Influence of phase transfer catalyst structure on selectivity

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A concise review is given of systematic studies concerned with the tuning of regio-, "frequentio-," chemo-, and diastereoselectivity by the structure or type of phase transfer catalyst.

Key words: phase transfer catalysis, regioselectivity, selectivity control, stereoselectivity, *C/O*-alkylation, *C/N*-alkylation.

There are numerous papers[1] and reviews[1–5] on various types of selectivity in phase transfer catalysis (PTC). Undoubtedly, the most exciting kind of selectivity is the enantioselectivity caused by the use of chiral catalysts. This has been recently reviewed[1,3–5] and will not be covered here. Instead, we shall concentrate upon various other types of preferences in PTC.

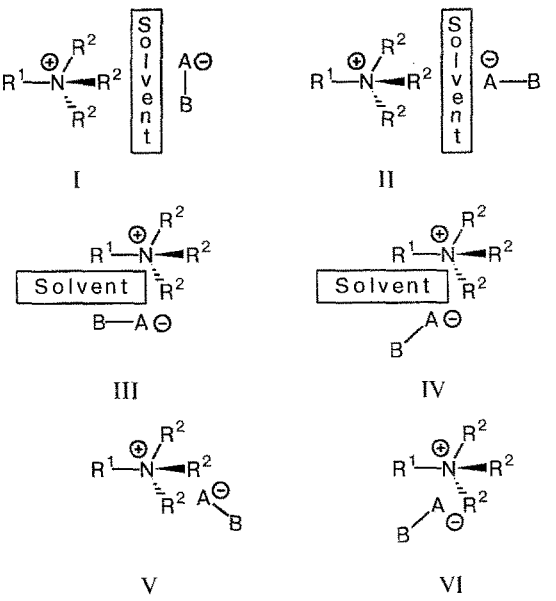
Most of the published material is concerned with selectivity differences between classical and phase transfer processes. The optimization of reaction conditions (solvent, base, reagent, temperature) is most often described. Usually just a few of the available catalysts are tested, and the best suited one is pointed out without in-depth analysis. Up to now there are only a few studies in which strong effects of catalyst structure on reaction paths are reported.

Regioselectivity

Competition of *O- vs. C*-alkylation. It is well known that ion pairs are involved in PTC processes. Let us consider the various possible arrangements of simple cation-anion combinations when the cation is $[R^1R^2_3N]^+$ and the anion is $[A—B]^-$, A being more electronegative than B. There are various possible close or solvent-separated ion pairs; six of those (I—VI) are shown in Scheme 1.

The relative preference of formation of an actual ion pair would depend on the steric requirements of R^1, R^2, and $[A—B]^-$, on the solvent, and on the nature of $[A—B]^-$. Subsequent chemical reactions of these species would be influenced by the degree of freedom of the anion. Shielding by counter-ion and solvent molecules might direct the attack of an alkylating agent more to A or more to B. Thus, an influence of the catalyst structure on the course of the reaction seems possible, but not inevitable.

Scheme 1



The early literature contains some indications of the influence of catalyst structure on *O- vs. C*-alkylation of enolate anions, but Sasson, Rabinovitz *et al.* were the first to study such affects in detail.[6,7] They investigated the alkylation of desoxybenzoins by dimethyl sulfate in the presence of 50% NaOH solution. It turned out that the *O/C*-alkylation ratios varied between 0.8 (NMe_4^+) to 1.95 (NPr_4^+). Conversion yields and *O/C* ratios could be linked to sterical accessibility of the charged central part of the onium salt.[6] Recently they have reported[7] about an additional correlation of the *O/C* ratio with the

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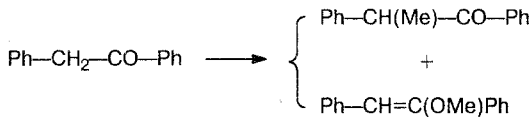
lowering of the interfacial tension caused by the quaternary ammonium ions.*

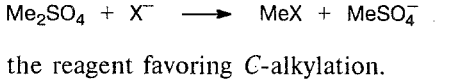


Subsequently this same reaction was investigated using a much larger array of catalysts.[8] It was confirmed that relatively low *O/C* ratio can be induced by the sterically unhindered catalysts (for instance NMe_4^+, $RNMe_3^+$). In addition, similar ratios of 0.8–1.2 were obtained in case of crown ethers (benzo-15-crown-5, 18-crown-6, dicyclohexano-18-crown-6, and others). Sterically shielded ($MeNBu^i_3Br$, *O/C* = 24) or highly delocalized cations (for example $(Me_2N)_3P{=}N{=}P(NMe_2)_3$, *O/C* = 63) lead to a much greater degree of *O*-alkylation, whereas "normal" catalysts effected in-between values. It is very important to note that catalysts with different counter-ions were tested, and invariably it was found that *O/C* ratios decreased in the order of HSO_4, Cl > Br > I. When $N(C_7H_{15})_4X$ was employed then the following *O/C* values were obtained: 7.3 (HSO_4); 5.7 (Cl); 5.3 (Br); 3.2 (I). Here a combination of several factors is operative.

(1) Tightness and array of the ion pair. Small, sterically available ions and crowns favor *C*-alkylation; sterically demanding and highly delocalized cations foster *O*-alkylation.

(2) The contribution from the noncatalyzed process (*O/C* ratio: 2.2). Its rate is slow, but it competes to some extent.

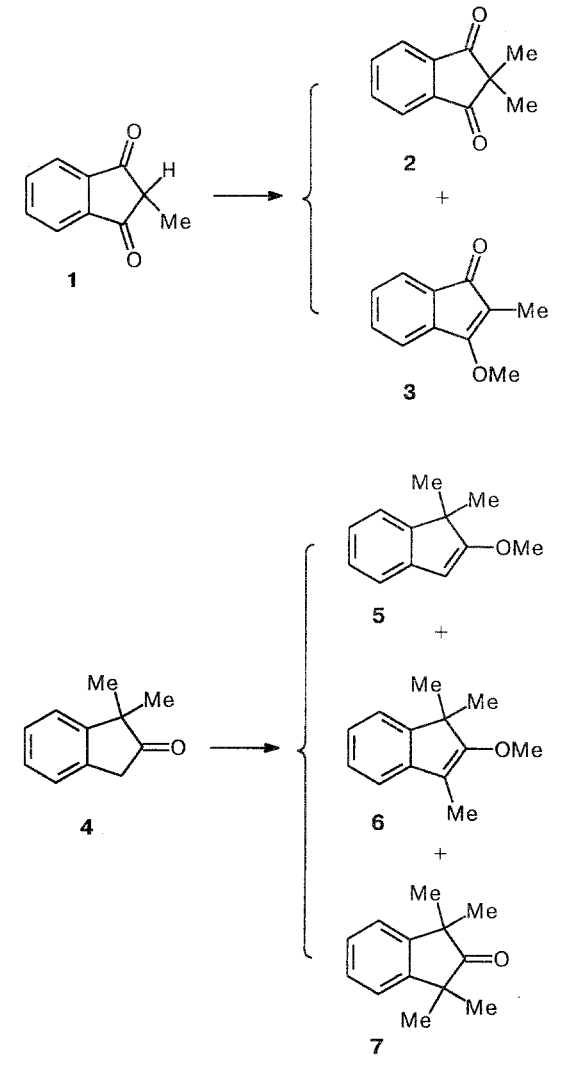
(3) The influence of the counter-ion. The degree of *C*-alkylation gradually increases on going from Me_2SO_4 over MeCl and MeBr to MeI. In this case the parallel catalytic reaction



produces the reagent favoring *C*-alkylation.

Unfortunately, these very substantial effects could not be widely generalized. In the author's laboratory a large number of systems were investigated, where the influence of the cation structure is weaker or just negligibly small. One may assume that relatively rigid anions would be strongly effected by the catalyst structure, but even that is not always the case. Thus, PTC alkylation of 2-methylindene-1,3-dione (**1**) with Me_2SO_4 (solid K_2CO_3, acetonitrile, 50 °C, 1–2 h) disappointingly leads to mixture of **2** and **3** in a 1 : 1 ratio independent of the catalyst (Scheme 2).[10] This reaction has two branching points as the mono *C*-alkylated product can be further *O*- or *C*-alkylated. Therefore, *O/C* ratios were determined for the first and second steps of the reaction.

Scheme 2



The *O/C* ratios in the noncatalyzed process are 0.4 and 0.5. It turned out that the catalysis by sterically unhindered cations and crowns produces similar *O/C* ratios for the first (**5**/(**6**+**7**)) and second (**6**/**7**) steps of the reaction, which are equal to 0.7–1.9 and 0.7–3.0 respectively. This group of catalysts includes benzo-15-crown-5, 15-crown-5, 18-crown-6, polyethylene glycol 2000, NMe_4Br, PPh_4Br, PPh_3MeBr and others. The application of conventional catalysts (such as triethylbenzylammonium chloride (TEBA), Aliquat 336, NBu_4HSO_4 and others) gives *O/C* values around 3–6 for the first step and much higher ones for the second

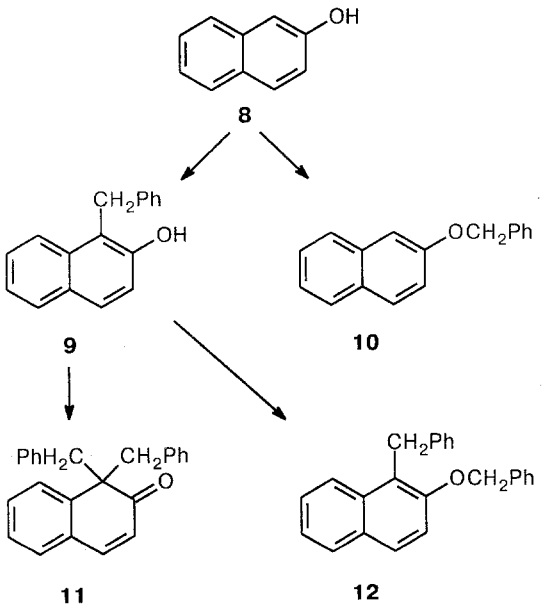
* Authors[7] believe that interfacial concentration of catalysts (measured by the fall of interfacial tension) is the key factor in this system. By all means this result should not be generalized. A more detailed study of the effect of phase transfer catalysts on interfacial tension in the dichloromethane—50% NaOH system showed that many poor catalysts exert a strong influence on the interfacial tension and *vice versa* (E. Dehmlow and J. Büker, unpublished results).

step. In this case the yield of **7** is very low. The transition to large cations (Ph_4AsCl, $[Ph_3P{=}N{=}PPh_3]Cl$, $[(Me_2N)_3P{=}N{=}P(NMe_2)_3]BF_4$) and [2.2.2]-cryptand results in formation of **5** in 91–95.5 % yield, corresponding to an *O/C* ratio of 10–21. The exclusive formation of **7** with any catalyst can be reached only with MeI as the alkylating agent. Thus were found the conditions needed for selective formation of **5** or **7**.

The selectivity of *O/C*-butylation of acetophenone was studied in the solid–liquid system without a solvent.[11] The use of a limited number of catalysts did not reveal significant structure influence. It is interesting to note, that *O/C* ratio depended on the catalyst concentration. The same was found in a more detailed study discussed below.

Another example that has some practical significance is the benzylation of sodium 2-naphthoxide (Na-**8**) in a solid–liquid system (toluene, 90 °C, 1 h) (Scheme 3).[12]

Scheme 3



The *O/C*-alkylation ratio (**10**/(**9**+**11**+**12**)) strongly depends on temperature in the range 20–55 °C, but less so at higher temperatures. At 30 °C the rates of catalyzed and noncatalyzed reactions are practically equal, but the *O/C* ratio of the first step (**10**/(**9**+**11**+**12**)) strongly depends on the catalyst concentration. In the case of TEBA this ratio rises from 0.02 (no catalyst) to 7.5 (100 mol. % of TEBA). In the absence of a catalyst, **9** is obtained in 90 % yield, and with an equimolar amount of TEBA, the yield of *O*-alkylated derivative **10** is 88 %. The comparison of catalysts at a constant concentration (10 mol. %) revealed a noticeable influence of a catalyst structure. For the first and the second steps of the reaction quite different *O/C* ratio values were obtained. Large, very lipophilic symmetrical ammonium ions (from $N(C_5H_{11})_4Br$ to $N(C_8H_{17})_4Br$) favor *O*-alkylation (*O/C* ratio = 1.1–1.3 at the first step, and 2.7–3.3 at the second step), and catalysts with small cations (NMe_4^+, $RNMe_3^+$) and benzocrown ethers favor *C*-alkylation (*O/C* ratio = 0.1–0.4 at the first step, and 0.9–1.7 at the second step). It is puzzling that the large cation with a delocalized charge $(Me_2N)_3P{=}N{=}P(NMe_2)_3^+$ falls into the intermediate class of catalysts, possibly due to solubility reasons.

Alkylation of other ambident ions. No clear-cut information is available yet on catalyst influence in the reactions of nitrite ion leading to mixtures of alkyl nitrite and nitroalkane.

The reactions of ambident SCN^- ion were studied repeatedly. Isothiocyanates are the more thermodynamically stable products and the isomerization

$$R{-}S{-}C{\equiv}N \longrightarrow R{-}N{=}C{=}S$$

can be carried out both thermally and by PTC catalysis.[13] The introduction of NBu_4Br exerts quite small influence on the *tert*-butyl thiocyanate/isothiocyanate ratio[14], and benzyl halides in the presence of 18-crown-6 (180 °C, *o*-dichlorobenzene) produced only isothiocyanates.[15] In the absence of a catalyst the isothiocyanate/thiocyanate ratio constituted 1 : 3.[15] The attempt to reproduce these results in the author's laboratory failed.[16] The reaction of benzyl chloride with solid KSCN was carried out at 180 °C in *o*-dichlorobenzene as in the above-mentioned work.[15] At the concentration of the catalyst 2.5 % in 90 min there were obtained mixtures of benzyl thiocyanate and benzyl isothiocyanate whose composition strongly depended on the catalyst. Isomerization of thiocyanate to isothiocyanate at 180 °C was accelerated by the all studied phase transfer catalysts, crown ethers and salts with large lipophilic cations being the most active ones. Working either in a solid–liquid or in a liquid–liquid PTC system at only 100 °C one can obtain pure thiocyanates. In this case the rate of the reaction was strongly catalyst depended, crowns and large lipophilic salts being again the best catalysts.[16]

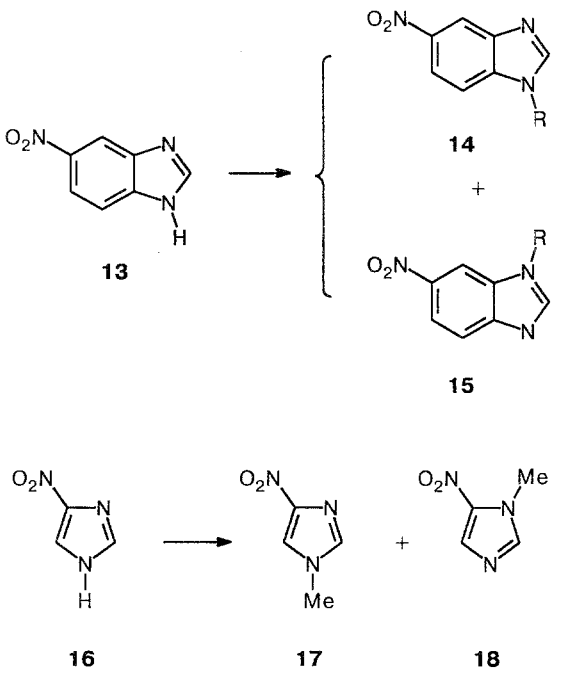
The influence of the catalyst on the *N- vs. C*-alkylation of indoles seems to be slight.[17] Similar small effects were observed in *N- vs. C*-alkylation of acridone and 4-pyridone.*

The problem of regioselectivity in *N*-alkylation of purines (Scheme 4) aroused much interest, but no effects of the catalyst structure were reported up to now. Instead there was determined the selectivity of *N*(1)- *vs.* *N*(3)-alkylation in compounds **13** and **16** (see Ref. 18).

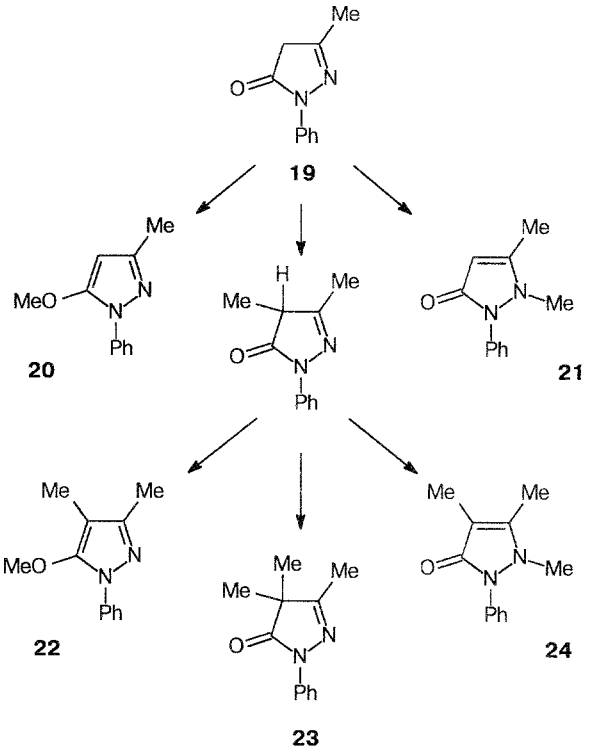
Both methylation and benzylation of **13** are phase transfer catalyzed (20 % KOH, CH_2Cl_2, 20 °C). All the investigated catalysts gave an equimolar mixture of *N*(1)-(**14**) and *N*(3)-alkylated (**15**) purines. A small catalyst

* E. V. Dehmlow and S. Schrader, unpublished results.

Scheme 4



Scheme 5



influence was observed in the methylation of diazole **16**. With dimethyl sulfate as the alkylating agent the extreme values of the **17**/**18** ratio were 68 : 32 (Aliquat 336 as the catalyst), and 87 : 13 (benzo-15-crown-5 as the catalyst). With MeI—benzo-15-crown-5 the yield of **17** reached up to 94 %.

In the case of some heterocycles *N*-, *C*-, and *O*-alkylations can compete. Methylation of pyrazolinone **18** with MeI was used as the test reaction in the 10% aqueous KOH—CH_2Cl_2 system (Scheme 5).[12]

Most successful was the application of relatively lipophilic catalysts, which practically did not influence the composition of product mixtures. A typical result obtained with Aliquat 336 was 13 % **19**, 28 % **21**, 6 % **22**, 23 % **23**, and 29 % **24**. It means that the selectivities of *O*-, *N*-, and *C*-alkylation at the first reaction step are 13 %, 28 %, and 58 % respectively. Some catalyst influence was observed with Me_2SO_4 as the alkylating agent. Extreme selectivity values provided such catalysts as NMe_4Br, $PhNMe_3Cl$ (58 % **19**, 35 % **21**, 2 % **22**, 7 % **24**) and $(Me_2N)_3P{=}N{=}P(NMe_2)_3Cl$ (72 % **19**, 24 % **21**, 1 % **22**, 4 % **24**).[12]

Even more complicated system is $(Et_2O)_2PO—NH—CO—C_2H_5$. Here in principle competition of alkylation at N, P=O-, and C=O-sites is possible.[19] The preliminary investigation under PTC conditions showed that mostly *N*-alkylation occurs, and the composition of the products depends only slightly on the catalyst.*

* E. V. Dehmlow and R. Richter, unpublished results.

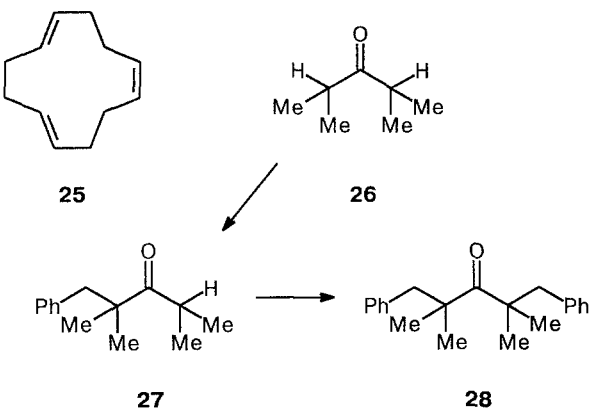
Frequentioselectivity = mono- vs. polyreaction

The term "frequentioselectivity" was introduced recently.[18] Starting compounds containing a number of similar reaction sites can react several times with the same reagent. In PTC this type of selectivity may often be controlled by reaction conditions. Low temperatures and low concentrations of the reagent and the catalyst usually favor mono-reaction. Nevertheless it may be safer and more convenient to use an inefficient highly hydrophilic catalyst with a small cation to ensure monoreaction, and a lipophilic one with drastic reaction conditions to obtain multiple interaction. As an illustration one could mention the addition of dihalocarbenes to polyolefins.[20] With NMe_4Cl as the catalyst cyclododecatriene **25** gives 72 % of monoadduct and 21 % of the bis-adduct of dichlorocarbene, and with $C_{16}H_{33}NMe_3Br$ only 5 % of the bis-adduct and 81 % of the tris-adduct under the same conditions. These results, however, are very sensitive to the concentrations of all reaction components including the catalyst.[20]

A unique case of "frequentioselectivity" was discovered recently.[18] 2,4-Dimethylpentane-3-on (**26**) can be benzylated with formation of the mono-product **27** and/or bis-product **28**. As the acidity of **26** is quite low, sodium hydride must be used for deprotonation. Nearly all the catalysts in toluene at full conversion of **26** lead to mono-product **27** in 97—100 % yield, and bis product **28** in 0—3 % yield. The appreciable yields of **28** can be

reached only in the presence of 15-crown-5 and 18-crown-6. At higher concentrations of these catalysts dibenzyl substituted ketone **28** becomes the main product. Apparently only the crown-sodium cation complexes are able to solubilize the bis-anion of **26** in toluene (Scheme 6).

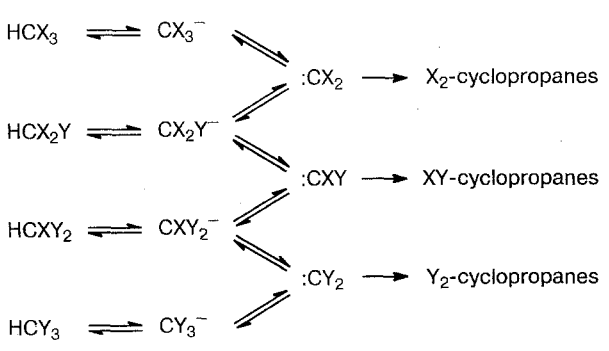
Scheme 6



Chemoselectivity

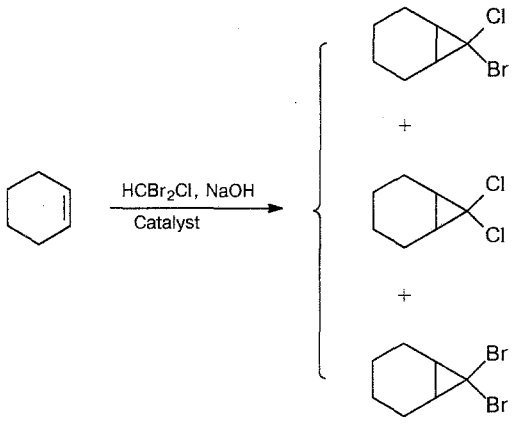
One of the most spectacular examples of catalyst controlled chemoselectivity was found in competing reactions of trihalomethyl anions and dihalocarbenes. Reaction of alkali metal hydroxide with haloform in the presence of a catalyst and an extraneous halide ion leads to the following well-known system of equilibria (Scheme 7). In the presence of most of the catalysts the exchange is quite fast and effective when X, Y = Cl, Br, or Br, I, or Cl, I.

Scheme 7



On the contrary, the addition of carbenes formed from mixed haloforms (such as $HCBr_2Cl$) to alkenes leads to dichloro-, bromochloro-, and dibromocyclopropanes in ratios strongly dependent on the nature of the catalyst. Following up the first observations of Fedorynski[21] (*cf.* also Ref. 22) a wide range of catalysts was used[23] in the reaction of cyclohexene with $HCBr_2Cl$ in the presence of concentrated NaOH at 45 °C. Although many catalysts were tested, only dibenzo-18-crown-6 and some of its derivatives along with tetramethylammonium chloride displayed high chemoselectivity in the formation of 7-bromo-7-chlorononcarane, the yield being 96–99 %. However tetramethylammonium salt is a very poor catalyst and the reaction rate is very low. The use of catalysts with very lipophilic cations having highly delocalized charge resulted in the intensive halide exchange.[25] (Scheme 8).

Scheme 8



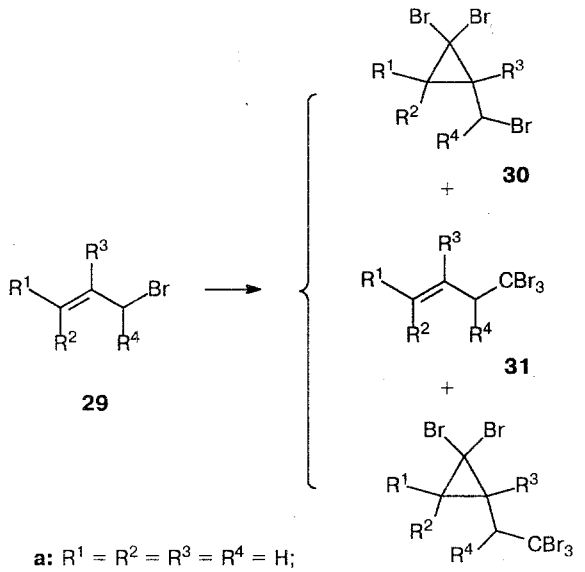
As to the HCX_3/NaOH system, PTC reaction generates the nucleophile CX_3^-, equilibrated with the electrophile $:CX_2$. Depending on the kind of reaction partners only one or both these species can be trapped. Allyl halides **29** are just such reagents, and compounds **30** and/or **31**, **32** could be produced as the result of carbene addition or trihalomethylide substitution. Compounds **32** are generated only from **31**, so the ratio **30**/(**31**+**32**) gives the addition/substitution ratio. Having in mind the results obtained by other investigators,[24,25] one can assume that the evaluation of the effects of a large number of catalysts in competing reactions on chemoselectivity was performed[26,27] (Scheme 9).

Just as in regioselectivity studies the catalysts fall into three classes.

1. Catalysts with sterically available onium fragments and some crown ethers that favor carbene addition.
2. "Classical" low selective phase transfer catalysts.
3. Catalysts with delocalized cation charge and sterically hindered salts favoring CX_3^--substitution.

All these effects are more pronounced in case of bromoform rather than chloroform. The extreme addition/substitution values are for **29a** 7.5 (NMe_4Cl) and 0.05 ($P[N{=}P(NMe_2)]_4$); for **29b** 10.6 (Cetrimid) and 0.2 ($AsPh_4Cl$); for **29c** 9.8 (benzo-15-crown-5) and 0.1 ($AsPh_4Cl$); and for **29d** even 92 (Cetrimid) and

Scheme 9



29 **30** **31** **32**

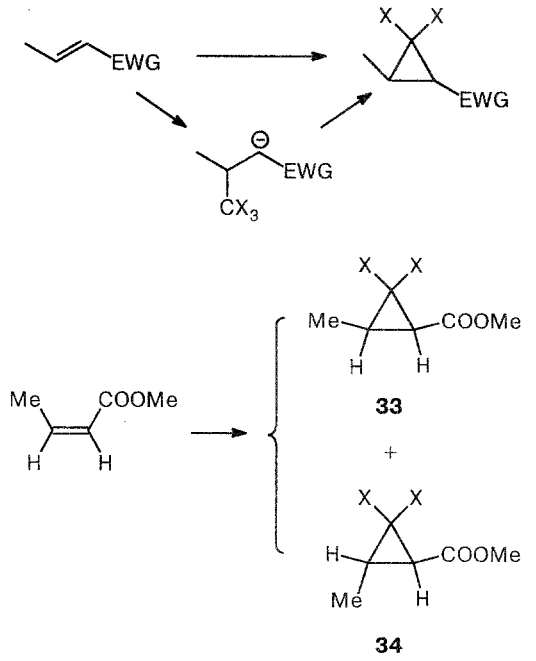
a: $R^1 = R^2 = R^3 = R^4 = H$;
b: $R^1 = R^2 = R^4 = H$, $R^3 = Me$;
c: $R^1 = R^2 = Me$, $R^3 = R^4 = H$;
d: $R^1 = Ph$, $R^2 = R^3 = R^4 = H$;
e: $R^1 = R^3 = H$, $R^2 ... R^4 = (CH_2)_3$.

0.01 ($AsPh_4Cl$)! It is rather difficult to explain why some catalysts (for example benzo-15-crown-5) do not behave similarly in all tested cases. Very specific interactions must operate sometimes.[27]

It is believed that "soft" catalysts of group (3) somewhat stabilize ion pairs $[Q^+CX_3^-]$, whereas "hard" catalysts of group (1) favor decomposition into carbene and an ion pair with a "hard" cation and anion. However, it is very important that all participating ion pairs are transient in the whole series of very complicated equilibria. To test the possible participation of CX_3^- carbenoids in real carbene generation/addition reactions, a series of experiments on competitive addition of CBr_2 and CCl_2 to cyclohexene, 2-methylbutene-2, and 2,3-dimethylbutene-2 in the presence of a large number of phase transfer catalysts was carried out.[28] Because no catalyst influence was observed, one can conclude that *in all cases the same free carbene is generated no matter what catalyst is used.*

Things are different if in competitive additions mixtures of electron rich and electron poor alkenes or just the latter ones are used.[27,29–33] Reaction of haloforms with acrylates leads to the formation of a mixture of cyclopropanes with the products of CX_3^- addition whose composition strongly depends on the catalyst,[31,32] and the competing addition of dibromocarbene to 2,3-dimethylbutene-2 or methyl acrylate with exclusive formation of cyclopropanes gives a mixture of products whose composition again strongly depends on the catalyst[27] (see also Refs. 30 and 32). The obtained results allows one to suppose that at least some cyclopropanation reactions *of electron poor double bonds* must proceed *via* initial Michael-like addition and subsequent ring closure (Scheme 10). This process can compete with the direct addition of dichlorocarbene.[31,32,34,35]

Scheme 10



33 **34**

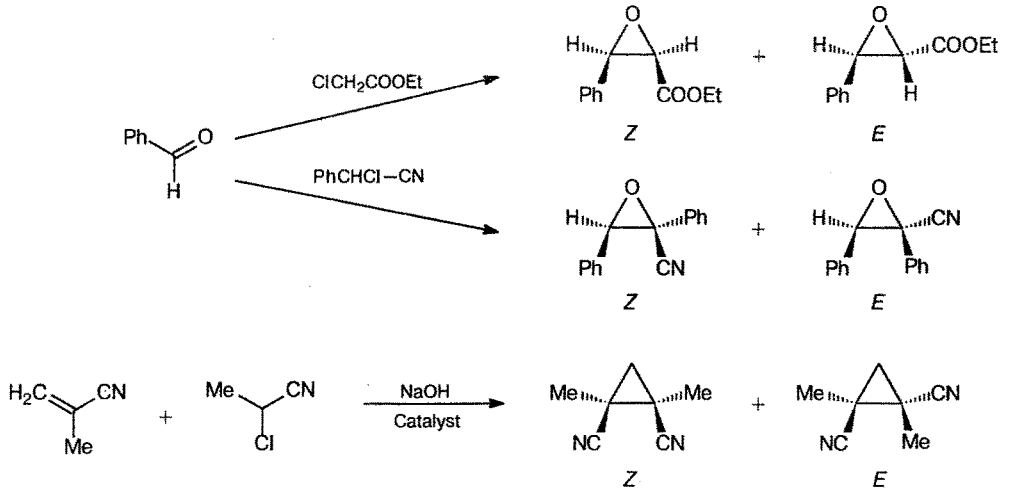
EWG — electron withdrawing group

To verify this assumption the reaction of methyl *cis*-crotonate with CX_2 (X = Cl or Br) under PTC conditions was performed. A surprising catalyst influence was observed there. Only in the presence of NMe_4Cl dichlorocarbene added stereospecifically giving **33** only. On the opposite, if the catalyst was $AsPh_4Cl$ a nonstereospecific reaction occurred *via* preliminary Michael-like addition giving *cis*- and *trans*- cyclopropanes **33** and **34** respectively (X = Cl) along with some by-products. In the reaction with dibromocarbene both products **33**, as well as **34** (X = Br), were formed independently of the catalyst.[32] These results prove the existence of competition between direct carbene addition and Michael-like addition with subsequent ring closure as shown on Scheme 10. In other words, this type of reactions is very sensitive to the nature of the catalyst.

Diastereoselectivity

A large number of works on Darzens-type reactions under PTC conditions are known. The Makosza group showed that under PTC conditions the stereoselectivity of the reaction of benzaldehyde with α-chlorophenylacetonitrile is changed.[34] Some catalyst influence on the *Z*/*E*-isomers ratio is also known for the benzaldehyde—

Scheme 11



ethyl chloroacetate reaction.[35,36] The values of the *Z/E* ratio are changed from 0.44 (dicyclohexano-18-crown-6) to 0.1 (PBu_4Br).[36] The outcome of the reaction is extremely sensitive to such parameters as reagent concentration and temperature. Recently this reaction was investigated in the author's laboratory using a large set of catalysts under standardized conditions (200 mmol benzaldehyde, 100 mmol ethyl chloroacetate, 0.2 mmol catalyst, 40 mmol of solid K_2CO_3, 6 ml chlorobenzene, 4 h, 132 °C).* The values of the *Z/E* ratio varied from 0.10 (no catalyst or $PhNMe_3Cl$, low conversion) through 0.12 (benzo-15-crown-5, higher conversion) to 0.96 (NBu_4Br or $N(C_6H_{13})_4Br$, almost quantitative conversion). Somewhat larger differences in the isomers ratio, varying from 0.5 (no catalyst) and 1.3 ($PhNMe_3Cl$) to 9–10 (very lipophilic catalysts), were discovered in the similar reaction of benzaldehyde with α-chlorophenyl acetonitrile.* Thus, the stereodifferentiation is relatively small and occurs at the first step, the carbanion addition to aldehyde. Interestingly, catalysts with small cations favor the formation of thermodynamically preferred intermediates. Catalysts with bulky cations exert the opposite influence because they form less rigid ion pairs (Scheme 11).

The formation of cyclopropane from methyl acrylonitrile and 2-chloropropionitrile under PTC conditions in the presence of a base proceeds by the mechanism similar to that discussed above for the Darzens reaction. Under standard conditions (10 mmol chloropropionitrile, 15 mmol methacrylonitrile, 0.2 mmol catalyst, 10 ml toluene, 10 ml 15% sodium hydroxide, ~20 °C, 1 h) *Z/E* ratio changed from just 1.4 (dibenzo-18-crown-6) to 0.6 ($Ph_3P{=}N{=}PPh_3Cl$). Here no reaction without the catalyst is possible.*

* E. V. Dehmlow and J. Kinnius, unpublished results.

Conclusions

When studies of PTC had just begun different catalysts were thought to differ only in their catalytic efficiency. Later it became clear that certain classes of catalysts *can have very pronounced effects on reaction selectivity*. In the most fortunate cases an almost total switch of the reaction pathway is possible. Unfortunately, it is still impossible to generalize the results obtained in the studies discussed here. Sometimes even seemingly closely related reactions are diversely affected by a phase transfer catalyst, and certain catalysts are less selective in a new reaction than one would expect from analogy. This is probably due to the very complicated character of PTC systems. The solubility of the ion pairs involved, reagent concentration, and reaction temperature along with specific interactions, all play their role.

In spite of these difficulties a possible catalyst control of selectivity is strongly recommended to be taken advantage in a newly tested reaction. For that purpose one should compare results obtained with a couple of catalysts taken from each of the above-mentioned 3 groups under standard conditions. In the author's laboratory it was found that for primary tests the following catalysts are the most suitable:

Group 1. Ammonium salts with small cations and crown ethers: NMe_4X, $PhNMe_3X$, benzo-15-crown-5.

Group 2. "Normal" catalysts: NBu_4X, TEBA.

Group 3. $AsPh_4X$, $NOct_4X$, $Ph_3P{=}N{=}PPh_3Cl$, or $(Me_2N)_3P{=}N{=}P(NMe_2)_3X$.

If substantial effects would be revealed, then in order to obtain optimal results other catalysts from 1 and 3 may be included.

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