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THE MECHANISM OF DIFLUOROCARBENE GENERATION FROM
PHENYL (TRIFLUOROMETHYL) MERCURY

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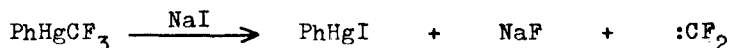
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SUMMARY

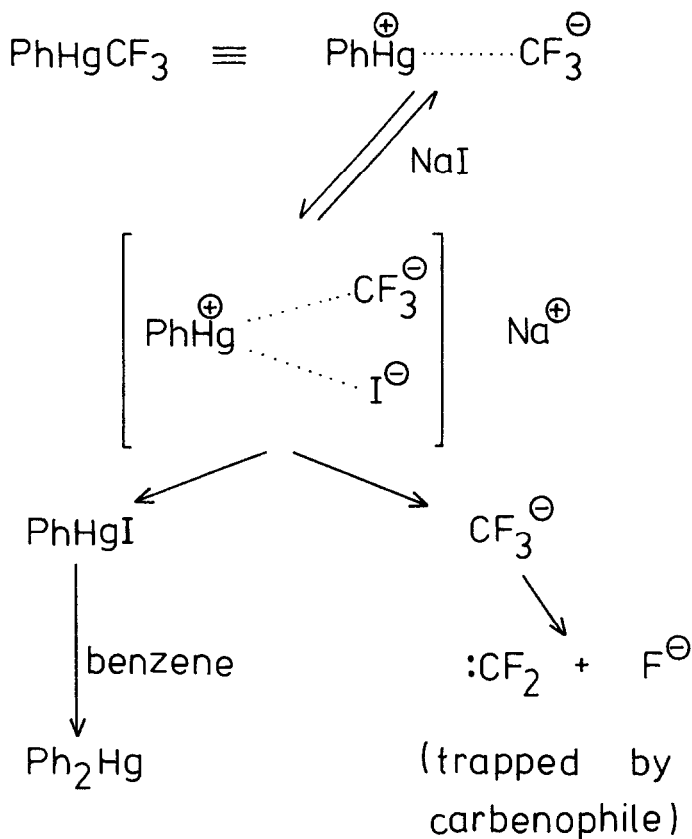
The difluorocarbene generation from phenyl(trifluoromethyl)mercury, PhHgCF_3 , is discussed. It is suggested that the nucleophilic attack of iodide anion on PhHgCF_3 followed by decomposition of such an intermediate is the key step in the mechanism. Phase-transfer catalyts do not influence this process.

Phenyl(trifluoromethyl)mercury is one of the most convenient difluorocarbene precursors. According to the procedure introduced by Seyferth *et al.* [1] it releases difluorocarbene relatively easily. This method has more advantages than the already known photochemical and thermal procedures [2-6].

In our research where PhHgCF_3 has been employed as a difluorocarbene precursor, suprisingly there has been found in the reaction mixture a significant amount of diphenylmercury (yield about 30-40%) besides other expected products. According to Seyferth *et al.* [1] the difluorocarbene generation can be simply expressed by the equation:



The generation of diphenylmercury seems to be a secondary process. On the basis of our observation of this reaction we would like to propose a scheme of difluorocarbene generation:



The enhanced acidity of mercury in PhHgCF_3 is caused by the presence of the CF_3 group. The very strong electronegative effect of three fluorine atoms is responsible for the fact that the structure of PhHgCF_3 can be treated as an ion-pair. In the reaction mixture, where PhHgCF_3 is completely dissolved in benzene and the NaI shows very low solubility, the iodide ion may be responsible for the cleavage of the $\text{Hg}^{\oplus} \cdots \text{CF}_3^{\ominus}$ bond. It can be assumed that the iodide anion will attack the most acidic center in the PhHgCF_3 molecule and cause the release of CF_3^{\ominus} . A two-phase mechanism of this process can also be considered.

The decomposition of CF_3^\ominus is an irreversible reaction which leads to the desired difluorocarbene. Moreover phenylmercuric iodide can react with benzene giving diphenylmercury, which has been observed in the reaction mixture.

To prove these conclusions, additional experiments have been carried out. The phenylmercuric iodide was refluxed in benzene for 24 hours giving 26% of diphenylmercury (the rest of the starting material remained unreacted). The direct reaction of phenyl(trifluoromethyl)mercury with benzene failed; after 4 days of refluxing the starting material remained unreacted, which was expected because of the known physico-chemical properties of PhHgCF_3 [1]. Whether the release of CF_3^\ominus group is caused by iodide anion remains a very interesting question. It is known that the generation of difluorocarbene in 1,2-dimethoxyethane (DME) - where sodium iodide is soluble - does not undergo any detectable acceleration and also reaction yields remain similar to those where benzene was used as a solvent in this reaction [7].

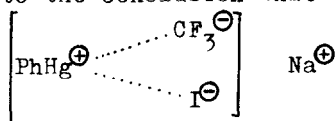
We have tested the use of phase-transfer catalysts to establish their influence on the reaction. The experimental data are collected in Table 1.

TABLE 1

The yield of 7,7-difluoronorcarane in the reaction:
 cyclohexane + $\text{PhHgCF}_3/\text{NaI} \longrightarrow$ 7,7-difluoronorcarane with
 different phase-transfer catalysts (reaction was carried out
 in a sealed tube for 10 hours at 100°C)

Catalyst	Yield of 7,7-difluoronorcarane	
n-Bu ₄ NCl	80%	
n-Bu ₄ NBr	84%	
n-Bu ₄ NI	90%	
TEBA	82%	
-	85%	83% [1]

No significant change was observed in the difluorocarbene generation. These results led us to the conclusion that the charge transfer type intermediate



and its stability are probably responsible for this phenomenon. It seems that the $\text{Hg}^{\oplus} \cdots \text{I}^{\ominus}$ bond is much weaker than the $\text{Hg}^{\oplus} \cdots \text{CF}_3^{\ominus}$ and the competitive cleavage of such an intermediate will determine the difluorocarbene generation. This process could proceed in solution or also as a two-phase process (solid NaI - dissolved PhHgCF_3).

EXPERIMENTAL

Phenyl(trifluoromethyl)mercury, PhHgCF_3 , was synthesized according to the known method [1] or by thermal decarboxylation of PhHgOCOCF_3 [8]. Crude product was crystallized from hexane and dried in a desiccator. Pure sodium iodide was dried at least 10 h at 140°C under vacuum ($p < 0.1$ mmHg). Before being used in the reaction the benzene was freshly distilled from CaH_2 .

The olefines, used as a difluorocarbene trap, were introduced to the reaction mixture usually in a ratio of 3 molar equivalents of olefine, 1 molar equivalent of PhHgCF_3 , 3 molar equivalents of NaI. Dry benzene was used as the solvent. The reaction mixture was refluxed for about 24 h, then the reaction mixture was filtered and the solution was chromatographed to give the required products. The solid residue contained NaI, NaF and PhHgI , whereas difluorocarbene-olefine adducts, Ph_2Hg and traces of PhHgCF_3 were usually present in the solution. Column chromatography was employed to separate these products.

Whenever volatile olefines were used as the difluorocarbene trap, the reaction was carried out in a sealed tube. After heating it in an oil bath at $90\text{--}100^{\circ}\text{C}$, the tube was connected to a vacuum line, the volatile products and benzene were removed and the expected olefine-difluorocarbene adducts were chromatographed on GC. The solid residue was then dissolved

in CHCl_3 and the components (Ph_2Hg and traces of PhHgCF_3) were separated using column chromatography.

Pure, commercially available phase-transfer catalysts: $n\text{-Bu}_4\text{NCl}$, $n\text{-Bu}_4\text{NBr}$, $n\text{-Bu}_4\text{NI}$ and TEBA (triethylbenzyl ammonium chloride) were used in catalytic amounts (5-10 mg) in the experiments described above.

All compounds mentioned in this paper are known in the literature and their structures have been proved by means of their MS, NMR, IR spectra and physical properties (melting points, etc.).

ACKNOWLEDGEMENT

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