References and Notes

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Acid Chloride Chemistry. I. Phosgenation of Carboxylic Acids, a Catalyst Screening Study[1]

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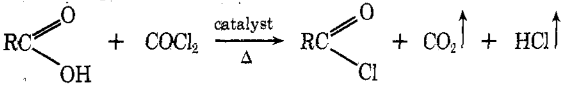
Imidazoles and several related structures with a $-\ddot{X}-Y{=}Z-$ system have been found to be excellent catalysts for phosgenation of lauric acid to lauroyl chloride. In contrast to carboxamide catalysts, imidazole can be recycled from batch to batch without appreciable loss of catalytic activity.

Over the past several decades the catalyzed phosgenation of carboxylic acids has become a prime preparative method (eq 1). Tertiary amines,[2] and more recently carboxamides,[3] have been used as catalysts for this phosgenation reaction. Both catalyst types, however, have restrictions which limit their large-scale application. Catalysis by tertiary amines[2] usually requires a reaction temperature in excess of 120°. Yields are variable, depending upon amine and type of carboxylic acid. Catalysis by carboxamides[3] normally provides high yields at reaction temperatures below 100°. Once the substrate acid has been consumed, however, the carboxamide-derived catalyst decomposes to nonactive tar. The tar can foul equipment[4] and has no catalytic value upon recycle to subsequent reactions.



$$RC(=O)OH + COCl_2 \xrightarrow[\Delta]{catalyst} RC(=O)Cl + CO_2\uparrow + HCl\uparrow \quad (1)$$

An ideal phosgenation catalyst should provide acid chlorides in high yield from an assortment of carboxylic acids at moderate reaction temperature and short residence time. Moreover, it should maintain its activity upon recycle with reaction residues from one batch reaction to another. We have found a number of catalysts which fit this description.

Results and Discussion

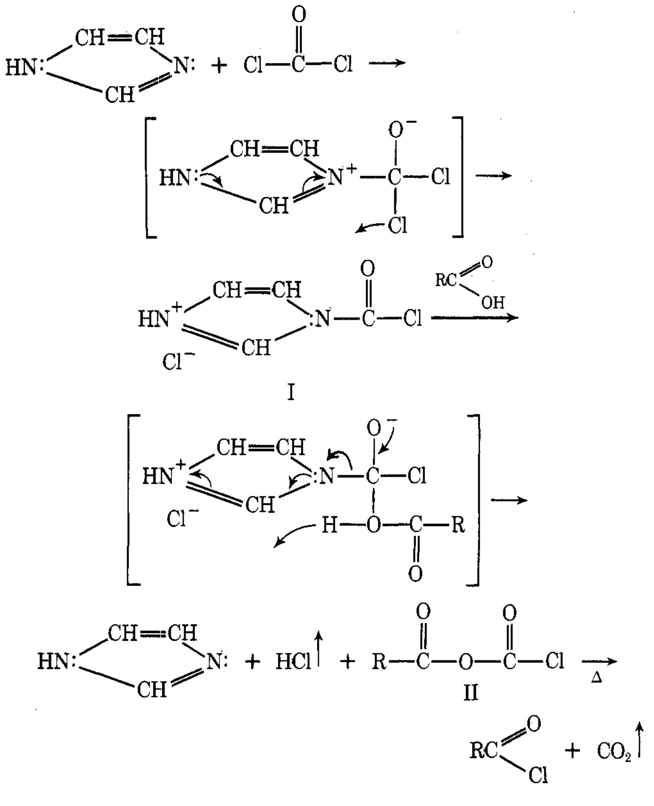
A large number of compounds have been tested as catalysts for the phosgenation of lauric acid to lauroyl chloride. The results of a number of these experiments are recorded in Table I. The catalysts in group A are five-membered heterocyclic compounds containing nitrogen, oxygen, or sulfur atoms adjacent to a carbon-nitrogen double bond. Most of these materials are excellent phosgenation catalysts, providing yields of lauroyl chloride in excess of 90% at reaction temperatures of less than 100°. Group B catalysts are six-membered heterocyclic compounds containing nitrogen, oxygen, or sulfur atoms adjacent to carbon-nitrogen unsaturation. Of those selected, the six-membered heterocyclics were less effective catalysts than the five-membered species. Group C is composed of compounds containing carbon-nitrogen unsaturation. The effectiveness of these materials for conversion of lauric acid to lauroyl chloride varies from excellent to essentially nil. This effectiveness is seen with the series of Schiff bases, isobutylidene-*n*-butylamine, *N*-benzylidenemethylamine, and *N*-benzylideneaniline, wherein the yield of lauroyl chloride varies inversely with aromatic substitution on the carbon-nitrogen double bond. Group D consists of isocyanates and compounds of carbon-carbon unsaturation. *n*-Butyl isocyanate provided an excellent yield of lauroyl chloride, whereas the aromatic specie did not. Carbon-carbon unsaturation provided poor conversion to lauroyl chloride, except for the enamine, 1-dimethylamino-2-methylpropene.

Carbon-nitrogen unsaturation, and in one case nitrogen-nitrogen unsaturation, is present in each compound in Table I which showed high catalytic activity. Usually, this unsaturation is adjacent to an atom possessing an available pair of electrons, the combination of which form the structure $-\ddot{X}-Y{=}Z-$. This XYZ structure is apparently responsible for the observed catalytic activity. Using

Table I
Phosgenation of Lauric Acid to Lauroyl Chloride[a]

Registry no.	Catalyst	Temp, °C	Phosgene consumed, mol %[b]	Yield, %[c]
	Group A			
	1-Butyl-4- (or 5-)methyl-1,2,3-triazole	66–91	100	96.6
143-07-7	2-Benzothiazole	88–95	103	96.4
112-16-3	Imidazole[f]	90–99	102	94.5
26588-27-2	2,5-Dimethyl-1,3,4-oxadiazole	82–100	97	93.8
95-16-9	1,2-Dimethylimidazole	90–105	99	93.0[e]
288-32-4	2-Methylimidazole	90–98	96	90.9
13148-65-7	2-Methylimidazole hydrochloride	93–98	75	69.8
1739-84-0	2-*n*-Butylimidazole	84–94	97	90.0
693-98-1	3,5-Dimethylpyrazole	90–98	93	88.5
36443-78-4	3,5-Dimethylisoxazole	93–103	90	82.9
50790-93-7	2-Thiazoline-2-thiol	94–106	86	77.4
	Group B			
67-51-6	1,5-Diazobicyclo[5.4.0]undec-5-ene	73–105	102	96.0
300-87-8	1,3,5-Triethyltriazine	93–90	103	94.5
96-53-7	Quinoxaline	91–100	92	88.9
6674-22-2	Phenazine	73–94	95	88.2
1009-74-1	Pyridazine	84–100	76	67.1
91-19-0	Pyrimidine	90–100	56	50.9
	Group C			
92-82-0	Isobutylidene-*n*-butylamine	66–94	100	93.0
289-80-5	Bicyclohexylcarbodiimide	78–99	97	95.5
289-95-2	*N*-Benzylidenemethylamine	88–102	70	61.8
6898-75-5	Acetone oxime	87–92	64	57.4
538-75-0	*N*-Benzylideneaniline	90–126	<10	*d*
	Group D			
622-29-7	*n*-Butyl isocyanate	98–100	103	97.8
127-06-0	1-Dimethylamino-2-propene	88–101	101	94.5
111-36-4	Toluene diisocyanate	85–100	66	70.6
2155-94-4	Tetravinylsilane	97–106	50	46.2
1321-38-6	Isobutyl vinyl ether	81–123	<10	*d*
1112-55-6	1-Hexyne	90–109	<10	*d*

[a] Unless otherwise specified 2.0 mol % catalyst based on acid was used. [b] Calculated from averaged flowmeter readings, and presented as mole per cent based on acid. [c] Yields based on lauric acid and 100% conversion of acid to acid chloride. Products distilled directly from completed reaction mixture was generally 99.0–100.5% pure as measured by Mohr (inorganic) chloride analysis. [d] Observed very sluggish reaction. Product not isolated. [e] A flocculant precipitate, apparently a complex of catalyst and acid chloride, was observed in the distilled product. [f] Used 0.5 mol % catalyst based on acid.



imidazole as the model, the depicted mechanism can be written for the catalyzed phosgenation of carboxylic acids to acid chlorides.

This mechanism shows the catalyst as the activator for phosgene in its reaction with carboxylic acid. Imidazole and phosgene yield reactive specie I, which reacts with carboxylic acid to yield acyl chloroformate (II), hydrogen chloride, and catalyst. Acyl chloroformate (II) decomposes at reaction temperature to yield acid chloride and carbon dioxide. Whether the catalyst is complexed with hydrogen chloride is a moot point. As seen in Table I, phosgenation in the presence of 2-methylimidazole is significantly more complete than in the presence of the preformed hydrochloride salt (2-methylimidazole hydrochloride). This data implies that catalyst is not complexed with hydrogen chloride.

The decomposition of the acyl chloroformate is perhaps the rate-determining step. Carbon dioxide is evolved from the reaction mixture at 90–100° following cessation of phosgene feed and hydrogen chloride evolution (see Experimental Section). This evolution indicates the decomposition of an intermediate after the last point at which hydrogen chloride is evolved. This phenomenon was observed with acids of acidities different from that of lauric acid, for instance benzoic and chloroacetic acids.[5]

For Schiff bases, the ease with which phosgene reacts with nitrogen of the carbon–nitrogen unsaturation, and subsequently the yield of acid chloride, should depend upon the ability of the adjacent groups to stabilize the resulting quaternary charge. The all-aliphatic, the aliphatic–aromatic, and the all-aromatic structures (see Table I) provided respective yields of lauroyl chloride of 93.0, 61.8, and <10%. This order of catalytic activity is in keeping with capacity to stabilize the quaternary charge, although steric factors associated with the aromatic groups may also contribute to decreasing activity within the series.

Recycle of Reaction Residues. A significant failure of carboxamide catalysts is the loss of activity once the substrate acid has been consumed.[4] Imidazole, and many of the other catalysts listed in Table I, retain their activity upon consumption of acid. The reaction residues remaining after product distillation can be recycled as useful catalyst for subsequent phosgenations. Data illustrating recycle experiments using imidazole as catalyst and lauric acid as substrate are shown in Table II.

Table II
Preparation of Lauroyl Chloride *via* Recycle of Imidazole Catalyst in Reaction Residues[a]

Expt. no.	Catalyst added[b]	Temp, °C	Time, hr	Phosgene consumed, mole %[c]	Yield, %[d]
1	0.5	89–98	5.0	101	93.4
2	0.0	88–100	5.0	97	93.8
3	0.0	84–97	5.0	99	92.9 93.4[e]

[a] Lauric acid (1.0 mol) phosgenated neat with 0.5 mol % imidazole catalyst in expt 1. In each succeeding experiment, 1.0 mol of acid was added to distillation residue of the previous reaction. [b] Mole per cent imidazole added during reaction, as based on 1.0 mol of acid added wth each experiment. [c] Calculated from averaged flowmeter readings, and presented as mole per cent based on acid. [d] Calculations based upon lauric acid and 100% conversion of acid to acid chloride. Products distilled directly from completed reaction mixture were of 99.4–100.0% pure as measured by Mohr (inorganic) chloride analysis. [e] Presented as overall yield.

Imidazole, in 0.5 mol % concentration based on acid, was used as catalyst in experiment 1. Upon complete reaction (see Experimental Section), the acid chloride product was removed by distillation under vacuum, and fresh lauric acid was added to the distillation residue. The phosgenation was repeated and the lauroyl chloride was collected as before. The process was repeated a third time. Although catalyst was added only to the initial charge, no difference in rate of reaction or yield and purity of lauroyl chloride was observed throughout the recycle series.

Experimental Section

Typical Phosgenation Experiment. A 500-ml, round-bottomed flask is fitted with a paddle stirrer, a gas inlet tube, a thermowell, and a Dry Ice-acetone deflamator (Dry Ice condenser). The flask and fittings are arranged so that gaseous phosgene could be fed below the surface of the stirred, reacting medium, and that phosgene escaping from the hot medium could be condensed on the Dry Ice-acetone deflamator and returned directly to the medium as a liquid. The deflamator is connected to two Dry Ice-acetone traps in series, the traps are connected to a water scrubber, and the scrubber is open to the atmosphere within the confines of a fume hood. (Caution! Phosgene is not sufficiently irritating at time of exposure to give warning of lethal amounts.) As by-products, hydrogen chloride and carbon dioxide are evolved from the reaction medium; they pass up through the deflamator, through the Dry Ice-acetone trap, and into the top of the water scrubber. In the scrubber, the gases react with a steady stream of water and pass down through a long glass column (4 ft) packed with glass beads. If the rate of phosgenation is too rapid, *i.e.*, an excessive reaction temperature, etc., phosgene entrained in the by-product gases will not be adequately condensed by the deflamator and began to appear in the Dry Ice-acetone trap. To this end, the incorporation of these traps in the off-gas system helps to establish facile reaction conditions.

The flask is charged with lauric acid (200 g, 1.0 mol) and catalyst (2.0 mol %, based on acid), and the mixture is heated with stirring to 90°. The stirred mixture is maintained at 90° for 1 hr, at which time gaseous phosgene (cylinder) is added below the surface of the liquid at a rate necessary to maintain a gentle phosgene reflux from the deflamator. Phosgene addition is regulated and calculated *via* a tubular flowmeter. Reaction is continued, generally within the range of 80–100°, until hydrogen chloride ceases to be evolved (cessation of heat generation at top of water scrubber). Phosgene feed is stopped and the reaction is held at 85–95° with gentle phosgene reflux from the deflamator until evolution of carbon dioxide ceases (30–60 min, as evidenced by cessation of gas at base of scrubber column). Occasionally, additional phosgene is required during this period to maintain phosgene reflux and to complete the reaction.

Following complete reaction, the deflamator is replaced by a 10-in. glass helix packed distillation column fitted with a total reflux head, and dissolved phosgene is removed from the stirred reaction product by sparging at 90° with dry nitrogen for 2 hr. The product is distilled at 10 mm as a single fraction.

The product is analyzed for contained chlorine *via* the Mohr (inorganic) chloride analysis (titration of chloride ion with silver nitrate solution).

Registry No.—$COCl_2$, 75-44-5.

References and Notes

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