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# HOW DO TRIALKYLAMINES CATALYZE REACTIONS OF DICHLOROCARBENE IN A TWO-PHASE SYSTEM?*

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At the end of 1974 Isagawa[1] reported that the generation of dichlorocarbene in a two-phase system from chloroform and concentrated aqueous NaOH is effectively catalyzed by trialkylamines. This result is very surprising since well known reactions of carbanions or halocarbenes generated in two-phase systems (aqueous sodium hydroxide as a base) are catalyzed by tetraalkylammonium compounds due to the formation of the organic phase soluble ion-pairs $>\overset{+}{N}<\ \overset{-}{C}\leq$[2]. It is obvious that trialkylamines are completely unable to act in a similar manner. As a matter of fact the alkylation of phenylacetonitrile with n-butyl bromide in the presence of aqueous NaOH is strongly catalyzed by tetraalkylammonium salts (but not by tributylamine). Therefore looking for the explanation of a strong catalytic effect of trialkylamines on the generation of dichlorocarbene, we should exclude the transport of $^{-}CCl_3$ anions to the organic phase. Thus, the only organic entity able to be transported into the organic phase seems to be dichlorocarbene. On the phase boundary $CHCl_3$/NaOHaq, the abstraction of protons (as evidenced by fast isotopic exchange[2b]) and subsequent formation of $CCl_3^-$ and dichlorocarbene does occur without any catalyst. The latter is apparently unable to react with alkene on the phase boundary. Its hydrolysis is also rather slow probably due to the fact that it exists in the intimate neighbourhood with $Cl^-$ anions (which are accumulated on the phase

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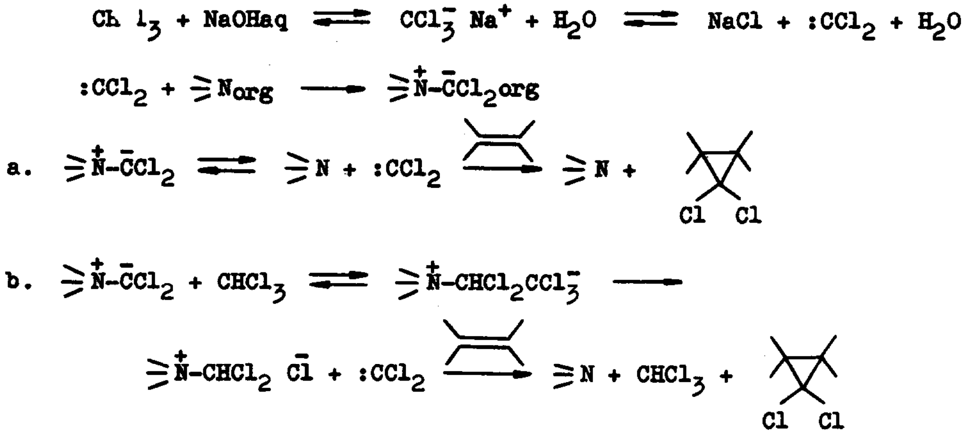
* Reactions of Organic Anions, Part LXVI; Part LXV: M.Mąkosza, B.Jerzak and M.Fedoryński, Roczniki Chem., in press.

boundary). Trialkylamines being, by no means, stronger nucleophiles are apparently able to react with dichlorocarbene on the phase boundary giving an ammonium ylide which comes to the organic phase where the following transformations can proceed (Scheme 1): a. the reverse dissociation of the ylide with the liberation of the dichlorocarbene, which is irreversibly consumed by the alkene; b. the acid-base equilibrium between the ylide and chloroform leading to the formation of the $CCl_3^-$ anion and then $:CCl_2$



$$Ch\ l_3 + NaOHaq \rightleftharpoons CCl_3^- Na^+ + H_2O \rightleftharpoons NaCl + :CCl_2 + H_2O$$

$$:CCl_2 + \geqslant N_{org} \longrightarrow \geqslant\overset{+}{N}-\overset{-}{C}Cl_2 org$$

$$a.\quad \geqslant\overset{+}{N}-\overset{-}{C}Cl_2 \rightleftharpoons \geqslant N + :CCl_2 \longrightarrow \geqslant N +$$

$$b.\quad \geqslant\overset{+}{N}-\overset{-}{C}Cl_2 + CHCl_3 \rightleftharpoons \geqslant\overset{+}{N}-CHCl_2CCl_3^- \longrightarrow$$

$$\geqslant\overset{+}{N}-CHCl_2\ \overset{-}{Cl} + :CCl_2 \longrightarrow \geqslant N + CHCl_3 +$$

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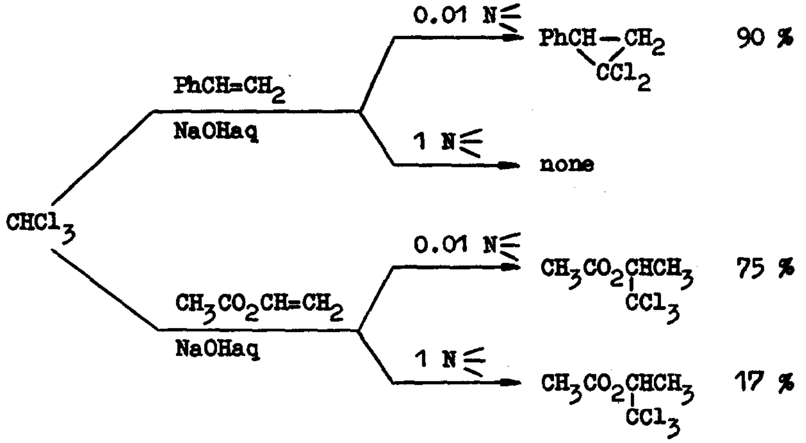
If the first pathway is operative, in the organic phase one can expect only the presence of dichlorocarbene but not trichloromethylanion. An electrophilic alkene, e.g. vinyl acetate should reacts with the former giving the adduct, 2,2-dichlorocyclopropylacetate. However the reaction with vinyl acetate yielded only 2,2,2-trichloroisopropyl acetate (yield 75 %). This result unambigously excludes the first pathway. The same conclusion comes from the fact that a trialkylamine, when used in stoichometric amount to chloroform, completely inhibits the formation of the dichlorocyclopropane from styrene, and considerably decreases the formation of the trichloromethyl derivative of vinyl acetate, thus the formation of the ylide cannot be reversible.



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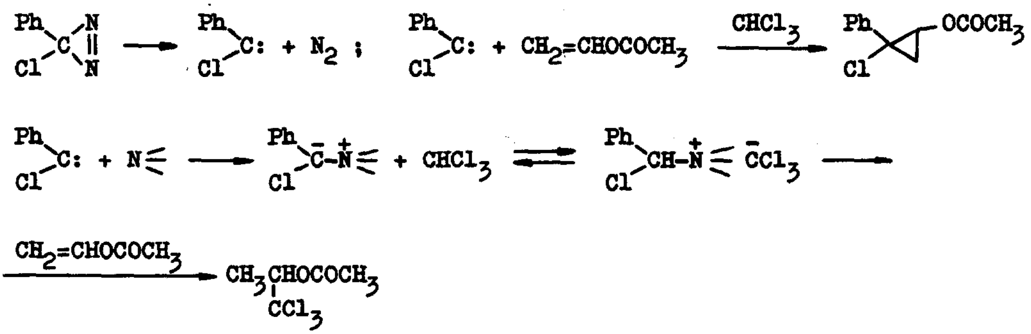
The formation of $CCl_3^-$ (and then $:CCl_2$) as a result of the equilibrium 1b. is quite possible if we consider better stabilization of the carbanion with Cl then with $\overset{+}{N}\lesssim$ substituents[3]. Thus, basicity of $\gtrsim\overset{+}{N}-\bar{C}Cl_2$ should be higher than that of $CCl_3^-$ and the equilibrium b would be shifted to the right. Since direct observation of such equilibrium is very difficult we have found an indirect proof that the reaction proceeds according to the pathway 1b. Phenylchlorocarbene generated by the thermal decomposition of phenylchlorodiazirine[5] reacts with vinyl acetate in chloroform solution giving 2-phenyl-2-chlorocyclopropylacetate; the same reaction carried out in the presence of triethylamine gave as a main product 2,2,2-trichloroisopropylacetate



Thus, phenylchlorocarbene does really react with trialkylamine giving a product of high basicity, able to abstract a proton from chloroform. The conclusion that trialkylamines catalyze the reactions of dichlorocarbene and trichloromethylanion in the two-phase systems, as shown on Scheme 1b, is therefore strongly supported.

Tributylamine in two-phase system catalyzes also very effectively the generation of dibromocarbene, which adds to alkenes giving dibromocyclopropane derivatives (e.g. from styrene 88 %, cyclohexene 76 %, 1-hexene 61 %, 1-heptene 67 %, 1-octene 75 %). These yields considerably exceed those obtained with tetraalkylammonium catalysts[6]. The effectiveness of trialkylamine catalysis in dibromocarbene generation allows one to prepare dibromocyclopropanes even from 1-alkenes, which do not react when dibromocarbene generation is catalyzed with tetraalkylammonium compounds. The detailed results will be published in near future.

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