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CHEMISTRY OF α-CHLOROETHYL CARBONATES AND CARBAMATES NUCLEOPHILIC SUBSTITUTION

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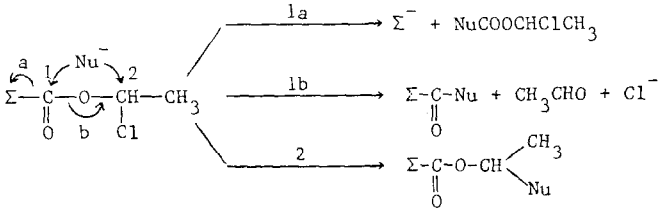
Abstract : It is shown that alkyl α-thiocyano and/or α-isothiocyano ethyl carbonates and carbamates can be obtained by reaction of the corresponding alkyl α-chloroethyl carbonates and carbamates with MSCN (M = NH_4, K). The first results obtained with octylchloroallyl carbonate are also reported.

Carbonates and carbamates are widespread derivatives in phytosanitary chemistry, and the synthesis of such new functionalized compounds are always under active investigations[1a,b,c,d]. Chloroalkylcarbonates[2a] and carbamates[2b] 1 and 2 easily obtained from the corresponding chloroformates could be good starting materials, if the chlorine atoms were easily replaced by a nucleophile.

$RO\text{-}COOCHClCH_3$ (1) $\qquad$ $R^1R^2N\text{-}COOCHClCH_3$ (2)

Besides their potential applications, these molecules pose an interesting reactivity problem. Indeed, they may be attacked by nucleophiles following different pathways and the laws governing their reactivity are not well known (Scheme).



SCHEME

Moreover, it would be of interest to know if path 2 would take place following an SN_2 or SN_1 mechanism. In our continuing interest on the chemistry of this series[3,4] we wish to

report here the first results dealing with the condensations of alcaline thiocyanates on some 1 and 2 derivatives as well as an octyl chloroallyl carbonate $C_8H_{17}OCOOCH=CH-CH_2Cl$ 3.

Condensations of MSCN (M = K, NH_4) on 1 (R = C_8H_{17}, Ph) are reported in Table I and some interesting features emerge from these results.

In aprotic solvents, there was no large behaviour difference between KSCN and NH_4SCN. On the contrary in protic solvents NH_4SCN was much more reactive. The presence of a salt as catalyst has a dramatic influence only in aprotic solvents. Interestingly the reagents were completely soluble in aprotic as well as in protic solvents, but the catalyst was soluble in protic solvents and only sparingly soluble in aprotic ones. So the activation observed in acetone could be due to a reaction taking place at the surface of the catalyst.

Variations of 4/5 ratios are difficult to explain in an aprotic solvent. In a protic solvent such as methanol a stronger specific solvatation of the nitrogen of SCN^- is certainly responsible for the high yields in thiocyanate 4.

Finally protic solvents may be of practical interest with sensitive substrates as illustrated with phenyl chloroethyl carbonate. In acetone, the essential reaction was the attack on the carbonyl group with elimination of phenol while in formamide substitution of chlorine took place in fair yields.

Some of the results obtained with chloroethyl carbamates 2 ($R^1 = R^2 = Et$, $R^1R^2 = (CH_2)_5$) have been gathered in Table II. On the contrary to what was observed with carbonates, protic solvents were of much more practical interest than aprotic solvents, the reaction time being shorter. In the absence of kinetic measurements, it is impossible to discuss the exact nature of the mechanism. However compared to carbonates it is clear that in carbamates, nitrogen conjugation with the carbonyl group allows more electron delocalization on the oxygen of the chloroethyl group to stabilised a potential cation. So SN_1 or SN_2 with like cation transition states must be more expected from carbamates than from carbonates thus explaining the favorable influence of protic solvents.

This hypothesis seems confirmed by the results obtained with octyl chloroallyl carbonate 3 (Table III). This compound must also have a strong tendency to condense following a SN_1 or a cation like transition state mechanism. So protic solvents are expected to be better than aprotic ones. That is what was observed. The values of the ratios of the different products formed will be much more difficult to interpret since interconversions between them were detected.

In a typical procedure, compound 1 (R = Oct, 10 mmoles, 2.36 g) was added to a magnetically stirred mixture of NH_4SCN (40 mmoles, 3.04 g) and PBu_4Br (2 mmoles, 0.67 g) in refluxing acetone (20 ml). After completion of the reaction (monitored by GLC 3 m 10 % SE 30) and usual aqueous workup, the products were isolated by flash chromatography on a silica column (eluent 92/8 Petroleum ether/Ethyl acetate).

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TABLE I

$ROCOOCHClCH_3$ (1 eq) + MSCN (4 eq) $\xrightarrow[(0.2\ eq)]{Catalyst}$ $ROCOOCH(SCN)-CH_3$ + $ROCOOCH(NCS)-CH_3$ + ROH

1 → 4 + 5 + 6

R	Solvent	M	Catalyst	Time (h)	T°C	4[a]/5[a]	4+5 % [b]	6 % [b]
Oct	Me_2CO	K	-	35	56	55/45	80	10
Oct	Me_2CO	NH_4	-	35	56	67/33	78	18
Oct	Me_2CO	NH_4	NEt_4Br	6.5	56	75/25	67	17
Oct	Me_2CO	NH_4	PBu_4Br	4	56	80/20	80	9
Oct	MeOH	K	-	73	25	93/7	70	19
Oct	MeOH	NH_4	-	27	25	100/0	64	21
Oct	$HCONH_2$	K	-	168	25	65/35	62	23
Oct	$HCONH_2$	NH_4	-	71	25	59/41	85	5
Oct	$HCONH_2$	NH_4	PBu_4Br	86	25	57/43	85	7
Ph	Me_2CO	NH_4	PBu_4Br	168	56	trace	trace	c
Ph	$HCONH_2$	NH_4	-	73	25	100/0	51	35

a : Identified by ^1H NMR and IR. All the microanalyses are satisfactory.

b : Yield of isolated products by flash chromatography on silica column.

c : 75 % of phenol isolated in mixture with thiocyanate (ratio determined by ^1H NMR).

TABLE II

$R^1R^2NCOOCHClCH_3$ (1 eq) + MSCN (4 eq) $\xrightarrow[(0.2\ eq)]{Catalyst}$ $R^1R^2NCOOCH(SCN)-CH_3$ + $R^1R^2NCOOCH(NCS)-CH_3$

2 → 7 + 8

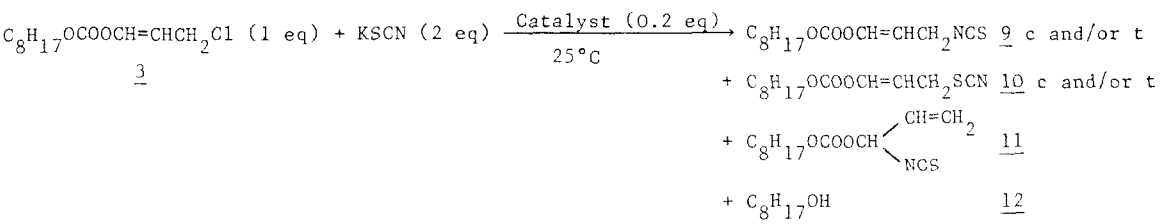
R^1	R^2	Solvent	M	Catalyst	Time (h)	T°C	7[b]/8[b]	7+8 % [c]
Et	Et	Me_2CO	NH_4	-	7.5	25	78/22	68
Et	Et	Me_2CO	NH_4	PBu_4Br	3.75	25	67/33	87
Et	Et	$HCONH_2$	NH_4	-	a	25	54/46	71
Et	Et	MeOH	NH_4	-	a	25	62.5/37.5	64
$(CH_2)_5$		$HCONH_2$	K	-	a	25	39/61	36
$(CH_2)_5$		$HCONH_2$	NH_4	-	a	25	44/56	64

a : Instantaneous reaction.

b : Identified by ^1H NMR and IR.

c : Yield of isolated products by flash chromatography on silica column. All these products are unstable.

TABLE III



Solvent	Catalyst	Ratio					Total yield[b] %	12[b] %
		Time (h)	9 c[a] %	9 t[a] %	10 c[a] %	10 t[a] %	11[a] %		
Me_2CO	-	39	8	41	6	0	45	64	23
Me_2CO	PBu_4Br	15	0	41	18	0	41	85	5
EtOH	-	4.5	7	27	9.5	5	51.5	97	0
EtOH	PBu_4Br	3	5	38	20	14	23	92	5

a : Identified by ^1H NMR and IR. All the microanalyses are satisfactory.

b : Yield of isolated product by flash chromatography on a silica column.

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