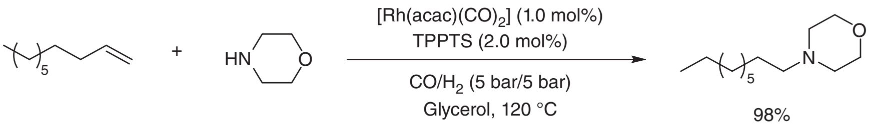
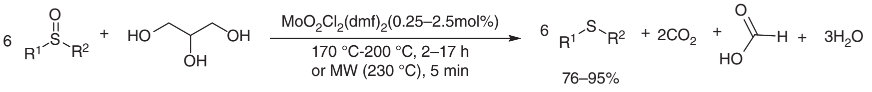
then undergoes metal-catalyzed hydrogenation with water as the only by-product. Glycerol acts as a hydrogen transfer agent and facilitates the Rh-catalyzed reduction of the enamine intermediate by ensuring that the reaction proceeds at relatively low pressure.



Scheme 1.58 Rh-catalyzed hydroaminomethylation reaction in glycerol.

Furthermore, glycerol has been demonstrated to be used as a solvent and reducing agent for the Mo-catalyzed chemically selective deoxidation of sulfoxides, where it acts only as a reducing agent and not as a hydrogen donor, as depicted in Scheme 1.59 [82].



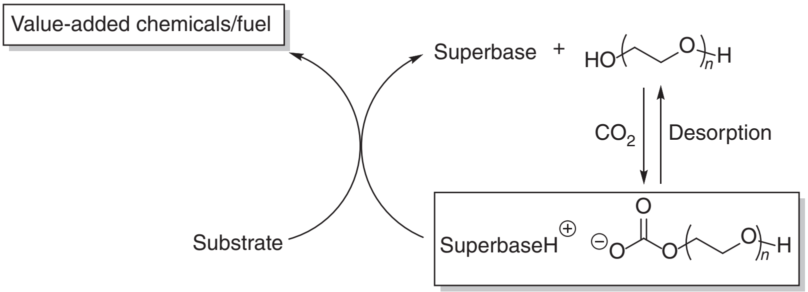
R^1=4-$CH_3C_6H_4$, C_6H_5, 4-BrC_6H_4, 4-ClC_6H_4, 4-CNC_6H_4, 2-$CO_2MeC_6H_4$, 4-$NO_2C_6H_4$
R^2= CH_3, 4-$CH_3C_6H_4$, C_6H_5, $CH_2C_6H_5$, 4-ClC_6H_4, cyclopropyl, etc.

Scheme 1.59 Glycerol as a chemical selective reductant of sulfoxide.

1.5 Miscellaneous

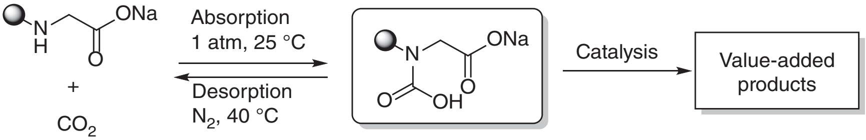
1.5.1 Polyethylene Glycol as a Solvent for CO_2 Capture and Conversion

PEG not only serves as an essential green solvent but also plays an important role in CO_2 capture and conversion. Recently, much attention has been focused on developing cost-effective and powerful absorption agents and CO_2 capture and storage (CCS) technologies. Nevertheless, the large energy input during desorption becomes a key obstacle to achieving practical CCS. Alternatively, reactions involving CO_2 are typically conducted at high pressures, which may be economically undesirable and a concern for safety. The challenge is to develop catalysts that can activate CO_2 at low pressure (preferably 1 atm) and thus catalyze the binding of CO_2 into the structures of organic molecules. In order to settle the problem of energy loss in the CCS procedure, PEG has gained attention as a CO_2-friendly material. A highly efficient binary system consisting of PEG/superbase has been developed to capture and simultaneously activate CO_2, thus successfully converting the captured CO_2 directly into value-added chemicals or fuels and avoiding desorption (Scheme 1.60) [83]. Experimental results have indicated that the superbase/PEG system has proven to be an excellent system for fast and reversible iso-molar CO_2 sorption, and that the amidazolium alkyl carbonate obtained by capturing CO_2 with superbase and PEG may be more reactive than free CO_2. As a consequence, CO_2 uptake may lead to its activation and the desorption process using this strategy requires few external energy inputs. In overview, the CO_2 fixation can be catalyzed into value-added chemicals/fuels under extremely mild reaction conditions (1 atm, 40 °C, metal-free process).



Scheme 1.60 CO_2 capture and activation by superbase/PEG and its subsequent conversion.

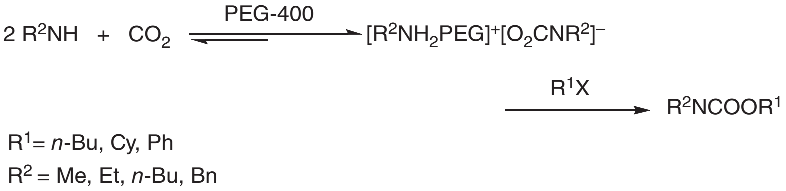
Similarly, the flexible PEG chains can coordinate with alkali metal cations, which can increase the capacity of the counterions. Readily available amino acid salts of *N*-substituted groups have a very high CO_2 capacity in PEG solutions, which are nearly equivalent to capture, and have been exploited to some extent in the field of CO_2 capture (Scheme 1.61) [84].



Scheme 1.61 Equimolar CO_2 capture by *N*-substituted amino acid salts and subsequent conversion.

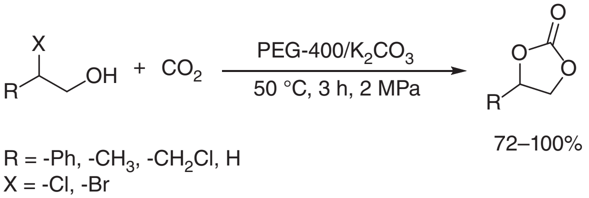
Besides, organo-carbamates have a great variety of applications in the medicinal industry and agriculture and are widely used as protecting groups or key intermediates in synthetic chemistry. Conventional organo-carbamate synthesis involves the use of highly toxic phosgene as a carbonylating agent, which requires organic solvents and can easily cause environmental problems. However, organo-carbamates which are chemically selectively synthesized from the PEG-enhanced amines, carbon dioxide, and alkyl halides have excellent features such as environmental friendliness and high efficiency. In this work, amines, CO_2, and alkyl halides are subjected to a three-component reaction with the help of K_2CO_3 and PEG (MW ¼ 400) to produce organo-carbamates under ambient conditions (Scheme 1.62) [85]. PEG in this reaction is used as a solvent and a PTC. Notably, the presence of PEG can also suppress the alkylation of amines and carbamates, thereby enhancing the selectivity for the targeted carbamates.

From the perspective of environmental protection and resource utilization, the chemical conversion of CO_2 into useful chemicals is of increasing interest. One of the most promising approaches for the chemical fixation of CO_2 is the synthesis of



Scheme 1.62 PEG-enhanced chemoselective synthesis of organic carbamates from amines, CO_2, and alkyl halides.

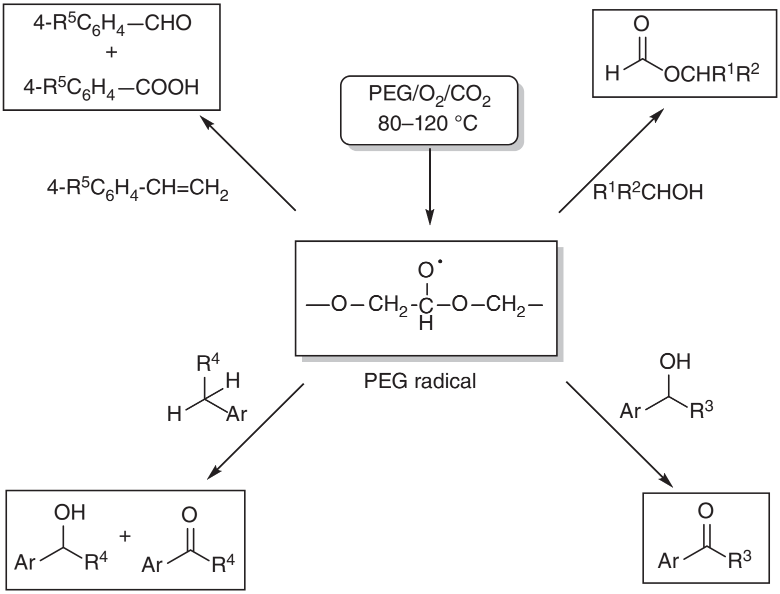
five-membered cyclic carbonates, which have been used in a range of applications, for instance, as polar nonprotonic solvents, intermediates for organic and polymer synthesis, chemical components for pharmaceutical/fine chemicals for biomedical applications, and as lithium secondary battery electrolytic components for lithium secondary batteries (Scheme 1.63) [86]. In this context, PEG has already been used as an efficient reaction medium to synthesize cyclic carbonates by reacting ortho–halo alcohols with carbon dioxide in the presence of a base. Notably, PEG-400 exhibits a unique impact on reactivity as an environmentally friendly solvent compared to conventional organic solvents. First, PEG-400 can come up with complexes via coordinating the potassium cation in the same way that crown ether does, which influences the basicity of K_2CO_3. Second, the "CO_2-expansion of PEG" impact alters the physical characteristics of the reaction mixture, such as viscosity and solubility of the reactants, which enhances the synthesis process. High yields and excellent selectivity of cyclic carbonates are achieved under mild reaction conditions. Furthermore, the product can be isolated easily by extraction, which is considered a cost-effective way to produce cyclic carbonate in an environmentally friendly manner.



Scheme 1.63 Synthesis of cyclic carbonate from vicinal halohydrins and CO_2 in PEG-400.

1.5.2 Polyethylene Glycol Radical-Initiated Oxidation Reactions in Compressed Carbon Dioxide

PEG and its derivatives are usually recognized as a thermally stable, cheap, toxicologically harmless, and relatively environmentally friendly medium for chemical reactions and as PTCs. On the other hand, PEG, being susceptible to oxidative attack by free radicals in the presence of oxygen at high temperatures (above 70 °C), can afford the formation of numerous complicated low-molecular-weight PEG peroxides through a random chain-breaking process. In this case, when combined with compressed CO_2, the PEG radicals induced by thermal oxidative degradation can initiate a series of radical reactions such as selective formylation of primary and secondary fatty alcohols, oxidation of benzyl alcohols, benzyl C—C bond cleavage and benzyl sp^3 C–H oxidation, as shown in Scheme 1.64 [87], representing great synthetic potential utility in a cost-effective, practical, and environmentally friendly manner. The whole procedure does not require any catalyst or additional free radical initiator. In this work, hexadecanol is chosen as the model compound for the preliminary study. As a consequence, hexadecanol is mixed with PEG-1000, oxygen (2.5 MPa), and carbon dioxide (13.5 MPa) at 100 °C for 12 h, hexadecyl formate in 68% isolated yield, and 15% palmitic acid is obtained along with 15% recovery of the hexadecanol. This method allows for a metal-free, cost-effective synthetic transformation with environmentally friendly characteristics compared to conventional processes.

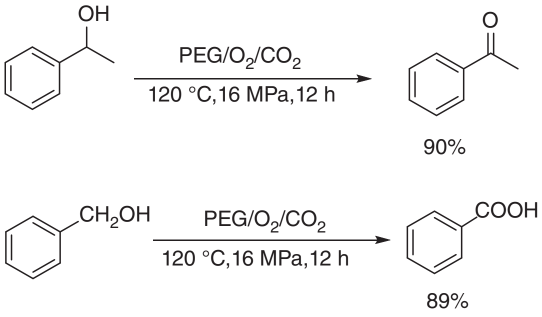


Scheme 1.64 Organic reactions involving PEG radicals in compressed carbon dioxide.

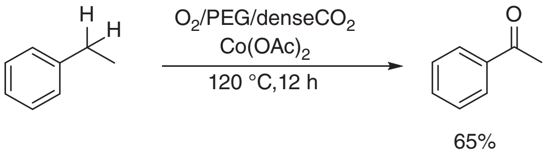
In this similar way, $PEG/O_2/CO_2$ is also used as an initiator, oxidizer, and solvent to oxidize primary and secondary alcohols to aldehydes or acids and ketones, respectively (Scheme 1.65) [88]. Compressed CO_2 here could offer a relatively safe environment for the oxidation of molecular oxygen as an oxidant in the reaction and could also be used to adjust the selectivity of the target product by altering its pressure to improve reactivity and to render product separation easier.

Based on the abovementioned experimental achievements, the application of PEG radicals in the oxidation of benzyl hydrocarbons is further explored (Scheme 1.66) [89]. In this regard, PEG oxidation/thermal degradation plays a critical role in the oxidation of ethylbenzene to acetophenone.

To investigate the oxidation reaction process during thermal degradation of PEG by *in situ* generation of radicals, the radical species, the trace formylation



Scheme 1.65 PEG radical-initiated oxidation of benzylic alcohols in compressed carbon dioxide.

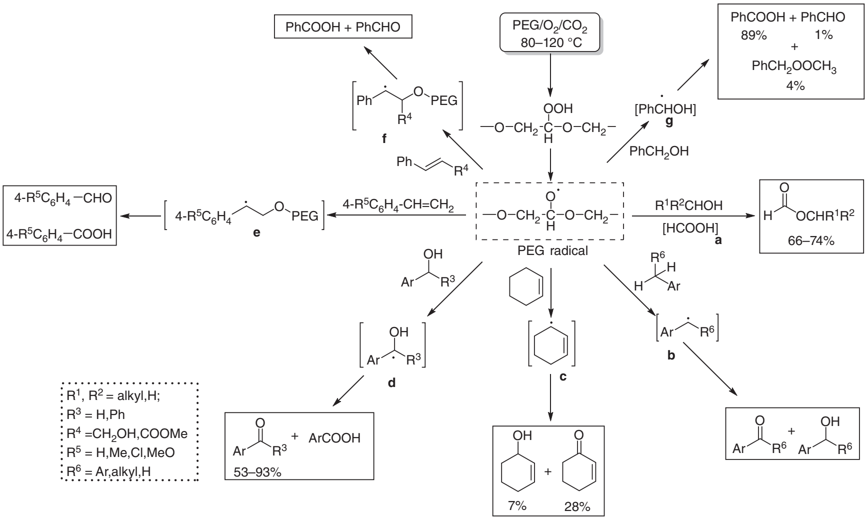


Scheme 1.66 PEG radical-initiated benzylic C—H bond oxygenation in compressed carbon dioxide.

products under the action of PEG radicals, the extended distribution of relative molecular masses of PEG, the generation of peroxide intermediates determined by KI/starch method, and the inhibition of the reaction by TEMPO (2,2,6,6-tetramethylpiperidine-1-yloxy) have been investigated, respectively. Then a rationalized radical mechanism is proposed, as shown in Scheme 1.67 [87]. The PEG radical generated by the reaction of PEG with oxygen initiates the substrate to produce a relatively stable radical, e.g. b–g, depending on the substrate structure. As expected, benzyl or allyl may favor the formation of benzyl radicals or allyl radicals, and thus primarily undergo oxidation, such as benzyl alcohol oxidation, benzyl C–C cleavage reactions, and benzyl/allyl sp_3 C–H oxidation, while aliphatic alcohols may preferentially pass through the formylation pathway.

1.5.3 Ring-Opening Reaction

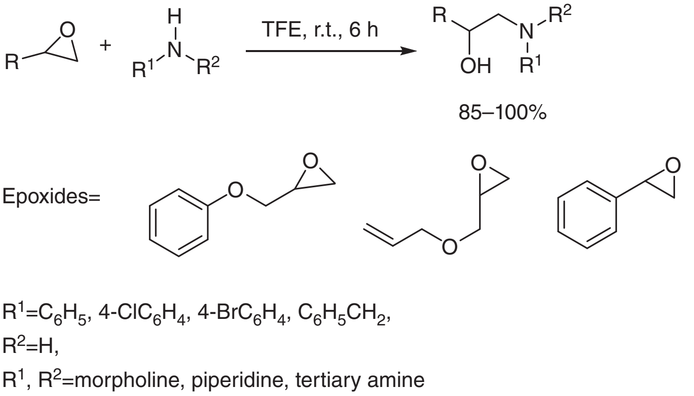
Fluorinated alcohols are good hydrogen bond donors and have high polarity, high ionizing power, and low nucleophilicity. Therefore, TFE and PFTB can promote the opening of epoxides by heteroatom or carbon nucleophiles. TFE and PFTB both contain highly nucleophilic fluorine atoms, which can act as nucleophilic reagents to react with epoxides, attacking the carbon–oxygen bond in epoxide molecules and opening up the ring structure. The fluorine atoms in fluorinated alcohols can polarize the O—H bond in the alcohol, making it more polar and thus more easily attracting nucleophilic reagents. In addition, fluorine atoms can also increase the electrophilicity of alcohols, thereby reducing the bond energy of the C—O bond and making epoxides easier to open. Therefore, fluorinated alcohols can promote the



Scheme 1.67 The structural formulae and proposed pathways of organic reactions initiated by PEG radicals generated by thermal oxidative degradation.

ring-opening reaction of epoxides by increasing the electrophilicity of oxygen atoms in epoxides and reducing the bond energy of the C—O bond.

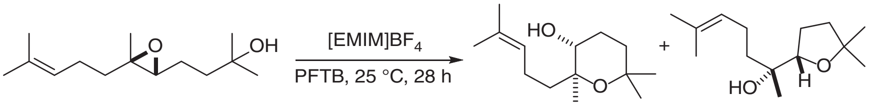
Epoxides are important and useful intermediates in organic synthesis because of their easy formation and high reactivity. In this method, TFE serves as both a reusable catalyst and medium, while aliphatic and aromatic amines act as nucleophiles to efficiently open the epoxide ring, resulting in the formation of β-amino alcohols with high yield and good regioselectivity (Scheme 1.68). It is worth noting that the high polarity and hydrogen bonding interactions between TFE and epoxides may be the reasons for promoting the reaction [90].



R^1=C_6H_5, 4-ClC_6H_4, 4-BrC_6H_4, $C_6H_5CH_2$,
R^2=H,
R^1, R^2=morpholine, piperidine, tertiary amine

Scheme 1.68 Ring opening of epoxides with amines.

In addition, the ring opening of epoxy alcohols usually occurs through the 5-*exo* selective pathway of producing THF rings, rather than through the desired 6-*endo* selective pathway of producing tetrahydropyran rings. The synergistic effect of PFTB and 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM]BF_4) can promote the internal selective ring-opening reaction of trisubstituted epoxides (Scheme 1.69). Starting from readily accessible homochiral polyepoxy alcohols with a methyl group at all the *endo*-cyclization sites, polyethers up to five consecutive fused 6-, 7-, and/or 8-membered rings can be constructed in one step. The partial positive charge on the stable transition state of BF_4 salt is used to further improve the internal selectivity. In the presence of [EMIM]BF_4, the reaction rate increases due to the small amount of HF produced by the dissolution of the BF_4 anion in the PFTB. When using [EMIM]BF_4, which is more easily soluble in PFTB than Ph_4PBF_4, the internal selectivity slightly increases [91]. Therefore, through the combined use of PFTB and [EMIM]BF_4, a selective inversion from *exo*-selectivity to *endo*-selectivity can be achieved, thereby quickly and effectively synthesizing the multi-ring porous core structure of marine stepped polyether molecules.



Scheme 1.69 The synergistic action of PFTB and [EMIM]BF_4 promotes the internal selective ring-opening reaction of triple-substituted epoxides.

1.6 Summary and Concluding Remarks

In this chapter, the different reactions involving various alcohol as solvents are summarized, among which the different roles of glycerol, PEG, and fluorinated alcohols in organic reactions are mainly introduced according to the functional characteristics of alcohols.

Alcohols are ideal media for many reaction processes as a cheap, abundantly available, and low-toxic solvent, mainly in reduction reactions, coupling reactions, and condensation reactions, but also in other reactions. Some bio-based alcohols that can be prepared by petrochemical industry procedures or from renewable sources are widely used in laboratories and industries, such as bioethanol, 2-propanol, and glycerol. In particular, glycerol, as an important green solvent combining the advantages of water and ionic liquids, has great advantages in improving the catalytic rate and selectivity in organic synthesis, product separation, and catalyst and solvent recovery, which provides an innovative solution to replace traditional volatile solvents. Interestingly, PEG is used as a green and cheap solvent for various types of organic transformations due to its good compatibility. Secondly, it has remarkable cationic complexing ability as an acyclic analog of crown ethers. In metal-catalyzed reactions, the catalytic system "PEG-metal" can be easily recovered and reused without significant loss of activity. Furthermore, fluorinated alcohols have unique properties and are a very attractive solvent for organic reactions, allowing for many challenging reactions, although it is not very green.

Although great strides have been made by utilizing alcohol as a solvent and a variety of valuable chemicals have been obtained, there is still major room for improvement in the future:

(1) The reason for glycerol as a solvent to facilitate the reaction needs to be further investigated in depth. Second, technical-grade glycerol (80%) is more desirable as a green solvent for direct industrial and laboratory applications, but there are few successful examples. Finally, glycerol as a high-boiling-point polar solvent faces the same problem as many ionic liquids, How to remove the polar compounds from glycerol? This is an important question that needs to be addressed.
(2) The interactions and mechanical details of the multiphase catalytic interface in the presence of PEG as a solvent are yet to be explored in depth. Second, the solvation of solutes in PEG is largely unknown, and the interaction of PEG with metal cations and how it affects the solvation of resistant anions also remains to be addressed. In addition, studies on how the phase behavior of PEG enhances product recovery are yet to be thoroughly investigated.
(3) Fluorinated alcohols are less used in green chemistry due to their corrosiveness, toxicity, and cost, and it is critical to develop methods that reduce the use of fluorinated solvents while continuing to utilize their inherent properties. Moreover, the interaction mechanism between fluorinated alcohols and substrates in the reaction process needs to be further studied.

In short, we hope that the content presented in this chapter will inspire organic chemists to give more consideration to alcohol solvents in their future research to achieve the goal of green chemistry.

Acknowledgments

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