

Do the Structures of Phase-transfer Catalysts influence Dihalogenocarbene–Carbenoid Selectivities?¹

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The selectivities of phase-transfer catalytically generated dichloro- and dibromo-carbenes towards alkenes are independent of the structure of the catalysts which indicates that free $:CX_2$ is involved in all cases in spite of the fact that there is a strong catalyst influence on certain reaction paths starting from $CX_3^- \rightleftharpoons :CX_2$.

The generation of free $:CCl_2$ in the phase transfer (PT) catalysed conversion of chloroform with NaOH² was established *via* selectivity experiments with $(C_8H_{17})_3N(Me)Cl$ as catalyst by Starks.³ Subsequently it became doubtful whether this result was valid for all types of PT catalysts. Following original leads by the groups of Baird,⁴ Kostikov⁵ and Fedoryn'ski⁶ a number of PTC $CX_3^- - CX_2$ reactions have been developed in which the nature of the PT catalyst has a profound influence on reaction paths. These are as follows.

(a) Conversions of allylic bromides give cyclopropanes 1 and/or substitution products 2. In the extreme case ($R^1 = R^3 = H$, $R^2 = Ph$), the catalyst cetrinide yields a ratio of 1:2 of 92:1, contrasting with 1:91 with Ph_4AsCl .⁷ Thus, the nature of the catalyst may determine the reaction course almost quantitatively.

(b) *tert*-Butyl acrylate, NaOH, $HCCl_3$ and a PT catalyst result in compounds 3 and 4 in ratios that vary strongly with the catalyst.^{7,8}

(c) Adduct ratios are very dependent on catalyst structures when intra- or inter-molecular competitions for dihalocarbene are executed between structural elements of types 5 and 6.^{7,9-11}

(d) Reaction of *cis*-crotonate 8 (+ $HCCl_3 - NaOH$) yields 9 stereospecifically only with NMe_4^+ catalysts whereas other catalysts lead to mixtures of 9 and 10. At least some of the reactions (b)–(d) must proceed *via* Michael addition intermediates of type 7.

(e) PTC dihalogenocarbene formations–additions starting with $HCBBr_2Cl$ lead to mixtures of 11 to 13 with most catalysts. Special catalysts (NMe_4^+ , benzo-crown ethers) give almost pure 11 with a selectivity of $\geq 98\%$.^{6,12} The formation of a proportion of 13 of up to 44% indicates the involvement of a fast halide exchange cascade in the presence of some catalysts.^{2,12}

These and other results allow PT catalysts to be grouped into three classes.²

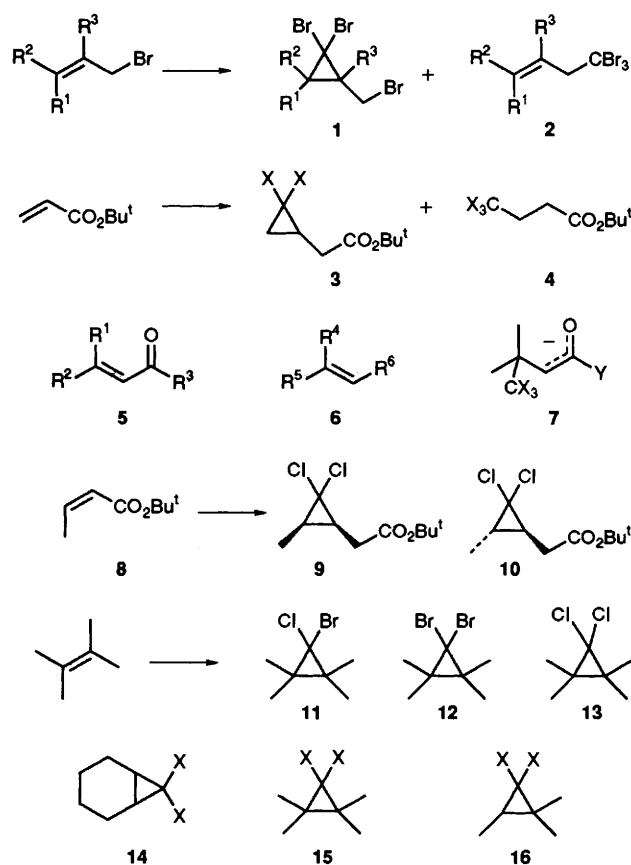
(i) Sterically shielded and highly delocalized cations [e.g., $AsPh_4^+$, $Ph_3P=N=PPh_3^+$, $(Me_2N)_3P=N=P(NMe_2)_3^+$]. These 'soft' ions seem to prefer reactions of CX_3^- anions.

(ii) Cations with a small, sterically unhindered head group (Me_3NR^+) and benzo-crown ethers. These seem to foster expulsion of CX_2 from ion pairs (cation+ CX_3^-) to give 'hard'–'hard' ion pairs (cation+ X^-).

(iii) Typical traditional PT catalysts (e.g. NBu_4^+ and

$PhCH_2NEt_3^+$ and similar ones) which do not have a strong directing effect on reactions (a)–(e).

We chose selectivity experiments to probe for a possible carbene–carbenoid dichotomy such as has been demonstrated, for instance, for $PhC-Br$ generated with $KOBu^t - PhCHBr_2$ in the presence and absence of a crown ether.¹³ To that aim, equimolar amounts of two alkenes in excess of



Scheme 1

Table 1 Phase-transfer catalytic selectivities of dichloro- and dibromo-carbene additions to cyclohexene, 2-methylbut-1-ene and 2-methylbut-2-ene^a

Catalyst Class	Compound	Dibromocarbene		Dichlorocarbene	
		15/14	16/14	15/14	16/14
(i)	[Me ₂ N] ₃ P=N=P(NMe ₂) ₃ BF ₄	2.5 ± 0.1	5.7 ± 0.1	5.8 ± 0.2	18.0 ± 0.4
(i)	[Ph ₃ P=N=PPh ₃]Cl	2.63 ± 0.03	5.60 ± 0.05	5.84 ± 0.04	17.9 ± 0.2
(i)	Ph ₄ AsBr	2.56 ± 0.04	5.7 ± 0.1	5.9 ± 0.1	18.0 ± 0.5
(ii)	NMe ₄ Cl	2.8 ± 0.1	6.15 ± 0.32	5.34 ± 0.05	17.9 ± 0.4
(ii)	Benzo-15-crown-5	2.47 ± 0.03	5.5 ± 0.1	6.0 ± 0.2	18.8 ± 0.1
(ii)	Dibenzo-18-crown-6	2.5 ± 0.3	5.6 ± 0.3	5.8 ± 0.1	19.1 ± 0.3
(iii)	PhCH ₂ NEt ₃ Cl	2.57 ± 0.04	6.0 ± 0.3	5.3 ± 0.1	18.4 ± 0.5
(iii)	N(C ₈ H ₁₇) ₄ Br	2.51 ± 0.04	5.80 ± 0.07	5.9 ± 0.2	17.4 ± 0.4

^a Conditions: 25 mmol of each alkene, 200 mmol of HCX₃, 5 mmol of 50% NaOH, 0.25 mmol of catalyst, 4 h stirring at room temp. GC analysis with 1,2-dibromocyclohexane as internal standard.

haloform were treated with dibromo- or dichloro-carbene generated in the presence of a catalyst and a limiting amount of 50% aqueous sodium hydroxide. Table 1 lists our results which were obtained from 3–5 independent experiments for each example in a well documented way.¹⁴ In some of these heterogeneous reactions the standard deviations are relatively high, but it is quite evident that there is no differentiation between the various groups of catalysts in spite of some numerical spread. In particular, there is no systematic deviation for any of the catalyst from the mean values.

Thus, the observed cases of reaction branching are not due to an inherent carbenoid-carbene stabilization or destabilization by various catalysts of classes (i)–(iii). We must rather assume that all reactions start from the (very rapidly) equilibrating system $CX_3^- \rightleftharpoons :CX_2 + X^-$. Depending on the relative reactivities of all potential reaction partners present, either an electrophilic reaction of the carbene (with an alkene or an halide ion) or a nucleophilic substitution or Michael-type addition, respectively, will be preferred.

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