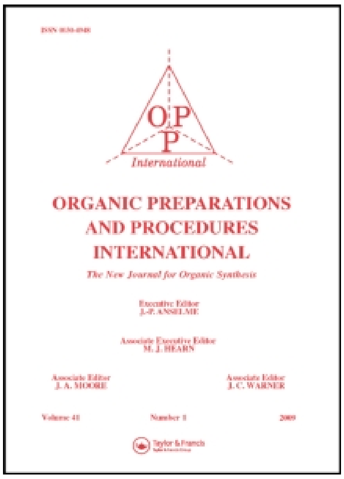

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RECENT ADVANCES IN THE USE OF ACYLIUM SALTS IN ORGANIC SYNTHESIS. A BRIEF REVIEW

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INTRODUCTION

Acylium salts have been the subject of intensive research throughout the past two decades. They deserve still more attention in view of their chemical potential as useful synthetic intermediates. The primary focus of the present review, which covers the literature to the end of 1988, is to survey the more recent progress in the increasing utilization of acylium salts in organic synthesis. Additionally, the chemical transformations of the initially formed products have been described.

I. SYNTHESIS AND SPECTROSCOPIC PROPERTIES OF ACYLIUM SALTS

The first reported stable isolated acylium salt was prepared as early as 1943 by Seel,[1] who reacted acetyl fluoride with boron trifluoride at low temperature. Since then, many other acylium salts have been prepared, especially by Olah and his coworkers.[2-7] Several methods have been applied to the

$$CH_3COF + BF_3 \longrightarrow CH_3CO^+ \; BF_4^-$$

preparation of acylium salts which include the reaction of acyl chlorides with Lewis acids or silver salts and the deamination method.[2-8] These methods have been successfully used to prepare primary, secondary and tertiary alkanoylium and aroylium salts,[2-4] as well as alkenoylium[7] and diacylium salts.[3]

Acylium salts have been studied by UV, IR and NMR spectroscopy. UV spectra

$$\mathrm{RCOX + MXn \xrightarrow[\text{Freon 113, }-20^{\circ}]{\mathrm{CH_2Cl_2}\text{ or}} RCO^{+}\ MX^{-}_{n+1}}$$

X = Cl, F; M = Sb, Al, Fe, Zn, Sn, B, P, As

$$\mathrm{RCOF + AgSbF_6 \xrightarrow[-25^{\circ}]{SO_2} RCO^{+}\ SbF_6^{-} + AgF}$$

$$\mathrm{RCONXO + NO^{+}SbF_6^{-} \longrightarrow RCO^{+}\ SbF_6^{-} + XO_2 + N_2}$$

X = C, S

of alkanoylium salts in 100% sulfuric acid show no absorptions above 215 nm, whereas aroylium cations show fairly intense absorptions in the region 250-350 nm.[9-12] IR spectroscopy has been used to differentiate between acylium salts 1 and complexes 2 formed by acyl halides and Lewis acids in the solid or liquid states.[13,15] Two conclusions have been made regarding the IR results of the reaction between acyl chloride and Lewis acids; the first is that the

$$\mathrm{RCOCl + MCl_n \longrightarrow \underset{\underline{1}}{RCO^{+}\ MCl^{-}_{n+1}}}$$

$$\mathrm{RCOCl + MCl_n \longrightarrow \underset{\underline{2}}{RC(Cl)O\ \ldots\ MCl_n}}$$

shift of the carbonyl frequency of the starting acyl halide to a lower frequency (1550-1650 cm^{-1}) indicates the formation of donor-acceptor complex 2.[13,16] On the other hand, a shift of the carbonyl frequency of the starting acyl halides to a higher frequency (2200-2300 cm^{-1}) has been attributed to the $C\equiv O^{+}$ stretching vibration of an acylium salt.[17] Whether an acylium salt 1 or a complex 2 is formed depends on R, X, the Lewis acid and the solvent (Table 1). Dynamic equilibrium between acylium salt 1 and complex 2 has been suggested by Oulevey, Susz[22,23] and others.[24] According to the vibrational stretching frequencies, acylium salts can be regarded as resonance hybrids of the canonical forms 1, 1' and 1" (when applicable).[25-28]

$$\underset{\underline{1}}{\mathrm{R{-}C{\equiv}\overset{+}{O}}} \longleftrightarrow \underset{\underline{1'}}{\mathrm{R{-}\overset{+}{C}{=}O}} \longleftrightarrow \underset{\underline{1''}}{\mathrm{\overset{+}{R}{=}C{=}O}}$$

TABLE 1. Infrared Absorptions of Carboxylic Halides/Lewis Acid Products.

Carboxylic Halide	Lewis Acid	IR (cm^{-1})	Ref.
CH_3COF	———	1848(vs)	18
CH_3COF	SbF_5	2294(vs) 1554(w) 1621(ms)	18
CH_3COCl	$SbCl_5$	2283(s) 1587(w) 1709(m)	18
CH_3COCl	$AlCl_3$	2305(vs) 1560(w)	17,19
CH_3COCl	$TiCl_4$	1620(s)	20
$(CH_3)_2CHCOF$	SbF_5	2270(vs) 1585(m)	4
$(C_6H_5)_2CHCOF$	SbF_5	1578(vs)	4
$4\text{-}CH_3C_6H_4COCl$	$SbCl_5$	1550(vs)	21
$4\text{-}CH_3OC_6H_4COCl$	$SbCl_5$	2185(vs) 1546(w)	21

NMR spectroscopy has also been used to study acylium cations.[2-4,28-31] This method has the advantage that acylium cations can be generated and studied at low temperature in solution. In the proton NMR spectra, transformation of an aliphatic acyl halide into an acylium cation results in a low field shift of all proton signals. Shifts of about 2 ppm for the α-protons are observed for acylium cations 1. Smaller deshielding effects of about 1 ppm for the α-protons are attributed to complex 2. Tables 2 and 3 include proton and carbon-13 NMR data of some alkanoylium and benzoylium cations.

II. SYNTHESIS OF HETEROCYCLIC RING SYSTEMS

Acylium salts have been reported to react with different nucleophilic substrates such as nitriles, cyanamides, carbodiimides, alkenes and alkynes following a stepwise cycloaddition process to yield various types of heterocyclic ring systems.

1. Synthesis of Substituted 1,3,5-Oxadiazinium Compounds

It is well established that acylium salts react with aryl nitriles to give 1,3,5-oxadiazinium salts.As early as 1892, Eitner and Kraft[32]observed that

TABLE 2. Proton Chemical Shifts (δ) of Alkanoylium and Benzoylium Cations

Acylium Cation	CH_3	CH	o-	m-	p-	Ref.
CH_3CO^+	4.14	—				29
$(CH_3)_2CHCO^+$	2.01	4.34				29
$(CH_3)_3CO^+$	2.37					29
$C_6H_5CO^+$	—	—	8.86	8.21	8.72	30

TABLE 3. ^{13}C Chemical Shifts (δ) of Alkanoylium and Benzoylium Cations

Acylium Cation	$R\ ^{13}CO^+$	ipso-	o-	m-	p-	Ref.
CH_3CO^+	149.5					31
$CH_3CH_2CO^+$	149.7					31
$C_6H_5CO^+$	154.9	87.8	142.4	133.0	149.5	28
$p\text{-}ClC_6H_4CO^+$	156.2	87.2	146.0	138.1	161.0	28

benzoyl chloride reacted with two equivalents of benzonitrile in the presence of aluminum chloride to give 3, the correct structure of which was recognized seventy years later by Schmidt.[33] Similarly Meerwein and his coworkers[34] studied the reaction of acyl chlorides with nitriles in the presence of Lewis acids (Table 4). The structures of the products have later[33] been confirmed to be substituted 1,3,5-oxadiazinium salts 3. These salts have been found to be useful intermediates for the synthesis of other heterocyclic rings[32,33,35] scheme 1. Triphenyl-1,3,5-oxadiazinium salt 3 (R = Ar = Ph) reacted with different nucleophilic reagents such as carbanions, ammonia, hydrazines, hydroxylamines, urea and thioureas to give substituted pyrimidines, s-triazoles, oxadiazoles, hydroxytriazines and mercapto-s-triazines, respectively.

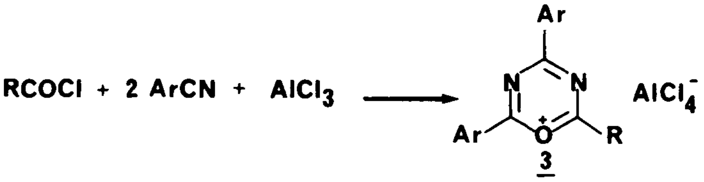
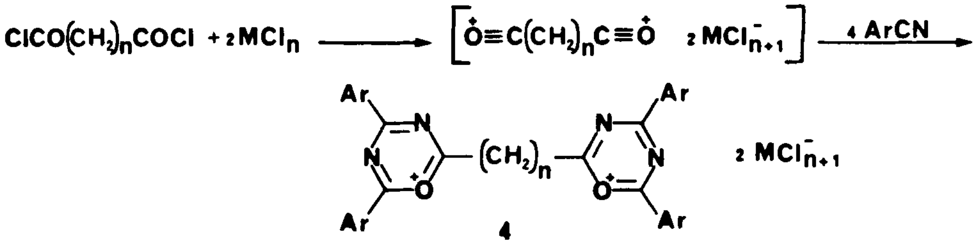


TABLE 4. Reaction of Acylium Salts with Aryl Nitriles

Ar	R	MCl_n	Yield(%)	Ref.
Ph	Ph	$AlCl_3$	—	32,34
Ph	$4\text{-}BrC_6H_4$	$AlCl_3$	83	34
Ph	α-naphthyl	$SnCl_4$	91	33
$4\text{-}ClC_6H_4$	$4\text{-}ClC_6H_4$	$SnCl_4$	80	33
Ph	CH_3	$SbCl_5$	67	38
Ph	CH_2Cl	$SbCl_5$	20	38

In addition, the hydrolysis of 3[33] and its reaction with primary and secondary amines[36] gave open-chain derivatives. Smit *et al.*[37] found that these salts could introduce a triazole ring into a carbohydrate moiety. Recently, we found[39] that diacylium salts, generated from the reaction of Lewis acid with diacyl chlorides in dichloromethane at -20°, reacted smoothly with aromatic nitriles to give bis-oxadiazinium salts, 4 (Table 5).



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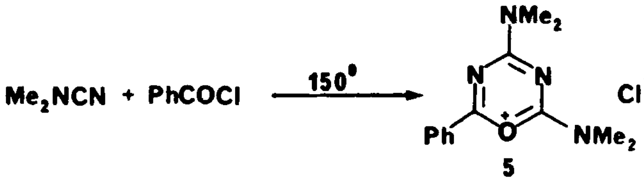
The reaction of dialkylcyanamides with acylium salts has been widely studied. Bredereck and Richter[40] found that benzoyl chloride and dimethylcyanamide, when heated together at 150° gave a crystalline compound 5, in 15% yield, while with other cyanamides only oily products were obtained.



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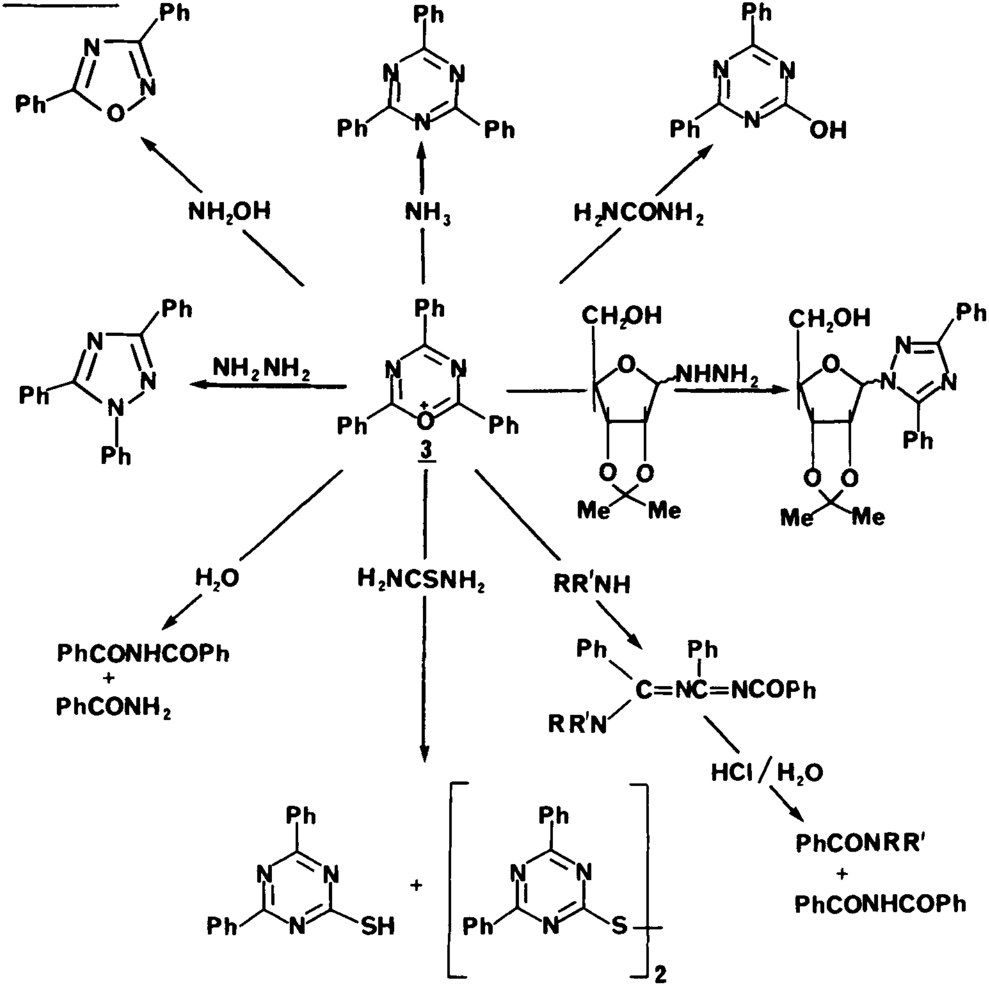
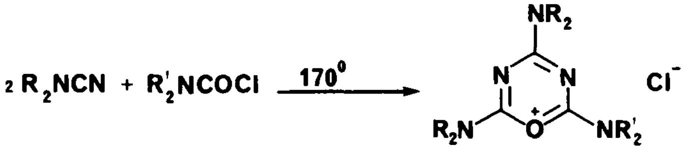
Similarly, Stevens and coworkers[41,42] reported that carbamoyl chlorides and dialkylcyanamides react upon heating to 170° to give amino substituted

Scheme 1



1,3,5-oxadiazinium salts 6. Recenlty,[43] we demonstrated that Lewis acids greatly promote the above reaction, due to the formation of the reactive acylium salt intermediates. Thus, benzoylium hexachloroantimonate reacts with



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two equivalents of dimethyl cyanamide at -20° to afford 85% of amino substituted 1,3,5-oxadiazinium salts 7. Other substrates reacted similarly[44-47] (Table 6).

TABLE 5. Reaction of Diacylium Salts with Aryl Nitriles[39]

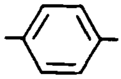
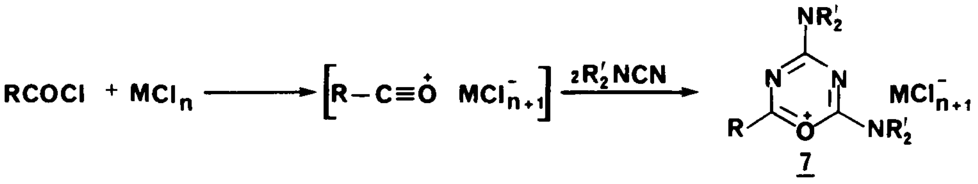
n	Ar	MCl_{n+1}	Yield(%)
0	$4\text{-}CH_3OC_6H_4$	$SbCl_6$	52
0	$4\text{-}CH_3OC_6H_4$	$FeCl_4$	34
2	$4\text{-}CH_3OC_6H_4$	$SbCl_6$	88
3	$4\text{-}CH_3C_6H_4$	$SbCl_6$	84
3	$4\text{-}CH_3OC_6H_4$	$SbCl_6$	85
4	$4\text{-}CH_3OC_6H_4$	$SbCl_6$	91
4	C_6H_5	$SbCl_6$	50
8	$4\text{-}CH_3OC_6H_4$	$SbCl_6$	97
8	$4\text{-}ClC_6H_4$	$SbCl_6$	71
	$4\text{-}CH_3OC_6H_4$	$SbCl_6$	71
	C_6H_5	$SbCl_6$	75
	$4\text{-}CH_3C_6H_4$	$SnCl_5$	90
	$4\text{-}CH_3OC_6H_4$	$SnCl_5$	85

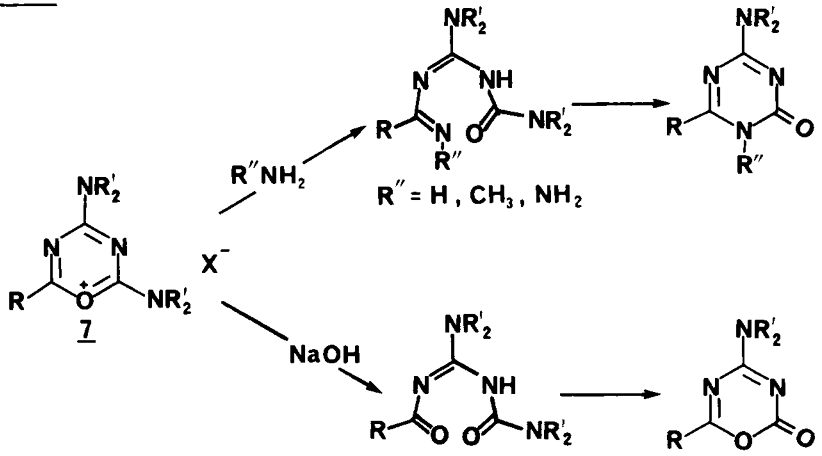
TABLE 6. Reaction of Acylium Salts with Dialkyl Cyanamides

R	R'	R'	MCl_{n+1}	Yield(%)	Ref.
CH_3	$(CH_3)_2CH$	$(CH_3)_2CH$	$SbCl_6$	82	43
C_6H_5	$-(CH_2)_5-$		$SnCl_5$	97	44
$4\text{-}CH_3C_6H_4$	$-(CH_2)O(CH_2)_2$		ClO_4	88	44
$4\text{-}NO_2C_6H_4$	$-(CH_2)_2O(CH_2)_2-$		$SbCl_6$	58	46
$4\text{-}CH_3OC_6H_4$	$-(CH_2)_2O(CH_2)_2-$		$SbCl_6$	87	46
2-Furyl	CH_3	CH_3	$SbCl_6$	65	47
2-Thienyl	$-(CH_2)_4-$		$SbCl_6$	62	47
2-Furyl	$-(CH_2)_2O(CH_2)_2-$		$FeCl_4$	80	47
2-Thienyl	$-(CH_2)_2O(CH_2)_2-$		$FeCl_4$	86	47



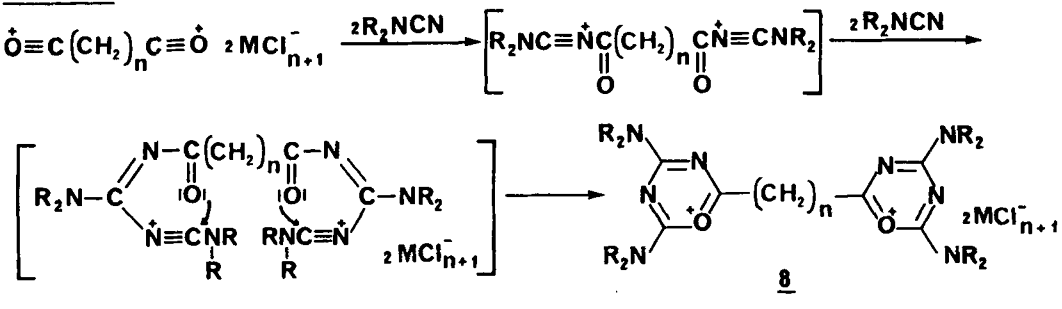
These 1,3,5-oxadiazinium salts have been used as potential precursors for the synthesis of other heterocycles,[40,44,45] scheme 2. Diacylium salts were reported to react with four equivalents of dialkyl cyanamides to afford the

<u>Scheme 2</u>



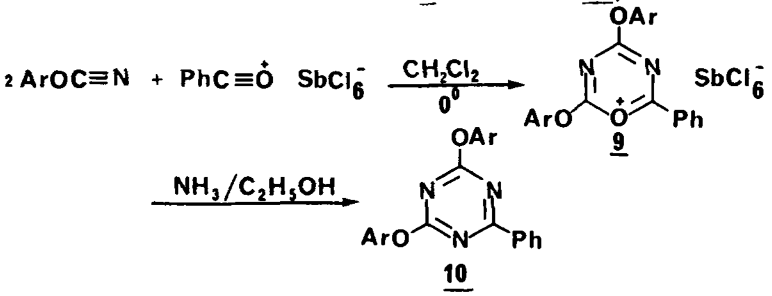
corresponding amino substituted bis-1,3,5-oxadiazinium salts 8, (Table 7).[46,48] The reaction is believed to proceed via a stepwise cycloaddition mechanism which involves cyanamidium salts, scheme 3. Evidence to support the intermediacy of acylium salts in the above reaction stems for the fact that the addition of the Lewis acid to a dichloromethane solution of diacyl chloride at -20° leads to a precipitation of the diacylium salt. The IR spectrum of this solid exhibits a strong absorption band between 2200-2300 cm^{-1} characteristic of the $-C\equiv\overset{+}{O}$ unit. In addition, substituents on the aromatic ring of the monoacyl chloride exert a great influence on the rate of the reaction, electron-releasing substituents strongly enhance the reaction, whereas electron-withdrawing substituents slow it down.

Scheme 3



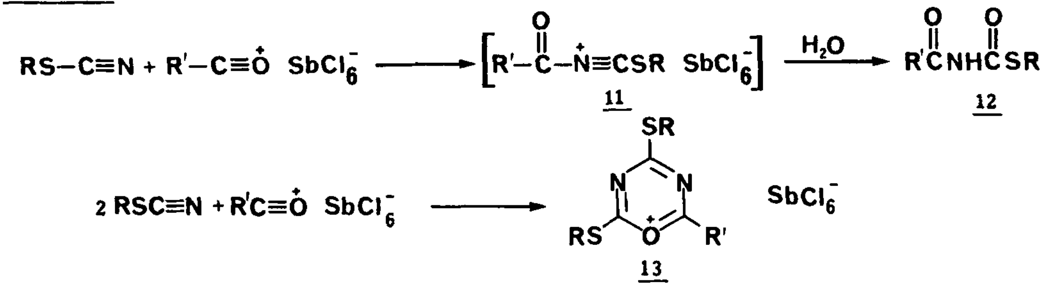
Similarly, aryl cyanates react with benzoylium salts to give oxadiazinium salts, 9. Ammonia converts these salts into s-triazines 10,[49,50] scheme 4.

Scheme 4



Alkyl thiocyanates react with acylium salts to give the unstable acylnitrilium salts 11 which can be trapped as imides 12 with water. However, acylium salts react with two moles of alkyl thiocyanates to give the corresponding 1,3,5-oxadiazinium salts 13,[51,52] scheme 5.

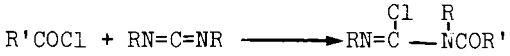
Scheme 5



$R = CH_3, C_2H_5;\ R' = C_6H_5,\ 3\text{-}CH_3C_6H_4,\ 4\text{-}CH_3C_6H_4,\ 4\text{-}NO_2C_6H_4$

2. Synthesis of Substituted 1,3,5-Triazinium Salts

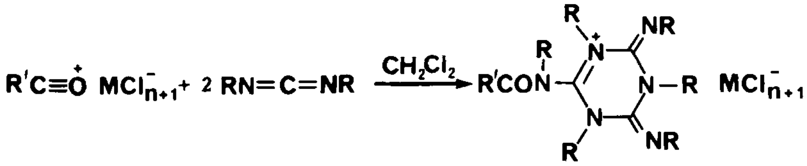
In contrast to the extensively studied reaction of acylium salts with aryl nitriles and cyanamides, their interaction with carbodiimides has rarely been explored. In the early 1960s, the first reaction of acyl chlorides and aliphatic carbodiimides was reported by Stachel[53] and Hartke.[54-56] The reaction was carried out without Lewis acids and gave acyl chloroformamidines 14 as the sole product. Recently, Jochims and Al-Talib have shown that Lewis



$$R'COCl + RN{=}C{=}NR \longrightarrow RN{=}\overset{Cl}{\overset{|}{C}}-\overset{R}{\overset{|}{N}}COR'$$

14

acids completely change the course of the above reaction.[43] Thus, acylium salts, derived from acyl chlorides and Lewis acids, readily react with three equivalents of aliphatic carbodiimides to give good to excellent yields of 3,4,5,6-tetrahydro-1,3,5-triazinium salts, 15. Similarly, 2-furyl and 2-thienyl acylium salts are reported to react with carbodiimides to give substituted 1,3,5-triazinium salts.[47] Table 8 compiles some representative results of the above reaction , which is limited to aliphatic carbodiimides; aromatic carbodiimides react with benzoylium hexachloroantimonate to afford an oil of unknown constitution.[43]



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$R' =$ alkyl, aryl, furyl, thienyl; $R = (CH_3)_2CH$, c-C_6H_{11}

$MCl_{n+1} = SbCl_6$, $ZnCl_3$, $FeCl_4$, $SnCl_6$

Recent work[57] in our laboratory has shown that a variety of diacylium salts readily react with six equivalents of aliphatic carbodiimides to give amino substituted bis-1,3,5-triazinium salts, 16. The reaction is quite clean, proceeding in nearly quantitative yields. It is worth noting that the reactions

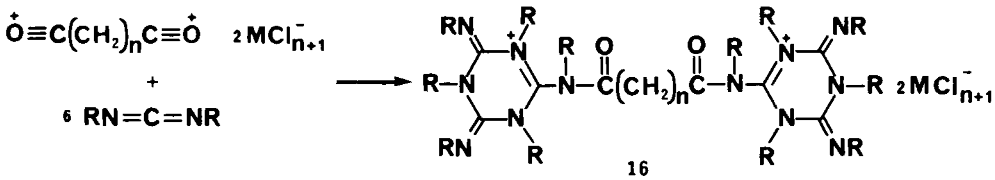

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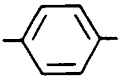
TABLE 8. Reaction of Acylium Salts $R\overset{+}{CO}\ MCl_{n+1}$ with Carbodiimides R'NCNR'

R	R'	MCl_{n+1}	Yield(%)	Ref.
CH_3-	$(CH_3)_2CH$-	$SbCl_6$	73	43
CH_3-	$(CH_3)_2CH$-	$ZnCl_3$	84	43
CH_3-	$(CH_3)_2CH$-	$FeCl_4$	86	43
CH_3-	c-C_6H_{11}-	$SbCl_6$	76	43
CCl_3-	$(CH_3)_2CH$-	$SbCl_6$	85	43
CCl_3-	c-C_6H_{11}-	$SbCl_6$	88	43
4-$CH_3C_6H_4$-	$(CH_3)_2CH$-	$SbCl_6$	71	43
4-$CH_3C_6H_4$-	$(CH_3)_2CH$-	$ZnCl_3$	71	43
4-$CH_3C_6H_4$-	$(CH_3)_2CH$-	$FeCl_4$	84	43
2-furyl-	$(CH_3)_2CH$-	$SbCl_6$	79	47
2-thienyl-	$(CH_3)_2CH$-	$SbCl_6$	88	47
2-furyl-	$(CH_3)_2CH$-	$SnCl_6$	84	47
2-furyl-	c-C_6H_{11}-	$SbCl_6$	78	47
2-thienyl-	c-C_6H_{11}-	$SbCl_6$	72	47

of oxalyl and phthaloyl acylium salts proceeded much more slowly than the reactions of other acylium salts.[57] The slowness is probably due to steric hindrance in the products. Several amino substituted bis-1,3,5-triazinium salts have been recently prepared and are compiled in Table 9.[58] The reaction is believed to proceed via a stepwise cycloaddition mechanism similar to that shown for the cyanamide reaction. It is of interest to contrast the behavior of acylium and diacylium salts with two and four equivalents of cyanamides, to give mono- and bis-1,3,5-oxadiazinium salts 7 and 8 respectively. It is possible that the driving force behind the cyclization to 7 and 8 is the formation of the stable aromatic oxadiazinium moieties. In the reaction with carbodiimides, the cyclization after the successive addition of two equivalents of carbodiimide to each acylium unit is not favored due to the fact

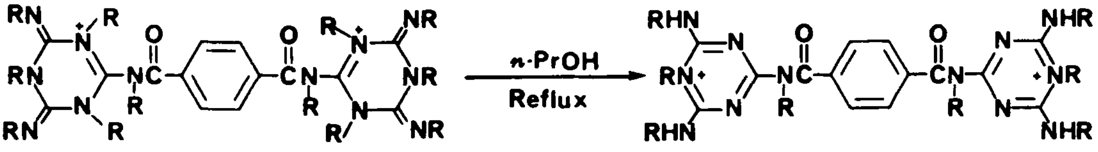
TABLE 9. Reaction of $\overset{+}{O}\equiv C(CH_2)_nC\equiv\overset{+}{O}$ $\overset{-}{MCl}_{n+1}$ with RN=C=NR

n	MCl_{n+1}	R	Yield(%)	m.p.(°C)
2	$SbCl_6$	$(CH_3)_2CH-$	84	136-139
2	$FeCl_4$	$(CH_3)_2CH-$	66	131-133
2	$ZnCl_3$	$(CH_3)_2CH-$	94	116-119
2	$SnCl_6$	$(CH_3)_2CH-$	69	132-135
2	$SbCl_6$	$c-C_6H_{11}-$	71	143-145
3	$SbCl_6$	$(CH_3)_2CH-$	85	162-165
3	$SnCl_6$	$(CH_3)_2CH-$	88	135-140
8	$FeCl_4$	$c-C_6H_{11}-$	83	102-106
8	$ZnCl_3$	$c-C_6H_{11}-$	90	117-119
	$SbCl_6$	$(CH_3)_2CH-$	80	173-176
	$FeCl_4$	$(CH_3)_2CH-$	85	142-145
	$SnCl_6$	$c-C_6H_{11}-$	73	136-139
	$FeCl_4$	$c-C_6H_{11}-$	78	132-135

that the product will be the non-aromatic tetrahydrooxadiazinium salt, 17. Instead a third equivalent is added to each acylium unit, followed by cyclization to afford 15, scheme 6.

Tetrahydro-1,3,5-triazinium and bis-tetrahydro-1,3,5-triazinium salts 15 and 16 are found to be thermally unstable.[43,58] Thus, boiling a solution of 16 in n-propanol under reflux results in loss of four isopropyl groups and the formation of the new bis-triazinium salt 18.

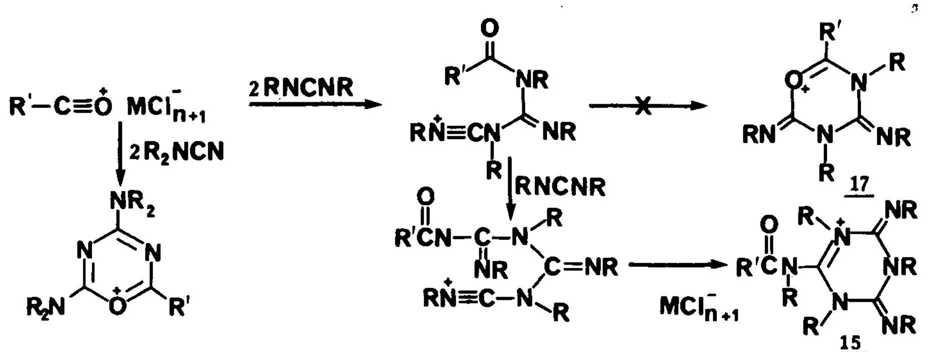
The loss of the isoropyl groups as propene was indicated by the decoloriza-



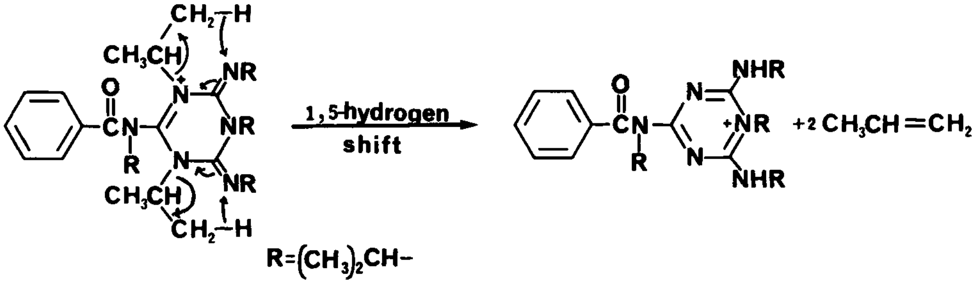
16 $R=(CH_3)_2CH-$, $c-C_6H_{11}-$

18

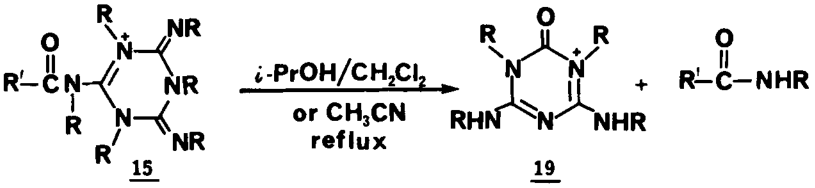
Scheme 6



tion of bromine in carbon tetrachloride solution.[58] The thermal degradation is believed to involve a 1,5-sigmatropic hydrogen shift. Also, it was reported

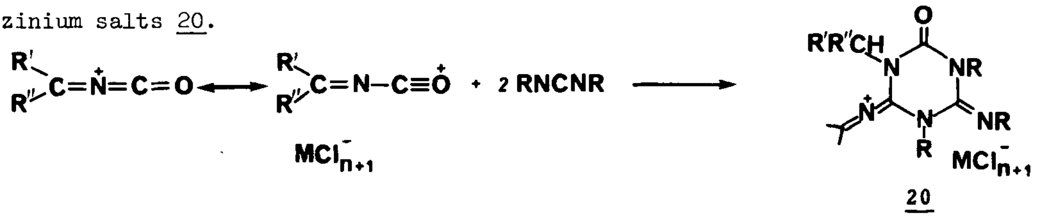


that heating tetrahydro-1,3,5-triazinium salts 15 in isopropanol/methylene chloride, and/or acetonitrile under reflux gave triazinium salt 19 and the N-isopropylarenamides.



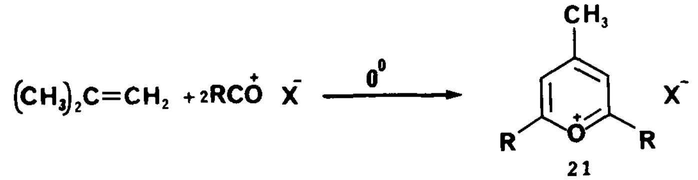
R = $(CH_3)_2CH-$, $c-C_6H_{11}-$; R' = aryl

In a recent report[59] Jochims and coworkers have shown that 1-oxa-3-aza-butatrienium salts behave in their reactions with carbodiimides as acylium salts, to afford in almost quantitative yield of substituted 2-oxo-1,3,5-triazinium salts 20.



3. Synthesis of Pyrylium and Furylium Salts

Pyrylium salts can be prepared by the reaction of acylium salts with olefins.[60-62] Thus, from isobutene and two equivalents of acylium salts the pyrylium salts 21 were obtained.[60,61] These compounds can also be prepared by acylation of α, β-unsaturated ketones with carboxylic anhydrides and sulfuric acid.[63] Cyclization of 3-acetonylbenzothiophene 22 (X = S) with acylium perchlorate afforded benzothienopyrylium salt 23 in good yield.[64] The latter salt can be readily transformed into benzothienopyridine 24 (X = S) by treatment with ammonia. In a similar fashion, the isomeric 2-acetonylbenzothiophene 25 (X = S) furnished the pyrylium salts 26 (X = S) upon acylation;[65] similar results have been recently reported for the cyclization of substituted benzofurans 22 (X = O) with acylium salts.[66]



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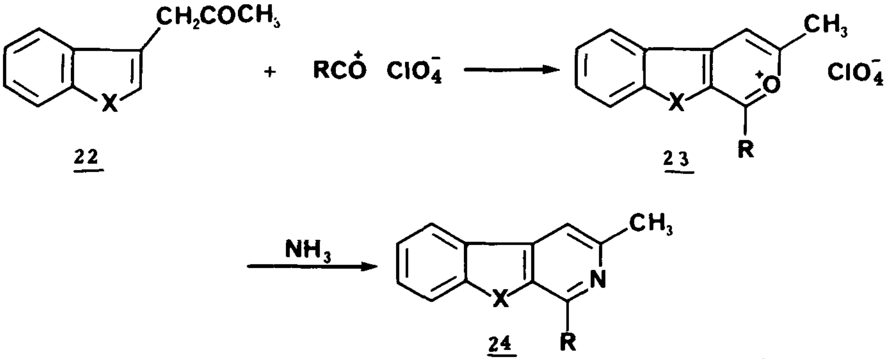

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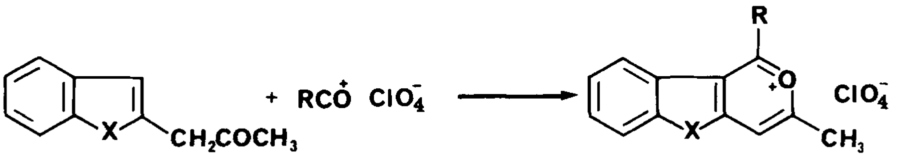
23

24



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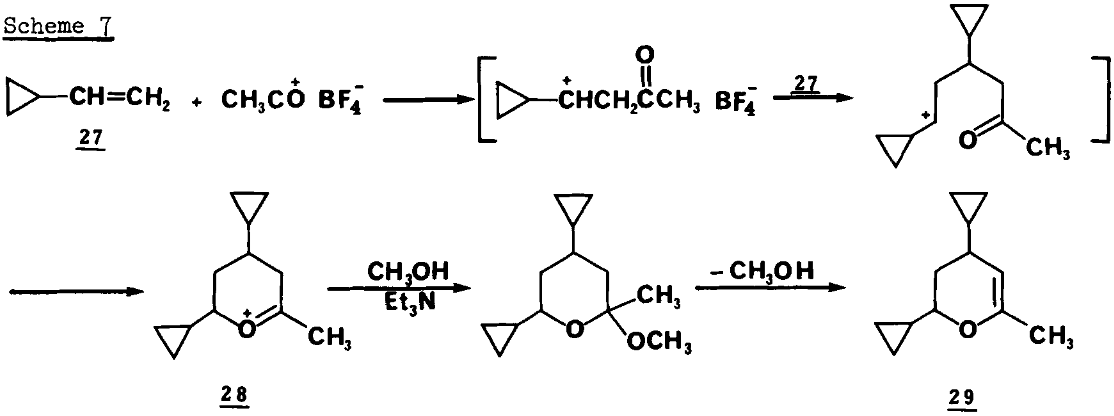
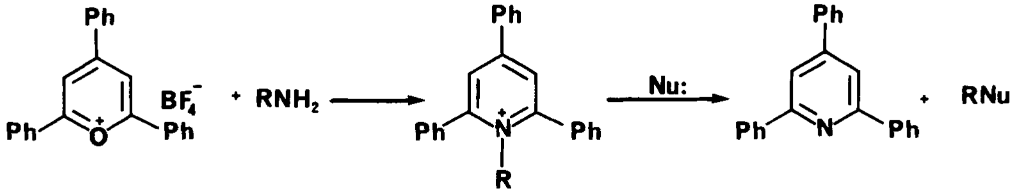
26

Phenylacetylene was reported to react with benzoylium hexachlorostannate or alkanoylium tetrafluoroborate to yield the corresponding substituted pyrylium salts.[67,68] The 3,4,5,6-tetrahydropyrylium salt 28, obtained from vinyl cyclopropane 27 and acetylium tetrafluoroborate, was isomerized to 29 by methanol-triethylamine,[69] scheme 7.

Scheme 7

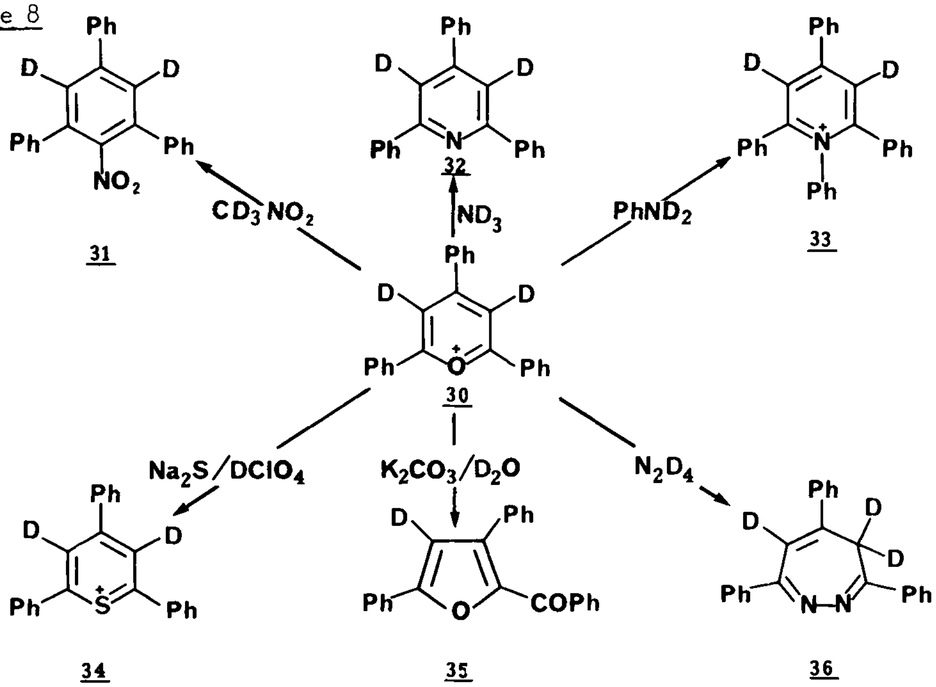


Pyrylium salts have become the most widely used precursors for the synthesis of substituted pyridinium salts.[70-76] Katritzky and his coworkers[70-72] reported that 2,4,6-triphenylpyrylium salt reacts readily with amines to yield the correspoding pyridinium salts, which transfer the N-substituent to a wide range of halide, O-, S-, N-, C- and H-nucleophiles and undergo elimination and rearrangement reactions. Other nitrogen containing nucleophiles, such as hydroxylamines, anilines, hydrazines,[73] amino acids,[74] 2-thiazolyl, 2-benzimidazolyl[75] reacted with pyrylium salts to give the respective pyridinium salts. Recently, Fischer and Mobius[76] have reported that pyrylium salts undergo fast isotopic exchange reactions on heating with catalytic amounts of bases in deuterated methanol or ethanol to give deuterated pyrylium salts 30. The use of pyrylium salts 30 as starting materials for synthesis of specifically deuterated carbo- and heterocycles was demonstrated by ring transformations of 2,4,6-triphenyl-{3,5-D_2}pyrylium perchlorate 30 to 2,4,6-triphenyl-{3,5-D_2}



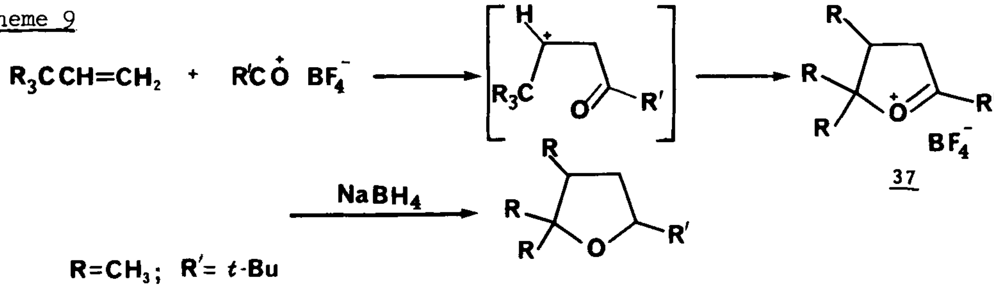
nitrobenzene 31, 2,4,6-triphenyl-{3,5-D_2}pyridine 32, 1,2,4,6-tetraphenyl-{3,5-D_2}pyridinium perchlorate 33, 2,4,6-triphenyl{3,5-D_2}thiopyrylium perchlorate 34, 2-benzoyl-3,5-diphenyl{4-D}furan 35 and 3,5,7-triphenyl{4,4,6-D_3}-4H-1,2-diazepine 36, scheme 8.

Scheme 8



Acylation of olefins, which lack a suitably activated allylic hydrogen, gave the trihydrofurylium salts 37 in high yields.[77-79] Compounds 37 can be easily reduced to substituted tetrahydrofuran derivatives upon reaction with hydrogen donors,[79] scheme 9. It has been demonstrated that the acylation

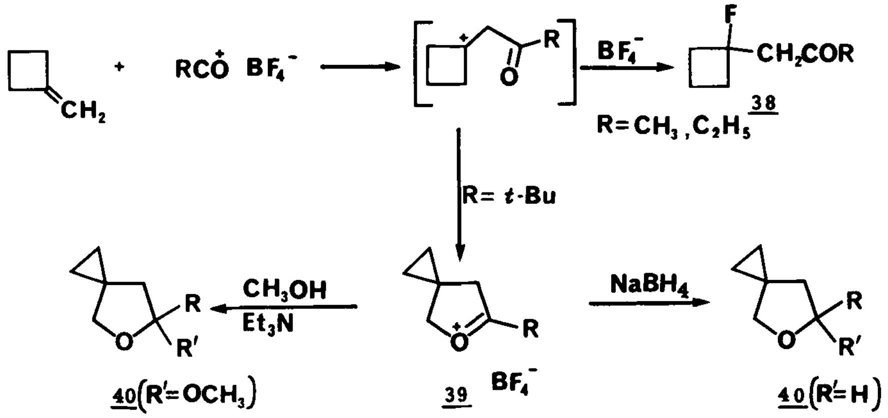
Scheme 9



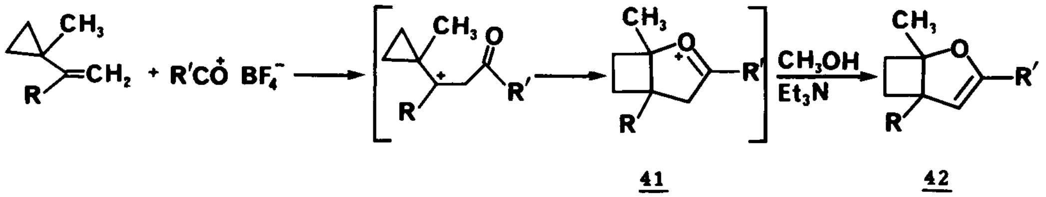
products of methylene cyclobutane were dependent on the type of acylium salts involved.[80-85] While acetylium and propionylium salts give β-fluoroketones

38, pivaloylium salt affords the rearranged products 40, most likely *via* the trihydrofurylium salt 39. However, butyrylium and isobutyrylium salts gave mixtures of 38 and 39, scheme 10. Analogous results were observed for the acylation of substituted cyclopropenes.[86] Acylation of vinylcyclopropane was

Scheme 10



accompanied by Wagner-Meerwein rearrangement to give the furylium salt intermediate 41 which leads to dihydrofuran 42 upon treatment with methanol.[87-88] Trihydro-furylium salts are also reported to be involved in the acylation of substituted cyclopropanes[89] and *tert*-butylacetylene.[90]

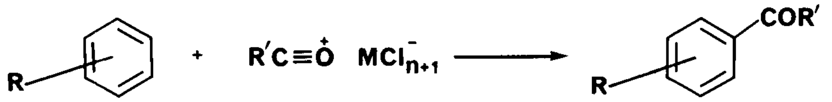


III. SYNTHESIS OF KETONES

The reaction of acylium salts with substituted benzenes to give the corresponding ketones is well documented. This general method known as Friedel-Crafts acylation, is the most important method for the preparation of ketones in which the carbonyl group is attached to an aromatic ring. Once formed, these ketones may be converted into many other important classes of organic compounds.[91,92]

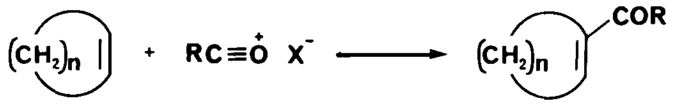
Although the Friedel-Crafts acylation of alkenes has been studied for more than eighty years, the reaction has not yet met with the success of the

Friedel-Crafts acylation of aromatic compounds. The lack of success is due to the formation of various side products, arising from electrophilic addition, elimination, isomerization and polymerization. In the following sections, we will survey the synthesis of different classes of ketones utilizing the acylation of alkenes and alkynes.



1. Synthesis of α,β-Unsaturated Ketones

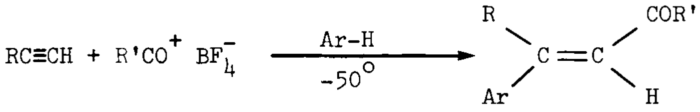
Acylation of simple cycloalkenes, such as cycloheptene or cyclohexene, has been known to give α,β-unsaturated ketones 43 for more than thirty years.[93,94] Recent work is mainly concerned with the acylation of alkynes.[95-99]



n = 4,5

43

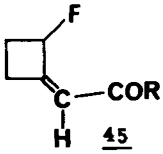
Terminal alkynes react with acylium salts in the presence of aromatic compounds to yield β-aryl-α,β-unsaturated ketones 44.[95-99] Ring expansion was observed



R = alkyl, aryl; R' = alkyl

44

in the reaction of cyclopropylacetylene with acylium salts at -30° , which leads to the substituted methylenecyclobutane 45. However under the same conditions 2,2-dichloro-1-methylcyclopropylacetylene reacts to give moderate yields of allenic ketones 46.[100] 2-Cyclopentenones 47 were obtained as the major products when the acylation of alkynes was carried out in non polar solvents at low temperatures.[101-104] This is a synthetic valuable modification of the well known Nazarov cyclization.[105] The formation of cyclopentenones appears to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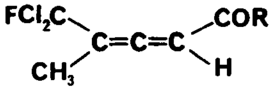
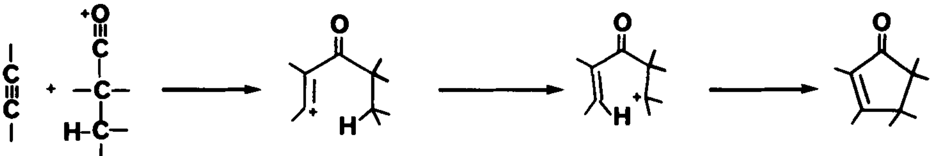

46

be a somewhat unusual process, since the nature of the product requires reaction of the saturated chain of the acyl residue. Mechanistic studies have shown that a facile intramolecular {1,5}-hydride shift from the β-carbon of the acylating agent to the initially formed vinyl cation occurs. Analogous {1,5}-hydride shifts were observed in the reactions of cyclohexyl[102,105] and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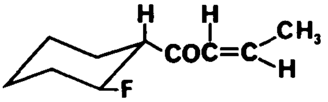
adamantyl[106] acylium salts with alkynes, which lead to ketones 48 and 49. The formation of cyclopentenones 47 in this reaction has successfully been used in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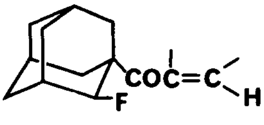
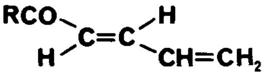

49

the total synthesis of naturally occurring prostanoids.[104]

Hindered α,β-unsaturated ketones were obtained in good yields from the reaction of trisubstituted alkenes with alkyl acylium salts.[107] Butadiene is stereoselectively acylated to give moderate yields of the trans ketones 50 at low temperatures.[108-110] The presence of acetic anhydride in the reaction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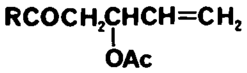

$RCOCH_2\underset{\mathrm{OAc}}{\underset{|}{C}}HCH=CH_2$

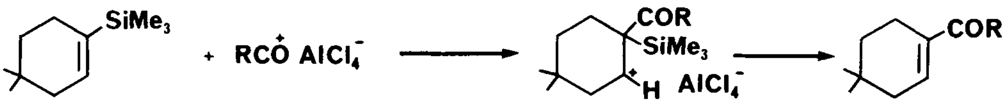
51

$RCOCH_2CH=CHCH_2OAc$

52

mixture changes the type of products obtained, and keto esters 51 and 52 instead of 50 were formed.[111]

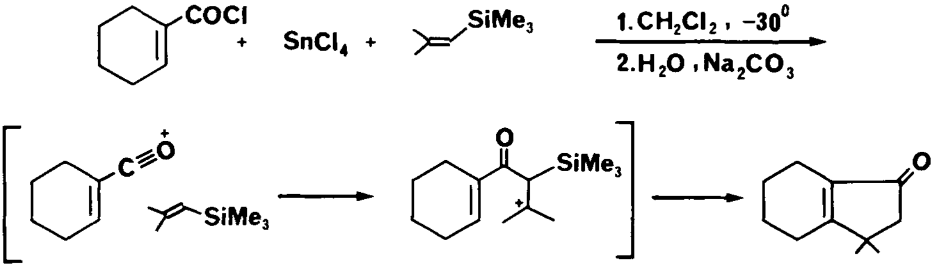
Vinyltrimethylsilanes 53 have been recently used to synthesize α,β-unsaturated ketones, 54.[112,113] Acylation occurs regioselectively at the carbon



53

54

bearing the trimethylsilyl group. This is expected because silicon stabilizes a positive charge in β-position. Vinylsilanes react with cyclic α,β-unsaturated acylium salts to produce bicyclic cyclopentenones 55.[114,115] Some naturally occurring furans such as Naginata ketone 56 and Isoegoma ketone 57, were synthesized using vinylsilanes as precursors.[116] 1-Phenylthio-1-trimethylsilylethene 58 was transformed into enone 59 upon its reaction with acylium salts.[117]



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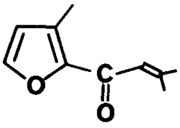

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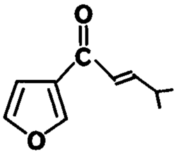

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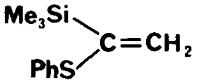

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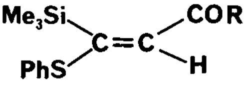
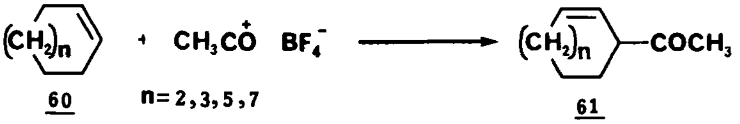


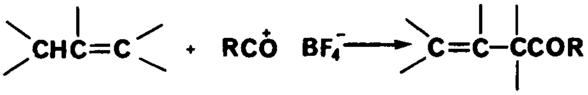
59

2. Synthesis of β,γ-Unsaturated Ketones

β,γ-Unsaturated ketones were obtained in moderate to good yields from the reaction of 1-alkylcyclohexenes with acetic anhydride in the presence of zinc chloride.[118,119] Cycloalkenes 60 were acylated with acetylium salts to yield β,γ-unsaturated ketones e.g. 61, which are partially isomerized to the corresponding α,β-unsaturated ketones when n=2 or 5.[120,121] According to Smit *et al.*[78,122] acylation of alkenes with activated allylic hydrogen atoms

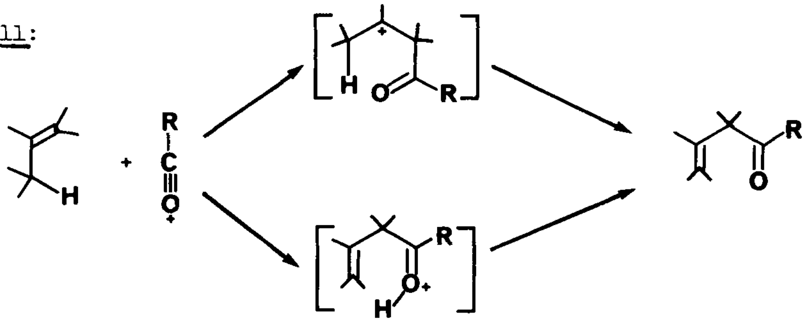


represents a versatile method for the preparation of β,γ-unsaturated ketones.



Similar results were reported for the reaction of the n-butyl acylium salt with cis- and trans-2-butene in dry SO_2 at -60°.[133] Two mechanisms have been proposed to rationalize the formation of β,γ-unsaturated ketones, one involved the intermediacy of β-keto carbenium ions,[78] while the other suggested a concerted ene mechanism,[121,124] scheme 11. Different classes of unsaturated ketones, including β,γ-unsaturated ones, were obtained from the acylation of cycloheptatriene,[125,126] 1,3-cyclooctadiene,[127] 1,5-cyclooctadiene[127] and cyclooctatriene.[128]

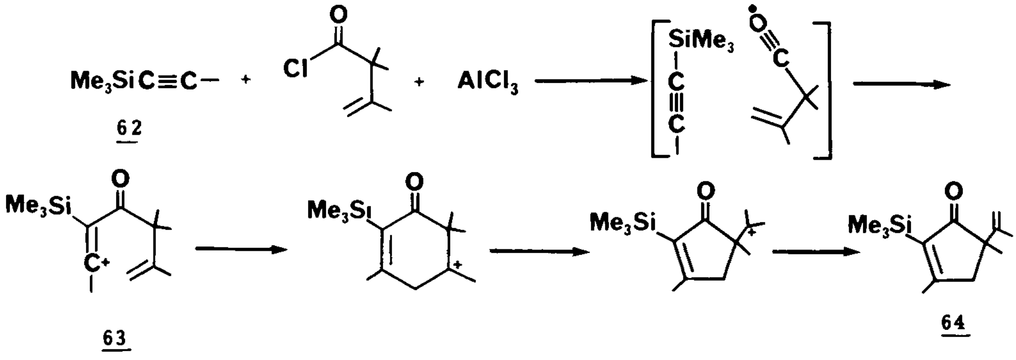
Scheme 11:



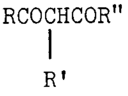
Substituted silyl acetylenes 62 react with α,α-disubstituted-β,γ-unsaturated acylium salts to give 5-substituted 2-cyclopentenones 64 through intramolecular cyclization of vinyl cations 63 and ring contraction.[129] In the case of acylium salts having at least one α-hydrogen, phenols were formed as final products.[129]

3. Synthesis of β-Diketones

Mono and dialkyl acetylenes react smoothly with acylium salts in polar

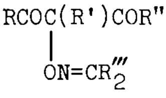


solvents such as nitromethane to afford β-diketones 65 as the sole product.[130] Nitromethane is assumed to be the source of the second oxygen of 65. Therefore, nitromethane should be considered as nucleophile and not only as solvent. Evidence



$$\underset{R'}{RCOCHCOR''}$$

65



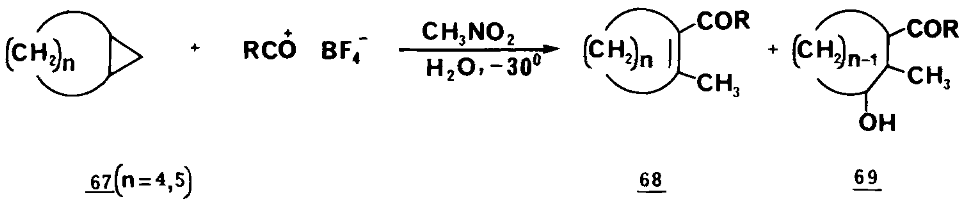
$$\underset{ON=CR'''_2}{RCOC(R')COR''}$$

66

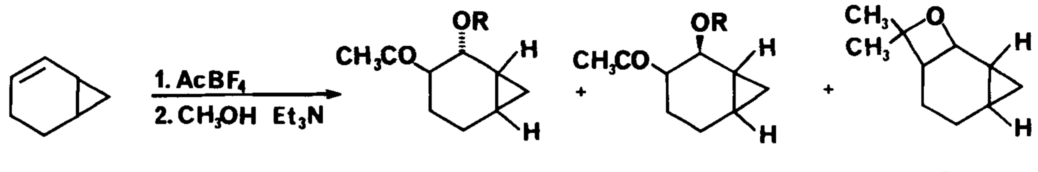
to support this assumption arises from the observation that nitrogen-containing adducts 66 were isolated on some occasions especially when a secondary nitroalkanes were used.[131] Trimethylsilylenol ethers of ketones undergo acylation with a variety of acid chlorides in the presence of Lewis acids to give as major products 1,3-diketones, resulting from C-acylation of the ether.[132,133]

4. Acylation of Bicyclic Systems

Norcarane 67 (n = 4) and its derivatives react rapidly with pivaloylium salt at -50° to afford a mixture of ketones after hydrolysis.[134,135] Bicyclic cyclopropanes 67 react similarly with pivaloylium salt to give unsaturated ketones 68 and 69 after hydrolysis.[136] The reaction of other bicyclo{n,1,0} systems with acylium salts have been studied.[137,138] Thus, even at -60° bicyclo



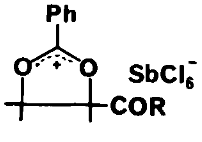
{4,1,0}hept-2-ene 70 gives *tricyclicoxonium* intermediates, which react further with alcohols to give moderate yields of *syn* and *anti* ketones 71, 72 and oxatricyclononane 73.[137]



70 71 72 73

IV. MISCELLANEOUS SYNTHESES VIA ACYLIUM SALTS

Besides the previously mentioned heterocyclic ring systems, acylium salt reactions were reported to afford other heterocycles.[139-145] Thus, treatment of 1,3-dicarbonyl compounds with benzoylium hexachloroantimonate gave acyl substituted 1,3-dioxolanium salts 74.[139] Likewise, the synthesis of substituted 1,3-dioxonium salts 75 has been described.[140] Shastin and Balenkova reported that the reaction of acetyl tetrafluoroborate with olefins in the presence of acetonitrile afforded moderate yields of substituted oxazine 76.[141,142] Recently, Roussel *et al*. reported a short, general and regioselective synthesis of 1,3,6,8-tetraalkyl-2,7-naphthyridines 78 by one pot tetraacylation of 2-methyl-1-propene or 2-methyl-1-propene precursors followed by treatment with liquid ammonia.[143,145] The reaction involves several pyrylium salts intermediates including 77.



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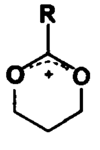

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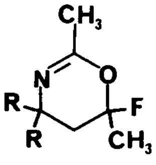

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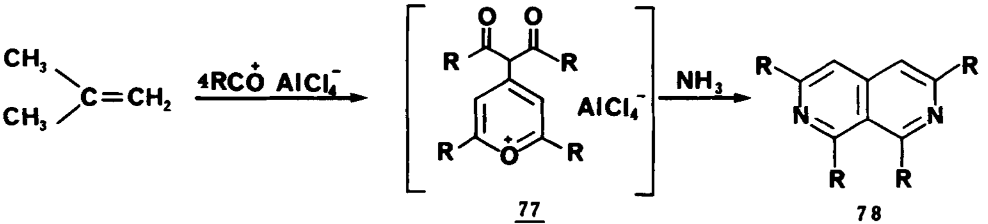
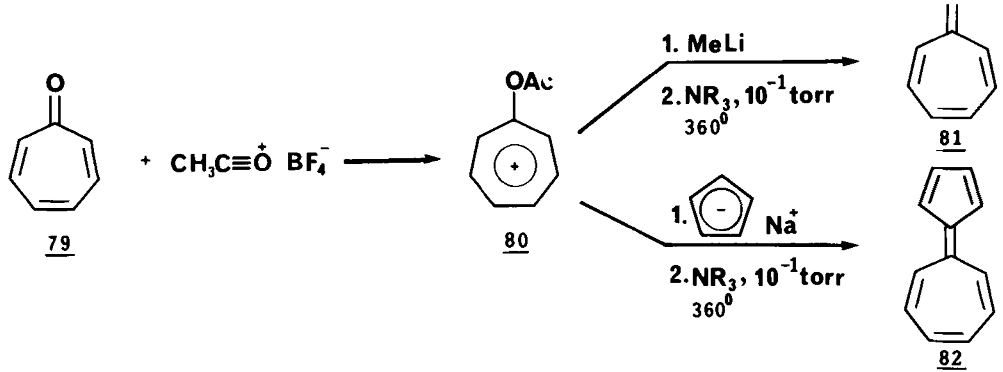
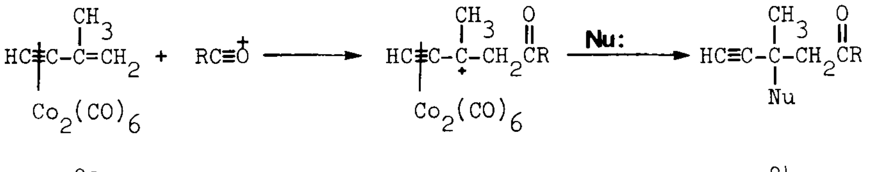


77 78

Tropone 79 undergoes O-acylation by acetylium tetrafluoroborate to give the corresponding acetoxytropylium salts 80.[146] This intermediate was converted to heptafulvene 81 and sesquifulvalene 82, respectively, upon its reaction with methyllithium and sodium cyclopentadienide followed by pyrolysis.



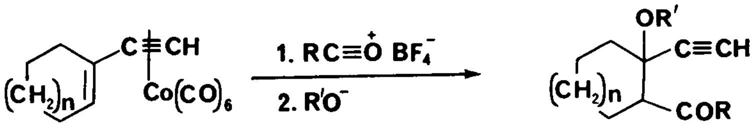
Recent work shows that transition metal complexes of alkenynes 83 react with acylium salts via a two-stage stepwise Ad_E mechanism.[147] The acetylenic moiety remained intact and acetylenic ketones 84 were obtained. Similarly,



$$\underset{Co_2(CO)_6}{HC\equiv C}-\overset{CH_3}{C}=CH_2 + RC\equiv\overset{+}{O} \longrightarrow \underset{Co_2(CO)_6}{HC\equiv C}-\overset{CH_3}{\underset{+}{C}}-CH_2\overset{O}{\overset{\|}{C}}R \xrightarrow{Nu:} HC\equiv C-\overset{CH_3}{\underset{Nu}{C}}-CH_2\overset{O}{\overset{\|}{C}}R$$

83 84

conjugated cyclic enynes 85 were selectively acylated at the double bond to give 86.[148] Bicyclic α,β-unsaturated ketones were obtained from the reaction of such cobalt complexes with acylium salts in the presence of allyl alcohols.[149]



85 (n = 1,2) 86

Substituted thiophene is acylated by ester substituted acylium salts 87, which leads to good yields of long chain acid esters 88 and carbinols 89 after dithioketalization and reductive desulfurization.[150] Acrolein undergoes O-acyl-

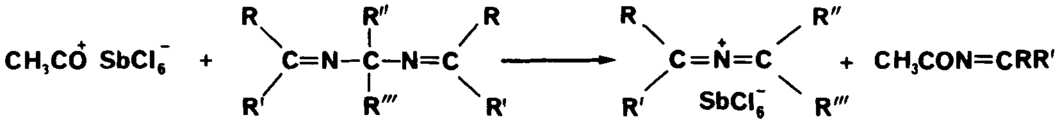
$CH_3OCO(CH_2)_yCO^+ \ SnCl_5^-$	$CH_3(CH_2)_xCOOCH_3$	$CH_3(CH_2)_xCH_2OH$
87, y = 2,4,7	88, x = 18,19,21-30	89

ation with acetylium salts to give good yields of vinylic esters 90.[151]

$$CH_2{=}CHCHO + CH_3\overset{+}{C}O\ BF_4^- \longrightarrow CH_3CH{=}CHOCOCH_3$$

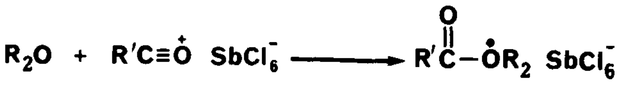
90

Wurthwein[152] reported that acetylium salts react with iminals 91 to yield 2-azaallenium salts 92 and N-acylimines 93 in good yields. Additionally, acylium salts react readily with dialkyl ethers at low temperature to afford the corresponding acyldialkyloxonium salts 94 which were further used as effective acylating agents.[153-154] Similarly, acylation of acetic anhydride gave triacyloxonium salts which were used as important catalysts for cationic telomerization of styrene or tetrahydrofuran in the presence of acetic acid.[155,156]



91 92 93

R = R' = R" = R‴ = Ph; R = R' = R" = Ph, R‴ = H; R = R' = Ph, R" = R‴ = H



$$R_2O + R'C{\equiv}\overset{+}{O}\ SbCl_6^- \longrightarrow R'\overset{O}{\overset{\|}{C}}{-}\overset{+}{O}R_2\ SbCl_6^-$$

94

V. CONCLUSION

The chemistry described in this brief survey suggests that acylium salts might serve as convenient and efficient tools for the synthetic organic chemist. Different heterocyclic ring systems have been directly prepared via these versatile and reactive intermdiates. In addition, different classes of ketones can be obtained by this methodology. Once formed, the initially resulting products react with a variety of nucleophilic reagents, which constitute an efficient and useful procedure of obtaining other classes of organic compounds and represent an adequate way for the construction of organic molecules.

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REFERENCES

1. F. Seel, Z. Anorg. Chem., 250, 331 (1943); 252, 24 (1943).
2. G. A. Olah, A. Germain and H. C. Lin, J. Am. Chem. Soc., 97, 5481 (1975).
3. G. A. Olah, Rev. Chem. (Bucharest), 7, 1139 (1962).
4. G. A. Olah, W. S. Tolgyesi, S. J. Kuhn, M. E. Moffatt, I. J. Bastien and E. B. Baker, J. Am. Chem. Soc., 85, 1328 (1963).
5. G. A. Olah and M. B. Comisarow, ibid., 88, 3313 (1966).
6. G. A. Olah and M. B. Comisarow, ibid., 88, 4442 (1966).
7. G. A. Olah and M. B. Comisarow, ibid., 89, 2694 (1967).
8. G. A. Olah, N. Friedmann, J. M. Bollinger and J. Lukas, ibid., 88, 5328 (1966).
9. W. M. Schubert, J. Donohue and J. D. Gardnet, ibid., 76, 9 (1954).
10. W. M. Schubert, J. Robins and J. M. Graven, J. Org. Chem., 24, 943 (1959).
11. G. A. Olah, C. V. Pettman, Jr. R. A. Waak and M. Doran, J. Am. Chem. Soc., 88, 1488 (1966).
12. D. W. Beistel, E. R. Atkinson and S. Safave, J. Mol. Spectrosc., 7, 174 (1967).
13. I. Cooke, B.-P. Susz and C. Herschmann, Helv. Chim. Acta, 37, 1280 (1959).
14. D. Cook, in "Friedel-Crafts and Related Reactions", Vol. I, G. A. Olah, Ed., 79, Interscience, 1963.
15. G. Oulevey and B.-P. Susz, Helv. Chim. Acta, 48, 630 (1965).
16. B.-P. Susz and I. Cooke, ibid., 37, 1273 (1953).
17. B.-P. Susz and J. J. Wuhrmann, ibid., 40, 722 (1957).
18. G. A. Olah, S. J. Kuhn, W. S. Tolgyesi and E. B. Baker, J. Am. Chem. Soc., 84, 2733 (1962).
19. D. Cook, Can. J. Chem., 37, 48 (1959).
20. D. Cassimatis and B.-P. Susz, Helv. Chim. Acta, 44, 943 (1961).
21. J. C. Jaccard and B.-P. Susz, ibid., 50, 97 (1967).
22. G. Oulevey and B.-P. Susz, ibid, 48, 1965 (1965).

23. G. Oulevey and B.-P. Susz, ibid., 47, 1828 (1964).

24. H. H. Perkampus and W. Weiss, Angew. Chem. 80, 40 (1968).

25. F. P. Boer, J. Am. Chem. Soc., 88, 1572 (1966), ibid., 90, 6706 (1968).

26. B. Chevrier, J. M. LeCarpentier and R. Weiss, ibid., 94, 5718 (1972).

27. D. Cassimatis, J. P. Bonnin and T. Theophanides, Can. J. Chem., 48, 3860 (1972).

28. G. A. Olah and P. W. Westermann, J. Am. Chem. Soc., 95, 3706 (1973).

29. G. A. Olah and A. M. White, ibid., 89, 3591 (1967).

30. G. A. Olah and A. M. White, "Carbonium ions", Vol. V, G. A. Olah and P. R. Schleyer, Eds., 2091, Interscience, 1976.

31. G. A. Olah and A. M. White, J. Am. Chem. Soc., 89, 7072 (1967).

32. P. Eitner and F. Kraft, Ber., 25, 2267 (1892).

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

34. H. Meerwein, H. Laasch, P. Mersch and J. Spille, ibid., 89, 209 (1956).

35. I. Shibuya and M. Kurabayashi, Bull. Chem. Soc. Jpn., 42, 2382 (1969); 46, 3902 (1973).

36. R. Fuks, M. Strebelle and A. Wenders, Synthesis, 788 (1977).

37. P. Smit, G. A. Stork and H. C. Van der Plas, Recl. Trav. Chem. Pays-Bas, 102, 453 (1983).

38. T. N. Sumarokova, R. A. Slavinskaya, I. G. Litvyak and N. Yu. Vykhrest, Zh. Obshck.Khim., 50, 2331 (1980).

39. H. Tashtoush, M. Al-Talib and M. Omari, Unpublished results.

40. K. Bredereck and R. Reichter, Chem. Ber., 99, 2454 (1966).

41. P. Rushton, C. H. Schwalbe and M. F. G. Stevens, Acta Cryst., C39, 476 (1983).

42. P. Rushton and M. F. G. Stevens, J. Chem. Soc. Perkin Trans I, 1533 (1985).

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

44. W. Schroth and H. Kluge, Z. Chem., 26, 94 (1986).

45. W. Schroth, H. Kluge and M. Gabler, ibid., 26, 95 (1986).

46. M. Al-Talib and H. Tashtoush, Tetrahedron Lett., 353 (1987).

47. M. Al-Talib and H. Tashtoush, Indian J. Chem., 27B, 934 (1988).

48. M. Al-Talib and H. Tashtoush, J. Heterocyclic Chem., 25, 1023 (1988).

49. D. Martin and A. Wise, Chem. Ber., 100, 3736 (1967).

50. D. Martin, Z. Chem., 7, 123 (1967).

51. J. Liebscher and H. Hartmann, Tetrahedron Lett., 2977 (1975).

52. D. Herrmann, J. Jachmann and S. Neuhaus, Ann., 1198 (1981).

53. H. D. Stachel, Angew. Chem., 71, 246 (1959).

54. K. Hartke and J. Bartulin, ibid., 74, 214 (1962).

55. K. Hartke, ibid., 74, 214 (1962).

56. K. Hartke and E. Palow, Chem. Ber., 99, 3155 (1966).

57. H. Tashtoush and M. Al-Talib, Org. Prep. Proc. Int., 20, 511 (1988).

58. M. Al-Talib, H. Tashtoush and K. Shwagfeh, Unpublished results.

59. M. Al-Talib, J. C. Jochims, L. Zsolnai and G. Huttner, Chem. Ber., 118, 1889 (1985).

60. A. T. Balaban and C. D. Nenitzescu, Ann., 625, 74 (1959); J. Chem. Soc., 3553 (1961).

61. P. F. Praill and A. L. Whitear, Proc. Chem. Soc., 312 (1959).

62. P. F. Praill and A. L. Whitear, J. Chem. Soc., 3575 (1961).

63. C. Roussel, Bull. Soc. Chim. Fr., 454 (1986).

64. V. I. Dulenko, V. I. Volbushko, L. V. Dulenko and G. N. Dorofeenko, Khim. Geterotsikl, Soedin., 273 (1974); C. A., 80, 133305b (1974).

65. N. A. Alekseev and S. V. Tolkunov, Khim. Geterotsikl. Soedin., 848 (1980); C. A., 93, 204499z (1980).

66. V. I. Dulenko and S. V. Tolkunov, Khim. Geterotsikl Soedin., 887 (1987); C. A., 108, 167343z (1988).

67. I. D. Gidnev, A. V. Shastin and E. S. Balenkova, Khim. Geterosikl. Soedin., 1562 (1983); C. A., 100, 103116e (1984).

68. R. Schmidt, Angew. Chem., 76, 437 (1964).

69. A. A. Vasilev, E. S. Balenkova, T. V. Levashova, A. A. Grigorev, N. V. Smirnova and Yu. N. Luzikov, Zh. Org. Khim., 17, 2018 (1981).

70. A. R. Katritzky, R. H. Manzo, J. M. Lloyd and R. C. Patel, Angew. Chem. Int. Ed. Eng., 19, 306 (1980).

71. A. R. Katritzky, Tetrahedron, 36, 679 (1980).

72. A. R. Katritzky, R. T. C. Brownlee and M. Musumara, ibid., 36, 1643 (1980).

73. E. A. Zvezdina, A. N. Popova, A. I. Pyschev and G. N. Dorofeenko, Khim. Geterotsikl. Soedin., 461 (1982); C. A., 97, 109834d (1982).

74. A. Dinculescu and A. Balaban, Chem. Patent Rom. RO 74, 733; C. A. 99, 158261q (1983).

75. A. Dinculescu and A. Balaban, Chem. Patent Rom. RO 76, 314; C. A. 99, 158262r (1983).

76. G. W. Fischer and G. Mobius, J. prakt. Chem., 327, 529 (1985).

77. O. V. Lyubinskaya, V. A. Smit, A. S. Shashkov, V. A. Chertkov, M. I. Kanishchev and V. F. Kucherov, Izv. Akad. Nauk. SSSR, Ser. Khim., 397 (1978); C. A. 89, 42942b (1978).

78. W. A. Smit, A. V. Semenovsky, V. F. Kucherov, T. N. Chernova, M. Z. Krimer and O. V. Lubinskaya, Tetrahedron Lett., 3101 (1971).

79. O. V. Lubinskaya, A. S. Shashkov, V. A. Chertkov and W. A. Smit, Synthesis, 742 (1976).

80. E. S. Balenkova, E. B. Frolov, S. N. Anfilogova and Yu. N. Lusikov, Vestn. Mosk. Univ., Ser. 2. Khim., 1978, 706; C. A., 90, 137312f (1979).

81. E. S. Balenkova, E. B. Frolov and S. V. Anfilogova, Zh. Org. Khim., 14, 1109 (1978).

82. E. B. Frolov, SSSR Patent, C. A., 92, 41389b (1980).

83. F. B. Frolov, SSSR Patent, C. A., 94, 156649v (1981).

84. S. N. Anfilogova, E. B. Frolov, Yu. N. Luzikov and E. S. Btenkova, Zh. Org. Khim., 15, 1432 (1979).

85. S. N. Anfilogova, E. B. Frolov and E. S. Balenkova, Vestn. Mosk. Univ., Ser. 2. Khim., 21, 611 (1980); C. A., 94, 139527m (1981).

86. E. B. Frolov, S. N. Anfilogova, I. A. Pomytkin, Yu. N. Luzikov and E. S. Balenkova, Zh. Org. Khim., 16, 1839 (1980).

87. I. A. Pomytkin, E. S. Balenkova and S. N. Anfilogova, ibid., 17, 1339 (1981).

88. I. A. Pomytkin, E. S. Balenkova and S. N. Anfilogova, ibid., 81, 532 (1982).

89. Yu. V. Tomilov, V. A. Smit and O. M. Nefedov, Izv. Akad. Nauk. SSSR, Ser. Khim., 2620 (1975);C. A. 81, 91109d (1974); 2744 (1978); C. A. 90, 103743d (1979).

90. S. V. Borodaev, E. V. Nanmova and S. H. Lukyanov, Zh. Org. Khim., 22, 1789 (1986).

91. G. A. Olah "Friedel-Crafts and Related Reactions", Vol. I and IV, Interscience, 1963; G. A. Olah and J. A. Olah, Vol. III, 1257 (1963).

92. R. T. Morrison and R. N. Boyd "Organic Chemistry" 5th Ed. P. 768, Allyn and Bacon Inc., London. 1987.

93. G. Baddely, H. T. Tayler and W. Pickles, J. Chem. Soc., 124 (1953).

94. N. Jones and H. T. Tayler, ibid., 4017 (1959).

95. V. A. Smit, A. A. Shchegolev and V. F. Kucherov, Izv. Akad. Nauk. SSSR, Ser. Khim., 2377 (1972); C. A. 78, 29379b (1973).

96. V. A. Smit, A. V. Semenovskii, G. V. Roitburd, A. A. Schchegolev, V. F. Kucherov and O. S. Chizov, Dokl. Vses. Konf. Khim. Atsetilena, 4th (1972); C. A., 79, 17980y (1973).

97. A. A. Shchegolev, V. A. Smit, S. A. Khurshudyan, V. A. Chertkov and V. F. Kucherov, Izv. Akad. Nauk. SSSR, Ser. Khim., 1093 (1977); C. A. 87, 134296f (1977).

98. S. A. Khurshudyan, A. A. Shchegolev, V. A. Smit, V. A. Chertkov and V. F. Kucherov, ibid., 2754 (1977); C. A. 88, 104844m (1978).

99. A. A. Schegolev, W. A. Smit, S. A. Khurshudyan, V. A. Chertkov and V. F. Kucherov, Synthesis, 324 (1977).

100. I. A. Pomytkin, E. S. Balenkova and S. N. Anfilogova, Zh. Org. Khim., 18, 2295 (1982).

101. A. A. Schegolev, W. A. Smit, V. F. Kucherov and R. Caple, J. Am. Chem. Soc., 97, 6604 (1975).

102. A. A. Schegolev, W. A. Smit, G. V. Roitburd and V. F. Kucherov, Tetrahedron Lett., 3373 (1974).

103. K. S. Jadhav, S. B. Thakur and S. C. Bhattacharyya, Indian J. Chem., 16B, 280 (1978).

104 M. I. Kanischev, A. A. Schegolev, W. A. Smit, R. Caple and M. I. Kelner, J. Am. Chem. Soc., 101, 5660 (1979).

105. C. Santelli-Rouvier and M. Santelli, Synthesis, 429 (1983).

106. M. I. Kanischev, W. A. Smit, A. A. Schegolev and R. Caple, Tetrahedron Lett., 1421 (1978).

107. J. A. Dubois, I. Saumatally and C. Loin, Bull. Soc. Chim. Fr., 133 (1984).

108. G. G. Melikyan, K. A. Atanesyan, K. A. Simongan, S. O. Simongan and Sh. O. Badanyan, Zh. Org. Khim., 19, 1158 (1983).

109. G. G. Melikyan, K. A. Atanesyan and Sh. O. Badanyan, Arm. Khim. Zh., 35, 408 (1982); C. A. 97, 162301d (1982).

110. G. G. Melikyan, K. A. Atanesyan, G. Kh. Astanyan, R. T. Grigorgan and Sh. O. Badanyan, Zh. Org. Khim., 23, 1627 (1978).

111. A. V. Shastin and E. S. Balenkova, ibid., 20, 956 (1984).

112. I. Fleming and A. Pearce, Chem. Commun., 633 (1975).

113. T. H. Chan and I. Fleming, Synthesis, 761 (1979).

114. F. Cooke, J. Schwindeman and P. Magnus, Tetrahedron Lett., 1995 (1979).

115. F. Cooke, R. Moerck, J. Schwindeman and P. Magnus, J. Org. Chem., 45, 1046 (1980).

116. J.-P. Pillot, B. Bennetau, J. Dunogues and R. Calas, Tetrahedron Lett., 4717 (1980).

117. D. J. Ager, ibid., 1945 (1982).

118. J. K. Groves and N. Jones, J. Chem. Soc. (C), 2215 (1968); 609 (1969).

119. J. K. Groves and N. Jones, Tetrahedron Lett., 1161 (1970).

120. S. N. Anfilogova, M. I. Kengerli and E. S. Balenkova, Zh. Org. Khim., 14, 1627 (1978).

121. H. M. R. Hofmann and T. Tsushima, J. Am. Chem. Soc., 99, 6008 (1977).

122. V. A. Smit, A. V. Semenovskii, O. V. Lyubinskaya and V. F. Kucherov, Doklady Akad. Nauk. SSSR, 203, 604 (1972); C. A. 77, 87955b (1972).

123. O. V. Lyubinskaya, V. A. Smit, A. V. Semenovskii and V. F. Kucherov, Izv. Akad. Nauk. SSSR, Ser. Khim., 1803 (1976); C. A. 85, 192154c (1976).

124. O. V. Lyubinskaya, V. A. Smit, A. S. Shashkov, V. A. Chertkov, M. I. Kanishchev and V. F. Kucherov, ibid., 397 (1978); C. A. 89, 42942b (1978).

125. J. A. Blair and C. J. Tate, Chem. Commun., 1506 (1969).

126. J. A. Blair, G. P. Mclaughlin and J. Paslawski, ibid., 12 (1967).

127. T. S. Centrell and B. L. Strasser, J. Org. Chem., 36, 670 (1971).

128. A. C. Cope, T. A. Liss and D. S. Smith, J. Am. Chem. Soc., 79, 240 (1957).

129. M. Karpf, Helv. Chim. Acta, 67, 73 (1984).

130. G. V. Roitburd, V. A. Smit, A. V. Semenovskii, A. A. Schchegolev and V. F. Kucherov, Doklady Akad. Nauk. SSSR, 203, 1086 (1972); C. A. 77, 87763n (1972).

131. G. V. Roitburd, W. A. Smit, A. V. Semenovsky, A. A. Schegolev, V. F. Kucherov, O. S. Chizhov and V. I. Kadentsev, Tetrahedron Lett., 4935 (1972).

132. I. Kopka and M. W. Rathke, J. Org. Chem., 46, 3771 (1981).

133. R. E. Tirpak and M. W. Rathke, ibid, 47, 5099 (1982).

134. Yu. V. Tomilov, V. A. Smit and O. M. Nefedov, Izv. Akad. Nauk. SSSR, Ser. Khim., 1439 (1974); C. A. 81, 91109d (1974).

135. Yu. V. Tomilov, V. A. Smit and O. M. Nefedov, ibid., 2512 (1976).

136. Yu. V. Tomilov, V. A. Smit and O. M. Nefedov, ibid., 2614 (1975).

137. A. A. Vasilev and E. S. Balenkova, Zh. Org. Khim., 20, 1336 (1984).

138. A. A. Vasilev, Yu. N. Luzikov and E. S. Balenkova, ibid., 20, 1007 (1984).

139. Yu. A. Zhdanov, S. M. Lukyanov, S. V. Borodov and S. V. Borodaeva, ibid., 22, 2376 (1986).

140. T. P. Kosuline, E. V. Gromachevskaya, L. A. Falina, A. G. Kolensikov and V. G. Kulenvich, Khim. Geterotsikl. Soedin., 464 (1983); C. A. 99, 22395d (1983).

141. A. V. Shastin and E. S. Balenkova, Zh. Org. Khim., 20, 1357 (1984).

142. I. D. Gridnev, A. V. Shastin and E. S. Balenkova, ibid., 23, 1546 (1987).

143. C. Roussel, A. Mercier and M. Cartier, J. Org. Chem., 52, 2935 (1987).

144. C. H. Erre and C. Roussel, Bull. Soc. Chim. Fr., 449 (1984).

145. C. H. Erre, A. Pedra, M. Arnaud and C. Roussel, Tetrahedron Lett., 25, 515 (1984).

146. W. K. Schank, R. Kyburz and M. Neuenschwander, Helv. Chim. Acta. 58, 1099 (1977).

147. A. A. Schegolev, W. A. Smit, Y. B. Kalyan, M. Z. Krimer and R. Caple, Tetrahedron Lett., 4419 (1982).

148. G. S. Mikaelyan, A. A. Schchegolev and V. A. Smit, Arm. Khim. Zh., 36, 194 (1983). C. A. 99, 105464b (1983).

149. G. S. Mikaelyan and V. A. Smit, Izv. Akad. Nauk SSSR, Ser. Khim., 11, 2652 (1984); C. A. 102, 95482v (1985).

150. S. J. Rao, V. T. Bhalerao and B. D. Tilak, Indian J. Chem., 26B, 208 (1987).

151. I. I. Ibragimov, V. G. Dzhafarov and V. A. Tarasov, Dokl. Akad. Nauk SSSR, 275, 892 (1984); C. A. 101, 130192d (1984).

152. E.-U. Wurthwein, Angew. Chem., 93, 110 (1981).

153. G. A. Olah, J. A. Olah and J. J. Svoboda, Synthesis, 490 (1973).

154. R. Szymanski, H. Wieczorek, P. Kubisa and S. Penczek, Chem. Commn., 33 (1976).

155. H. Boekhoff and W. Heitz, Macromol. Chem., 180, 1055 (1979).

156. D. L. Rakhmankulov, R. T. Akhmatdinov and E. A. Kantor, Russ. Chem. Rev., 53, 888 (1984), C. A. 101, 210081g (1984).

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