

Room Temperature Ionic Liquid Assisted Thiocyanation Of Substituted Ketones And Study Of Its Green Context

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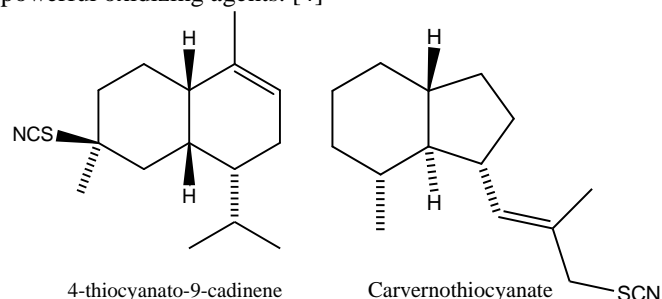
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Abstract: RTIL catalysed thiocyanation of substituted ketones has been carried using ethyl methyl imidazolium chloride with zinc chloride using acetonitrile solvent. The method is applicable to various ketones as well as best suited for the reagent ammonium thiocyanate. Wide applicability, good to excellent yield and recyclability of ionic liquid are important features of this method.

Keywords: RTIL, Ammonium thiocyanate, Aromatic ketones

I. INTRODUCTION

Thiocyanated ketones are important intermediate for synthesis of sulfur containing heterocyclic compounds. They can be frequently found in the many natural compounds which have pharmacologically importance.[1] Thiocyanato functionality of these ketones can be used as mercapto group which can yield compounds such as thiazolidine that have capacity to show some herbicidal properties. [2] There are different methods reported for synthesis α -thiocyanato ketones or simply α -thiocyanation of enolizable ketones but yields are typically very low due to poor nucleophilicity of SCN⁻ anion. [3] However many of these methods uses poisonous metal thiocyanates, sometimes expensive thiocyanating agent with powerful oxidizing agents. [4]



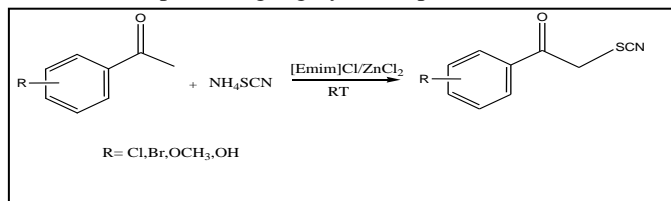
Thiocyanation of aromatic ketones is one of the most important reactions in organic synthesis. Thiocyanato substituted compounds in which thiocyanate group readily transformed into sulfur bearing functionalities. [5] They are acting as versatile reagent for synthesis of various organic compounds. Many times in medicines different methodologies are developed for α -thiocyanation of aromatic ketones using diverse types of reactions. [6] The classical methods of preparation include many more steps in synthetic sequence and high temperature ultimately harsh conditions. [7] The present work shows direct α -thiocyanation method for aromatic ketone using ethyl methyl imidazolium chloride with zinc chloride.

II. MATERIALS AND METHODS

¹HNMR spectra were recorded in CDCl₃ at 400 MHz IR spectra were recorded on a Shimadzu FTIR, Mass spectra were recorded on LC-MS using ionization technique. The progress of the reactions was monitored by TLC. All the chemicals were purchased from Sigma Aldrich and Spectrochem. Melting points were recorded on Veego digital melting point apparatus.

III. GENERAL PROCEDURE

In this present work ketones are treated with ammonium thiocyanate (1:1.5) in presence of RTIL(1-ethyl-3-methyl imidazolium chloride/ZnCl₂) as catalyst, acetonitrile is solvent at room temperature to get desired α -ketothiocyanates within short duration producing high yield of product.



Scheme: Thiocyanation of substituted ketones

IV. RESULTS AND DISCUSSION

Thiocyanation of aromatic ketones is investigated at various reaction conditions. In the absence of ionic liquid, when reaction was not progresses but in the presence of very small amount it the reaction accomplish with good results. It proves that ionic liquid is effectively acting as a catalyst towards the thiocyanation of aromatic ketones. The ionic liquid was recovered by distillation and reused for three times. It gives good to excellent yield in short reaction time because ethyl methyl imidazolium chloride with zinc chloride have been reveals the various interesting properties. So, this method have more superiority than other methods.

RECYCLING EFFECT OF IONIC LIQUID ON THIOCYANATION OF KETONES

Sr. No.	Ionic Liquid Reuse	Yield (%)
1.	I st recycle	92
2.	II nd recycle	90
3.	III rd recycle	85

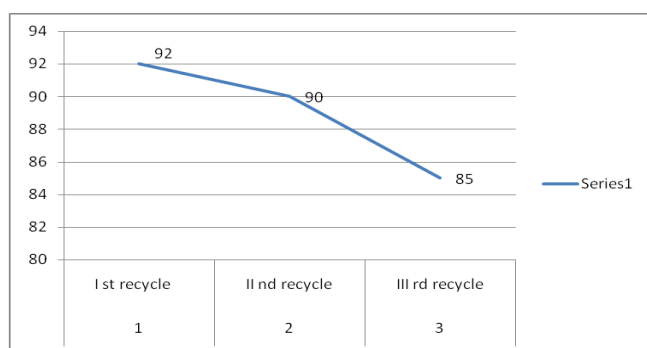


Figure 1: Graphical Representation of Catalyst Recycling

OPTIMIZATION OF REACTION CONDITION AND SOLVENT FOR THIOCYANATION OF SUBSTITUTED KETONES

Sr. No.	Solvent	Temperature(°C)	Time(h)	Yield (%)
1	Methanol	RT	6	65
2	Ethanol	RT	7	69

3	Water	RT	5	86
4	Acetonitrile	RT	2	92

RTIL ASSISTED GREEN α -THIOCYANATION OF KETONES

Entry	Substrate	Product	Reaction Time (h)	Yield (%)	M.P. (°C)
a			5	78	124-126
b			4.5	82	70-72
c			3.5	84	115-117
d			6	81	120-122
e			6.5	91	107-109
f			6	75	135-137
g			5.5	88	166-168
h			5	76	188-190
i			4.5	89	129-131
j			4	90	139-141

V. SPECTRAL DATA

A. 1-(4-CHLOROPHENYL)-2-THIOCYANATOETHANONE

IR-(cm⁻¹): 2055(SCN), 1623(C=O), 1400(C=C), 746(C-Cl)

¹HNMR- (CDCl₃)δ: 7.88(d,1H), 7.88(d,1H), 7.43(d,1H), 7.43(d,1H), 3.58(s,2H)
¹³CNMR -(CDCl₃)δ: 197.01, 139.6, 135.4, 129.8, 128.9, 110.8, 26.7
Mass -(m/z): 211.7(m⁺),239.8,287.9

B. 1-PHENYL-2-THIOCYANATOETHANONE

IR-(cm⁻¹): 3177(C-H), 2062(SCN), 1622(C=O),1403(C=C),
¹HNMR- (CDCl₃)δ: 4.16(s 2H);7.36(d 1H);7.62(d 1H);7.73(d 1H)
¹³CNMR -(CDCl₃)δ: 44.23, 112.48, 116.36, 118.69, 150.00, 161.42
Mass -(m/z): 151.2,177.4(m⁺),218.4,322.3

C. 4-METHYL-1-PHENYLETHANONE

IR-(cm⁻¹): 3156(C-H), 2923(C-C), 2061(SCN), 1621(C=O)
¹HNMR- (CDCl₃)δ: 1.1(s 3H); 7.39(d 1H);7.52(d 1H);4.01(s 3H)
¹³CNMR -(CDCl₃)δ: 182.2,142.6,130.9,131.5,125.3,22.8
Mass -(m/z): 134.1(m⁺),119.1

VI. CONCLUSION

Here we have developed new, green α-thiocyanation of ketones by using RTIL ethyl methyl imidazolium chloride with zinc chloride as catalyst with ammonium thiocyanate as reagent and acetonitrile solvent having non-hazardous technique. Ionic liquid used is easily recycled and reused for three times with considerable, good yield of the product. Reported procedure is good and more practical alternative to the existing methodologies for such α-thiocyanation of ketones. Recyclability of RTIL is attractive feature of this method

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