0.15 h. The adduct charge was 0.26.

3.17 The formation of Mg.1,porphin. 4-(5-acetyl-2-dehydro-1-methyl cyclopent-3-en-1yl)-but-1,3-dien-1yl

It is assumed that the Mg.1,4-(5-acetyl-2-dehydro-1-methyl cyclopent-3-en-1yl)-but-1,3-dien-1yl porphin may be promoted to a higher energy state by ultraviolet excitation, as

Mg.1,4-(5-acetyl-2-dehydro-1-methyl cyclopent-3-en-1yl)-but-1,3-dien-1yl porphin \rightarrow



Mg.porphin.N⁺

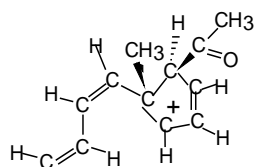
Mg.1,porphin.4-(5-acetyl-2-dehydro-1-methyl cyclopent-3-en-1yl) but-1,3-dien-N1-yl (23) [20]

$$\Delta H = -0.03069 \text{ h}$$

No activation was required for this reaction. The adduct charge was 0.22.

At this stage in the sequence of the mechanism it is possible for the molecule in an excited state to cyclise and form the prospective C-ring of the steroid progesterone. However, two conformation changes must first occur, namely the formation of the 3-cis conformation of the substituted but-diene, as shown here,

Mg.1,porphin.4-(5-acetyl-2-dehydro-1-methyl cyclopent-3-en-1yl) but-1,3-dien-N1-yl \rightarrow



Mg.porphin.N⁻

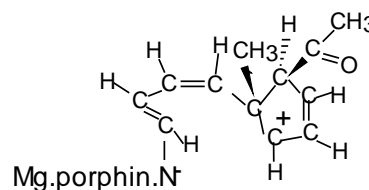
Mg.1,porphin.4-(5-acetyl-2-dehydro-1-methyl cyclopent-3-en-1yl)-but-1,3-dien-N1-yl (cis) (24)

[21]

$$\Delta H = 0.01783 \text{ h}$$

This activation and enthalpy change are feasible. A further conformation change may convert the adduct to a transition state conformation, with a gauche bond of the substituted but-diene entity that may then cyclise, as shown,

Mg.1,porphin.4-(5-acetyl-2-dehydro-1-methyl cyclopent-3-en-1yl)-but-1,3-dien-N1-yl (cis) \rightarrow



Mg.porphin.N⁺

Mg.1,porphin.4-(5-acetyl-2-dehydro-1-methyl cyclopent-3-en-1yl) but-1,3-dien-N1-yl (gauche) (25) [22]

$$\Delta H = -0.00210 \text{ h}$$

This activation and enthalpy change are favourable.

3.18 The formation of Mg.1,porphin. 9H-1-acetyl-8-methyl-inden-N4-yl

The Mg.1,porphin. 4-(5-acetyl-2-dehydro-1-methyl cyclopent-3-en-1yl)-but-1,3-dien-1yl (gauche) may cyclise with activation as shown,

Mg.1,porphin. 4-(5-acetyl-2-dehydro-1-methyl cyclopent-3-en-1yl)-but-1,3-dien-N1-yl (gauche) \rightarrow

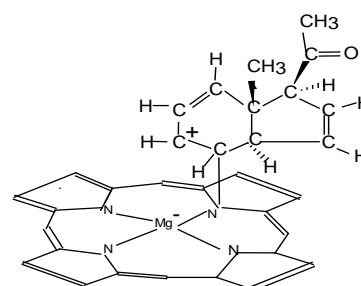


Fig.5.Mg.1,porphin.9H-1-acetyl-8-methyl-inden-N4-yl. (26) [23]

$$\Delta H = 0.21171 \text{ h}$$

The adduct charge was 0.77. The Mulliken charges with H included on the steroid C11 and C12 are, -0.02 and 0.21, respectively at this stage in the synthesis.

4 Conclusion

The photochemically catalyzed copolymerization of the simple gases, ethyne and propyne in the order peppe predicts the 17- β acetyl and 13- β methyl groups, the electrophoricity of 11-C, and the formation of the trans C & D rings in an exciting, orienting electromagnetic field. Further work at a higher accuracy may alter the values given here.

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