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RADICAL INITIATORS, REAGENTS AND SOLVENTS USED IN RADICAL CHEMISTRY

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ABSTRACT

This review article describes the developments towards the free radical reactions in respect of radical initiators, reagents and solvents used in radical chemistry. Various tin-free reagents developed in the last 20 years has been covered in this paper. Now, radical reactions were successfully occurred with hydrophilic initiators in water solvent also.

Keywords: Free radicals, reagents, radical initiators and solvents.

1. INTRODUCTION

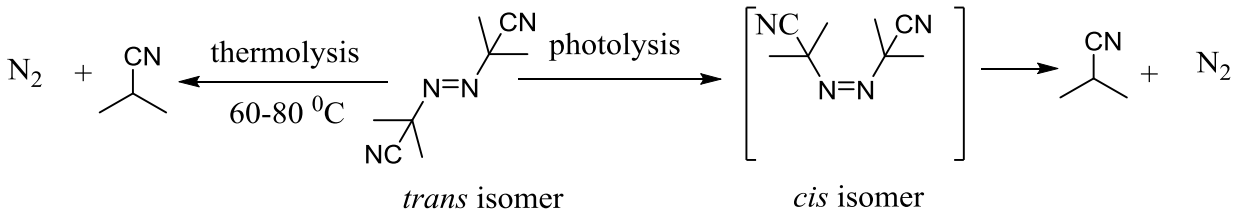
Radical chemistry has become a very important tool in the organic synthesis since the discovery of the triphenylmethyl radical by Moses Gomberg more than a century ago.[1] Now-a-days, free radical reactions and radical intermediates were considered as reactive intermediate to be used in the synthesis of carbocycles, heterocycles as well as natural products.[2] Radical reactions are very useful for the preparation of spirocyclic compounds employing an intramolecular radical strategy with cyclic olefin or alkyne, or cyclization of a radical species containing a preoccupied quaternary carbon center.[3] Radical reactions are successfully utilized for synthesis of drugs and pharmaceutical molecules in medicinal chemistry. This protocol is also emerging as one of the leading methods in many industrial processes-especially for the production of 'plastics' or polymers. These results underscore the importance of developing new, efficient protocols in the radical chemistry. As a result, thousands of new protocols have been developed by the researchers by application of new radical initiators, reagents and solvents. Some of the radical reactions are associated with atom or group transfer, inter- or intramolecular radical addition, cascade reactions, radical translocation, one-electron oxidation, or ionic chemistry etc. Radical reactions are generally accompanied under very mild conditions. Thus, various sensitive functional groups are tolerated under free radical conditions.

For the production of free radicals, a covalent bond has to be cleaved homolytically into two parts so that each fragment possess one electron on the atom which shared the covalent bond. Generally, the cleavage of the bond is achieved by the application of energy in the form of heat, light, or radiation. In this review, the developments towards representative radical initiators and radical reagents that produce radicals easily has been described. These radical initiators generally require mutually conflicting properties: they should be stable at room temperature but decompose to produce radicals under mild conditions.The updates on the green solvents used in radical chemistry is also covered in this article.

2. Generation of radicals with different mode of energy supply

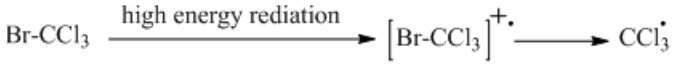
Various methods such as thermolysis, photolysis, radiation and redox systems are widely used in the generation of radicals. In thermolysis process, a covalent bond is generally cleaved to its radical fragments at high temperature (> 800°C). Covalent bonds that can be cleaved at low temperatures are limited to the weak bonds having dissociate energy 30-40 kcal/mol.[4] *Azo* compounds, peroxides, nitrite esters *etc* having low bond dissociation energy are used as radical initiators in radical

chemistry. Among these, *azo* compounds are widely used as a radical initiator which produce radical *via* homolytic fission of covalent bonds by the thermal decomposition at 60-80 °C.
Another widely used method for the generation of radicals is the photolysis. In this technique, the azo compounds under undergoes the unstable *cis*-isomer by the absorption of light energy to produce radicals (**Scheme 1**).[6] Similarly, alkoxy radicals and acyloxy radicals are produce from peroxides on absorption of light energy.



Scheme. 1: Decomposition of *azo* compound

High energy radiation such as X-rays and γ–rays are also used for the generation of radicals.[4] However, this technique has very limited applications in organic synthesis. On the other hand, oxidation-reduction i.e. redox reaction[7], has great utility in the generation of radicals by an intermolecular electron transfer. The Kolbe reaction is a representative example for such type of reaction.[8]

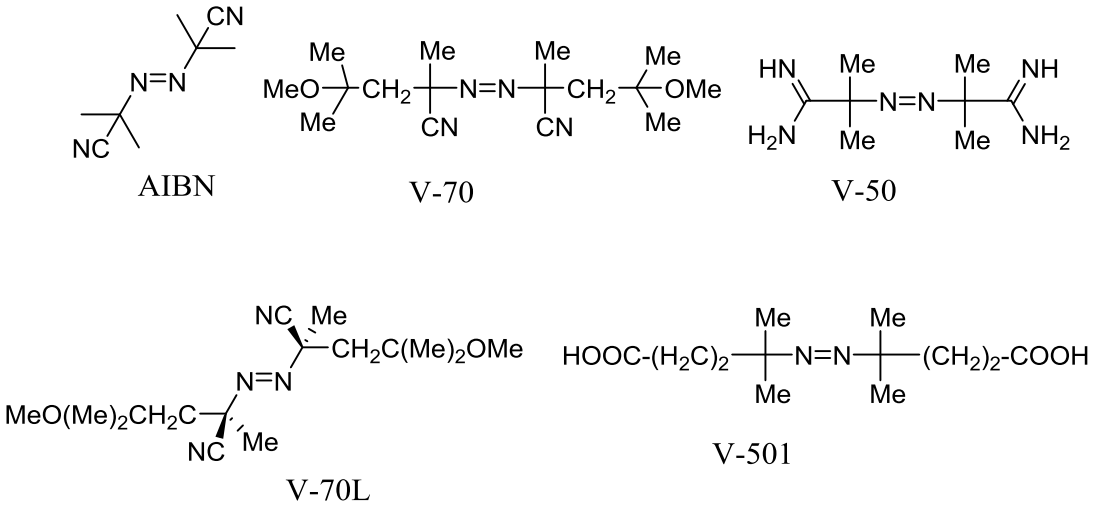


Scheme. 2: Radical generation by high radiation

3. Radical initiators used in the radical reactions

(a) *Azo*compounds as radical initiators

Nitrogenous*azo* compounds such as 2,2 '-azobisisobutyronitrile (AIBN), 2,2'-azobis(4-metlzoxy-2,4-dimethylvaleronitrile) (V-70), 2,2'-azobis (2-methyl propionamidine)dihydrochloride) (V-50)*etc*. are extensively used as radical initiators in organic synthesis.[4] This is because of high decomposition ability of *azo* compounds and produces the stable radical. Azo compounds are decomposed by heat or absorbing light by the *cis* form to produce the corresponding alkyl radicals and nitrogen.Among the *azo* compounds, AIBN is one of the most widely used radical initiators in organic synthesis. It is commercially available as white crystals, whose melting point is 65 °C with a half-life of 10 h in toluene at 65 °C. It is often used with trialkyltin hydrides in synthetic reactions.[9]
Recently, many azo-type radical initiators that work below room temperature have also been discovered. For example, 2,2'-azobis(4-metlzoxy-2,4-dimethylvaleronitrile) (V-70) is a radical initiator that acts below the room temperature. It is extensively used in the stereoselective formation of carbon-carbon and carbon-heteroatom bonds via the generation of radical species in neutral and mild conditions.[10] It was observed that V-70 is melted at 50-96 °C with a half-life of 10 h in toluene at 30 °C. Interestingly, it is quite stable for a few months when stored in a refrigerator. It is commercially available as a mixture of *meso* and *racemic* form. (*2RS,2'RS*)-Azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70L) is the racemic form isomer purified from V-70 that exhibits a higher activity compared to V-70 as a radical initiator. This initiator is applied for the preparation of enantiomeric pure compound via radical reaction. V-70L is commercially available, white crystalline compound; whose melting point is 59.2-62.3 °C and half-life is 1h in toluene at 30 °C. It could be stored for a few months in a refrigerator.



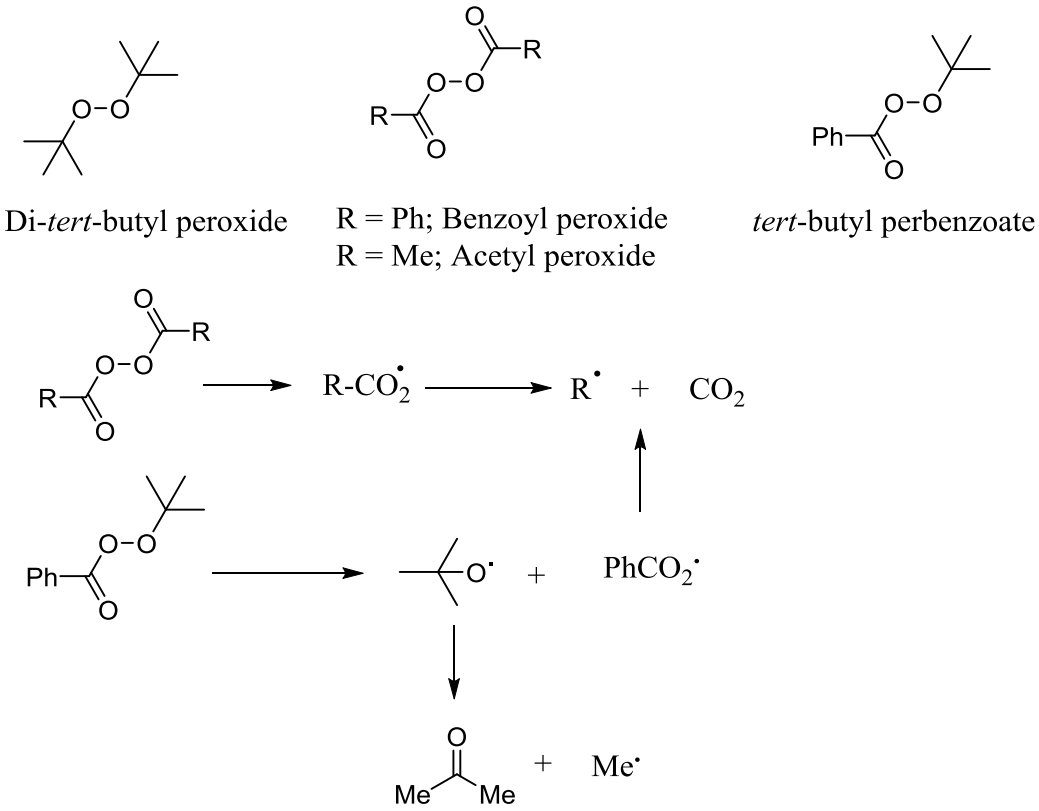
Scheme. 3: Some important radical initiators

Furthermore, it was reported that azo compounds possessing the hydrophilic functional groups act as effective initiators in aqueous media.[11] In this aspect, molecular design to find out the water-soluble radical initiators has been performed.[12] Researchers observed that V-50 and V-501 are two azo type compounds that efficiently worked as radical initiators in water. V-50contains an amino group that increased the hydrophilicity of the molecule and thus, acts as a hydrophilic radical initiator. It is a white crystalline commercially available compound having melting point 160- 169 ^{o}C. Similar to AIBN, V-50 also worked as an initiator at moderate temperature.Its half-life period is 10 h in water at 56°C. Another, hydrophilic radical initiator is 4,4'-azobis(4-cyanopentunoic acid) (V-501) which has a carboxylic group in the molecule. It is also white crystalline solid, and commercially available. Its melting point is 120-123°C having a half-life of 10 h in water at 69°C.

(b) Peroxide radical initiators

Several peroxides has been used radical initiators in organic synthesis for a long time. Thermolysis of peroxide produces alkoxy radical and acyloxy radical by the cleavage of the peroxide bond. Benzoyl peroxide, acetyl peroxide,*tert*-butyl perbenzoate, *di-tert*-butyl peroxide (*t*BuO-O-*t*Bu) are the widely used peroxides in radical chemistry (Scheme 4).

Among these, benzoyl peroxide is one of the most widely used peroxide radical initiators in organic synthesis.[4] It is a white crystalline compound, commercially available and its melting point is 105-106°C. This compound on decomposition by heat producesphenyl radical and carbon dioxide *via* benzoyloxy radical.It was observed that aromatic diacyl peroxides are generally more stable than their aliphatic counterparts. Acetyl peroxide decomposes at 25 ^{o}C, so that careful handling is required to avoid dangerous explosion. These compounds are sensitive to shock, light, heat and metals. Among the known peroxides, di-*tert*-butyl peroxide has a relatively stable structure. It produces methyl radical via *t*-butoxy radical (**Scheme 4**).



Scheme. 4: Some peroxides used as radical initiator

It has been observed that several organoboranes are act as radical initiators. Among these, trialkylborane analogs have been used as radical initiators for long time. Triethyl borane (Et_3B) is effective at -79 ^oC and particularly used in the selective organic preparation.[13] Other organo borane compounds such as 9-BBN is also used as an efficient radical initiator in the seteroselective organic synthesis.[14]

4. Reagents used in radical cyclization

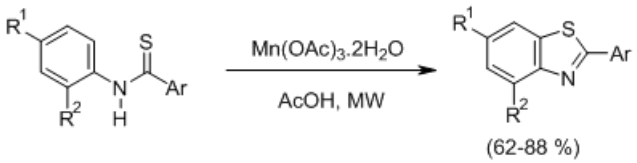
Till date, various tin hydride reagents such as tri-*n*-butyltin hydride ($^nBu_3SnH$), trimethyltin hydride (Me_3SnH), and triphenyltin hydride (Ph_3SnH) have been used in the most of the radical reactions.[15] The alternative procedure is also known involving a small amount of tri-*n*-butyltin chloride ($^nBu_3SnCl$) with sodium cyanoborohydride for *in situ* generation of tri-*n*-butyltin hydride.[16] However, these tin based radical reagents have several drawbacks. One of the major problems is the toxicity of the trialkyl tin hydrides.[17] Furthermore; complete removal of thetoxic tributyltin residues from the reaction mixtures is very difficult and hence, it is very difficult to purify the product(s) from the reaction mixture.[18] These drawbacks strongly limit the applications of tin-based reagents in the synthesis of drugs and medicines.

Various efforts have been directed towards the tin free radical chemistry.[19] Tributylgermanium hydride (Bu_3GeH),[20] tris(trimethylsilyl)silane [$(TMS)_3SiH$ or TTMSS][21] and polymethylhydrosiloxanes[22] are superior alternatives to $^nBu_3SnH$. Other reagents, such as samarium diiodide,[23] Cp_2TiCl_2,[24] indium[25]have good potential to replace the toxic Bu_3SnH for radical cyclizations. Triphenylgermanium hydride mediated radical carbonylation/ cyclization reactions[26] are also very useful. Triethylborane (Et_3B) is a powerful reagent for radical cyclization.[27] But such reagents are highly expensive.

Phosphorous compounds are proved to be excellent alternatives to organotin hydrides.[28-30] Barton *et al*. have exposed a radical reaction using hypophosphorous acid.[31] Kita *et al*. reported a radical reduction in aqueous isopropyl alcohol using the radical initiator VA-061, hypophosphorous acid, and triethyl amine.[32] Diethyl phosphite[33] [$(EtO)_2P(O)H$] and diethyl thiophosphite [$(EtO)_2P(S)H$] were also proved to be an useful alternative and more versatile reagent for radical cyclization.[34]

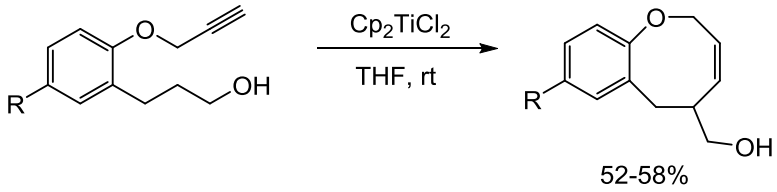
Indium based compounds are also utilized in the radical reaction. For example, indium mediated atom transfer radical cyclization reaction has been explored[35] using a catalytic amount of indium and iodine. The reductive radical cyclization using an excess of indium and iodine without the use of a radical initiator such as AIBN or Et_3B/O_2 is also reported. Recently, several indium-mediated reactions have initiated by single-electron transfer (SET) in tandem carbon-carbon bond-forming processes.

Dihalogenoindium hydride ($HInX_2$) can be generated from $InCl_3$ or $InBr_3$, is also an effective alternative radical reagent to Bu_3SnH. Several metal hydrides[36] such as $NaBH_4$[37] DIBALH[38] and Et_3SiH[39] are also some efficient alternative to Bu_3SnH used in the radical reactions.
Manganese(III) triacetate[40] is also found to be an excellent one-electron oxidant that has been widely employed to produce free radicals for cyclization reactions. For example, arylbenzothiazoles have been prepared from arylthioformanilides using manganese triacetate $Mn(OAc)_3.2H_2O$ in acetic acid under microwave irradiation. (**Scheme 5**).[41]



Schemem. 5: $Mn(OAc)_3$-catalyzed radical reaction

In another approach, Cp_2TiCl_2 is proved to be an excellent alternative to organotin hydrides in radical reactions.[42] Treatment of the epoxy ethers with Cp_2TiCl in THF under argon afforded the 8-membered cyclic ethers in moderate yields(**Scheme 6**).[43]

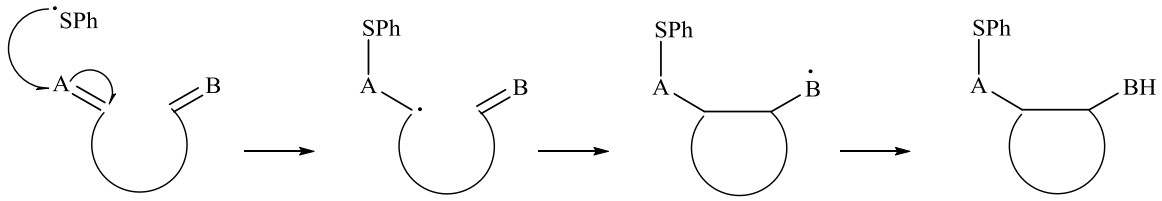


Scheme. 6: Cp_2TICl_2-mediated radical cyclization

Recently, Ce (IV) reagents, Ceric ammonium nitrate (CAN)[44] and ceric-tetra-*n*-butylammonium nitrate (CTAN)[45] are widely applied for the generation of radicals and radical cations that can further react with other substrates to form carbon-carbon bonds.[46] The use of CTAN has been exemplified in the oxidative additions of 1,3-dicarbonyl substrate to allyltrimethylsilane.[47] The oxidative coupling of *β*-carbonyl imines and allyltrimethylsilane with CTAN were investigated in CH_3CN and CH_2Cl_2 as solvent.[48]

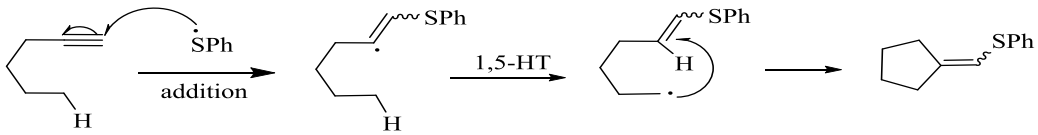
5. Thiol-mediated radical reaction

Of late, thiol-mediated tin free methodology has been developed for the construction of carbon-carbon bonds based on sulfanyl radical addition-cyclization.[49] These radical reactions proceed by the addition of a sulfanyl radical to an unsaturated bond to form a carbon-centered radical species. Subsequent intramolecular addition of the resulting carbon-centered radical to another multiple bond followed by the abstraction of hydrogen from thiophenol to afford the product **(Scheme 7)**.



Scheme. 7: Thiol-mediated radical cyclization

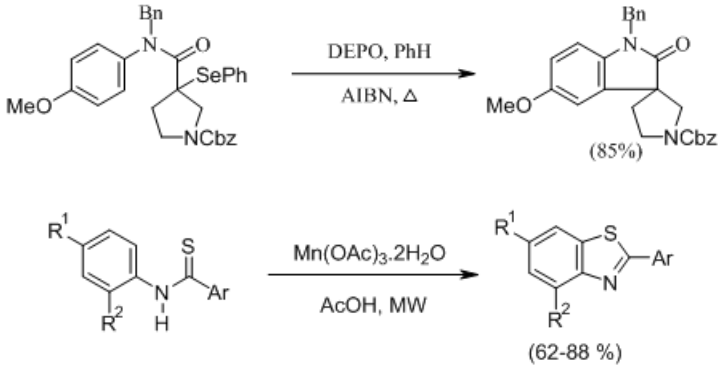
Another approach a sulfanyl radical, generated from thiol and AIBN adds to the terminal of the triple bond to create a alkenyl radical, which undergoes 1,5-hydrogen atom transfer. After translocation, the new radical species undergoes an intramolecular cyclization to give the product (**Scheme 8**).



Scheme. 8: Thiol-mediated radical cyclization *via* hydrogen transfer

6. Solvents used in the radical reaction:water is the greenest solvent

Most of the radical reactions are carried out in organic solvents such as- benzene, toluene, xylene, THF, *t*-butanol etc. The use of water as a solvent in radical cyclization reactions is an excellent achievement from both economic and environmental point of view.[50] In this aspect, Jang *et al*. reported[51] an efficient and mild methodology for the synthesis of heterocyclic compounds with phosphorous functionality by radical cyclization of dienes in water. Nambu *et al*.[52] also performed the radical reaction by using VA-061 as the water-soluble initiator and 1-ethylpiperidine hypophosphite (EPHP) as the chain carrier.Murphy and coworkers synthesized indolines from the reaction of iodoarenes with diethylphosphine oxide (DEPO) in water at 80°C *via* aryl radical formation, hydrogen atom abstraction, and cyclization.[53] In order to synthesize alkaloid horsfiline, they also used phosphorous centered radical obtained from ethyl piperidine hypophosphite and DEPO.[54] The authors observed that DEPO was highly effective for this cyclization at 80°C;but this reaction is difficult with Bu_3SnH (**Scheme 9**).



Scheme. 9: Synthesis of alkaloids applying phosphorous centered radical reaction

7. CONCLUSION

In this paper, various radical initiators, reagents and solvents used in the radical reactions has been discussed. Various efforts have been paid towards the development of tin free radical chemistry. The radical initiators possessing the hydrophilic functional groups act as effective initiators in aqueous media. Many radical initiators are also effective at room temperature. Several phosphorous compounds are proved as excellent alternative to organotin reagents in radical reactions. Tributylgermanium hydride, samarium, indium, titanium, manganese, nickel based compounds were widely used in radical reactions. However, these reagents are costly. Thiophenol is an attractive alternative to tin reagents. This methodology is cost effective than other metal-based reagents. Among the several solvents, water is the greenest solvent used in the radical reaction.

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Conflict of interest: The authors declare that there are no conflicts of interest.

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