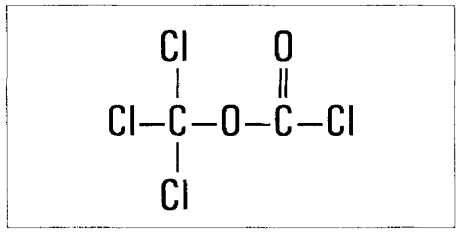
Trichloromethyl chloroformate "Diphosgene"



Phosgene Substitute

Diphosgene is an easy to handle liquid substitute for phosgene; it has a higher boiling point (128°) than phosgene (8.2°) which is a gas at room temperature[1]. Due to its low vapor pressure (10 mm at 20°) diphosgene can be easily measured at room temperature. Phosgene on the other hand is more cumbersome to handle; it either comes as a gas in cylinders or as toluene solution. Diphosgene is thus safer than phosgene although it is also toxic. In most applications 1 mol of diphosgene reacts equivalently to 2 mols of phosgene. Depending on reaction conditions, diphosgene reacts with 1 equivalent of a nucleophile (alcohol, amine, etc.), to give the appropriate chlorocarbonyl or trichloromethoxycarbonyl derivative. If desired, diphosgene can be conveniently converted into phosgene by dissolving in carbon tetrachloride in the presence of a basic catalyst (diphosgene in carbon tetrachloride – pyridine 400: 1 for 30 minutes yields 90% phosgene[2]).

The following transformations have been conveniently performed with diphosgene

- **chloroformates** from alcohols[1,3–5],
- **symmetrical** or **unsymmetrical carbonates** from alcohols[4,6–10],
- **carbamates** from alcohols and amines[6],
- **carbamoyl chlorides** from amines[11],
- **isocyanates** from amines[1,12–14],
- **symmetrical** or **unsymmetrical ureas** from amines[11,15–18],
- **imidic chlorides** from amides[19,20],
- **carboxylic chlorides** from carboxylic acids[1,12,21],
- **isocyanides** (isonitriles) from N-monosubstituted formamides[22,23],
- **N-carboxy-α-amino acid anhydrides** from α-amino acids[24–26],
- various **heterocycles** from bifunctional compounds[1,27–31].

Some further applications are e.g. as reagent in the preparation of phosphine dichlorides[32] and dichlorotriaminophosphoranes[33] from phosphine oxides and phosphoric triamides respectively, and in the epoxidation of olefins by potassium superoxide[34].

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23261 **Trichloromethyl chloroformate** ("Diphosgene") **pract.** ~97% (GC); 1 lt ≈ 1.64 kg 10 ml sFr. 28. US$ 21.00
B.P. 128°; d_4^{20} 1.639; n_D^{20} 1.459 50 ml sFr. 120. US$ 90.00
$Cl_3COCOCl$ $C_2Cl_4O_2$ M_r 213.83 [503-38-8]

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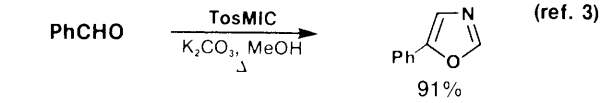
TosMIC
Tosylmethyl Isocyanide

Since its discovery[1] over a decade ago, **tosylmethyl isocyanide** (TosMIC) has become a useful synthetic reagent in the repertoire of the organic chemist. The diverse chemistry exhibited by this stable, white crystalline compound includes the efficient preparation of a variety of nitrogen heterocycles, the syntheses of cyclic and acyclic ketones, and a convenient preparation of nitriles.[2]

Heterocycle Synthesis:

Oxazole:



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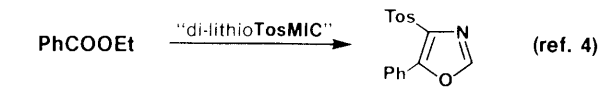
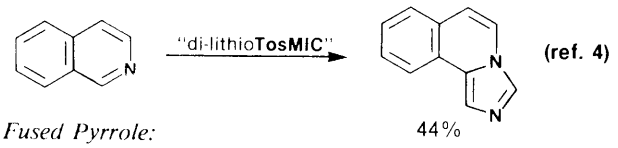


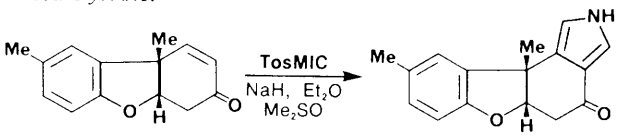
(ref. 4)

Fused Imidazole:



(ref. 4)

Fused Pyrrole:



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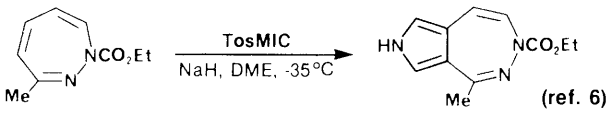
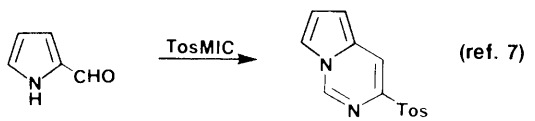


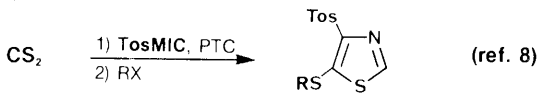
(ref. 6)

Fused Pyrimidine:



(ref. 7)

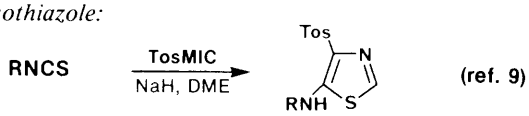
5-Mercaptothiazole:



(ref. 8)

R = alkyl, Bn, allyl, Bz, Ac

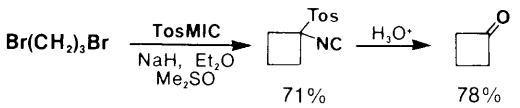
5-Aminothiazole:



(ref. 9)

R = alkyl

Cyclic Ketone Synthesis:



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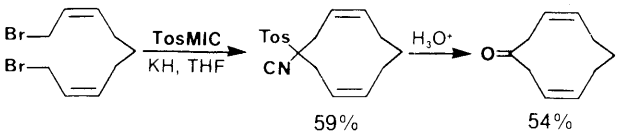
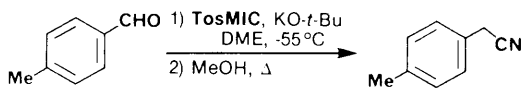


Nitrile Synthesis:

(ref. 11)



(ref. 12)

(ref. 13)

R = H, OMe

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18,820-4 Tosylmethyl isocyanide (TosMIC) 5g $16.55
25g $58.35