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A Review on the Types of Organic Reactions in Water

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Abstract – In recent years, water has proven to be a versatile solvent for organic chemistry. Water as a solvent is not only cheap and safe for the environment, but it also creates entirely new reactivity. Pericyclic reactions, carbanion equivalent reactions, carbocation equivalent reactions, radicals and carbene reactions, transitionmetal catalysis, and oxidations-reductions are just a few of the types of organic reactions in water that we will cover in this instructional review. Aqueous organic reactions have a wide range of applications, including the production of biological substances from carbohydrates and biomolecule chemical modification.

Key Words – Organic Reactions, Water, Carbanion Equivalent, Radicals and Carbenes, Oxidations, Pericyclic

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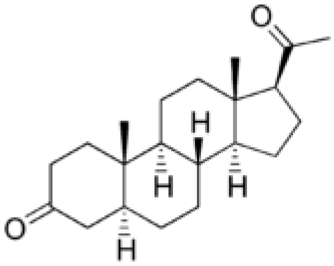
1. INTRODUCTION

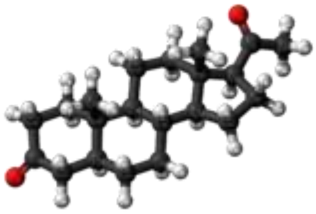
Organic chemistry is a discipline of chemistry concerned with the structure, characteristics, and interactions of organic molecules containing carbon in covalent bonds. The structural formula is determined by studying the structure. Physical and chemical qualities are studied, as well as chemical reactivity, to better understand their behaviour. The chemical synthesis of natural products, medicines, and polymers, as well as the laboratory and theoretical (in silico) research of individual organic molecules, are all part of the study of organic processes.

Hydrocarbons (compounds having solely carbon and hydrogen) and compounds based on carbon but also including additional elements, such as oxygen, nitrogen, sulphur, phosphorus (found in many biochemicals), and the halogens, are among the substances investigated in organic chemistry. The study of carbon–metal bonding is known as organometallic chemistry.[1]

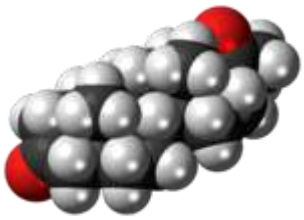
Organometallics such as transition metals such as nickel, cobalt, and chromium as well as the lanthanides are also being studied in the context of contemporary research in organic chemistry.



Line-angle representation



Ball-and-stick representation



Space-filling representation

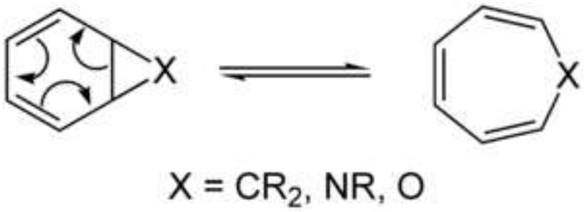
Three depictions of the steroid hormone 5-Dihydroprogesterone (5-DHP), which is an organic molecule. Color compounds show carbon atoms as black, hydrogen atoms as grey, and oxygen atoms as red. Line angle depiction assumes carbon atoms at every line terminal and vertex, while hydrogen atoms are assumed to occupy the remaining valences (up to 4).

The great majority of chemicals on Earth are made up of organic molecules, which are the building blocks of life. There are a number of ways in which carbon may be used in organic compounds since it has a valence that allows for a wide range of structural diversity, as well as many different types of applications. They constitute the foundation of, or are ingredients of, numerous commercial items including medicines; petroleum and agricultural chemicals produce lubricants, solvents; polymers; fuels and explosives; and other items. Inorganic chemistry encompasses not just biochemistry and organometallic chemistry, nevertheless, the study of organic materials, polymer chemistry, and pharmaceutical chemistry.[2]

In an aquatic environment, life, the most complex form of organic molecules on Earth, needs the formation of chemical bonds. Water should be thought of as a flexible solvent for organic chemistry, as it is in nature. Organic reactions in water have received a lot of attention when it was discovered that using water instead of organic solvents significantly accelerated Diels–Alder reactions. Other examples, in addition to Diels–Alder reactions, include practically all of the most useful organic reactions, including those involving watersensitive chemicals. Water is, without a doubt, the most cost-effective and ecologically friendly solvent. Water as a solvent, in many circumstances, not only increases reaction speeds but also improves reaction selectivities owing to hydrophobic effects, even when the reactants are sparingly soluble or insoluble in this media. Furthermore, the limited solubility of oxygen gas in water, which is a crucial feature in the early development of life in an anaerobic environment, might make air-sensitive transition-metal catalysis easier in open air. The use of water as a solvent also means that time-consuming protection–deprotection steps for certain acidic-hydrogen-containing functional groups are no longer necessary, which improves overall synthetic efficiency. Water-soluble molecules, such as carbohydrates, can be employed without the requirement for time-consuming derivatization, When organic compounds are separated from water, water-soluble catalysts can be reused. Chemical biology, which use chemical instruments to analyse biological processes, relies heavily on aqueous organic chemistry. Because of this, it is not covered in the majority of current textbooks, even though aqueous organic chemistry has numerous useful applications and looks promising in the near future. Non-specialists will be able to fill up the gaps in organic chemistry textbooks by reading this introduction. [3]

2. TYPES OF ORGANIC REACTIONS IN WATER

1. Pericyclic reaction



This type of reaction is one where the transition state of the molecule is circular and the reaction occurs in a coordinated manner. The bond orbitals of the bonds participating in the reaction overlap in a continuous cycle at this point. It is on the one hand possible to think of pericyclic reactions and coarctate reactions as distinct from linear reactions, which cover the majority of organic transformations and have no transition state. On the other, linear reactions have an acyclic transition state. Predominant pericyclic reactions are those that result in a reorganisation or addition. The pericyclic reactions shown in the following table are the most common (the three most important classes are shown in bold). Dyotropic reactions and group transfer reactions, on the other hand, are extremely rare. Ene and cheletropic reactions are commonly categorised as group transfer events. [4]

- **Mechanism of pericyclic reaction**

Pericyclic reactions, by definition, involve a concerted mechanism involving a single cyclic transition state. As a result, they were jokingly referred to as "no-mechanism reactions" comprehension of the pericyclic processes in terms of the idea of orbital symmetry conservation prior to. However, many reactions with pericyclic processes have comparable stepwise mechanisms that proceed through radical or dipolar intermediates and are likewise feasible. In some cases, the mechanism of pericyclic reactions, such as [2+2] ketene cycloaddition events, may be "contentious." Furthermore, metal-catalyzed analogues of pericyclic reactions are common, albeit they are typically not properly pericyclic since they proceed via metal-stabilized intermediates and are therefore not coordinated.

As a result of these limitations, pericyclic reactions possess a theoretical knowledge that is as intricate and well-developed as that of any organic reaction in existence. There are a number of factors that determine whether a pericyclic mechanism is likely or desirable, and the Woodward–Hoffmann guidelines are among the most important of these factors. Butadiene and ethylene [4+2] reactions, for example, are projected to be pericyclic reactions under heated conditions, while the addition of two ethylene molecules to each other is not predicted to be. It appears that the former has an orderly, coordinated transition state, whereas the latter has a multistep radical process. This is consistent with experimental observations. Several similar techniques, as seen below, get the same results.

The aromatic transition state hypothesis assumes that the pericyclic process's minimal energy transition state is aromatic, with the amount of electrons involved dictating the reaction topology. Four-electron systems may have transition states with Möbius topology, where the orbitals of reacting molecules interact with an odd number of nodes. The related antiaromatic (4n + 2)-electron Möbius and 4n-electron Hückel transition states are consequently significantly disfavored. The generalised Woodward–Hoffmann principles may be stated very easily using aromatic transition state theory: During a pericyclic process, electron pairs with odd numbers of electrons enter a Hückel transition state, whereas electron pairs with even numbers of electrons enter a Möbius phase. [5]

2. Reactions of carbanion equivalent

The metal-mediated carbanion based reaction is an important method for generating carbon–carbon bonds. As a result of the necessity for low temperatures and strict avoidance of moisture, many metal-mediated carbanion-based reactions using organomagnesium and organolithium reagents have proved challenging to handle. They have recently been adapted to operate well in water by employing metal mediators such as indium, tin, and zinc in carbonyl compound and imine reactions with allyl halides. aryl or alkenylboronic acids to a,b-unsaturated carbonyl compounds and a 1,2-addition to aldehydes were shown to be rhodium-catalyzed additions in aqueous organic mixtures. Related asymmetric conjugate additions have been reported by Hayashi and colleagues (most notably). In water and in an environment of air, Rh(I) [$Rh(COD)_2C_l$ or $Rh(COD)_2BF_4$]-catalyzed Grignard-type phenylation of carbonyl compounds from trimethylphenylstannane with aldehydes 21 happens smoothly. When the methyl groups in organotin compounds are replaced by halogens, the reaction necessitates the addition of a base, which generates $PhSn(OH)nX_{32}n$ species in situ and increases their reactivity. Carbonyl alkylation of the Barbier-Grignard type may also be done in water. Various aldehydes 24 react with alkyl iodides 25 in the presence of Zn/CuI and a catalytic amount of InCl to produce the necessary alcohol products 26 in water through a Barbier–Grignard type reaction. It's important to know that an aldehyde's hydroxyl group does not need to be protected prior to the water reaction. Regio and stereoselective Barbier-type allylation reactions using metals produce a-adduct products, however this is highly rare. When using water as a solvent, it is possible to do allylation with a high degree of selectivity (adduct against c-adduct). A 100 percent c-adduct 29 is created in the presence of just 2 mL of water solvent, whereas 99 percent of the a-adduct 30 is formed in the presence only 6 equivalents of water solvent. The reaction between 1 mmol aldehyde 27 and 1.2 mmol allyl bromide (28) generates 100% c-adduct 29. Water is not only an excellent solvent for the allylation reaction in this case, but it is also required for the creation of an oxonium ion intermediate, which yields a-adduct products. The development of the oxonium intermediate is thought to be totally suppressed when there is too much water solvent present. [6]

3. Reactions of carbocation equivalent

Carbocations are frequently started in organic processes by the coordination/reaction of protonic and Lewis acids. Many Lewis and protonic acid-catalyzed carbocation equivalent reactions have been created, and many of these have been used in industry. However, because most acids react with water rather than the substrates, even a tiny quantity of water can block the reactions. Various protonic and Lewis acids have recently been discovered to preserve catalytic activity in aqueous environments. Many of them, in particular, are not only compatible with water, but also activated by it. $Sc(OTf)_3$ and $Yb(OTf)_3$ are rare earth metal salts that can be employed in aqueous organic processes. In aqueous solution, for example, $Yb(OTf)_3$ is found to be extremely successful in catalysing the Mukaiyama aldol reaction of benzaldehyde (34) with silyl enol ether 35, but in dry organic solvents it is considerably less effective. The increase in reaction rate generated by water is most likely owing to a change in the acid catalyst's structure and activity, or to the active catalyst's regeneration from the appropriate intermediate, which is quicker in water than in dry organic solvents. The majority of catalytic asymmetric carbocation reactions are carried out in aprotic anhydrous solvents such dry toluene, dichloromethane, and propionitrile at low reaction temperatures (e.g., 278 uC). In an aqueous solution, Cu(II) and a chiral ligand have recently been shown to be useful for the asymmetric aldol processes. The desired aldol product 40 is produced in a high yield and with acceptable enantioselectivity by reacting benzaldehyde (38) with silyl enol ether 39 in the presence of a catalytic amount of Cu(OTf)2 and bis(oxazoline) ligand 37. When compared to wet organic solvents, such as wet ethanol and wet dichloromethane, dry organic solvent yields and selectivities are lower. The increased enantioselectivity in water might be due to the quick hydrolysis of the silyl cation equivalent formed during aldol processes, which is responsible for the reduction in enantioselectivity by catalysing racemic aldol reactions. [7]

The limited solubility of most organic substrates in water is one of the fundamental disadvantages of utilising water as a solvent. Surfactants, which solubilize organic molecules in water, might help to solve the problem. In contrast to the reaction of silyl enol ether 42 with the catalytic quantity of $Sc(OTf)_3$ in water, the reaction with sodium dodecyl sulphate (a surfactant) and $Sc(OTf)_3$ in water provides a high yield of the matching aldol product 43, which is desired.. "Lewis acid-surfactant combined catalyst (LASC)" is a novel type of catalyst that was recently created. It works as a Lewis acid to catalyse the reaction as well as a surfactant to make organic substrates soluble in water. Scandium tris(dodecyl sulphate) ($Sc(DS)_3$) is an excellent example since it catalyses the reaction of benzaldehyde (41) with silyl enol ether 42 in water extremely well. [8]

4. Reactions of radicals and carbenes

Because strong O–H bonds (enthalpy 436 kJ $mol^2 1$) are difficult to attack, water is the preferred solvent for radical and carbene reactions. Water has recently been investigated as a solvent for these processes. In atom-transfer radical cyclizations, significant solvent effects have been seen. When allyl iodoacetate 66 is treated in water with triethylborane, a radical initiator, the matching lactone product 67 is produced in 78 percent of the time. The reaction is slow in organic solvents including hexane, benzene, methanol, tetrahydrofuran (THF), DMSO, and others, and gives no or little lactone product.

In addition, the radical cyclization that produces medium- and large-ring lactones is substantially more efficient in water than in organic solvents. In a 69 percent yield, a-iodo ester 68 reacts with triethylborane in water to produce nine-membered lactone 69. In organic solvents like hexane, benzene, and methanol, on the other hand, the atom-transfer radical cyclization produces no or very little lactone. Similarly, radical cyclization produces the eighteen-membered lactone in water significantly more effectively (70 percent yield) than in benzene. Water's enormous dielectric constant and high cohesive energy density, according to ab initio calculations, are both responsible for the cyclization's acceleration. [9]

In water, organic halides undergo a rapid radical reaction, resulting in the desired reduced products. Many organic halides 72 can be reduced to 73 by reacting them with phosphinic acid (hypophosphorous acid) and azo-bis-isobutryonitrile (AIBN) and NaHCO3, respectively, in aqueous ethanol.

D_3PO_2 is also effective for radical deuteration of organic halides. Organic halides 74 are reduced with D_3PO_2 in D_2O to produce labelled compounds 75 that may be measured in vivo. Free-radical polymerization may also be done with water as a solvent. Water's high heat capacity enables for efficient heat transmission from polymerization. Water's strong polarity differentiates many monomers from polymers in a striking way when compared to organic solvents. Aqueous free-radical polymerization is now widely used in industry. Carbene reactions occur in water as well. Water-soluble ruthenium alkylidenes 76 with cationically functionalized phosphine ligands, for example, are stable in water and start lefin metathesis processes. In aqueous settings, monomer 77 is quantitatively polymerized in the presence of 76. [10]

5. Transition-metal catalysis

In contemporary organic chemistry, the use of late transition metals for catalysing reactions is becoming increasingly important. Traditionally, organometallic chemistry and transitionmetal catalysis have been carried out in an inert gas environment, with moisture exclusion being critical. The explanation for this might be that water, as a ligand, frequently takes up coordination sites on metals. When water comes into contact with metal–carbon bonds, it can either transfer a proton (electrophilic reaction) or release oxygen (oxygenation) (nucleophilic reaction). Recent studies have shown that open air and water catalysis is both promoted and operable. In addition to being used as organic syntheses, amides 80 may also be used as raw materials for polymers and detergents, as well as for lubricants. Nitriles have historically been hydrated with acids or bases such as H_2SO_4 and NaOH. Many functional groups, such as carbon–carbon double bonds, are not able to withstand this action. Furthermore, especially under acidic settings, hydrolysis of amide compounds produces carboxylic acid byproducts. For the classical hydration of nitriles to amides, carefully regulated conditions with one equivalent of water in relation to the starting material nitriles are required. The hydration of different nitriles provides quantitatively the corresponding amide products in water with the easily produced, affordable, and supported ruthenium hydroxide catalyst $Ru(OH)x/Al_2O_3$. [11]

Carbon–carbon double bonds, as well as other functional groups, may endure this hydration procedure. In industrial, the hydration of acrylonitrile (81), which produces acrylamide in large quantities, gives (82). Hydration of carbon–carbon double bonds or the polymerization of acrylonitrile are not possible side reactions. The transition metal catalyst can be reused thanks to the water solvent. Filtration makes it simple to remove the $Ru(OH)x/Al_2O_3$ catalyst from the reaction mixture. After separation, the catalyst can be re-used at least twice more without losing much of its activity. arylboronic acids have been studied extensively in conjunction with rhodium catalysed addition to activated olefins (i.e. olefins having electron-withdrawing groups). It is, however, a prerequisite of this procedure to activate olefins with electron-withdrawing groups. By switching organic solvents to water, the reaction substrates are enlarged from activated olefins to general unactivated olefins. For the production of "Heck-type" products 85, several unactivated arylboronic acids 84 are reacting with various unactivated styrenyl olifins 83 in water with the help of the water-soluble phosphine ligand TPPDS, while vinyl heteroaromatic compounds 86 reacting with the same arylboronic acids 84 yield addition–hydrolysis products 88. For water-soluble sulfonated ligands or triphenylphosphines, the inorganic solvent responds slowly or not at all. Water may also be used to create palladium-catalyzed C–N bonds. Un-reactive aryl chlorides 90 are smoothly reacted with amines 91 in water using a phosphine ligand 89 and a palladium catalyst to provide the appropriate amination products 92.[12]

6. Oxidations–reductions

Heavy metal reagents or moisture-sensitive oxidants have frequently been used in oxidation processes. Water-compatible oxidants like O_2 and H_2O_2 have recently evolved novel oxidative processes in aqueous settings.

In water, ruthenium catalyst $Ru(OH)x/Al_2O_3$ can convert moderate to outstanding yields of biaryl compounds employing solely clean, safe, and cost-effective molecular oxygen as the oxidant for a variety of 2-naphthols and phenol substitutes. 2-Naphthol (101) undergoes an oxidative coupling in water, yielding 1,19-binaphthalene-2,29-diol (BINOL) (102) in the presence of 5 mol% $Ru(OH)x/ Al_2O_3$ and 1 atm O_2, which is a highly significant buildingblock and ligand. It's worth noting that even after the seventh recycling run, the $Ru(OH)x/Al_2O_3$ catalyst may be reused without losing any catalytic activity.[13]

A novel amphiphilic resindispersion of palladium nanoparticles may be utilised to catalyse the oxidation of alcohols in water using molecular oxygen (ARP-Pd). Aldehydes are formed in the presence of the nano-palladium catalyst, while ketones are formed in water when primary and secondary alcohols are present. Despite repeated usage, ARP-Pd retains its catalytic activity. Aqueous oxidative polymerization simplifies product separation. Poly(2,6-dimethyl-1,4-phenyleneoxide) (PPO) 112 is an important engineering plastic produced by the oxidative polymerization of 2,6-dimethylphenol (DMP) 111 in aqueous NaOH solution. NaOH solution dissolves the DMP monomer but not the PPO polymer product. After the reaction, simple distillation separates the precipitated product from the reaction mixture, and the aqueous solution can be reused for polymerization.[14]

Another water-compatible oxidant, hydrogen peroxide, is frequently utilised in aqueous oxidative processes. Various alcohols are transformed into the matching aldehyde or ketone products in water in the presence of polyoxometalate, $Na_{12}[WZnZn_2(H_2O)_2(ZnW_9O_{34})_2$, which is readily produced in one step in water from simple salts. The polyoxometalate catalyst, which was synthesised in situ, could be recycled in water.[15]

3. CONCLUSION

Organic reactions in water have received a lot of attention in the last decade, and research and development in this field is continuing growing at a rapid pace. This review serves as an introduction to this field. Organic reactions in water have now become as varied as those in organic solvents. It's worth noting that in water, whole new reactivities of reactions have been identified. The widespread use of aqueous organic reactions also serves as a driving factor for the field's future growth.

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