Kirk-Othmer Encyclopedia of Chemical Technology.

CATALYSIS, PHASE-TRANSFER

Phase-transfer catalysis (PTC) is a technique by which reactions between substances located in different phases are brought about or accelerated. Typically, one or more of the reactants are organic liquids or solids dissolved in a nonpolar organic solvent and the coreactants are salts or alkali metal hydroxides in aqueous solution. Without a catalyst such reactions are often slow or do not occur at all; the phase-transfer catalyst, however, makes such conversions fast and efficient. Catalysts used most extensively are quaternary ammonium or phosphonium salts, and crown ethers and cryptates. Although isolated examples of PTC can be found in the early literature, it is only since the middle of the 1960s that the method has developed extensively.

Traditionally, the reactions to be considered here are performed in homogenous medium, either in hydroxylic solvents or in polar aprotic solvents. In comparison, PTC has the following advantages: no need for expensive aprotic solvents; simpler work-up; shorter reaction time and or lower reaction temperature; use of aqueous alkali hydroxides instead of other expensive bases.

Undoubtedly cost factors and environmental considerations (recycling of solvents, less toxic or less hazardous materials) will lead to increasing industrial application of this methodology.

1. The Fundamental Process in Displacement Reactions

Figure 1 shows the mechanistic picture developed by C. M. Starks (1, 2) for liquid–liquid PTC in a graphical form. The catalyst cation Q^+ extracts the more lipholilic anion Y^- from the aqueous to the nonpolar organic phase where it is present in the form of a poorly solvated ion pair $[Q^+Y^-]$. This then reacts rapidly with RX, and the newly formed ion pair $[Q^+X^-]$ returns to the aqueous phase for another exchange process: $X^- \longrightarrow Y^-$. In practice most catalyst cations used are rather lipophilic and do not extract strongly into the aqueous phase so that the anions are exchanged at the phase boundary.

This general scheme has been supported by a wealth of detailed investigations. The organic-phase reaction is usually rate limiting. Of special importance are the observations that the rate of reaction is proportional to the catalyst concentration and independent of the stirring speed (size of the interphase) above the minimum required for efficient mixing. A certain number of water molecules are coextracted with the anion (3). This phenomenon has a decisive influence on the relative, eg, Cl vs Br vs I, and absolute rate of reaction. In solvents of relative low polarity, eg, CH_2Cl_2, $CHCl_3$, benzene, the ion pair, not the anion, is the dominant nucleophile (4). Absolute rates may be higher than in polar aprotic solvents.

2. Types of Phase-Transfer Processes

There are several types of processes depending on the nature of the phases, the character of the extracted species, and the direction of extraction.

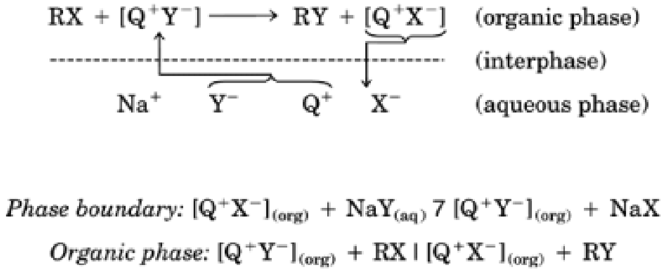


Fig. 1. Mechanism for liquid–liquid PTC.

2.1. Phases

Often there are two liquid phases (liquid–liquid PTC) or one solid, one liquid (solid–liquid PTC). If the catalyst is bound to a polymeric matrix this may comprise a third phase (triphase catalysis). Examples of gas–liquid, gas–solid, and solid–solid PTC are still relatively rare. In the latter two cases, a small amount of liquid, eg, water, is probably present as an unnoticed third phase.

2.2. Character of the Extracted Species

Most PTC reactions are initiated by the extraction of some anion, be it a nucleophile, a base, or an oxidant, by lipophilic cations. However, relatively hydrophilic cations can be extracted by large anions from an aqueous or solid phase into an organic solvent for electrophilic reactions. These include, for instance, diazonium ions and stable carbocations. But applications of this type are not yet widespread. Uncharged compounds HY can also be transferred if they form relatively strong hydrogen bonds to the halide in NR_4X catalysts. Among these are hydrogen halides, phenols, carboxylic acids, hydrogen peroxide, hydrazine, and even amines. Complexes, eg, $[NR^+_4\ Cl^- \cdots HCl]$, are known in crystalline form. A last group of extracted species are metal atoms. Crown ethers can make alkali metals soluble in solvents like THF for reductions; anthracene solubilizes magnesium.

2.3. Direction of Extraction

The “normal” PT process involves the transfer of a reactive agent from a solid or aqueous environment into a nonpolar organic solvent. But the exact opposite can be executed: extraction from an organic phase into an aqueous phase, for example, for changing selectivities. This “inverse PTC” is done relatively rarely.

3. Types of Phase-Transfer Reactions

There is an enormous potential of PTC for numerous reactions and no single type of mechanism explains everything. Among the more frequently used reactions involving anion extraction, two classes can be distinguished: (*1*) reactions without added bases; and (*2*) reactions in the presence of alkali metal hydroxides, potassium carbonate, or other inorganic bases. Numerous substitutions $RX + Y^- \longrightarrow RY + X^-$ are of the first type. The leaving group, X^-, is normally a halide or sulfonate, and the nucleophile can be almost any anion, eg, halide, CN^-, SCN^-, N^-_3, NO^-_2, carboxylate, phenolate, sulfide, thiolate, and many others. Another group of reactions without added base are oxidations with permanganate, hypochlorite, chlorite, chlorate, peroxydisulfate, $[Ce(NO_3)_6]^{2-}$, hexacyanoferrate(III), superoxide radical-anion, hydrogen peroxide, perborate, and others. Reductions with complex hydrides, dissolving metals, dithionite, formate, and others, as well as transfer hydrogenations can also be accelerated by phase-transfer catalysts.

Class (*2*) reactions are performed in the presence of dilute to concentrated aqueous sodium hydroxide, powdered potassium hydroxide, or, at elevated temperatures, solid potassium carbonate, depending on the acidity of the substrate. Alkylations are possible in the presence of concentrated NaOH and a PT catalyst for substrates with conventional pK_a values up to ~ 23. This includes many C–H acidic compounds such as fluorene, phenylacetylene, simple ketones, phenylacetonitrile. Furthermore, alkylations of N–H, O–H, S–H, and P–H bonds, and ambident anions are well known. Other basic phase-transfer reactions are hydrolyses, saponifications, isomerizations, H/D exchange, Michael-type additions, aldol, Darzens, and similar additions to multiple hetero bonds, β-eliminations, and basic autoxidations. Additional reactions of this class are α-eliminations to form carbenes, Wittig- and Horner-Emmons reactions, reactions of sulfonium ylides, a multitude of rearrangements, etc.

There are two very active special fields of phase-transfer applications that transcend classes (*1*) and (*2*): metal–organic reactions both with and without added bases, and polymer chemistry. Certain chemical modifications of side groups, polycondensations, and radical polymerizations can be influenced favorably by PTC.

4. Factors Influencing the Usefulness of Phase-Transfer Catalysis

In the following reaction under phase catalytic conditions

$$\mathrm{RX} + \mathrm{KY}_{(\mathrm{water})} \xleftarrow{\mathrm{N(C_4H_9)_4X}} \mathrm{RY} + \mathrm{KX}$$

the relative rate for $X = \mathrm{Cl}^-, \mathrm{Br}^-, \mathrm{I}^-$ is determined by two factors: the actual chemical reaction with I^-, Br^-, or Cl^-; and the magnitude of the competitive extraction of Y^- vs X^-. If the second factor is very unfavorable for Y^-, PTC may be impossible. Thus it is important to have some insight into the order of magnitude of the factors involved. The conditional extraction constant E_{QX} of the salt QX is defined as:

$$E_{\mathrm{QX}} = \frac{[\mathrm{QX}]_{(\mathrm{org})}}{[\mathrm{Q}^+]_{(\mathrm{aq})} \cdot [\mathrm{X}^-]_{(\mathrm{aq})}}$$

where the bracketed expressions stand for activities, or concentrations, in organic or aqueous media, respectively.

4.1. Solvent.

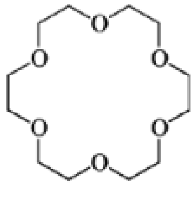
For PTC the solvents should be nonmiscible with water and non-hydroxylic; $CHCl_3$ and CH_2Cl_2, chlorobenzene, toluene, acetonitrile, and even petroleum ethers are employed. Alternatively, one can work without extra solvent if the substrate is liquid.

4.2. Catalyst Cation

The logarithms of extraction constants for symmetrical tetra-*n*-alkylammonium salts (log E_{QX}) rise by ca 0.54 per added C atom. Although absolute numerical values for extraction coefficients are vastly different in various solvents and for various anions, this relation holds as a first approximation for most solvent–water combinations tested and for many anions. It is important to note, however, that the lipophilicity of phenyl and benzyl groups carrying ammonium salts is much lower than the number of C atoms might suggest. Benzyl is extracted between *n*-propyl and *n*-butyl. The extraction constants of tetra-*n*-butylammonium salts are about

140 times larger than the constants for tetra-*n*-propylammonium salts of the same anion in the same solvent–water system.

For practical application in mixtures of water–organic solvent, only ammonium and phosphonium salts containing 15 or more C atoms are sufficiently lipophilic. In empirical catalyst comparisons crown ethers (hexaoxacyclooctodecanes) **(1)–(3)** were often as effective as the best onium salts.



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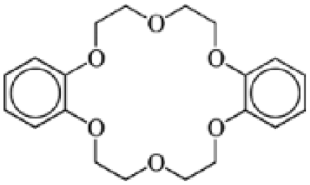

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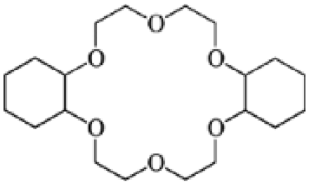


(3)

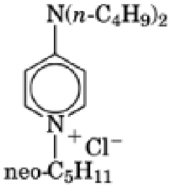
Other complexing agents sometimes advocated are cryptates, especially the compound dubbed [2.2.2] (Kryptofix 222) [23978-09-8] (see Chelating agents). Crown ethers were originally advocated for reactions in the presence of solid reagents (liquid–solid PTC). It is now known, however, that onium salts are equally suitable in many cases.

Often poly(ethylene glycol)s or derivatives thereof can be used instead of crowns or onium salts advantageously, although their catalytic activity frequently tends to be somewhat lower. The possible toxicity of crowns and cryptands and the price difference between these compounds and onium salts (100:1 to 10:1) are other important factors to be considered. Thus **(1)** [17455-13-9], **(2)** [14187-32-7], and **(3)** [16069-36-6] and cryptands are used more often in laboratory work, whereas onium salts are more important for industrial processes.

Benzyltriethylammonium chloride [56-37-1] is the most widely used catalyst under strongly basic conditions. Methyltrioctylammonium chloride [5137-55-3] (Aliquat 336, Adogen 464) is probably the least expensive catalyst. Others of high activity and moderate price are tetra-*n*-butylammonium chloride [1112-67-0], bromide [1643-19-2], hydrogen sulfate [32503-27-8], tetra-*n*-butylphosphonium chloride [2304-30-5], and other phosphonium salts of a similar number of C atoms. Many other onium salts can also be utilized.

4.2.1. Stability

The stability of the catalysts is another important factor. Reactive nucleophilic anions can attack their own counter ion, leading to Hofmann-type elimination or simple dequaternization. Rates of these processes can vary from zero to very fast depending on structures both of anion and cation, solvent, temperature, and especially the presence and concentration of alkali metal hydroxides. Contrary to an earlier suggestion, quaternary phosphonium salts are generally not more stable than ammonium salts. High temperature stabilities (up to ca 200°C) are exhibited by 4-dialkylaminopyridinium salts such as **(4)** [93103-34-5] (5), tetraphenylarsonium chloride **(5)** [507-28-8] (6), and especially the phosphoiminium salts bis[tris(dimethylamino)phosphine]iminium chloride [123048-82-8] **(6)** and tetratris[tris(dimethylamino phosphinimino] phosphonium chloride [122951-89-7] **(7)**. Only the last two catalysts are also very stable in the presence of hot concentrated NaOH (6).



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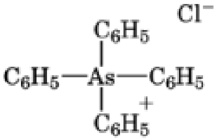

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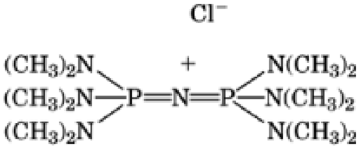

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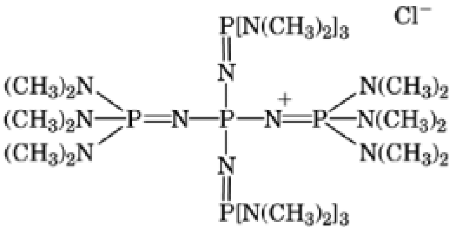

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4.2.2. Selectivity

Steering of reaction directions by the type of catalyst cation, eg, O- vs C-alkylation (7), substitution vs dihalocarbene addition (8), as well as enantioselective alkylations by optical active catalysts (9) have been achieved in some systems. Extensive development is necessary, however, to generate satisfactorily large effects.

Table 1. Anion Extraction Constants E_{QX}, of Tetra-n-Butylammonium Ion Pairs Between Water and Chloroform

Anion	E_{QX}	Reference	Anion	E_{QX}	Reference
Cl^-	0.78	10	$CH_3CO_2^-$	7.6×10^{-3}	12
Br^-	15.9	10	$C_6H_5CH_2CO^-{}_2$	1.86	12
I^-	1023	10	$C_6H_5CO^-{}_2$	2.45	12
ClO_4^-	3020	10	salicylate	263	12
NO_3^-	24.5	10	3-hydroxybenzoate	0.03	12
OH^-	$\sim 10^{-4}$	11	phenolate	0.93	12
			picrate	8.1×10^5	12
			p-toluene sulfonate	214	12
			naphthalene-2-sulfonate	2818	12
			anthracene-2-sulfonate	1.3×10^5	13
			trinitrobenzenesulfonate	2.9×10^4	12

4.3. Competitive Extraction of Anions

The successful extraction of the necessary anion into the organic phase is crucial for PTC. Often three anions compete for the catalyst cation: the one that is to react, the one formed in the reaction, and the one brought in originally with the catalyst. Table 1 lists the widely differing E_{QX} values of tetra-*n*-butylammonium salts. The big difference in the halide series is noteworthy and preparatively important. Hydroxide is $\sim 10^4$ times more difficult to extract than chloride (11) and the divalent and trivalent anions $SO^{2-}{}_4$ and $PO^{3-}{}_4$ are still more hydrophilic. Thus for practical applications hydrogen sulfate or chloride are recommended as the original anions in the catalysts. Bromide is more lipophilic than the smaller organic anions, and iodide can tie up the catalyst more or less quantitatively. Organic compounds carrying larger groups are naturally more easily extractable than the ones shown. Also noteworthy are the large differences in E_{QX} effected by seemingly slight structural changes (of acetate–benzoate, salicylate–3-hydroxybenzoate). It must be remembered that, within certain limits, relatively unfavorable extraction constants can be outmaneuvered by using a large excess of the less easily extracted salt.

Hydroxide ion is very hydrophilic and can be extracted in appreciable concentration into an organic medium only if the catalyst cation is very lipophilic and if the competition situation with other anions is favorable. Almost all other common inorganic and organic anions are more lipophilic, and in most cases not only the anion originally brought in with the catalyst, but mainly the one formed in the reaction tend to pair with the catalyst cation. At best the use of a large excess of concentrated aqueous sodium hydroxide or application of molar amounts of catalyst with a very hydrophilic original anion, eg, sulfate, can force this mechanism. In this case, the extraction of OH^- ions is rate limiting. An alternative mechanism (14) does not involve the extraction of QOH.

$$\textit{Phase boundary}: \quad \text{Substrate}{-}\text{H}_{(\text{org})} + \text{NaOH}_{(\text{aq})} \rightleftharpoons \text{Substrate}^-_{(\text{org})} + \text{H}_2\text{O} + \text{Na}^+_{(\text{aq})}$$

$$\textit{Phase boundary}: \quad \left[\text{Q}^+\text{X}^-\right]_{(\text{org})} + \text{Substrate}^-_{(\text{org})} \rightleftharpoons \left[\text{Q}^+\text{substrate}^-\right]_{(\text{org})} + \text{X}^-_{(\text{aq})}$$

$$\textit{Organic phase}: \quad [\text{Q}^+\text{substrate}^-]_{(\text{org})} + \text{RX} \longrightarrow \text{R}{-}\text{substrate} + [\text{Q}^+\text{X}^-]_{(\text{org})}$$

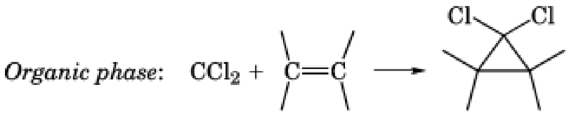
Here substrate molecules are deprotonated at the interface. Without catalyst the anions formed are immobilized because their counterion is in the opposite phase. Catalyst action is seen in detaching substrate anions from the boundary by anion exchange. The competitive situation for this is very favorable since most organic weak acids are much more lipophilic than halide ions except for iodide. Supporting evidence for the importance of interfacial processes is that some closely related alkylations proceed without catalyst in systems with negligible mutual solubility of the phases.

In dihalocarbene generation by phase-transfer catalysis the following steps seem to be involved (15): formation of $CX^{-}{}_{3}$ anions dynamically anchored at the boundary; reversible detachment with the help of the catalyst; reversible carbene formation $[Q^{+}CX_{3}^{-}] \rightleftharpoons [Q^{+}X^{-}] + CX_{2}$; addition to olefin.

$$\textit{Phase boundary}: \quad HCCL_{3(org)} + NaOH_{(aq)} \rightleftharpoons CCl^{-}_{3(org)} + H_{2}O + Na^{+}_{(aq)}$$

$$\textit{Phase boundary}: \quad CCl^{-}_{3(org)} + \left[Q^{+}Cl^{-}\right]_{(org)} \rightleftharpoons \left[CCl_{3}^{-}Q^{+}\right]_{(org)} + Cl^{-}_{(aq)}$$

$$\textit{Organic phase}: \quad \left[CCl_{3}^{-}Q^{+}\right]_{(org)} \rightleftharpoons \left[Q^{+}Cl^{-}\right]_{(org)} + CCl_{2}$$



In practice, 1–10 mol % of catalyst are used most of the time. Regeneration of the catalyst is often possible if deemed necessary. Some authors have advocated systems in which the catalyst is bound to a polymer matrix (triphase-catalysis). Here separation and generation of the catalyst is easy, but swelling, mixing, and diffusion problems are not always easy to solve. Furthermore, triphase-catalyst decomposition is a serious problem unless the active groups are crowns or poly(ethylene glycol)s. Commercial anion exchange resins are not useful as PT catalysts in many cases.

5. Typical Applications

From the many thousands of patents and journal publications, only a few typical examples are given here.

5.1. Displacement Reactions

The reactions $RCl \longrightarrow RCN$ are carried out by heating a threefold excess of concentrated aqueous NaCN solution with the alkyl chloride and 2 mol % tributylhexadecylphosphonium bromide for 2 h (1) (see Nitriles).

5.2. Formation of Esters.

$RBr \longrightarrow RCOOCH_{3}$ proceeds in 1–2 h by heating a concentrated $CH_{3}COOK$ solution with the halide, with or without solvent, and 1 mol % Aliquat 336 catalyst at 100°C (16). Esterification of higher acids, including sterically hindered ones, is carried out by neutralizing one equivalent of acid and one equivalent of tetrabutylammonium hydrogen sulfate with two moles of aqueous sodium hydroxide and boiling the mixture with the alkylating agent in $CH_{2}Cl_{2}$ for 15–30 min (17) (see Esterification).

5.3. Formation of Ethers.

Very high ether yields can be obtained from alcohols and phenols with dialkyl sulfates in CH_2Cl_2 and concentrated NaOH–tetrabutylammonium chloride at room temperature or slightly elevated temperature within 1–5 h (18). Using excess aqueous caustic–$N(C_4H_9)_4HSO_4$, unsymmetrical aliphatic ethers can be prepared with alkyl chlorides at 25–70°C in 3–4 h (19) (see Ethers).

5.4. Alkylation of Carbanions.

Concentrated NaOH–benzyltriethylammonium chloride is the base/catalyst system normally used for this type of process (20). Classes of compounds alkylated in this way include: phenylacetonitriles, benzylketones, simple aliphatic ketones, certain aldehydes, aryl sulfones, β-ketosulfones, β-ketoesters, malonic esters and nitriles, phenylacetic esters, indene, and fluorene (see Alkylation).

5.5. Nucleophilic Aromatic Substitution.

An activated aromatic halide is heated at 100–200°C with the alkali metal salt of the nucleophile (ArO^-, RO^-, F^-, CN^-/Cu^+, carbanion, etc) and the catalyst in an inert solvent (toluene, chlorobenzene) for a few minutes to a day (21–24).

5.6. Alkylation of N-Heterocycles.

Indoles (25), imidazoles (26), pyrazoles (27), benzotriazoles (27), or other heterocycles are generally alkylated in the presence of 50% aqueous NaOH and catalyst benzyltriethylammonium chloride without solvent or in chlorobenzene or toluene.

5.7. Polymerization of Butyl Acrylate.

An aqueous solution of $K_2S_2O_8$ and a solution of butyl acrylate [141-32-2] and catalytic amounts of Aliquat 336 in ethyl acetate are heated at 55°C (28) (see Acrylic ester polymers).

5.8. Oxidations.

5.8.1. $KMnO_4$

In neutral solution with Aliquat 336 and benzene as organic solvent, olefins yield carboxylic acids (1, 29).

5.8.2. NaOCl

Sodium hypochlorite proves to be a useful reagent under PTC conditions for the following transformations (30):

$$\mathrm{ArCH_2OH} \longrightarrow \mathrm{ArCHO}$$

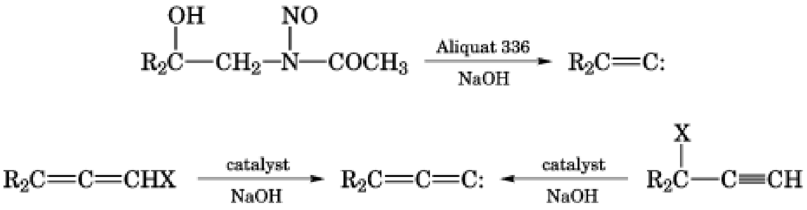
$$\mathrm{R_2CHOH} \longrightarrow \mathrm{R_2C{=}O}$$

$$\mathrm{RCH_2NH_2} \longrightarrow \mathrm{RCN}$$

Applications of phase-transfer catalysis with these additional oxidants are known: peracetic acid, air–KOH, $K_3[Fe(CN)_6]$, KO_2, K_2CrO_4, H_2O_2–heavy-metal oxide (31), H_5IO_6, ceric ammonium nitrate, KNO_2, $NaBrO_3$, and $NaClO_2$.

5.9. Carbene Reactions.

The best procedure for preparing dihalocarbene adducts of olefins consists in stirring a haloform–methylene chloride solution with an excess of concentrated aqueous caustic soda in the presence of benzyltriethylammonium chloride. Even sterically hindered and electronically deactivated compounds give excellent yields (32). Mixed dihalocarbenes, CXY ($X, Y =$ F, Cl, Br, I), except for CF_2, can be prepared. Insertions into tertiary C–H bonds can be carried out with moderate yields. Among other less common reactions improved by the use of PTC-generated CCl_2 are the carbylamine synthesis ($RNH_2 \longrightarrow R-NC$) (33). Alkylidene carbene ($R_2C{=}C{:}$) and alkenylidene carbene ($R_2C{=}C{=}C{:}$) adducts have also been prepared (34, 35).



$$R_2\overset{\overset{\text{OH}}{|}}{C}-CH_2-\overset{\overset{\text{NO}}{|}}{N}-COCH_3 \xrightarrow[\text{NaOH}]{\text{Aliquat 336}} R_2C{=}C{:}$$

$$R_2C{=}C{=}CHX \xrightarrow[\text{NaOH}]{\text{catalyst}} R_2C{=}C{=}C{:} \xleftarrow[\text{NaOH}]{\text{catalyst}} R_2\overset{\overset{\text{X}}{|}}{C}-C{\equiv}CH$$

Other reactions assisted by PTC are described in the general references.

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