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Addition of Dichlorocarbene on Organic Azides in Solid-Liquid Phase-Transfer Catalysis.

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Abstract: The addition of dichlorocarbene on organic azides in homogeneous medium leads to isocyanide dihalides. In the conditions of the solid - liquid phase transfer catalysis, tetrachloroaziridines and isocyanide dihalides are obtained respectively as main products depending on whether a hydrogenated organic or whether a 2-F-alkylethyl azide is used.

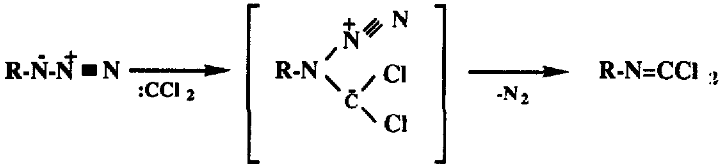
Isocyanide dihalides are very versatile compounds because of the presence in the molecule of two chlorine atoms with a different reactivity. They have attracted considerable attention and their reactivity have been extensively investigated [1,2].

There are basically three main synthetically useful methods for the preparation of isocyanide dihalides [3-16]:

- The addition of halogen to isocyanides and the halogenation of compounds such as isothiocyanates, isocyanates and imidoyl chlorides.
- The addition of dichlorocarbene to compounds such as carbodiimides, azirines, aziridines and organic azides.
- From cyanogen chloride.

Among these methods, we were interested in the addition of dichlorocarbene to organic azides [17]. The isocyanide dihalides are obtained with a good yield by stirring n-alkyl azides in pentane at 0°C in the presence of excess potassium t-butoxide in chloroform [17].

The mechanism suggested by the authors involves the addition of a dichlorocarbene as electrophile on the nitrogen atom bounded to the alkyl chain of the alkyl azide, followed by the elimination of molecular nitrogen according to the Scheme 1 :



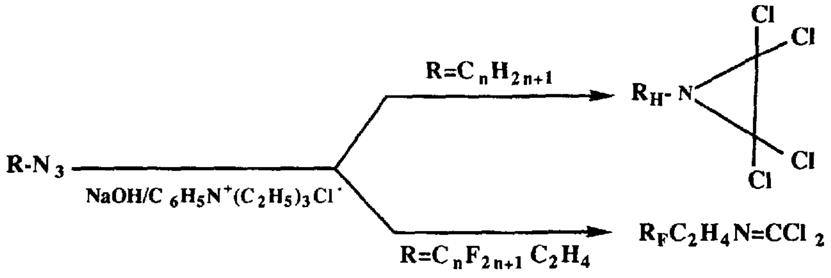
Scheme 1

This kind of reaction needs anhydrous conditions and an inert atmosphere.

We should like to report an easy and convenient alternative procedure to promote the addition of carbene on organic azides, and the different behaviour of hydrogenated organic azides and 2-F-alkylethyl azides in the presence of dichlorocarbenes generated in the conditions of the phase-transfer catalysis.

Makosza and Wawrzyniewicz [18] have shown that dichlorocarbene may be generated efficiently from chloroform and 50% aqueous NaOH in a heterogeneous system by use of the phase-transfer catalyst triethylbenzylammonium. The mechanism generally accepted is anion generation in the aqueous phase, transfer of the anion into the organic phase, and reaction with the substrate [19-22]. Carbene generation using solid-liquid phase-transfer catalysis has been carried out with potassium t-butoxide as base and crown ethers as catalyst [23]. The mechanism postulated for this case is base transfer to the organic phase by means of the cation-complexing effect of the catalyst. More recently is was found that quaternary ammonium compounds can also work as solid liquid phase-transfer catalysts using sodium hydroxide as base [24-26].

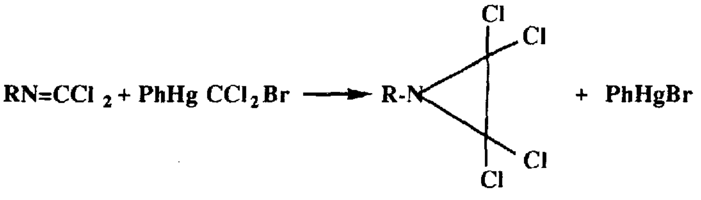
We have used solid-liquid phase-transfer catalysis to generate dichlorocarbene in the presence of organic azides and have obtained depending on whether hydrogenated organic or whether a 2-F-alkylethyl azide [27-28] is used, a tetrachloroaziridine or an isocyanide dihalide respectively as main product, according to the Scheme 2 :



Scheme 2

Typical yields are summarized in the table below.

The results obtained in this work demonstrate that the conditions of the solid-liquid phase-transfer catalysis promote the addition of dichlorocarbene not only to the negatively charged nitrogen atom of the organic azide, but also to the C=N bond of the isocyanide, which was only possible from isocyanide dihalides with particular reagents [29] in homogeneous medium :



(1)

The difference of behaviour of the different organic azides used can be thought as coming from the different inductive effects of the alkyl, aryl and F-alkyl part of the molecules.

The reactions were performed in chloroform using powdered sodium hydroxide and a catalytic amount (1mole %) of triethyl benzyl ammonium chloride (TEBAC). The reaction proceeds fast and is strongly exothermic (it must be carried out in a efficient fume hood because of the toxicity of some isocyanide dihalide).

The advantages of this method are its simplicity and the use of readily available reagents.

Table
Addition of Carbene on Organic Azides

Azide	Isocyanide dihalides (yield %)	Tetrachloroaziridine (yield %)	Boiling Point (°C/mmHg)
$C_4F_9C_2H_4N_3$	39[a]	17[b]	40/30 [c]
$C_6F_{13}C_2H_4N_3$	60[a]	12[b]	40-45/1.75 [c]
$C_8F_{17}C_2H_4N_3$	50[a]	9[b]	65/1.70 [c]
$C_8H_{17}N_3$	21[a]	75[a]	68/0.40 [c] 85-90/0.40 [d]
$C_9H_{19}N_3$	15[a]	60[a]	85-90/1.5 [c] 115/1.5 [d]
$C_6H_5CH_2N_3$	23[b]	28[a]	110/20 [c] 135/20 [d]

a. Yield of product isolated by distillation; ^{1}H NMR, ^{19}F NMR and GC-MS spectra in accordance with the structure proposed.

b. Yield of product in gas-chromatography GC-MS; spectra in accordance with the structure proposed.

c. Boiling point of the isocyanide dihalide.

d. Boiling point of the tetrachloroaziridine.

Further investigations in the field of the comparative carbene chemistry between hydrogenated and F-alkylated organic azides are in progress.

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