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THE REACTION OF ACYLIUM SALTS WITH DIALKYLCYANAMIDES

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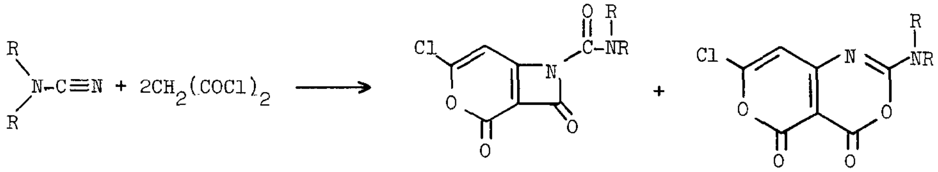
Abstract:

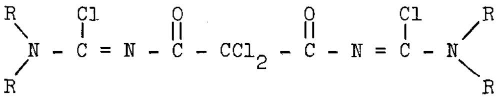
Aliphatic and aromatic acid chlorides react with dialkylcyanamides in the presence of Lewis acid at low temperature. The reaction proceeds via a stepwise mechanism to afford 1,3,5-oxadiazinium salt in good yields.

The reaction of dialkylcyanamides with acyl chlorides has been the subject of continuing interest as described in a number of reports of recent research[1-3]. Ried and coworkers[1] have reported that malonyl chloride reacts with dialkylcyanamide to give pyranoazetedione 1 and the pyrano-oxazinediones 2 (Eq.1). However, dichloromalonyl chloride reacts with dialkylcyanamide to give the corresponding open chain derivative bischloroformamadine 3. Recently, Al-Talib and others[4] reported that the reaction of heterobutatrienium salts 4 with dialkylcyanamides gives 5, (Eq.2). In this reaction compound 4 behaves as an acylium salt.



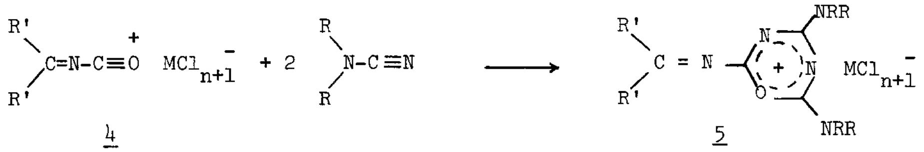
(Eq.1)

1 2

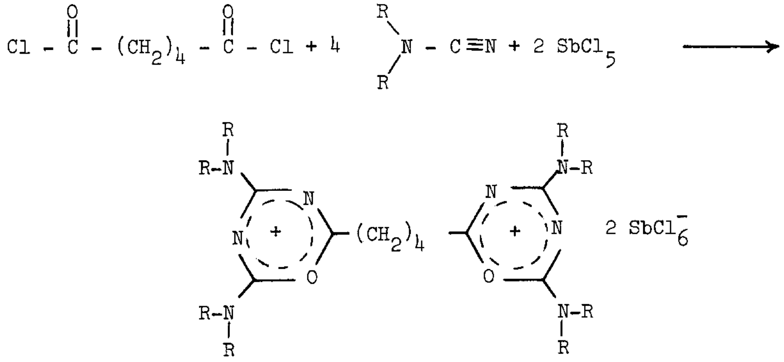


$$R_2N-\underset{}{\overset{Cl}{C}}=N-\overset{O}{\overset{\|}{C}}-CCl_2-\overset{O}{\overset{\|}{C}}-N=\overset{Cl}{C}-NR_2$$

3


(Eq.2)

Only a few 1,3,5-oxadiazinium salts were described in the literature[5-8]. We now wish to report the results of our work on the reaction of dialkylcyanamide with acyl chlorides in the presence of Lewis acid. Adipoyl chloride was found to rapidly react with diisopropylcyanamide in the presence of a Lewis acid such as $SbCl_5$ or $FeCl_3$ to give exclusively oxadiazinium salt, 6, in good yield (Eq.3). The generality of the reaction was demonstrated by showing that other alkanedioyl chlorides react under similar reaction conditions to give the corresponding oxadiazinium salts. The results are listed in Table 1.

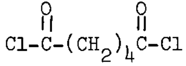
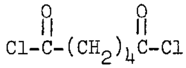
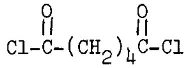
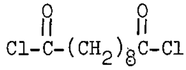
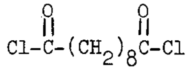
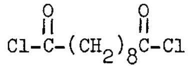
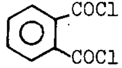
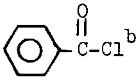
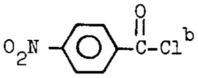
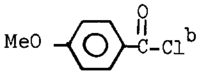
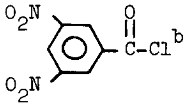

(Eq.3)

6

The above reaction is believed to proceed via a stepwise mechanism, in which two nitrile units are added to the acylium cationic intermediate. The involvement of the acylium ion was confirmed by showing that treatment of acyl chloride with Lewis acid leads to the formation of this cation as evidenced from the IR band at around 2250 cm^{-1} characteristic of $C\equiv O^+$. In addition, it was observed that electron-releasing substituent ($-OCH_3$) enhances the reaction of benzoyl chloride, whereas electron-withdrawing substituent ($-NO_2$) strongly slows down the reaction.

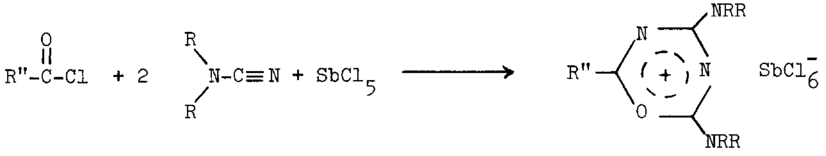
It is worth mentioning that acyl chlorides are reported[5] to react with dialkylcyanamide at high temperature to give low yields of oxadiazinium salts 7. We found that the above reaction can be carried out in presence of a Lewis acid at low temperature with high improvement in yields (Eq.4). The results are included in table 1.

Table 1: Reaction of acyl chloride with RRN-CN in presence of Lewis acid MCl_n (M=Sb or Fe) to yield oxadiazinium salts.

Acyl chloride	R	Conditions	%Yield[a] or 6 or 7
 $\mathrm{Cl{-}C({=}O){-}(CH_2)_4{-}C({=}O){-}Cl}$	$(CH_3)_2CH$	$SbCl_5$, 3h	87
 $\mathrm{Cl{-}C({=}O){-}(CH_2)_4{-}C({=}O){-}Cl}$	$(CH_3)_2CH$	$FeCl_3$, 3h	84
 $\mathrm{Cl{-}C({=}O){-}(CH_2)_4{-}C({=}O){-}Cl}$	CH_3	$SbCl_5$, 2h	75
 $\mathrm{Cl{-}C({=}O){-}(CH_2)_8{-}C({=}O){-}Cl}$	$(CH_3)_2CH$	$SbCl_5$, 3h	88
 $\mathrm{Cl{-}C({=}O){-}(CH_2)_8{-}C({=}O){-}Cl}$	$(CH_3)_2CH$	$FeCl_3$, 4h	92
 $\mathrm{Cl{-}C({=}O){-}(CH_2)_8{-}C({=}O){-}Cl}$	CH_3	$SbCl_5$, 3h	78
	CH_3	$SbSl_5$, 22h ($SbCl_5$, reflux 10h)	46 (64)
 [b]	CH_3	$SbCl_5$, 3h	85
 [b]	CH_3	$SbCl_5$, 6h	58
 [b]	CH_3	$SbCl_5$, 1.5h	94
 [b]	CH_3	$SbCl_5$, 18h	42

a. Isolated yield.

b. Molar ratios of acyl chloride: Lewis acid is 1:1.


7

(Eq.4)

The general procedure for the reaction includes the dropwise addition of antimony pentachloride (10.0 mmol) in anhydrous dichloromethane (10 ml) to a solution of alkanedioyl chloride (5.00 mmol) in anhydrous dichloromethane (10 ml) at -20°C. Then, dialkylcyanamide (20.0 mmol) in anhydrous dichloromethane (10 ml) was added. The reaction mixture was slowly warmed to 25°C and stirred for few hours at this temperature. When the reaction was complete[9], aboslute ether (30 ml) was added to afford a powder precipitate. The products were recrystallized from acetonitrile[10]. The reactions of these heterocyclic salts are now under further investigation.

Aknowledgments:

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References and Notes:

(1) W. Ried, J. Nenninger and J. W. Bats, Chem. Ber. 118, 4707 (1985).

(2) W. Ried and J. Nenninger, Chem. Ber. 119, 129 (1986).

(3) M. Al-Talib and J. C. Jochims, Chem. Ber. 118, 1304 (1985).

(4) M. Al-Talib, J. C. Jochims, L. Zolnai and G. Huttner, Chem. Ber. 118, 1887 (1985).

(5) K. Bredereck and R. Richter, Chem. Ber. 99, 2454 (1966).

(6) R. R. Schmidt, Chem. Ber. 98, 334 (1965).

(7) D. Herrmann, J. Jachmann and S. Neuhaus, Liebigs Ann. Chem. 1981, 1198.

(8) R. Gompper and F. Towae, Synthesis, 1975, 522.

(9) The completion of the reaction was indicated by the disappearance of the absorption bands between 2225-2250 cm^{-1} in the IR spectrum of the reaction mixture.

(10) All new products give satifactory elemental analysis (C,H,N), ^{1}H-NMR and ^{13}C-NMR spectra.

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