

MINI REVIEW

Conversion Reaction of Benzyl-Type Chlorinated Hydrocarbons into Functional Groups

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Benzyl chloride and its derivatives are important intermediates, the benzyl-type chlorinated hydrocarbons tend to have reaction with kinds of nucleophilic reagents, such as OH^- , OR^- , CN^- , NH_3 , *etc.*, give new functional groups. This review summarizes these reactions and makes discussions according to introduce different groups and compares different kinds of reactions.

Key Words: Benzyl-type chlorinated hydrocarbons, Functional, Ether linkage, C=C bond, R-CO-R, Hydroxyl group, Amine, heterocyclic.

INTRODUCTION

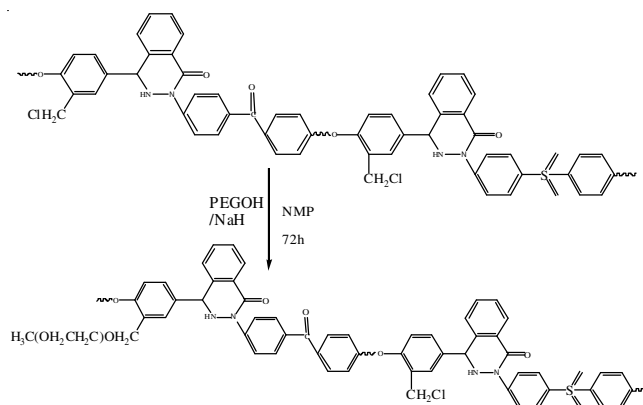
Blanc chloromethylation of aromatics is a class of reaction that gives benzyl chloride and its derivatives as the major products in a polyformaldehyde-HCl system and the reaction process is a mature and widely use in technology. Benzyl chloride and its derivatives are important intermediates because they can easily have substitution reaction with nucleophilic reagents to provide new polymers or copolymers with monomers and also obtain kinds of new derivatives by introducing the necessary functional groups, so as to achieve the target materials or improve the performance of products¹. In recent years, there are several studies in various fields such as ion exchange resin, functional polymer microsphere, separation and purification of biological macromolecule and surfactant, *etc.*

Introduction of ether linkage: The chloride ion of chloromethylation reacts with hydroxyl group *via* substitution reaction can introduce ether linkage and the Williamson synthesis of ether with sodium alkoxide, alcohol and hydroxybenzene is a common preparation of symmetry and asymmetry ether.

The reaction of chloromethyl intermediate with sodium alkoxide always requires long time and with out catalyst the yield is comparatively low and the sodium alkoxide needs harsh experimental conditions. It is liable to deliquesce and the presence of water will reduce the yield, even result in no activity. Zhan *et al.*² made the alkylation.

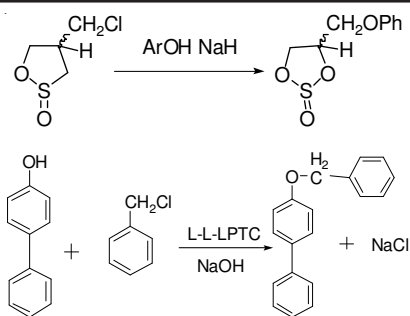
Liping *et al.*³ got the products extracted with chloroform and ethanol three times and then returned by Soxhlet extractor

for 48 h. So the reaction need long reaction time, low yield and tedious post-processing.



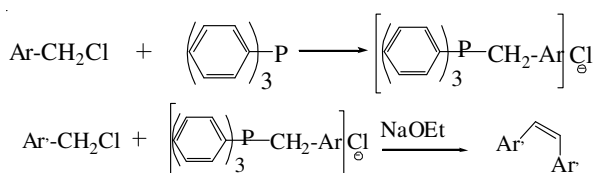
Moczar *et al.*⁴ synthesized acridine derivants by the same method. Bredikhina *et al.*⁵ realized the substitution reaction with hydroxybenzene. This reaction needs short time and high yield and also the solvent can be recycled. Yadav *et al.*⁶ reported the *o*-alkylation (etherification) in a *tri*-liquid PTC system. This system is environmental friendly, high yield, good selectivity and promising field.

Introduction of C=C Bond: It is well known that the polymers containing double bonds are tending to cross-link with other groups or materials to realize modification or chemical modified. Through radical polymerization cross-linking branched-chains of different properties can make the polymers have better overall performances than block

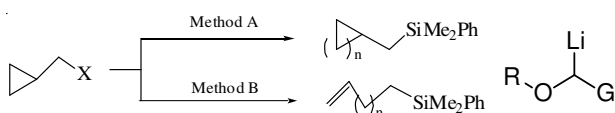


copolymers and have further development in emulsifier, solubilizer, surfactant, phase transfer catalyst and biomedical material, *etc.* In short, the introduction of C=C bond has great significance in improving the material properties and enlarging the applying scope⁷. Such reports mainly concentrated in witting rearrangement, Grignard type of reaction, Heck reaction, elimination reaction, *etc.*

Witting reaction is an important way to introduce olefinic bond, with mild reaction condition, high yield and no isomers. It can also synthesize some acid-sensitive olefins⁸. To overcome the difficult separation, the workers use phosphate instead of triphenylphosphine to prepare witting reagent.



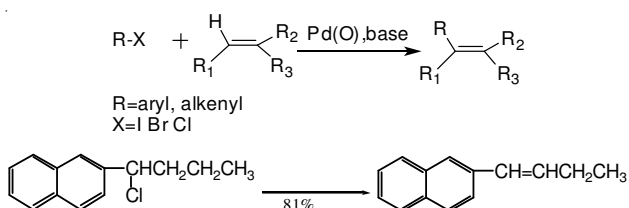
The reaction of alkyl halide with lithium in non-polar solvent with good selectivity has been reported in many papers. Yue and his group members have done a lot of researches since 1996⁹⁻¹⁴.



This method with mild conditions, easy getting material is only applicable to compound that can load negative charge at a position of G group, such as ethylene, benzene, or acetylene. When there is unstable substituent to negative charge such as H, R will be difficult to migrate. Also Li is so lively that can be broken down when reacted with water, alcohol, acid, so it should pay attention when preparation and use.

Palladium-catalyzed Heck reaction has been among the most important ways in synthetic organic chemists for C=C in the last 30 years. To overcome the catalyst, difficult purification and shorter life, loading Pd on the inorganic or organic polymer carriers are reported¹⁵.

Also benzyl-type chlorinated hydrocarbon can carry out the elimination reaction.

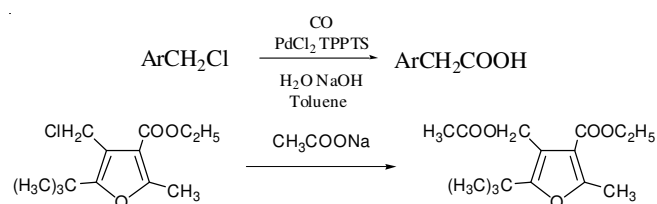


They can also react with hydroxyl, carboxyl, carboxylic acid with C=C bond.

Introduction of R-CO-R: Carbonylation of benzyl-type chlorinated hydrocarbons in the presence of nucleophilic reagent, such as H₂O, ROH, RNH₂ or RCOOH can respectively provide carboxylic acid, ester, amide or the mixture.

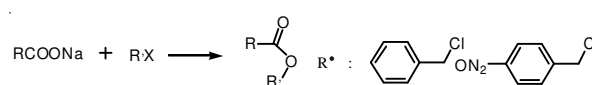
Benzyl-type chlorinated hydrocarbons tend to occur elimination reaction with nucleophiles. So its carbonylation needs large amounts of catalyst and phase transfer agent and the recovery and recycling can restrict industrial application, but green, simple and low cost.

Pevzne¹⁶ achieved esterification with long time and tedious post-processing.

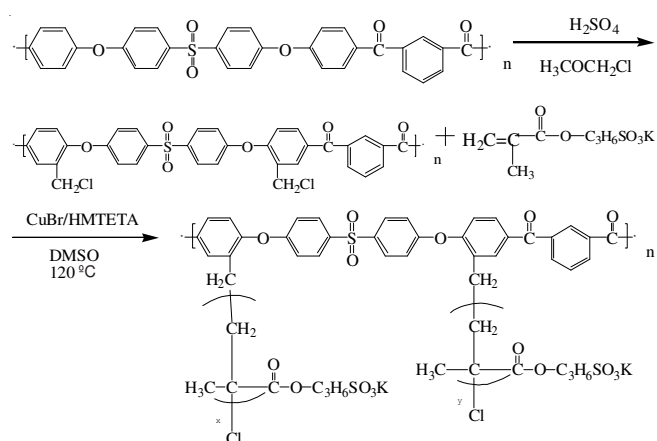


Qiujiang¹⁷ studied this route in the presence of PTC, which made shorter time and higher yield.

Brinchi and his group achieved this reaction in ionic liquid, with mild reaction condition, simple post-processing, easy products separation, no use of toxic solvents and recycled ionic liquid¹⁸.

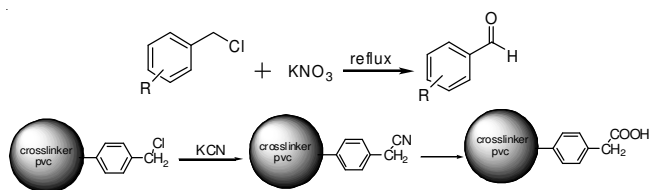


Zeng *et al.*¹⁹ synthesized the copolymer *via* atom radical polymerization.

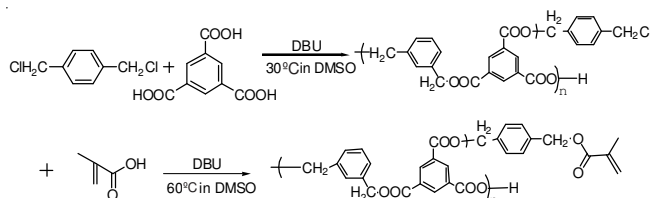


There are many researches on oxidation of benzyl-type chlorinated hydrocarbons, such as Sommelet oxidation, Hass. Bender oxidation, Krohnke and Komblum oxidation, which usually produce a large pollution. New methods that adsorb oxidation on a variety of inorganic carriers or take ionic liquid as reaction media, but the preparation is too complex and expensive, so they only stay at academic level²⁰.

The reaction with NaCN/KCN is easy. But the toxic reagent is not good to operator and environment.

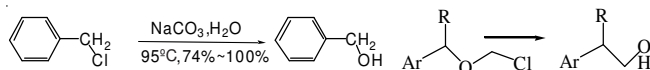


The reaction with carboxyl groups catalyzed by DBU as a base is also common with short reaction time, simple post-processing, high selectivity and yield, but the side chain such as hydroxyl would affect the selectivity²¹.



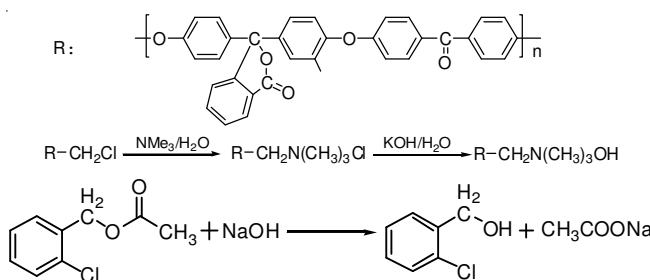
Introduction of hydroxyl group: The introduction of -OH group can improve the polymer hydrophilic. The common paths are hydrolysis, Grignard reaction with lithium, hydrolysis after quaternary ammonium, *etc.* The hydrolysis is easy to carry out.

Gomez *et al.*²² used the lithium Grignard reaction under mild condition.



Xiong *et al.*²³ added OH indirectly, but the separation is difficult and more steps.

Quijiang *et al.*¹⁷ got chlorobenzylalcohol. Reducing rate of benzyl ether can reduce the environmental pollution and improve the yield of target.

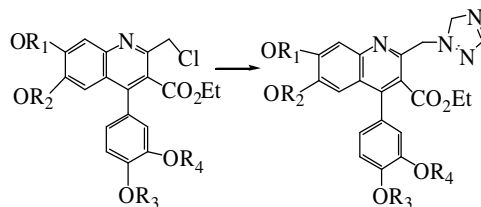
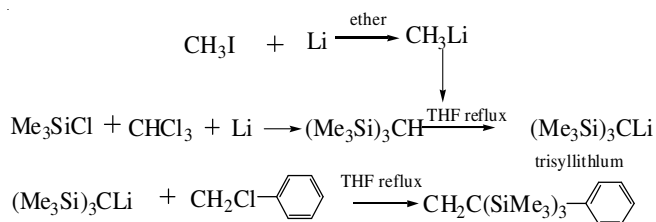


Introduction of heterocyclic ring: Introducing the required heterocycle to modify polymers can make them better performance.

The C=N imine of Schiff base complexes is a very lively group, which can be reduced to amines or react with Grignard reagent to synthesis important organic intermediates^{24,25}. Combining C=N can make add different organic or inorganic polymers more flexible.

Safa and Babazadeh²⁶ realized modification of organic silicon with good thermal stability, high weatherability, selective permeability. But it was strict to temperature and also easy polymerization of targets.

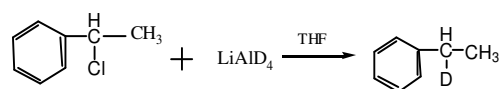
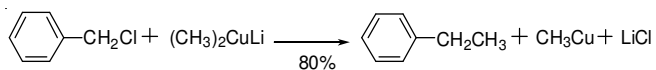
Mizuno *et al.*²⁷ designed to product metabolites by Friedel-Crafts reaction.



Reaction with amino compounds: The benzyl-type chlorinated hydrocarbon tends to occur substitution with amine, the most common type is Menshutkin reaction. Some have been commercialized, for example benzyl triethyl ammonium chloride is an excellent phase-transfer catalyst²⁸⁻³⁰. But this reaction should be in high polar organic media and always need long time and the quaternized attack has steric hinderance when the stereostructure is complex and the separation is difficult too.

-CH₂Cl can be substituted by NHR₂(H) getting mon-amine, di-amine, *tri*-amine which are important organic intermediates^{24,31}.

Generation of aromatics: The most common methods to give aromatics are direct reduction and Corey-House reaction.



Corey-house gets products from Benzyl chloride and dialkyl copper lithium. It is an important path to get complex alkanes or aromatics and even fit to inactive halogenated hydrocarbon; but the latter adopts lithium aluminum hydride as reducing agent which only can be in anhydrous medium, although it is able to synthesize optically active alkane, but there are few reports because of its defects such as the stereochemistry of product is not obvious with difficult hydrogenolysis and slow process, *etc.*

Conclusion

Benzyl chloride and its derivatives are important precursors of many functional polymers. Using these as starting materials various functional polymers can be obtained *via* further reactions. Such reactions should pay attention to adopt paths of safe, effective, easy preparation and recovery, also take the place of technology, which use toxic reagents or unfavourable to the industrial extension. Although in recent years reports about these reactions are diversified, some routes with high yield are studied because of the use of ionic liquid and harsh reaction conditions limit the industrialization.

We believe that the study of mechanism could make the route design more effective, with the progress of chemical industry these reactions are expected to be widely used in wider fields. In summation, they can play an active role in benefiting mankind and promoting social progress.

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