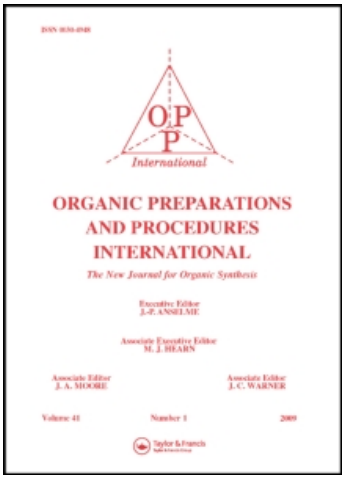

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A ONE-POT PREPARATION OF SUBSTITUTED BIS-1, 3, 5-TRIAZINIUM SALTS

Hasan Tashtoush[a]; Mahmoud Al-Talib[a]
[a] Department of Chemistry, Yarmouk University, Irbid, JORDAN

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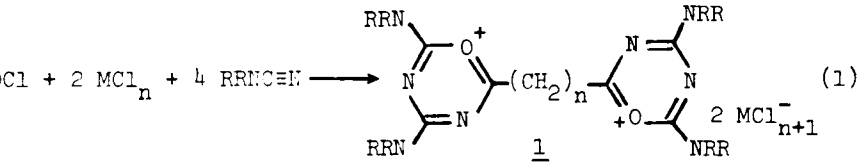
A ONE-POT PREPARATION OF SUBSTITUTED BIS-1,3,5-TRIAZINIUM SALTS

Hasan Tashtoush and Mahmoud Al-Talib*

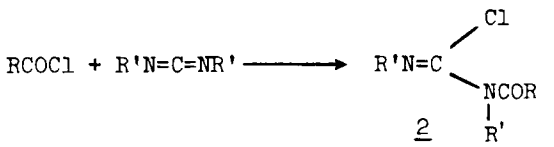
Department of Chemistry
Yarmouk University, Irbid, JORDAN

The chemistry of acylium salts has attracted much attention recently because of their importance as useful synthetic intermediates.[1-4] A previous paper[1] described the facile reaction of diacyl chlorides with N,N-dialkylcyanamide in the presence of Lewis acids (Eq. 1) to afford amino substituted bis-1,3,5-oxadiazinium salts 1, the reaction was shown to involve acylium salts as intermediates. The reaction of acyl chlorides with dialkylcarbodi-



(1)

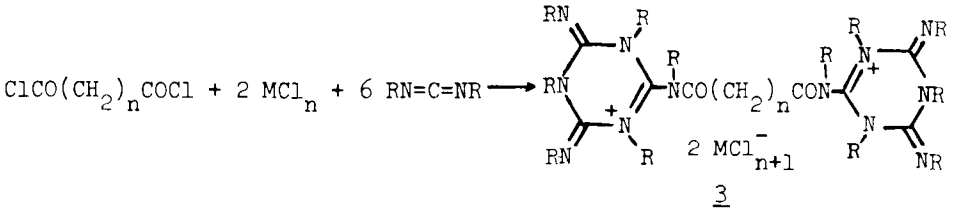
imides has been found to give acyl chloroformamidines (2) as the sole product (Eq. 2).[5,6] Little is known about the reaction of acylium salts with



(2)

dialkylcarbodiimides. A recent report by one of the present authors has shown that acylium salts reacted with three equivalents of dialkylcarbodiimides to afford substituted 1,3,5-triazinium salts. The present study describes a detailed investigation on the preparation of amino substituted bis-1,3,5-triazinium salts (3) via the reaction of diacylium salts with dialkylcarbodiimides (Eq. 3).

Adipoyl chloride reacted with six equivalents of diisopropylcarbodi-

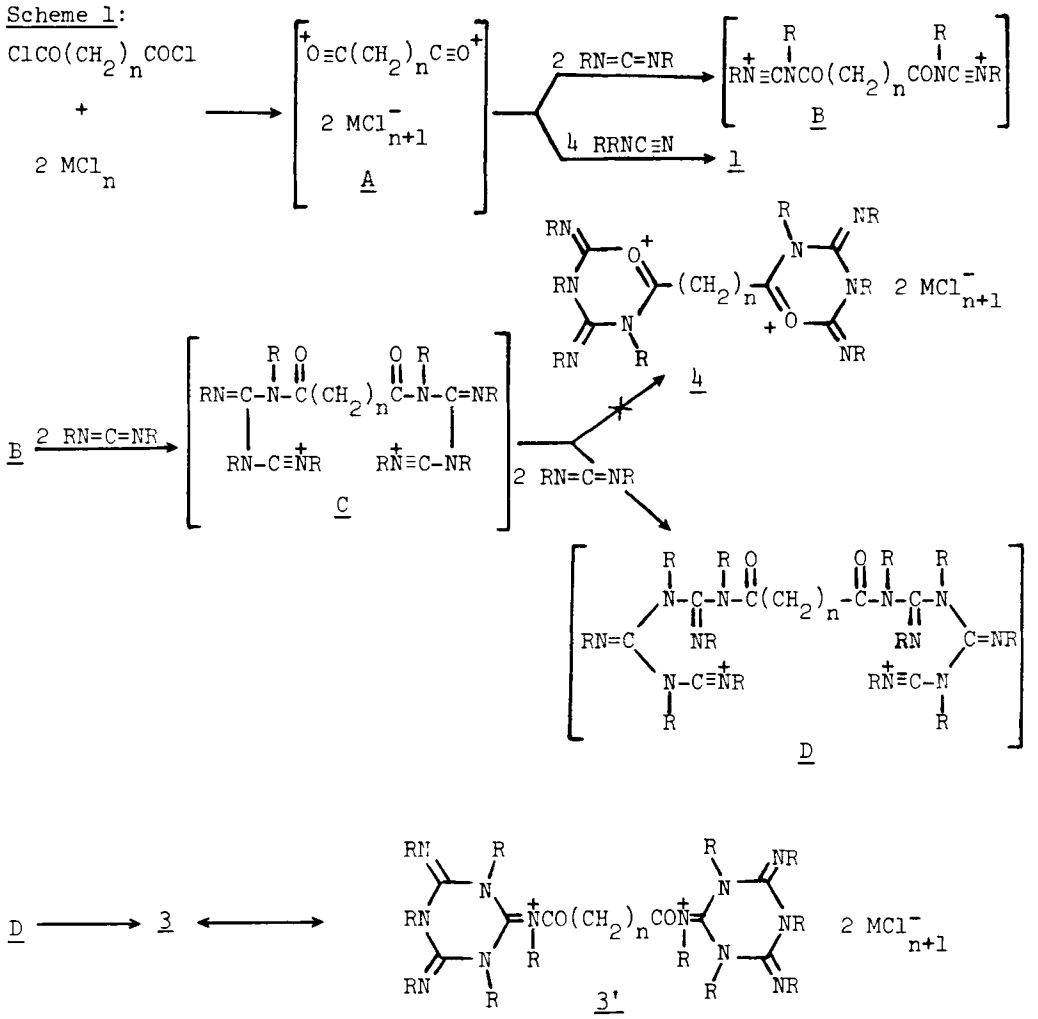


(3)

3

imide in the presence of two equivalents of antimony pentachloride to give the amino substituted bis-1,3,5-triazinium salt 3c. The reaction was quite clean, proceeding in nearly quantitative yield (Table 1). The structure of 3c was confirmed by ^{1}H-NMR, ^{13}C-NMR, IR spectroscopy and elemental analysis. Other Lewis acids such as $SnCl_4$, $FeCl_3$ and $ZnCl_2$ were also effective in promoting the reaction (Table 1). Among the tested Lewis acids, stannic chloride was the most efficient in promoting the reaction of adipoyl chloride with diisopropylcarbodiimide, and only one equivalent of it was sufficient for the completion of the reaction in less than one hour. The reaction was extended to include other diacyl chlorides as well as other dialkylcarbodiimides; the results are shown in Table 1. It was observed that oxalyl and phthaloyl chlorides are much slower in their reactions with dialkylcarbodiimides and give lower yields than other diacylchlorides. This may be attributed to steric hindrance in the products. The reaction is believed to proceed as shown in scheme 1 via the addition of the acylium salt intermediate A to two equivalents of carbodiimide yields a cyanamidium salt B which then reacts with another two equivalents of carbodiimide to give intermediate C. Intermediate C reacts further with another two equivalents of carbodiimide to give D which undergoes cyclization to afford the products 3(a-l).[2,7,8]

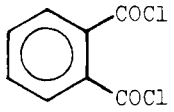
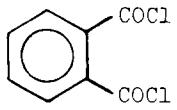
It is interesting to contrast the behavior of diacyl chlorides with four equivalents of N,N-dialkylcyanamide in the presence of a Lewis acid to give amino substituted bis-1,3,5-oxadiazinium salts (1).[1] We suggest that the driving force for the cyclization to 1 is the tendency to form the stable



aromatic oxadiazinium moieties, while in the present case, the cyclization after the successive addition of two equivalents of dialkylcarbodiimide to each acylium unit is not favored due to the fact that the product will be the nonaromatic tetrahydrooxadiazinium salt 4. Instead, a third equivalent of dialkylcarbodiimide adds to each acylium unit in C. The driving force for such addition rather than ring closure is the formation of the more resonance stabilized guanidinium moieties (3⟷3'). The products are stable at room temperature and can be stored under dry conditions for months without any changes. However these products were found to be thermally unstable. An

attempt to crystallize compound 3c from hot acetonitrile was accompanied by a change in the original product. The new product lost some isopropyl groups and found to contain N-H bonds as evidenced from IR and ^{1}H-NMR apectra.

TABLE 1. Reaction of Diacyl Chlorides with Dialkylcarbodiimides

Product No	Diacyl chloride	R	Conditions	mp (°C)	Yield[a] (%)
3a	ClCOCOCl	$(CH_3)_2CH$-	$SbCl_5$, 12h	142-145(dec)	64
3b	ClCOCOCl	c-C_6H_{11}-	$SbCl_5$, 36h	168-170	55
3c	$ClCO(CH_2)_4COCl$	$(CH_3)_2CH$-	$SbCl_5$, 3h	143-146(dec)	94
3d	$ClCO(CH_2)_4COCl$	c-C_6H_{11}-	$SbCl_5$, 5h	125-128(dec)	85
3e	$ClCO(CH_2)_4COCl$	$(CH_3)_2CH$-	$FeCl_3$, 3h	128-130(dec)	85
3f	$ClCO(CH_2)_4COCl$	$(CH_3)_2CH$-	$ZnCl_2$, 8h	116-118(dec)	88
3g	$ClCO(CH_2)_4COCl$	$(CH_3)_2CH$-	$SnCl_4$[b], 1h	133-136(dec)	98
3h	$ClCO(CH_2)_8COCl$	$(CH_3)_2CH$-	$SbCl_5$, 3h	115-118	90
3i	$ClCO(CH_2)_8COCl$	c-C_6H_{11}-	$SbCl_5$, 5h	108-112(dec)	93
3j	$ClCO(CH_2)_8COCl$	$(CH_3)_2CH$-	$SnCl_4$[b], 2h	130-132(dec)	95
3k		$(CH_3)_2CH$-	$SbCl_5$, 24h	125-127(dec)	68
3l		c-C_6H_{11}-	$SbCl_5$, 48h	128-130(dec)	60

a) Isolated yields. b) Molar ratios of diacyl chloride: Lewis acid: dialkylcarbodiimide is 1:1:6. The counter anion is $SnCl_6^{2-}$.

EXPERIMENTAL SECTION

Mps were determined with Electrothermal melting point apparatus and are uncorrected. Microanalyses were performed by M-H-W laboratories, Phoenix, Az. Elemental analysis data is given in Table 2. The IR spectra were recorded as potassium bromide pellets on a Pye-Unicam SP3-300 spectrophotometer. The ^{1}H-NMR spectra were measured with a Bruker MW-250 MHz and are reported in δ values with TMS as the internal standard. The ^{13}C-NMR spectra were recorded on Bruker MW-63 MHz (Table 3). The reaction was monitored by IR spectroscopy by following the disappearance of the bands between 2100-2300 cm^{-1} characterstic of the starting substrate. Diacyl chlorides are commercially available. Diisopropylcarbodiimide and dicyclohexylcarbodiimide were

purchased from Fluka.

TABLE 2. Elemental Analysis Data of Compounds 3(a-l)

Compound No	Formula	Elemental Analysis Calcd (Found) C	H	N
3a	$C_{44}H_{84}N_{12}O_2.2SbCl_6$	35.66 (35.69)	5.71 (5.75)	11.39 (11.53)
3b	$C_{80}H_{132}N_{12}O_2.2SbCl_6$	48.95 (48.90)	6.78 (6.66)	8.56 (8.79)
3c	$C_{48}H_{92}N_{12}O_2.2SbCl_6$	37.48 (37.28)	6.03 (5.94)	10.93 (10.83)
3d	$C_{84}H_{140}N_{12}O_2.2SbCl_6$	49.97 (50.14)	6.99 (7.02)	8.32 (8.18)
3e	$C_{48}H_{92}N_{12}O_2.2FeCl_4$	45.59 (45.70)	7.33 (7.20)	13.29 (13.30)
3f	$C_{48}H_{92}N_{12}O_2.2ZnCl_3$	47.54 (47.30)	7.65 (7.65)	13.86 (13.57)
3g	$C_{48}H_{92}N_{12}O_2.SnCl_6$	49.29 (49.09)	7.93 (7.63)	14.37 (14.05)
3h	$C_{52}H_{100}N_{12}O_2.2SbCl_6$	39.18 (39.26)	6.32 (6.31)	10.54 (10.66)
3i	$C_{88}H_{148}N_{12}O_2.2SbCl_6$	50.94 (50.75)	7.19 (7.24)	8.10 (8.09)
3j	$C_{52}H_{100}N_{12}O_2.SnCl_6$	50.93 (51.03)	8.22 (8.11)	13.71 (13.69)
3k	$C_{50}H_{88}N_{12}O_2.2SbCl_6$	38.54 (38.69)	5.69 (5.66)	10.79 (10.65)
3l	$C_{86}H_{136}N_{12}O_2.2SbCl_6$	49.47 (49.73)	6.88 (6.71)	8.44 (8.19)

TABLE 3. Spectral Data of Compounds 3(a-l)

Compound No	^{1}H NMR Solvent, δ	^{13}C NMR	IR(cm^{-1})
3a	CD_3CN 4.52 (m, 6 H, CH); 4.30 (m, 4 H, CH); 3.40 (m, 2 H, CH); 1.60-1.42 (m, 36 H, CH_3); 1.29-1.12 (m, 36 H, CH_3).	174.4, 157.3, 135.4 (C=O, C=N); 56.7, 54.4, 49.7 (CH); 22.8, 22.4, 21.3, 21.0, 20.2, 19.8 (CH_3).	1685, 1660

TABLE 3 cont.

3b	CD_3CN 4.08 (m, 6 H, CH); 3.58 (m, 4 H, CH); 3.07 (m, 2 H, CH); 2.47-1.24 (m, 120 H, CH_2 of cyclohexyl).	———	1710(sh.), 1670,1610 (sh.).
3c	CD_2Cl_2 4.50 (m, 6 H, CH); 4.30 (m, 4 H, CH); 2.79 (br. 4 H, 2 CH_2); 1.77 (br. 4 H, 2 CH_2); 1.57-1.45 (m, 36 H, CH_3); 1.31-1.12 (m, 36 H, CH_3).	175.5, 158.8, 136.8 (C=O, C=N); 58.6, 56.2, 51.6 (CH); 34.9, 24.9 (CH_2); 24.5, 23.9, 23.7, 23.3, 22.7, 22.5, 22.4, 22.3, 22.1, 21.9, 21.6, 21.0, (CH_3).	1675, 1650
3d	$CD_3CN/CDCl_3$(2:1) 4.18-3.61 (m, 12 H, CH); 2.84 (br. 4 H, 2 CH_2); 2.10 (br. 4 H, 2 CH_2); 1.77-1.10 (m, 120 H, CH_2 of cyclohexyl	175.2, 158.5, 136.4 (C=O, C=N); 67.1; 62.8, 59.1, 58.9, 57.7, 56.1 (CH); 34.8, 24.7 (CH_2).	1685, 1660, 1500.
3e	———	———	1680, 1660, 1500.
3f	$CDCl_3$ 4.72 (m, 4 H, CH); 4.23 (m, 6 H, CH); 3.35 (m, 2 H, CH); 2.60 (br. 4 H, 2 CH_2); 1.91 (br. 4 H, 2 CH_2); 1.54-1.13 (m, 72 H, CH_3).	175.5, 158.3, 136.2 (C=O, C=N); 58.2, 55.2, 55.1, 53.7, 51.0, 50.5 (CH).	1650, 1505
3g	$CD_3CN/CDCl_3$ (1:1) 5.05 (m, 2 H, CH); 4.64 (m, 4 H, CH); 4.27 (m, 4 H, CH); 3.39 (m, 2 H, CH ; 3.01 (br. 4 H, 2 CH_2); 1.88 (br. 4 H, 2 CH_2); 1.59-1.47 (m, 36 H, CH_3); 1.37-1.14 (m, 36 H, CH_3).	175.9, 158.5, 136.5 (C=O, C=N); 58.3, 55.2, 53.7, 51.1 (CH); 34.7, 24.1 (CH_2).	1680, 1580, 1510.
3h	CD_2Cl_2 4.64 (m, 4 H, CH); 4.32 (m, 6 H, CH); 3.39 (m, 2 H, CH); 2.85 (br. 4 H, 2 CH_2); 1.91 (m, 4 H, 2 CH_2);	175.3, 158.3, 135.8 (C=O, C=N); 59.8, 58.6, 56.4, 51.3 (CH); 35.1-20.9 (CH_2 and CH_3).	1680, 1660, 1510.

TABLE 3 cont.

	1.65-1.47 and 1.32-1.15 (two m, 80 H, CH_3 and 4 CH_2).		
3i	$CDCl_3$ 4.25 (m, 2 H, CH); 3.97 (m, 8 H, CH); 3.72 (m, 2 H, CH); 2.81 (br. 4 H, 2 CH_2); 2.48-1.18 (m, 132 H, 6 CH_2 and CH_2 of cyclohexyl).	174.9, 157.2, 135.3 (C=O, C=N); 66.4, 61.3, 61.0, 58.5 (CH).	1650, 1510.
3j	CD_3CN 4.55 (m, 6 H, CH); 4.30 (m, 4 H, CH); 3.40 (m, 2 H, CH); 2.77 (br. 4 H, 2 CH_2); 1.67-1.14 (m, 84 H, 6 CH_2 and CH_3).	176.1, 159.0, 136.9 (C=O, C=N); 58.6, 56.1, 51.5, 47.0 (CH).	1655, 1580, 1520.
3k	$CDCl_3$ 7.75 (br. 4 H, aromatic); 4.92 (m, 4 H, CH); 4.20 (m, 6 H, CH); 3.35 (m, 2 H, CH); 1.74-1.12 (m, 72 H, CH_3).	170.0, 156.1, 135.2 (C=O, C=N); 133.5, 131.2, 128.2.	1660, 1500 (br.).
3 l	CD_3CN 8.09 (br. 4 H, aromatic); 4.32 (m, 4 H, CH); 4.00 (m, 6 H, CH); 3.32 (m, 2 H, CH); 2.46-1.24 (m, 120 H, CH_2 of cyclohexyl).	———	1650, 1510 (br.).

Amino Substituted bis-1,3,5-Triazinium Salts (3). General Procedure.- To the diacyl chloride (5.0 mmol) in dry dichloromethane (10 ml) was added dropwise at -20° a solution of a Lewis acid (10.0 mmol) in dry dichloromethane (10 ml) followed by the dropwise addition of a solution of dialkylcarbodiimide (30.0 mmol) in dry dichloromethane (15 ml). The reaction mixture was allowed to become ambient and then stirred for a period of time (Table 1). When IR showed that the starting materials were consumed, slow addition of ether (50 ml) afforded a colorless powder. The products were collected and recrystallized at room temperature from dichloromethane-ether (1:1) or

acetonitrile-ether (1:2). The following compounds were prepared by the general procedure.

N,N'-diisopropylethanediamido-N,N'-bis{3,4,5,6-tetrahydro-1,3,5-triisopropyl-4,6-bis(N-isopropylimino)-1,3,5-triazine-2-yl-1-ium} bis hexachloroantimonate (3a), N,N'-dicyclohexylethanediamido-N,N'-bis{1,3,5-tricyclohexyl-4,6-bis(N-cyclohexylimino)-3,4,5,6-tetrahydro-1,3,5-triazine-2-yl-1-ium} bis hexachloroantimonate (3b), N,N'-diisopropylhexanediamido-N,N'bis{3,4,5,6-tetrahydro-1,3,5-triisopropyl-4,6-bis(N-isopropylimino)-1,3,5-triazine-2-yl-1-ium}bis hexachloroantimonate (3c), N,N'-dicyclohexylhexanediamido-N,N'-bis{1,3,5-tricyclohexyl-4,6-bis(N-cyclohexylimino)-3,4,5,6-tetrahydro-1,3,5-triazine-2-yl-1-ium}bis hexachloroantimonate (3d), N,N'-diisopropylhexanediamido-N,N'-bis{3,4,5,6-tetrahydro-1,3,5-triisopropyl-4,6-bis(N-isopropylimino)-1,3,5-triazine-2-yl-1-ium}bis tetrachloroferrate (3e), N,N'-diisopropylhexanediamido-N,N'-bis{3,4,5,6-tetrahydro-1,3,5-triisopropyl-4,6-bis(N-isopropylimino)-1,3,5-triazine-2-yl-1-ium}bis trichlorozincate (3f), N,N'-diisopropylhexanediamido-N,N'bis{3,4,5,6-tetrahydro-1,3,5-triisopropyl-4,6-bis(N-isopropylimino)-1,3,5-triazine-2-yl-1-ium}hexachloro stannate (3g), N,N'-diisopropyldecanediamido-N,N'-bis{3,4,5,6-tetrahydro-1,3,5-triisopropyl-4,6-bis(N-isopropylimino)-1,3,5-triazine-2-yl-1-ium}bis hexachloroantimonate (3h), N,N'-dicyclohexyldecanediamido-N,N'bis{1,3,5-tricyclohexyl-4,6-bis(N-cyclohexylimino)-3,4,5,6-tetrahydro-1,3,5-triazine-2-yl-1-ium}bis hexachloroantimonate (3i), N,N'-diisopropyldecanadiamido-N,N'-bis{3,4,5,6-tetrahydro-1,3,5-triisopropyl-4,6-bis(N-isopropylimino)-1,3,5-triazine-2-yl-1-ium}hexachlorostannate (3j), N,N'-diisopropylphthaldiamido-N,N'-bis{3,4,5,6-tetrahydro-1,3,5-triisopropyl-4,6-bis(N-isopropylimino)-1,3,5-triazine-2-yl-1-ium}bis hexachloroantimonate (3k), N,N'-dicyclohexylphthaldiamido-N,N'-bis{1,3,5-tricyclohexyl-4,6-bis(N-cyclohexylimino)-3,4,5,6-tetrahydro-1,3,5-triazine-2-yl-1-ium}bis hexachloroantimonate (3l).

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