CRDEEPJournals SJIF Imapct Factor: 2.912
Global Journal of Current Research Abdel-Malek & Ewies Vol. 3 No.1 ISSN: 2320-2920
Global Journal of Current Research Vol. 3 No. 1. 2014. Pp. 1-21

Review Research Paper

Phase-Transfer Catalysis in Organic Syntheses

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Abstract

Phase-transfer Catalysis (PTC) can increase yields, reduce cycle times, eliminate hazardous or expensive reagents and solvents, and provide numerous other benefits to organic chemical manufacturers, so that much effort has been directed toward the coupling of phase-transfer catalysis with asymmetric synthesis. There are hundreds of industrial applications of PTC for a variety of processes of organic synthesis and major advantages of PTC in industrial applications; which easily recognized in the given examples. Also, many synthetic approaches of PTC are discussed in this review.

Keywords: *Phase-Transfer Catalysis, Organic Synthesis, Carbanions, Application*

Introduction

Organic synthesis is the principal way to produce chemical products of practical applications such as pharmaceuticals, plant protection agents, dyes, photographic chemicals, polymers etc. Transformation of starting materials into desired final products usually require a number of chemical operations in which additional reagents, catalysts, solvents, etc, are used. Thus, in the course of synthesis, besides the desired products, many waste materials are produced because transformations of educts into products are not quantitative and selective processes particularly due to the use of these additional components. These wastes should be regenerated, destroyed and disposed, consuming much energy and creating heavy burden on the environment. It is there for of great importance to develop and use synthetic methodologies that minimize these problems. Perhaps one of the most general and efficient methodologies that fulfill this requirement is phase-transfer catalysis (PTC): (Makosza and Serafin 1965, Makosza and Fedornski 1987, Makosza 2000, Starks 1971, Starks et al 1994, Starks and Owen 1973, O'Donnell and Dennett, 1989, Dehmalo and Dehmalow 1993) (Figure 1).

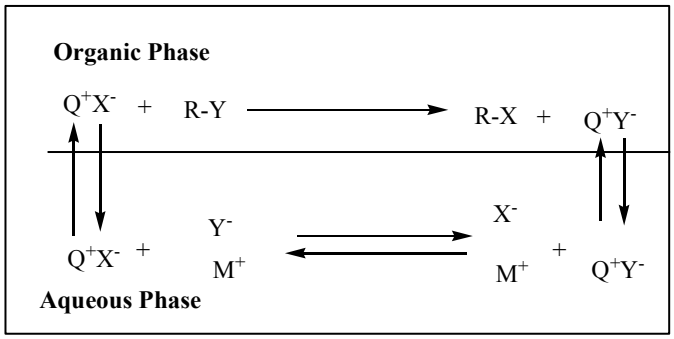


Figure 1. Phase-Transfer Catalysis

The PTC method (Makosza 2000) involves bringing together a substrate (e.g. R-Br) which is soluble in an organic layer and an anion (e.g. CN^-) which prefers to be in an aqueous layer. The substrate and anion are brought together by a catalyst, usually an alkyl quaternary ammonium salt (R_4N^+) (Kulinski and Jonczyk 1992, Pielichowski and Popielarz 1984, Pielichowski and Bogdat 1989) which transports the anion into the organic phase where it can react with the substrate (Figure 2).

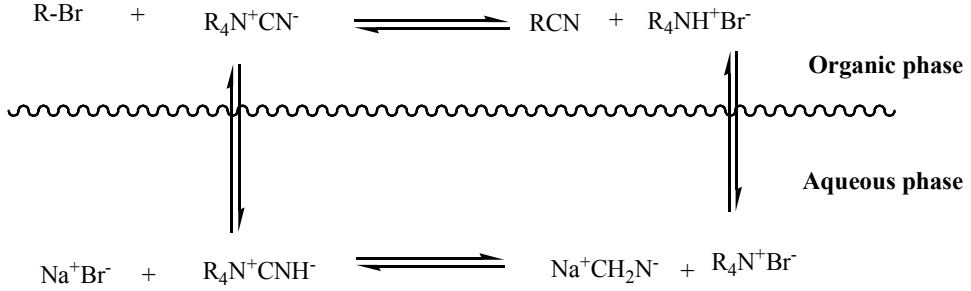


Figure 2: Phase-Transfer Catalysis method

There are several advantages for the PTC system over single-phase systems including improved reaction rates, lower reaction temperatures and the absence of expensive anhydrous or aprotic solvents. In fact, certain reactions have been found to proceed in a PTC system that would not otherwise work.

Reagents used as Phase Transfer Catalysts

1. **Quaternary Ammonium Salts**

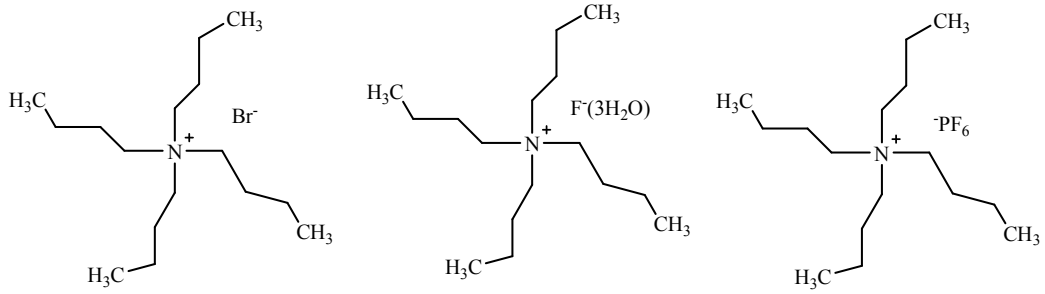


Figure 3: Quaternary Ammonium Salts

1. **Cinchona Alkaloid-Derived Quaternary Ammonium Salts** (Gockel and Weber 1978, Dalko and Moisan 2001, O'Donnell 1993, Sasson 1997).

Cinchona alkaloids are a family of natural products that can be isolated from cinchona trees. The following four alkaloids are the most abundant and can be easily isolated from the bark of the trees. :

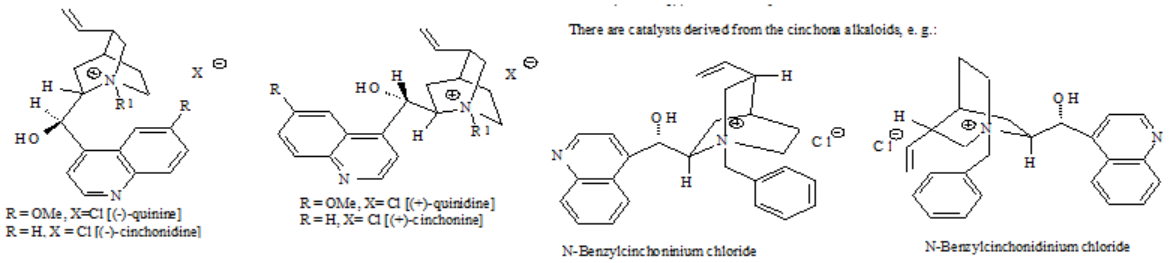
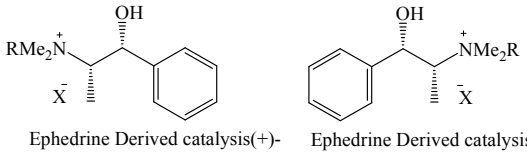


Figure 4: Cinchona Alkaloid-Derived Quaternary Ammonium Salts

2. **Ephedrine-Derived Catalysts** (Brunner et al 1995, Lygo et al 1997, Loupy and Zaparucha 1993)



R = $-CH_2-C_6H_5$; X= Cl

Figure 5: Ephedrine-Derived Catalysts

3. **Maruoka Catalysts (Quaternary Ammonium catalysts with C_2 symmetry)** (Ooi et al 1999, 2000, 2001)

Maruoka (Ooi et al 1999) designed an array of C_2-symmetric, biaryl spiro ammonium catalysts.

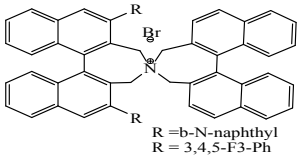


Figure 6: Quaternary Ammonium catalysts with C_2 symmetry

4. **Quaternary Phosphonium salts** (Kisch et al 1986, Alper 1981, McNulty et al 2004, Dehmlov 1977)

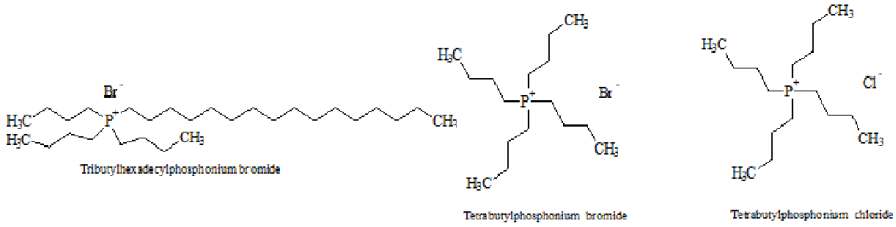


Figure 7: Quaternary Phosphonium salts

5. **Crown Ethers** (Pugia 1986, Mathias and Carraher 1984, Ganboa 1986, Valentine 1975, Artamkina et al 1984, Salisova 1979, Vogtle 1803, Gockel 1976, Izatt et al 1971, Baker 1981, Wingfield 1980)

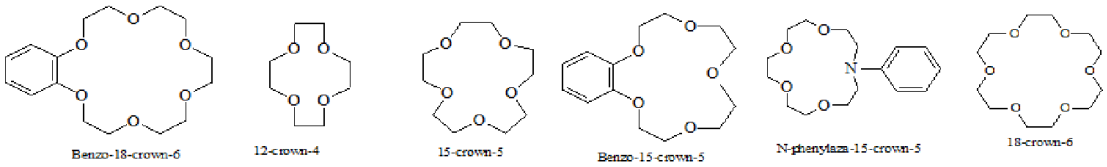


Figure 8: Crown Ethers

6. **Polyethylene glycol (PEG)**(Neumann 1985)
   $HO(C_2H_4)_nH$

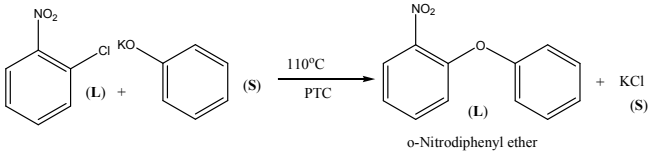
Modes of operations of Phase transfer catalysis

There are two modes of operations in PTC

1- Liquid-liquid phase transfer catalysis (L-L)PTC(Lygo et al 1999)
2- Solid-liquid phase transfer catalysis (S-L)PTC (Yadav 2004)

Phase transfer catalysis has been applied in many industrial processes. A large number of PTC processes use the liquid-liquid phase transfer catalysis (L-L PTC) mode of operation. PTC has been quite successful for C,N,O and S-alkylations involving SN_2 type reactions in fine chemical industries, apart from dehydrohalogenations.

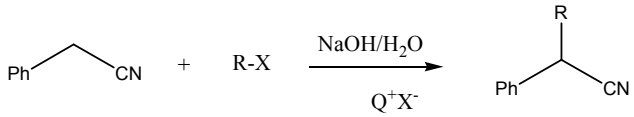
o-Nitrodiphenyl ether (Yadav 2004) is an important intermediate in the fine chemical industry and used in a number of drugs. This ether is typically prepared from *o*-chloronitrobenzene (OCNB) by condensation with alkli metal phenoxide in toluene or xylene in presence of copper or cuprous chloride and the process requires a high temperature to initiate the formation of the cuprous salt of phenol. Once initiated, the reaction is exothermic and can sometimes become uncontrolled leading to the formation of tarry masses. However, synthesis of *o*-nitrodiphenylether was accomplished by reacting o-chloronitrobenzene with solid potassium phenoxide using tetra-*n*-butylphosphonium bromide as catalyst under solid-liquid phase transfer catalysis (S-L PTC) (Scheme 1). The advantages of solid-liquid phase transfer catalysis (S-L PTC) are that the reaction is conducted at controllable temperature, the reaction rate are increased by orders of magnitude and the reaction is 100% selective, in comparison with liquid-liquid phase transfer catalysis (L-L PTC) which is very slow and yields by-products. The mechanism based on homogenous solubilization of solid resulting in the formation of an active ion-pair with nucleophile, was found to prevail in the system.



Scheme 1

Phase transfer catalysis in the chemistry of carbanions

From the original work of Makosza in 1965, to the pioneering efforts of Starks (1971), and onward to the advances of O'Donnell (1989); Phase-transfer catalysis (PTC) has played a large role in organic syntheses .Alkylation of carbanions with alkyl halides; a process of great commercial value, was studied as a good model for such PTC reactions, using tetraalkylammonium (quat) salt (Q^+X^-) as PTC catalyst. Particularly important for pharmaceutical industry is alkylation of phenylacetonitrile .This reaction was the first practical example of the application of PTC in organic syntheses and industry (Makosza 1965). Many characteristic features of this type of catalysis have been disclosed using this example as a model process.

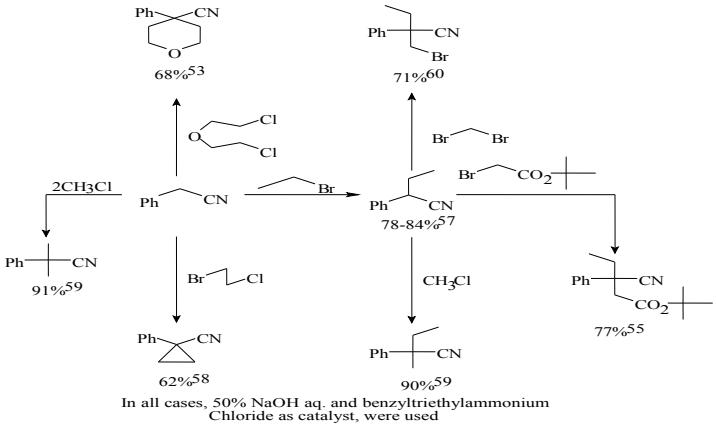


Scheme 2

No reaction occurs when a mixture of phenylacetonitrile, an alkyl halide and 50% aq. NaOH is vigorously stirred. Upon introduction of tetraalkylammonium halide in a catalytic amount, usually 1% molar, an exothermic reaction occurs and produces phenylalkylacetonitrile (Makosza 1976) (Scheme 2). The Phase transfer catalysis alkylation of carbanions, exemplified by the reaction of phenyl acetonitrile, is a general process applicable to a great variety of carbanion precursors such as arylacetonitrile derivatives (2-alkoxy (Makosza 1972), 2-dialkylamino (Makosza et al 1968), ….etc), Schiff bases derived from acetonitrile (O'Donnell 1994), many ketones (Jonczyk et al 1971) (acidic hydrocarbons, cyclopentadiene (Menchikov et al 1985), indene (Makosza 1966), benzyl-,(Golinski et al 1979), halomethyl-(Jonczyk 1975), allylphenyl (Jonczyk 1983) and Reissert compounds) (Makosza 1969).

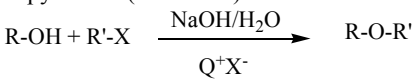
Alkylation

Nearly every type of haloalkane can be used in alkylation reactions: mono- and dihaloalkanes(Makosza 1966), halonitriles (Lange 1967), esters of haloacetic acids (Makosza 1969), etc. PTC conditions are very favorable for cycloalkylation reactions with α,ω-dihaloalkanes (Scheme 3)



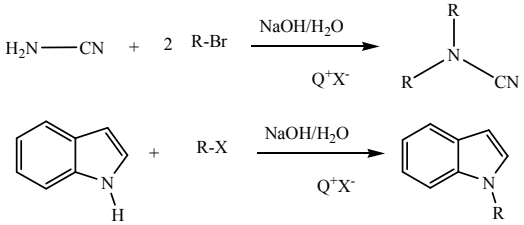
Scheme 3 alkylation reactions *via* PTC

High selectivity of mono- and not dialkylation is usually observed under Phase transfer catalysis conditions compared to other base/solvent systems(Makosza 1968). Also, Phase transfer catalysis is an efficient methodology for O, N, S and P alkylation of alcohols, phenols, amides, Heterocycles, thiols, phosphorus compounds, etc, via corresponding anion. For example, a variety of dialkyl ethers can by synthesized conveniently by the treatment of alcohols and alkyl halides or sulfones with concentrated aqueous sodium hydroxide or even anhydrous potassium carbonate and PTC catalyst, instead of the traditionally used sodium hydride, sodium amide, sodium metal or lithium diisopropylamide (Scheme 4).



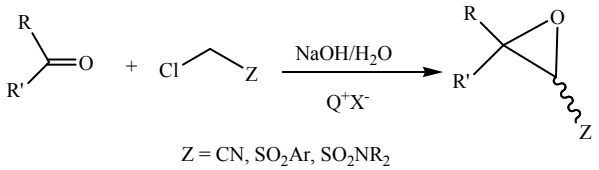
Scheme 4: PTC alkylation of alcohol to yield dialkyl ethers

Many examples exist of the value of PTC for N-alkylation of nitrogen heterocycles such as pyrrole, indole, benzothiazine, imidazole, etc, as well as amides and imides. PTC is also the system of choice for nitroarylation of these O-, N-, and S-aniones (Scheme 5).



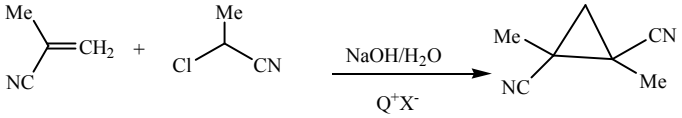
Scheme 5: PTC for N-alkylation of nitrogen heterocycles

PTC is also very convenient for many others reactions of carbanions, especially those containing leaving groups such as a halide (Jonczyk et al 1972 and Golinski 1978), or a sulfonium group (Merz 1973). Drazens condensation of α-halocarbanions or sulfur ylides with aldehydes and ketones blonges to this category (Scheme 6)



Scheme 6: Drazens condensation of α-halocarbanions or sulfur ylides with aldehydes and ketones

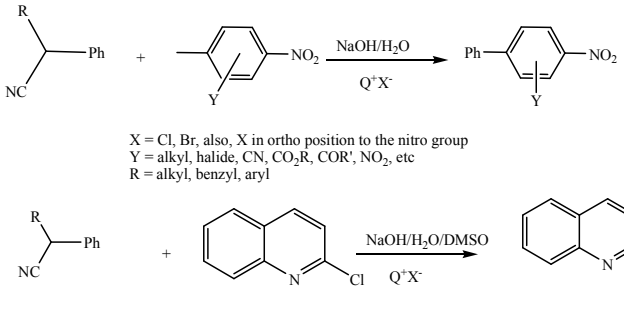
Another example is addition of these active intermediates to electrophilic alkenes, followed by an interamolecular SN_2 reaction, leading to cyclopropane derivatives (Scheme 7)



Scheme 7: synthesis of cyclopropane derivatives

Nitroarylation

For nitroarylation of active carbaninos, such as phenylacetonitrile derivatives, PTC conditions offer the most convenient route(Makosza et al 1974). When other base/solvent systems (e.g. sodium amide/liquid ammonia) are used to generate carbanions, the nitroarylation proceeded much less efficiently or not at all. Halides in some heteocycles (9-chloroacridine (Wilizynski et al 1977), 2-chloroquinoline (Jawdosiuk et al 1979), 4-chloropyridine-N-oxide (Jawdosiuk et al 1979), etc) can undergo substituted by 2-phenylalkanenitrile carbanions under PTC conditions(Gallo et al 1984) (Scheme 8)



Scheme 8: Nitroarylation of active carbaninos via PTC

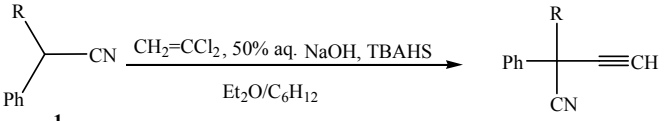
Application of phase-transfer catalysis (PTC) to reactions of C-H acids with chloroethylenes

1,1-Dichloroethylene (vinylidene chloride VC), cis-1,2-dichloro-ethylene (cis-DE) or trichloroethylene (TRE) easily eliminate hydrogen chloride with formation of chloroacetylene (CA)(Kulinski 1992) or dichloroacetylene (DCA)(Pielichowski 1984, 1989), respectively, when treated with an alkali metal hydroxide in the presence of a quaternary ammonium salt (Kulinski 1992 and Pielichowski 1984), or in aprotic dipolar solvent (Pielichowski 1989), (phase-transfer catalysis, PTC)(Makosza et al 2003). Both CA and DCA exhibit electrophilic properties hence easily add nucleophiles. From practical point of view, the nucleophiles are usually present in reaction mixture, adding to *in situ* generated CA or DCA. Thus, PTC technique was successfully applied to reactions of TRE with oxygen(Pielichowski 1988), selenium (Martynov et al 1985, 1988, 1989) and nitrogen (Pielichowski 1984, 1994, 1995, Bogdat 1994) nucleophiles leading to formation of the corresponding 1,2-dichlorovinyl substituted derivatives and/or other products

1-

2- Reaction of 2-substituted phenylacetonitriles with vinylidene chloride (VC) or cis-dichloroethylene (cis-DE).

Nucleophiles, including carbanions, add to the mono-substituted triple bond usually in trans-fashion with formation of cis-products (Makosza 1966, Deslongchamps 1983, Jonezyk 1996). cis-Adducts formed from carbanions and CA should easily eliminate hydrogen chloride giving ethynylated C-H acids. Indeed, stirring of 2-alkyl substituted phenylacetonitriles **1a-g** with VC, 50% aq. sodium hydroxide and tetra-n-butylammonium hydrogensulfate (TBAHS) as a catalyst, resulted in 2-ethynyl substituted nitriles **2a-g** in good yields(Jonezyk 1991, and Kulinski 1994)(Scheme 9)



R 1,2	a Me	b Et	c i-Pr	d CH_2=$CHCH_2$	e $PhCH_2$	f $PhCH_2$	g i-Pr-$N(CH_2)_2$
Yield %	61	81	70	75	83	89	90
Purity %	≥98	≥98	95	92	92	≥98	≥98

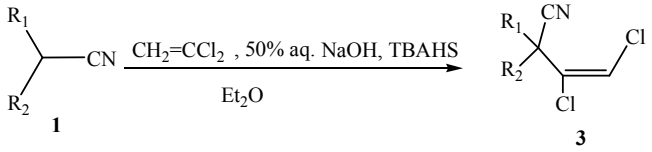
Scheme 9: reaction of 2-substituted phenylacetonitriles with VC or (cis-DE)

The process was carried out at reflux (ca. 40°C) of cyclohexane/ethyl ether mixture, for 2.5-5h, but preparation of the sterically crowded *i*-propyl derivative **1c** required longer time, under inert gas. The use of the latter is essential to prevent oxidation of nitriles **1** to the corresponding phenones and the violent burning of chloroacetylene in air. For the latter reason the use of ethyl ether is very desirable since it stabilizes chloroacetylene by formation of complexes (Hopf 1995) the process did not take place without the catalyst. Essentially the same results gave cis-DE, but its use did not show any advantages. Also, it is much more expensive than VC. Careful examination of a mixture from the reaction of **1a** with VC carried out at 18°C revealed the presence of a small amount of trans-2-chlorovinyl- and 1-chlorovinyl substituted derivatives, the latter was converted into **2a** after prolonged reaction. These compounds may result from cis-addition of **1a** to CA and its addition to C-1 of CA, respectively.

3- Reactions of C-H acids with trichloroethylene (TRE)

a- Reactions of 2-substituted phenylacetonitriles

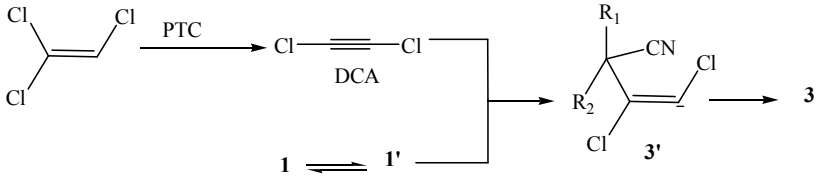
Different products namely trans-1,2-diclorovinyl substituted nitriles **3** were formed in high yields when 2-substituted phenylacetonitriles 1 were allowed to react with TRE under PTC conditions (Scheme 10)



1,3	a	b	c	e	h	i	j	k	l	m
R1	Ph	Ph	Ph	Ph	Ph	Ph	Ph	Ph	Ph	Ph
R2	Me	Et	i-Pr	$PhCH_2$	$Me_2N(CH_2)_2$	Me_2N	$O(CH_2CH_2)N$	MeO	i-PrO	Cl
3 Yield %	66	67	75	76	70	60	69	65	65	61

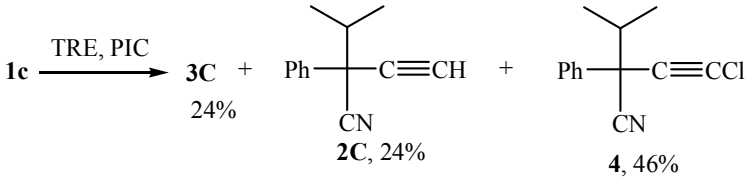
Scheme 10: Reactions of C-H acids with (TRE)

A reasonable route of formation of **3** is representing by (Scheme 11)



Scheme 11: formation of trans-1,2-diclorovinyl substituted nitriles (3)

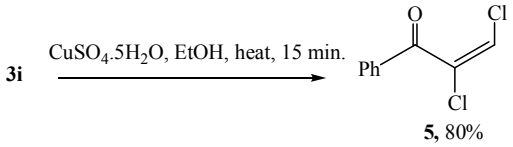
The carbanion **1** by *trans*-addition to DCA produces highly basic dichlorovinyl anions **3** which after protonation afforded *trans* products **3**. The process was carried out at 5-10°C in ethyl ether. Benzyltriethylammonium chloride (BTEAC) was less effective as a catalyst than TBAHS. When the reaction. When the reaction of nitrile **1c** with TRE was performed at *ca* 35°C products **2c** and **4** predominated, (yields determined by GC) (Scheme 12).



Scheme 12

Product **4** may be formed either *via* a cis-addition of **1c** to DCA and subsequent elimination of hydrogen chloride, *via* halogenophilic reaction of **1c** with DCA or less probably, via addition of this anion to TRE, followed by elimination of two equivalents of hydrogen chloride. All these mechanisms were identified in reactions of nucleophiles with TRE or DCA (Miller 1976 and Kende 1984). Ethynyl substituted derivative **2c** probably results from a halgenophilic attack by any anion present in the system on **4**.

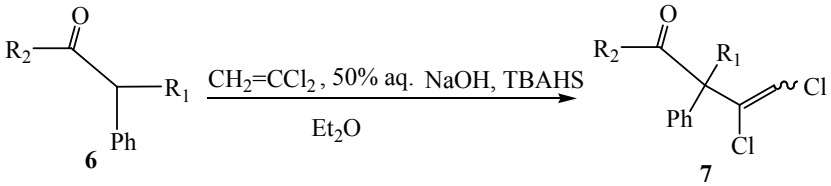
Dichlorovinylation of nitriles substituted at C-2 with a heteroatom afforded products **3i-m** which after unmasking of the carbonyl group should give dichlorovinyl-substituted ketones. This transformation was exemplified by efficient conversion of nitrile **3i** into *trans*-dichlorovinylphenyl ketones **5** (Scheme 13).



Scheme 13: conversion of nitrile 3i into *trans*-dichlorovinylphenyl ketones 5

b- Reactions of α-substituted desoxybenzoines and α-substituted phenylacetaldehydes

Desoxy-benzoines α-substituted with alkyl (**6a-e**) or heteroatom (**6f-h**) group react with TRE in the presence of 50% aq. sodium hydroxide and TBAHS as a catalyst in ethyl ether to give the expected products **7** usually as mixtures of *trans*- and *cis*-isomers (Jonczyk 2000, 2001) (Scheme 14).



6,7	a	b	c	d	e	f	g	h	i
R1	Me	Et	i-Pr	$CH_2=CHCH_2$	$PhCH_2$	Cl	PhO	PhS	CN

R2	Ph	Ph	Ph	Ph	Ph	Ph	Ph	Ph	Ph
7 Yield %	63	71	62	54	79	62	76	83	40

Scheme 14: reaction of Desoxy-benzoines α-substituted with TRE

Results of these investigations indicate that simple PTC methodology allows synthesizing a variety of ethynylated, 1,2-dichlorovinylated or 2-chlorovinylated C-H acids using cheap cholroethylenes. Utilization of other C-H acids, elucidation of mechanistic aspects of these processes as well as application of the products formed in organic synthesis, is actually searched.

Chiral Phase-Transfer Catalysis

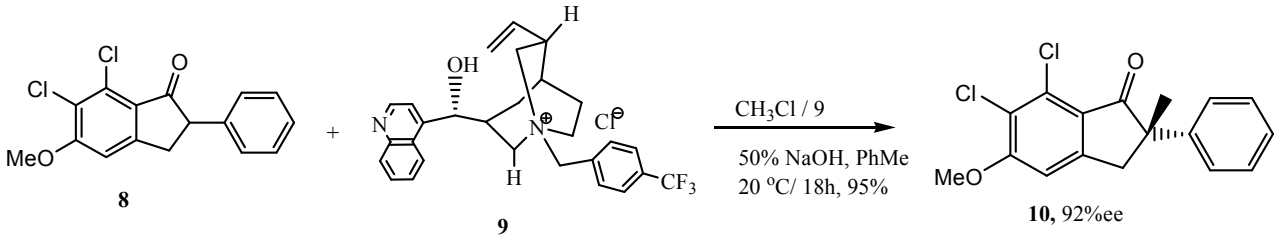
The growing importance of enantiomerically pure compounds for life-science applications has fueled a wealth of research in asymmetric synthesis. The importance of the field was underscored in 2001 when the Nobel Prize in Chemistry was awarded to W. S. Knowles, K. B. Sharpless, and R. Noyori for their work in asymmetric analysis. Numerous commercial processes involving asymmetric synthesis are now practiced.

Given that Phase-transfer Catalysis can increase yields, reduce cycle times, eliminate hazardous or expensive reagents and solvents, and provide numerous other benefits to organic chemical manufacturers, so that much effort has been directed toward the coupling of phase-transfer catalysis with asymmetric synthesis. Examination of asymmetric PTC reactions began in the mid-1970's and has continued at an accelerating pace, along with asymmetric catalysis in general, to become the most active area of academic PTC research. Excellent reviews exist on the subject of chiral PTC, and these may be consulted for additional information (Starks et al 1994, O'Donnell et al 1994, Sasson et al 1997, O'Donnell 2001, Dolling et al 1984). In particular, review by O'Donnell (1993) is exceptionally comprehensive through 1999

This article provides an overview of the reactions of Chiral Phase-transfer Catalysis, highlighting key results from the first low enantiomeric excess reactions, through the development of catalysts based on cinchona alkaloids (Dalko 2001), ephedrinium salts (Brunner 1995), the Maruoka catalysts (Ooi 1999) and the crown ethers (Pugia 1986). A wide variety of reactions have been examined, but the bulk of the publications have dealt with alkylations, Michael addition reactions, Darzens reaction, Aldol reactions and epoxidations:

1. Alkylations

One of the most impressive uses of chiral PTC involves the alkylation of 6,7-dichloro-5-methoxy-2-phenyl-1-indanone (**8**) with methyl chloride with chiral catalyst **9** to give **10**. Through a systematic study of reaction conditions, kinetics and reaction mechanism, a 92% ee of adduct **10** was obtained (Dolling et al 1984) (Scheme 15).



Scheme 15: uses of chiral PTC involves the alkylation of 6,7-dichloro-5-methoxy-2-phenyl-1-indanone (8)

The proposed interactions between the enolate and the catalyst are π-π stacking interactions, a hydrogen bond between the oxygen anion and the hydroxyl group of the catalyst as well as electrostatic effects (Lipkowitz et al1991).

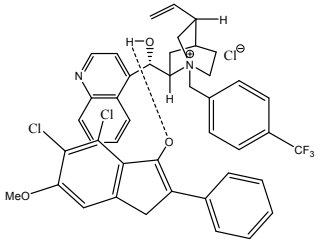
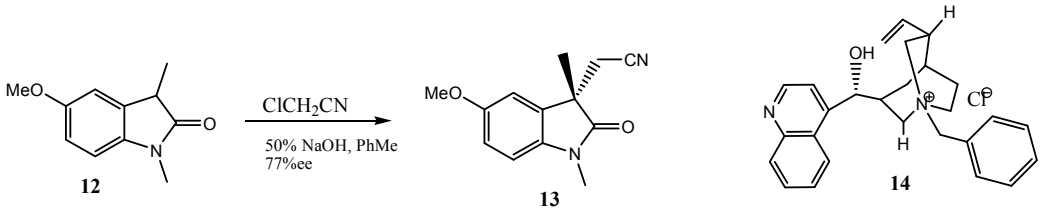


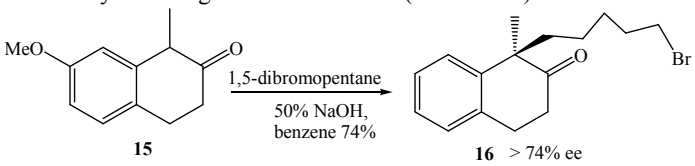
Figure 9

Another alkylation which used asymmetric PTC methods was the key step in the synthesis of (-)-physostigmine (11) (Lee et al 1996). Alkylation of **12** to give **13** was produced in good yield and in 77% ee, using the catalyst **14** (Scheme 16).



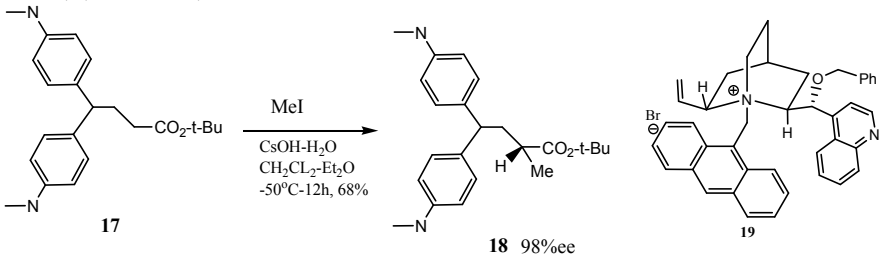
Scheme 16: synthesis of 2-((S)-5-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)acetonitrile (13)

An asymmetric PTC alkylation was also achieved by treating tetralone **15** with 1,5-dibromopentane in the presence of catalyst **9**. This yielded alkylated species **16** in 74% yield and greater than 74% ee (Scheme 17).



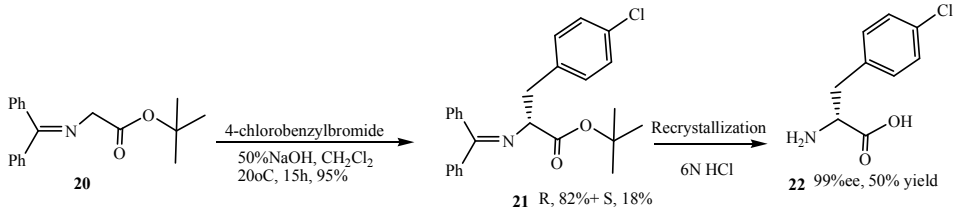
Scheme 17: treating tetralone 15 with 1,5-dibromopentane

Tert-butyl 4,4-bis(4-(methylamino)phenyl)butanoate**17** was alkylated to give **18** with a number of electrophiles in the presence of catalyst **19** (Corey et al 1998) (Scheme 18).



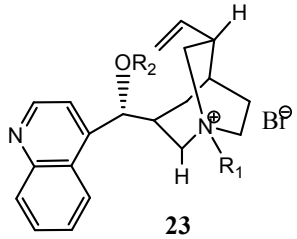
Scheme 18: alkylation of tert-butyl 4,4-bis(4-(methylamino)phenyl)butanoate

The synthesis of optically pure amino-acids has long been a goal of synthetic chemists (Williams 1989), and the use of asymmetric PTC in the enantio-selective synthesis of α-amino-acids has been achieved (O'Donnell et al 1997). The original work, published in 1978, was on the racemic alkylation of glycine Schiff base esters such as **20** (O'Donnell 1978). The first generation of chiral catalyst for alkylation of Schiff base (t-butylglycinate benzophenoneimine) **20** was achieved using catalyst **14** and gave, after recrystalization and deprotection, compound **22** in a 99% ee (O'Donnell 1989) (Scheme 19).



Scheme 19: the racemic alkylation of glycine Schiff base esters

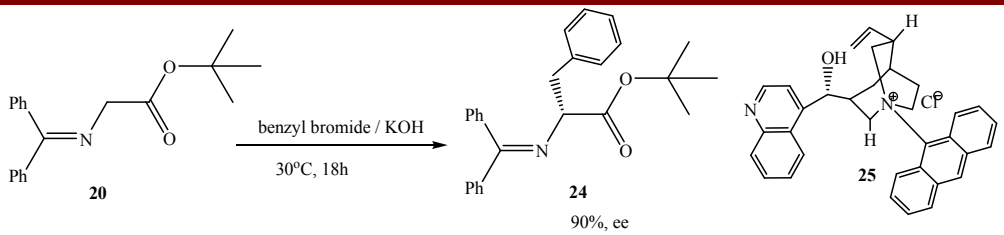
Over the years, several improvements to the alkylation of the Schiff bases were developed. The first involved the preparation of a second generation of chiral catalysts, the N,O-dialkylated salts (**23a-c**) which gave higher initial selectivities in the alkylation of **20** (up to 81% ee) (O'Donnell 1994) (Fig. 10). Strong evidence from this work indicated that the oxygen on catalysts such as **14** was alkylated *in situ* and that the N,O-alkylated salts were the catalysts responsible for stereoselectivity.



a, R1 = Bn, R2 = Bn
b, R1 = allyl, R2 = alkyl
c, R1 = Bn, R2 =allyl

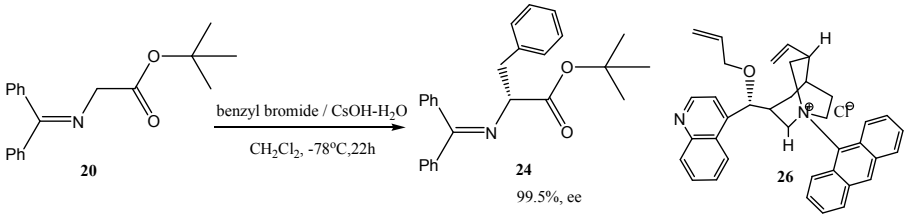
Figure 10: chiral catalysts, the N,O-dialkylated salts

A third generation of catalysts; the N-9-anthracenylmethyl salts (**25** and **26**), was developed independently by Lygo (1997) and Corey (1997). The Lygo group used catalyst **25** to alkylate Schiff base **20** in good to excellent ee's. An example is using benzyl bromide as the electrophile (Scheme 20).



Scheme 20: uses of catalyst 25 to alkylate Schiff base 20

The Corey (1997) group used a similar catalyst **26** and alkylated **20** with **11** different halides. Their changes in the reaction conditions (CsOH-H_2O, -60 to –78°C, CH_2Cl_2) led to very impressive enantiomeric excesses, an example, again by using benzyl bromide (Scheme 21).



Scheme 21: used catalyst 26 to alkylate Schiff base 20 with different halides

A novel approach to the alkylation of **20** using PTC as a heterogeneous catalyst was recently reported. This method used Schwesinger bases in conjunction with chiral catalyst **27** or **28** to achieve asymmetric induction in a heterogeneous reaction mixture (O'Donnell et al 1999). Enantiomeric excesses ranging from 56-94% with a variety of alkyl, allylic and benzylic halides were observed. Syntheses of the naturally occurring bis-α-amino acids units *via* asymmetric PTC alkylation of a glycine imine, using *N*-anthracenylmethylcinchonidium chloride, as catalyst (Figure 11)

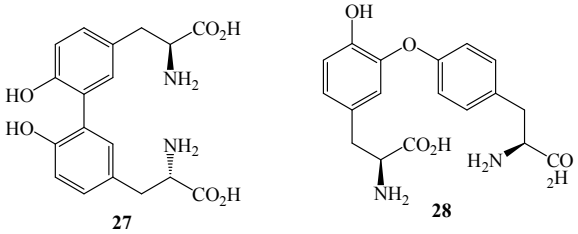
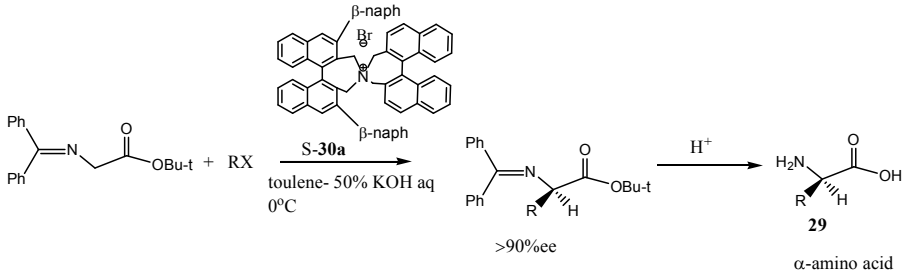


Figure 11: heterogeneous catalyst

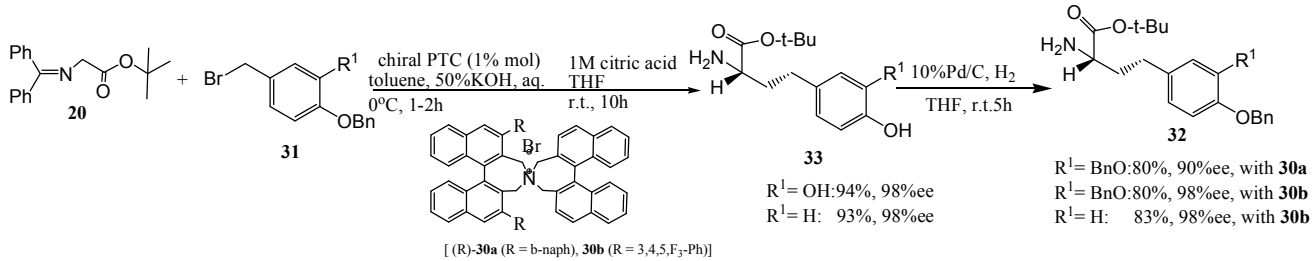
Recently, the fourth generation of the Maruoka catalysts (Ooi et alv1999) has reported the rational molecular design of C_2-symmetric chiral quaternary ammonium salt (S)-**30a** as a new chiral phase-transfer catalyst and demonstrated its remarkable efficiency in the catalytic enantioselective alkylation of *tert*-butyl glycinate-benzophenone Schiff base (**20**) under mild phase-transfer conditions. Since both enantiomers of the catalyst of type **30** can be readily assembled in exactly the same manner starting from either (R)- or (S)-binaphthol, a wide variety of natural and unnatural α-amino-acids **29** can be synthesized in an enantiomerically pure form by the phase-transfer catalytic alkylation of substrate **20**. A successful utilization of this advantage for the facile synthesis of L-Dopa (L-3,4-dihydroxyphenylalanine) esters (Brunner-Guenat et al 1995), was described (Scheme 22).



Scheme 22

Catalytic phase-transfer alkylation (Ooi et al 2000) of **20** with benzyl bromide derivative **31** (R^1 = OBn) (1.2 equiv.) in toluene-50% KOH aqueous solution (volume ratio = 3:1) proceeded smoothly at 0°C in the presence of (R)-**30a** (1 mol%) to furnish fully protected L-Dopa *tert*-butyl ester, which was subsequently treated with a 1M citric acid in THF at room temperature for 10 h to afford the corresponding amino-ester **32** (R^1 = OBn) in an 80% isolated yield. Although the enantiomeric excess was determined to be 90% ee by chiral HPLC analysis, it did not seem fully satisfactory because further purification such as recrystalization would be required to increase the enantiomeric purity. Therefore, (R)-**30b** was employed as a catalyst (Ooi et al 2000) and found that the alkylation of **20** with (R)-**30b** (1 mol%) and **31** (R^1=OBn; 1.2 equiv.) under otherwise indentical conditions gave rise to the amino-ester **32** (R^1=OBn) with excellent enantioselectivity (98% ee). Debenzylation of **32** (R^1=OBn) under catalytic hydrogenation conditions produced the desired L-Dopa tert-butyl ester (**33**, R^1 = OH) in 93% yield. Being exemplified by the feasibility of

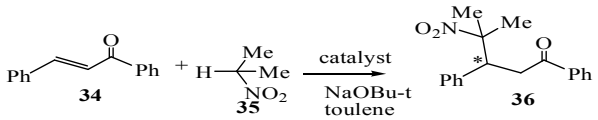
asymmetric synthesis of natural tyrosine tert-butyl ester (**33**, R^1 = H), the present concise and practical procedures should enable highly enantioselective synthesis of various L-Dopa analogues and related α-amino-acids (Scheme 23).



Scheme 23: Catalytic phase-transfer alkylation

2. Michael addition reactions

Michael addition of carbon nucleophiles to conjugated enones is one of the most powerful methods for carbon-carbon bond formation. Due to its relevance in the synthesis of biologically active compounds, much efforts have been focused on carrying out this reaction in a stereoselective way. One of the most attractive types of asymmetric synthesis is that in which chiral products are generated under the influence of chiral catalysts. In this respect, asymmetric Michael addition of 2-nitropropane (**35**) to chalcone **34** catalyzed by chiral crown ethers were found to fulfil the optimum conditions for the reaction to give good yield with high stereoselectivity of the corresponding Michael adduct **36**. The catalytic activity of the crown ethers (as phase transfer catalysts) in this reaction was studied under solid-liquid phase transfer conditions using toluene as a solvent and solid sodium *ter*-butoxide as a base at room temperature (Scheme 24).



Scheme 24: Michael addition of carbon nucleophiles to conjugated enones

Bako et al.(1997, 1999) synthesized a series of optically active crown ethers **37a-j** and their effects as phase transfer catalysts on the above reaction were investigated (Figure 12).

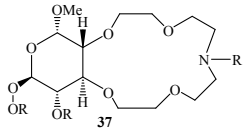
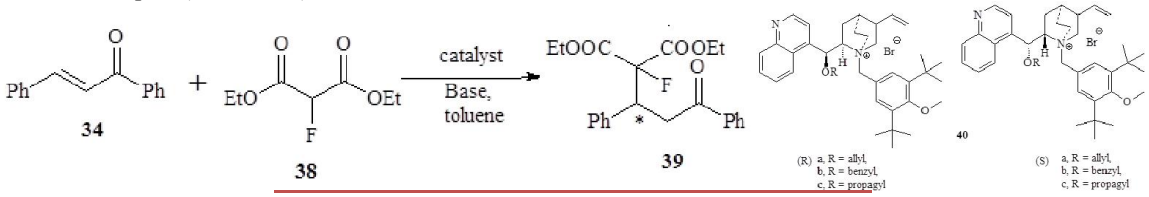


Figure 12: optically active crown ethers

Addition of 2-nitropropane (catalyzed by **35**) to chalcone **34** (catalyzed by **37a-j**)

catalyst	R	R'	Yield (%)	ee (%)	Time (h)
37a	H	Me	68	34 (S)	15
37b	H	Bu	82	90 (S)	9
37c	H	Ac	65	47 (S)	14
37d	Ts	Me	25	6 (S)	22
37e	Ts	Bu	35	10 (S)	18
37f	Ts	Ac	23	5 (S)	22
37g	Bu	Bu	49	45 (S)	20-24
37h	$(CH_2)_3OMe$	Bu	53	55 (S)	20-24
37i	CH_2Ph	Bu	40	27 (S)	20-24
37j	CH_2CH_2Ph	Bu	43	42(S)	20-24

The catalytic enantioselective Michael reaction of diethyl fluoromalonate (Kim et al 2003) **38** to chalcone derivatives **34** was achieved by using the cinchona alkaloid-derived quaternary ammonium salts **40**. In order to determine suitable reaction conditions, the reaction system was investigated using 10 mol% of catalyst with diethyl fluoromalonate **38** as the Michael donor and chalcone **34** as the Michael acceptor (Scheme 25).



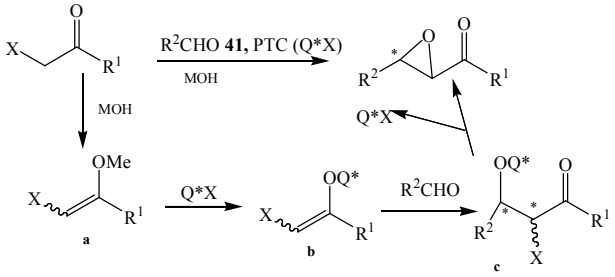
Catalysts 40		Base	Time (h)	Yield (%)	ee (%)
(R)	**40a**	K_2CO_3	18	64	37
(R)	**40b**	K_2CO_3	18	38	23
(R)	**40c**	K_2CO_3	18	20	27

(S)	**40a**	K_2CO_3	15	63	39
(S)	**40a**	Cs_2CO_3	9	38	11
(S)	**40a**	Rb_2CO_3	9	63	33
(S)	**40b**	K_2CO_3	18	30	33

Scheme 25: catalytic enantioselective Michael reaction of diethyl fluoromalonate

Darzens reaction

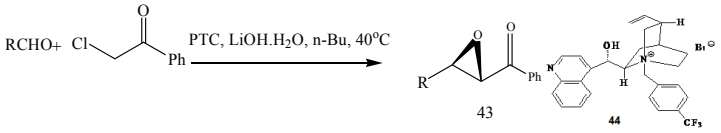
The Darzens reaction is one of the most important carbon-carbon bond forming reactions in synthetic organic chemistry because of the multifunctionality and utility of the α,β-epoxy carbonyl products. Although many examples are known with diastereoselective control in the Darzens reaction (Ohkata et al 1996), a few successful results involving enantiocontrol using chiral catalysts or reagents has been reposted. Thus, obtaining a reasonable enantiomeric excess in the catalytic asymmetric Darzens reaction still remains a challenge. A significant problem to be solved is the establishment of an efficient catalytic cycle in which the inorganic salts or related compounds generated from both substrates and reagents are converted into effective reactive species. Past enentiselective Darzens reaction promoted by metal reagents required stoichiometric amounts of chiral source because of the metal reagents and harsh reaction conditions employed (Ohkata et al 1996), (Scheme 26).



Scheme 26: Darzens reaction

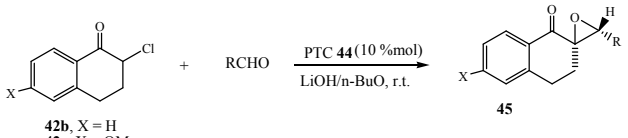
Catalytic asymmetric Darzens reaction promoted by a chiral phase transfer catalyst derived from cinchonine is described. The desired α,β-chloro cyclic and acyclic ketones as substrates with moderate to high enantiomeric excesses under mild reaction conditions (Arai et al 1999).

The reaction of commercially available α-chloroketone **42a** with various aldehyde (Arai 1998) **41**, yields the desired epoxyketone **43**, using the catalyst N-(4-trifluoromethylbenzyl)cinchonium bromide **44**(10 mol%), LiOH monohydrate (2.0 equv.) in dibutyl ether (1.0 M) at 4°C (Scheme 27).



Scheme 27: reaction α-chloroketone with various aldehyde using PTC

The reaction of α-chloro-cyclic ketones (**42b** and **42c**) as starting substrate with aldehydes **41** using PTC **44** was also investigated (Scheme 28).

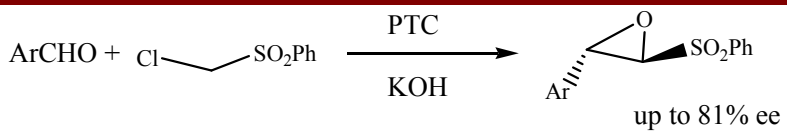


42b, X = H
42c, X = OMe

Ketone	Aldehyde 41		Time (h)	Yield of 45 (%)		ee of 45 (%)
42b	**41a**	R = i-Pr	61	**45a**	90	69
42b	**41d**	R = t-Bu	63	**45b**	86	75
42b	**41e**	R = t-$BuCH_2$	4	**45c**	86	86
42b	**41f**	R = Et_2CH	252	**45d**	67	84
42b	**41h**	R = c-Hex	62	**45e**	80	69
42b	**41i**	R = Ph	43	**45f**	67	59
42c	**41d**	R = t-Bu	48	**45g**	65	50
42c	**41e**	R = t-$BuCH_2$	63	**45h**	90	75
42c	**41a**	R = i-Pr	94	**45i**	96	35

Scheme 28: reaction of α-chloro-cyclic ketones aldehydes using PTC

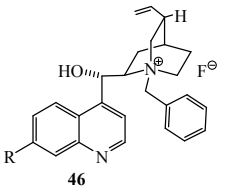
The catalytic asymmetric synthesis ofα,β-epoxysulfones *via* Darzens reaction (Arai et al 1998) under PTC conditions, using chloromethylphenyl-sulfone with various aromatic aldehydes in presence PTC 44 (10 mol %) with KOH at room temperature, was also investigated (Scheme 29).



Scheme 29: catalytic asymmetric synthesis ofα,β-epoxysulfones *via* Darzens reaction

Aldol reactions

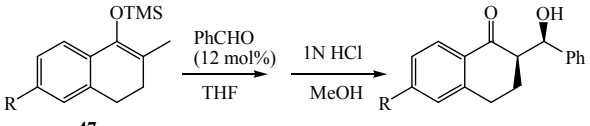
Catalytic asymmetric synthesis that enables transformation of prochiral molecules to optical active ones with propagation of chirality has been recognized as one of the most important subjects in modern synthetic organic chemistry. Especially, development of chiral catalysts for carbon-carbon bond forming reactions represented by Aldol reactions has attracted much attention. Although several excellent asymmetric Aldol-type reactions which are catalyzed by chiral metal complexes or lewis acids have been reported (Faruta et al 1991), a few reports have been known on the use of the chiral quaternary ammonium fluoride **46** as a catalyst (Colonna et al 1978) (Fig. 13).



46

Figure 13: chiral quaternary ammonium fluoride catalyst

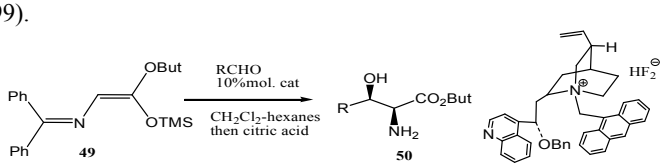
The Aldol reaction of silyl enol ethers with aldehydes (Ando et al 1993) was investigated by using the fluoride **46** as a catalyst. The silyl enol ethers of 2-methyl-1-tetralon derivatives **47** were allowed to react with benzaldehyde in the presence of 12 mol% of **46** in THF at –70°C for several hours, and then the silylated Aldols were hydrolyzed with 1N hydrochloric acid to give **48**. After a usual work-up, the diastereomeric ratios and the enantiomeric excesses were determined by HPLC measurement having a chiral stationary phase column (Scheme 30).



47 **erythro-48**
70%ee (R = H)

Scheme 30

The system is extended to synthesis of chiral β-hydroxy-α-amino acids **50** by Aldol coupling of aldehydes with the trimethylsilyl enol ether derivative of *tert*-butylglycinate benzophenone Schiff base **49** using cinchonidine-derived bifluoride salts **51** as a catalyst (Scheme 31) (Horikawa et al 1999).



49 **50** **51**

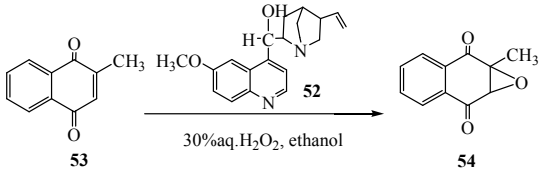
Scheme 31: synthesis of chiral β-hydroxy-α-amino acids 50

5- Epoxidations

The epoxide function plays an important role in metabolic processes (Sheehan et al 1958). However, the synthesis of optically active epoxides leaves much to be desired.

It was reported that the base-catalyzed hydrogen peroxide or t-butyl hydrogen peroxide mediated epoxidation of electron-poor olefins is subject to catalytic asymmetric induction. Using quaternary ammonium salts derived from alkaloids (Wynberg 1975) under phase transfer conditions it was possible synthesize a number of optically active epoxides starting from chalcones, a quinones and similar electron-poor olefins. Chemical yields are excellent in all cases, while the enantiomeric excess, as determined in one case, amounted only to 25% (Helder et al 1976).

Initial experiments performed with quinine **52** as the catalyst in a mixture of 30% aq. H_2O_2 and ethanol showed that quinone **53** gave the corresponding epoxide **54** in 90% chemical yield. However, asymmetric induction was minimal and the results were erratic (Scheme 32).



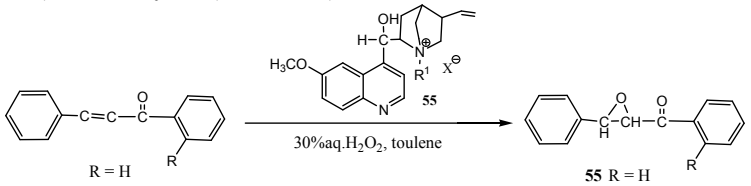
53 **54**

Scheme 32: Epoxidation of quinone 53

However, chalcones and related compounds could be transformed in excellent chemical yields into optically active epoxides, using quaternary salts derived from quinines (e. g. **55**, $R^1 = C_6H_5CH_2$) as chiral phase-transfer catalysts in the two phase system toluene / water (Scheme 33).

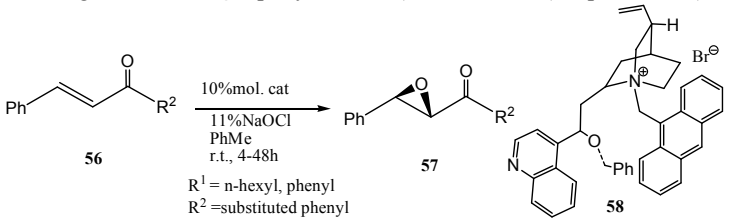
Thus when a solution of chalcone (R=H) in toluene was vigorously stirred for 24 hrs at room temperature with a solution of NaOH in 30% aq. H_2O_2 and the salt **55** ($R^1 = C_6H_5CH_2$), the yellow color of chalcone (R=H) had disappeared completely.

Work-up of the reaction mixture and elution of the crude product on silica gel / CH_2Cl_2 (in order to remove the catalyst) gave the optically active epoxide **56** (R=H) in a 99% yield (Scheme 33).



Scheme 33: optically active epoxide 56

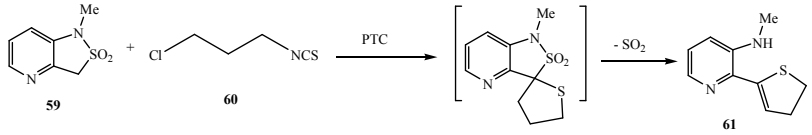
Recently, a study on the enantioselective epoxidation of α,β-unsaturated ketones utilizing Cinchona alkaloid-derived quaternary ammonium phase-transfer catalysts bearing an *N*-anthracenylmethyl **58** function was presented (Lygo 1999). It has been found that the *O*-benzyl derivatives of these catalysts in conjunction with sodium hypochloride give high enantio- and diastereoselectivities in the epoxidation of a range of substrates $R^1CH=CHCOR^2$ **56**, where R^1= alkyl or aryl and R^2= aryl. In the cases where R^2= alkyl, high enantioselectivity has also been observed, however the rate of reaction is substantially reduced. Application of this process to the enantioselective synthesis of a range of *trans*-α, β-epoxy ketones (**57**, ee 71-90%) is presented (Scheme 34).



Scheme 34: enantioselective epoxidation of α,β-unsaturated ketones

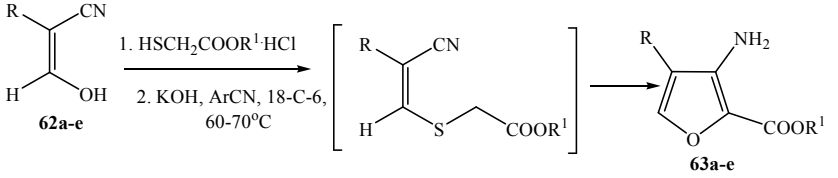
Uses of PTC in syntheses of five-membered heterocycles compounds

The reaction of pyridosultam **60** with 3-chloropropylthiocyanate **60** under the condition (toluene/aq. NaOH/TBAB) yielded the corresponding dihydrothiophene derivative **61** (Modrzejewska 2005) (Scheme 35).



Scheme 35

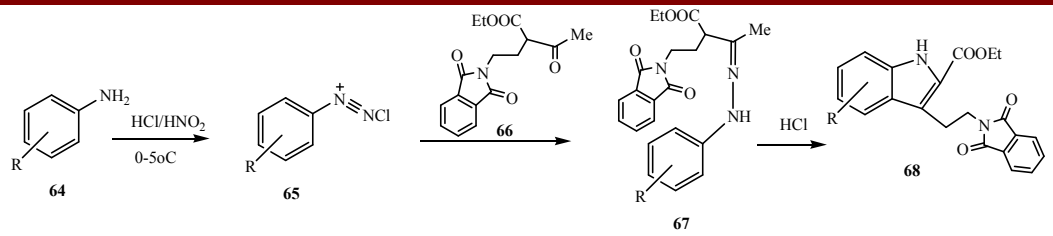
Methyl or ethyl 3-amino-4-arylthiophenes-2-carboxylates **63a–e** were synthesized by Thorpe reaction through the treatment of 3-hydroxy-2-arylacrylonitriles **62a–e** and methyl or ethyl thioglycolates with hydrochloric acid by using different TC conditions (solid-liquid or liquid-liquid). The solid-liquid PTC conditions using 18-crown-6 along with potassium hydroxide as a catalyst are the method with excellent yields. The reactions were carried out in acetonitrile at RT (Shah 2011) (Scheme 36).



R	R^1
a, Ph	COOEt
b, 4-OMe	COOMe
c, benzo[b]furyl-2	COOMe
d, thinyl-2	COOMe
e, dimethyl2,5-thinyl	COOMe

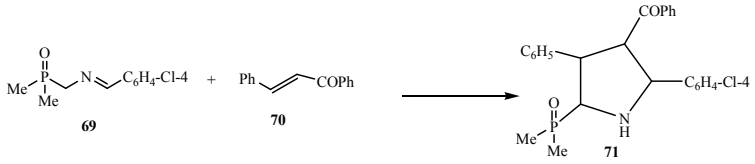
Scheme 36: synthesis of methyl or ethyl 3-amino-4-arylthiophenes-2-carboxylates 63a–e

In Japp-Klingemann reaction the indole derivatives **67** have been prepared as indicated in Scheme 37. The addition of a suitable PTC catalyst **66** to the reaction could significantly improve the reaction process. Firstly, aryl amines **64** were diazotized **65** and reacted under alkaline conditions ethyl 2-[2-(1,3-dioxo-1,3-dihydro-2*H*-isoindol-2-yl)ethyl]-3-oxobutanoate **66** using PTC-promoted Japp-Klingemannreaction to form the ring-opened aryl hydrazones **67**. These aryl hydrazones were cyclized and converted into the corresponding indole derivatives **68** by adding hydrochloric acid in ethanol (He et al 2005) (Scheme 37).



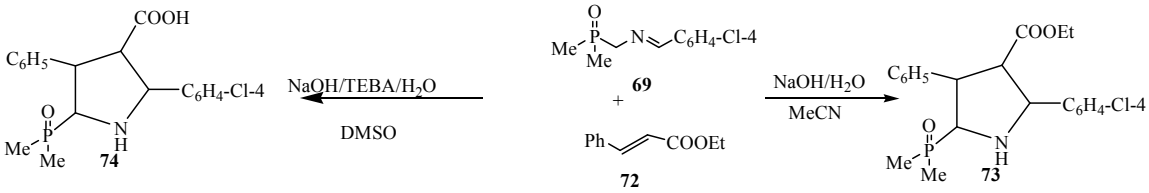
Scheme 37: synthesis of indole derivIA atives 67 Japp-Klingemann reaction

Synthesis of dimethyl phosphinyl substituted tetrahydropyrroles **71** via 1,3-cycloaddition reaction of the azomethine **69** to electron deficient alkenes such as α,β-unsaturated ketones (e.g., benzylideneacetophenone **70**), esters, andnitriles took place in high yield and low diastereoselectivity in phase-transfer catalysis conditions (solid potassium carbonate, triethylbenzylammoniumchloride (TEBA)) in acetonitrile as a solvent (Cholakova et al 2005) (Scheme 38).



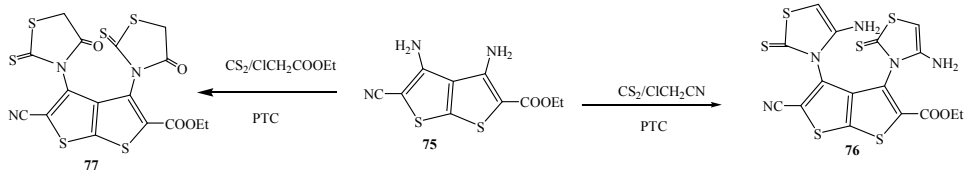
Scheme 38: Synthesis of dimethyl phosphinyl substituted tetrahydropyrroles 71

When Schiff base **69** and ethyl cinnamate **72** reacted under different phase-transfer catalysis conditions (10 equivalents of aqueous NaOH (50%)/TEBA/DMSO), the ester of pyrrolidinecarboxylic acid **73** has not been formed; instead the acid itself **74** was obtained as a mixture of two diastereoisomers (Cholakova et al 2005) (Scheme 39).



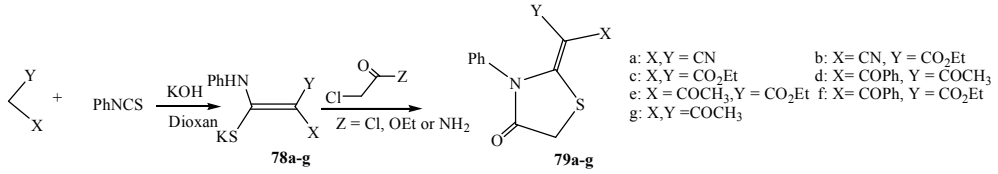
Scheme 39: reaction of Schiff base 69 and ethyl cinnamate 72 under different phase-transfer catalysis conditions

The addition reaction of ethyl 3,4-diamino-5-cyanothieno[2,3-b]thiophene-2-carboxylate **75** to carbon disulfide, followed by cyclization reaction through the treatment with chloroacetonitrile or ethyl chloroacetate under PTC conditions (K_2CO_3, TBAB, dioxane), furnished 3,4-bis(4-amino-2-thioxo-1,3-thiazol-3(2*H*)-yl)-5-propanoylthieno[2,3-*b*]thiophene-2-carbonitrile **76** and 3,4-bis(4-oxo-2-thioxo-1,3-thiazolidin-3-yl)-5-propanoylthieno[2,3-*b*]thiophene-2-carbonitrile **77**, in satisfactory yields (Khodairy et al 2011) (Scheme 40).



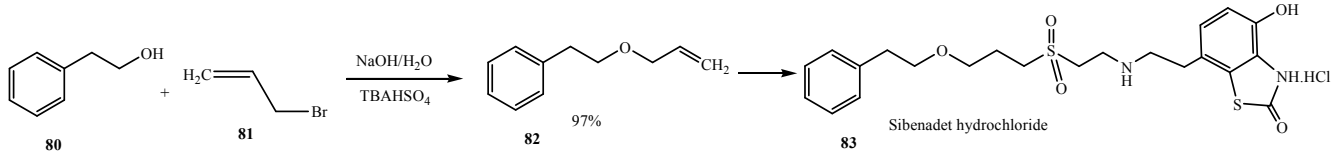
Scheme 40: addition reaction of ethyl 3,4-diamino-5-cyanothieno[2,3-b]thiophene-2-carboxylate 75 to carbon disulfide

A variety of 4-thiazolidinone derivatives **79a–g** were successfully synthesized via in situ formation of ketene-N,S-acetals **78a–g** which in turn was reacted with ethylchloroethyl acetate, chloroacetamide, or chloroacetyl chloride followed by ring closure to afford the desired 4-thiazolidinones **79a–g** (Farhat et al 2007) (Scheme 41).



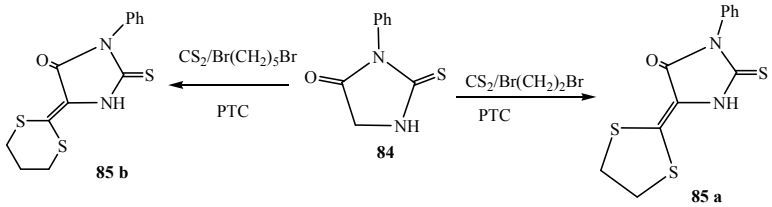
Scheme 41: synthesis of4-thiazolidinone derivatives 79a–g

One of the medicinal applications for PTC techniques is synthesis of sibenadet hydrochloride **83** which is a potentdrug used for treatment of chronic obstructive pulmonary disease. This bioactive molecule was synthesized by O alkylation of phenylethanol **80** with the alkyl bromide **81** under PTC condition to form the alkylated product **82** in 97% yield. Reaction of **82** with benzothiazole derivative led to formation of the desired product **82** (Fedory et al 2008) (Scheme 42).



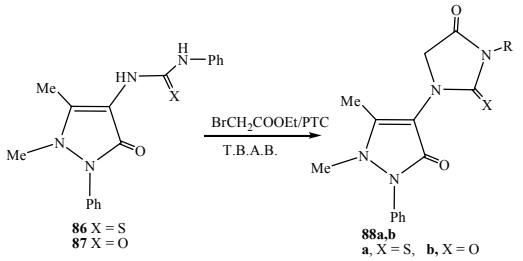
Scheme 42: synthesis of sibenadet hydrochloride

The PTC reaction of 3-phenyl-2-thiohydantoin **84** with dihalocompounds, namely, ethylene dibromide or 1,3-dibromopropane, with CS_2, yielded 1,3-dithioxane derivative **85a** or 5-(1,3-dithian-2-ylidene)-3-phenyl-2-thioxoimidazolidin-4-one derivative **85b**, respectively (Abou El-Regal et al 2007) (Scheme 43).



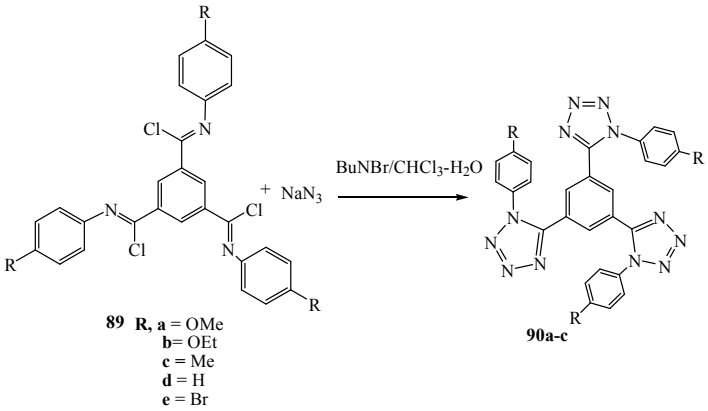
Scheme 43: PTC reaction of 3-phenyl-2-thiohydantoin 84 with dihalocompounds

Treatment of the thiourea **86** and urea **87** derivatives with ethyl bromoacetate under PTC condition using TBAB as a catalyst and benzene/anhydrous K_2CO_3 as liquid-solid phases gave imidazolidinediones **88a**, **b** via ring closure pathway (El-Metwally et al 2010) (Scheme 44).



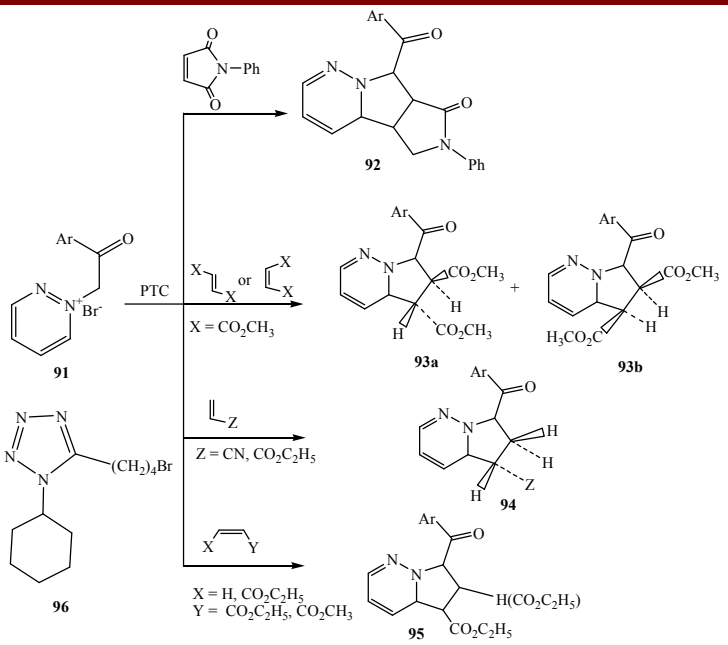
Scheme 44: Treatment of the thiourea 86 and urea 87 derivatives with ethyl bromoacetate under PTC

Functionally substituted tetrazoles have been synthesized from the corresponding *N,N',N''*-triarylbenzene-1,3,5-tricarboxamides **89** via sequential transformation of these compounds into imidoyl chlorides and treatment of the latter with sodium azide under conditions of phase-transfer catalysis. As a result, a number of heterocyclic structures **90a**–**e** containing three tetrazole rings has been isolated (Zatsepina et al 2008) (Scheme 45).



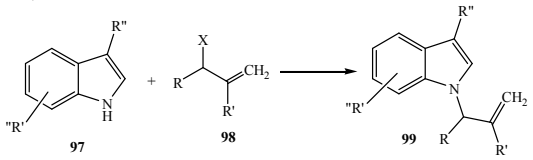
Scheme 45: synthesis of substituted tetrazoles

Treating of pyridazinium ylides **91** with N-phenylmaleimide, maleic and fumaric esters, resulted in the cycloadduct products **92**–**95** with high stereospecificity in the presence of KF and trioctylmethylammonium chloride or without solvent in the presence of aliquat **96** as phase transfer catalyst (Butnariu et al 2009) (Scheme 46).



Scheme 46: Treatment of pyridazinium ylides 91 with N-phenylmaleimide, maleic and fumaric esters

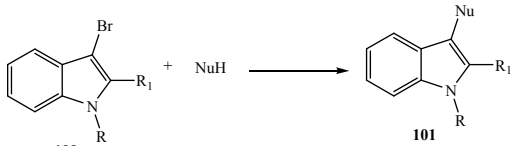
N-allylindoles **99** were easily carried out *via N*-allylation of the proper indoles **97** with the suitable allyl halides **98**. The reaction was accomplished in diethyl ether *via* a phase transfer process in which 18-crown-6 was employed as the transfer agent and *t*-BuOK as the base (Guazzelli et al 2007) (Scheme 47).



R, R' = H, CH_3; R" = H, CH_3, $CH_2CH_2OCH_3$, CHO, CH_2COOCH_3;
R"' = H, CH3, 7-CH3, X= halgen

Scheme 47: *N*-allylation of the proper indoles 97 with the suitable allyl halides 98

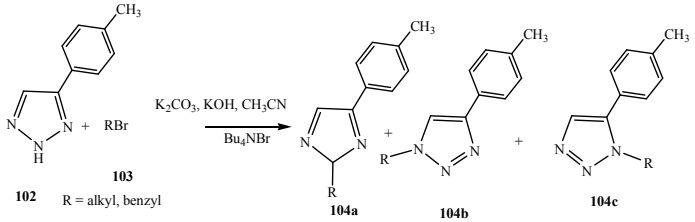
Barraja et al. heated 2-substituted-3-bromoindoles **100** with excess of different nucleophiles, solid KOH, and dibenzo-18-crown as a phase transfer catalyst to afford the corresponding 3-substituted indoles **101** in a satisfactory increase of yield (Barraja et al 2008) (Scheme 48).



R = H, CH_3; R_1 = Ph, 2-NO_2-C_6H_5, 2-$NH_2C_6H_5$, CO_2Et
Nu = SAr, O-Ar, NR(Ar, cyclic)

Scheme 48: synthesis of 3-substituted indoles 101 via PTC

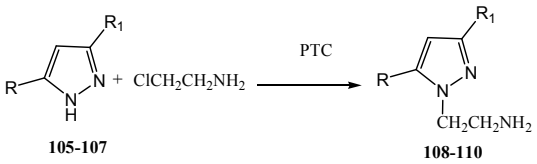
Reaction of 4-substituted-1,2,3-triazol **102** with alkyl bromide **103** under basic condition using PTC Bu4NBr produced N-substituted 1,2,3-triazole derivatives **104a-c** (Jagerovic et al 2010) (Scheme 49).



Scheme 49: reaction of 4-substituted-1,2,3-triazol 102 with alkyl bromide 103

Alkylation reaction of pyrazoles **105**–**107** with 2-chloroethylamine under the condition of phase-transfer catalysis was carried out in a liquid-solid system using benzene as an organic solvent and BTEAC as a catalyst. Reaction between equimolar amounts of reactants led to poor yields (20–40%) of the alkylated products **108**–**110** due to concurrent dehydrochlorination of 2-chloroethylamine.The yield was considerably decreased in going frompyrazole (**105**) to 3,5 dimethylpyrazole (**107**) whereas the maximal yield of alkylated products (70–80%) was obtained by using one of the following ratios: pyrazole:NaOH:2-

chloroethylamine 1:2:2, 3-(5) methylpyrazole :NaOH: 2 chloroethylamine 1:3:3, or 3,5-dimethylpyrazole :NaOH: 2-chloroethylamine 1:5:5 (Attaryan et al 2008) (Scheme 50).



105-107 **108-110**

105, 108 R =R1 =H; **106, 109** R = Me, R1 =H, Me; **107, 110**. R, R1 = Me

Scheme 50

Conclusion

There are hundreds of industrial applications of PTC for a variety of processes of organic synthesis. Sulfonyl fluorides are of interest owing to their insecticidal, germicidal and enzyme inhibitory properties. Synthesis of *p*-toluenesulfonyl fluoride was accomplished by reacting *p*-toluenesulfonyl chloride with solid potassium fluoride using PEG-400 as (PTC) catalyst (Yadav 2005). Toluenesulfonyl fluoride is used as peroxygen bleach activator. It is also used in the treatment of Alzheimer's disease (Auld et al 2001). L-Dopa (L-3,4-dihydroxyphenylalanine)esters (Ooi et al 2000) which have usually been prepared in an enzymatic way and tested as potential drugs for the treatment of Parkinson's disease (Brunner-Guenat et al 1995), are also produced *via* PTC.
Always these technologies require less investments, consume less energy, and generate much less industrial wastes as compared to the traditional ones. It is obvious that all measures which save energy and investments offer directly or indirectly substantial benefits to the environment of great importance is direct effect generation of smaller volume of wastes. Major advantages of PTC in industrial applications are listed below:

Elimination of organic solvents, Elimination of dangerous and inconvenient reactants (NaOH, KOH, K_2CO_3 etc. instead of NaH, $NaNH_2$, *t*-BuOK, etc), High reactivity and selectivity of active species, High yields and purity products.
Simplicity of the procedure, Low investment cost, Low energy consumption and Minimization of industrial wastes
These numerous and important advantages of PTC are easily recognized in the above given examples. One should stress that when a new synthetic process is developed, the possibility to apply PTC should be considered first. Due to the specific features of PTC and its advantages presented above, it should be considered as a most efficient and general green technology.

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