Hetrocyclization of Acetylenes with nitriles catalyzed by chromium Complex

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Abstract

A development of prospective synthetic methods to produce Pyridine including those of complex structure will allow to makes the latter more available and hence Pyridine bases will be widely used in industry. In this paper the Hetrocyclization of Acetylenes with nitriles catalyzed by chromium Complex has been carried out. We have limited our aim to study the chromium catalyzed activation of bifunctional vinyl halide a-Bromoacrylic amides with 1, 3 dines and alkynes to form an unsaturated butyrolactums. The compounds so obtained is 1.1-(4- Methoxyphenyl)-3(1 phenyl-(E)- methylidene)- 2,3,3a,4,5,7a- hex hydro- 1H-2-indolone and 1N-(4-Methoxyphenyl)-2-bromo-3-phenyl-(Z)-2-propenamide.

Keywords: chromium complex, 1.1-(4- Methoxyphenyl)-3(1 phenyl-(E)- methylidene)- 2,3,3a,4,5,7a- hex hydro- 1H-2-indolone

1. Introduction

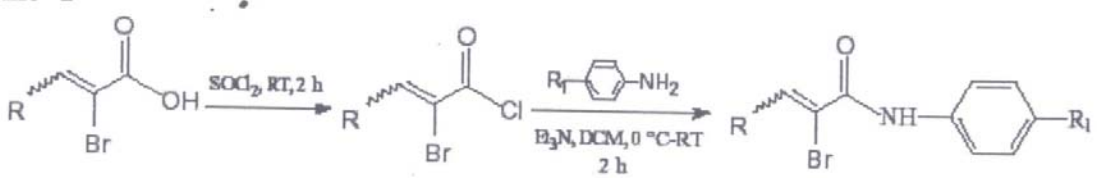
A Development of Prospective Synthetic and Methods To Produce Pyridine Including Those Of Complex Structure. In Synthesis Of Substituted Pyridine By Acetylene Hetrocyclization With Nitriles ($RC{=}NCR{=}CH_3$,Ph,Ph,Ch_2) In The Presence Of Co-Containing Complex Catalysts Was Published By Japanese Researches And The Carbon Hetro Bond Formation Reaction Catalyzed By The Transmission Metal Complex Has Been Very Attractive Formation Of Idols Aziridines And Other Heterocyclic Which One Part Of Biologically Interesting Products And The Synthesis Of Pyridine Basis Including Those Of Natural Structure With The Use Of Metal Complex Catalyst .The Transition Metal (Co ,Ni,Cr ,Pd ,Zr) And Rare Earth Elements Reactions Of Hetrocyclization Of Acetylene ,Liquids Phase Condensation Of Aldehyde With Amines ,Linear And Cyclic Oligomerization Of Vinyl Pyridines With Olefins Acetylenes Tertiary Alcohols To Give Substituted Pyridines Quoins And Phenanthrolines Of A Structure

2. Experimental Details

Our Aim Is To Study The -Catalyzed Activation Of Bifunctional Vinyl Halide A Bromoacrylic Amide With 1,3 Dina And Alkynes To Form An Unsaturated Butyrolactums Reaction Involved Formation Of Oxidative Addition Complex With Vinyl Halide And Then The In Sertion Of 1,3 Dines B/W The Carbon chromium In Bonds Leading To P Allyl chromium Bond Leading Complex And The heteroatom nucleophile attack on the p-ally chromium complex, which leads to expected lactums.

The synthesis of various Bromoacrylic amides and palladium catalyzed reaction of bromo acrylic amides were synthesized from the corresponding a- substituted anilines in the presence of triethylamine at room temperature.

Scheme -1

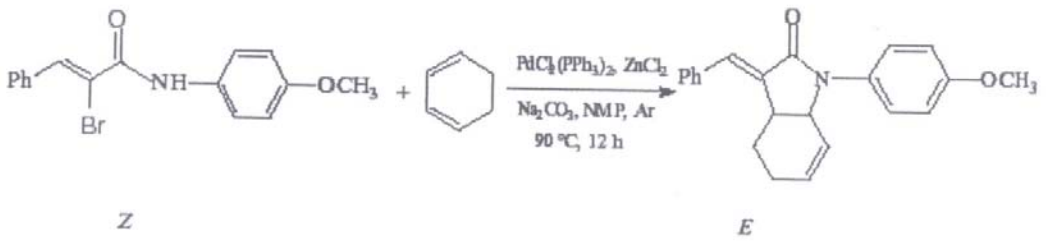


R = Ph, Me

$R_1 = NO_2, OCH_3$

Initial study was on the reaction of 1N- (4 Methoxyphenyl)-2- bromo-3-phenyl-(E)-2-propenamyde with1,3 cyclohexadiene catalyzed by $PdCl_2$ $(PPh_3)_2$ and co- catalyst, zinc chloride to yield the expected butyrolactums , 1 –(4-methoxyphenyl)-3-(1- phenyl-(E)-methylidene)-2,3,3a,4,5,7a-hexa-hydro1 H-2-indolone as shown scheme below;

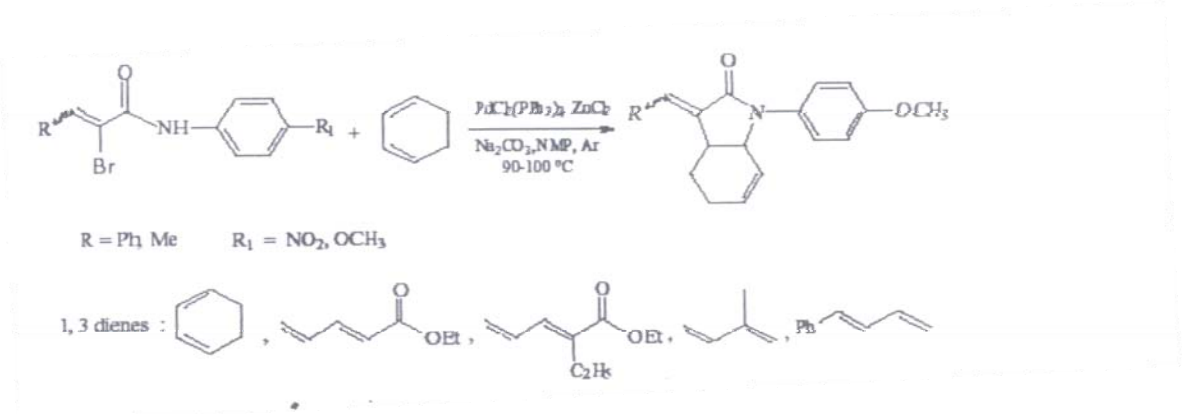
Scheme - 2



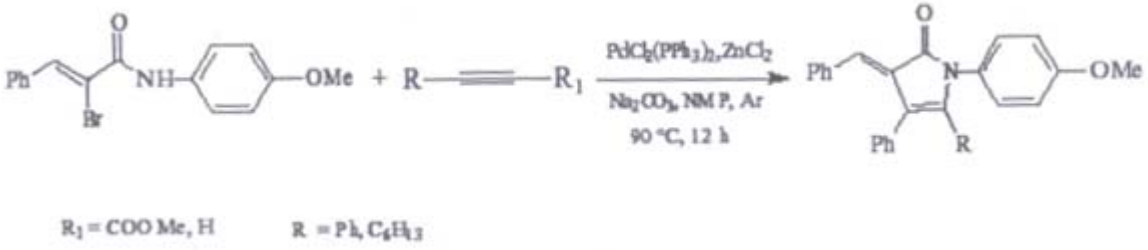
Z E

Similar reaction of various a-Bromoacrylic amides with different 1,3-dienes and alkynes were carried out in the presence of $CrCl_2(PPh_3)$ and zinc chloride at 90-100 ^oC under argon atmosphere to yield the corresponding substituted butyrolactums in good yield(scheme-3 & 4). The result of reactions of a- Bromoacrylic amides with 1, 3 dines are tabulated in third chapter.

Scheme-3

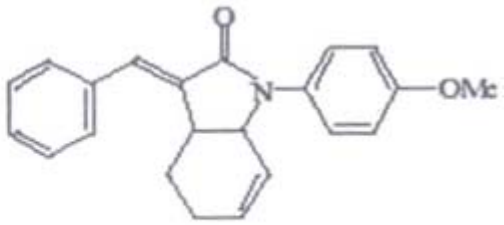


Scheme-4



General procedure for the chromium - catalyzed reaction of a- Bromoacrylic amides with 1, 3-dienes.

A 25 mL RB flask equipped with a magnetic stirring bar, reflux condenser and argon balloon was charged with a- Bromoacrylic amide (1 mmol), 1, 3- dines (2 mmol), $PdCl_2(PPh_3)_2$ (0.07 g, 0.1 mmol), sodium carbonate (0.275 g, 2 mmol), zinc chloride (0.067g, 0.5 mmol) and degassed N-,methylpyrrelidone (4 mL). the reaction mixture was flushed with argon thrice an d allowed to stir at 90 ^oC for 2-48h. The reaction mixture was neutralized with dil. HCl and the product was extracted with ethyl acetate (3 – 5 mL). The combined organic layer was dried over anhydrous sodium sulphate and concentrated under reduced pressure to give crude product. The crude product on silica gel column chromatographic purification using a mixture of petroleum ether and ethyl acetate gave the corresponding butyrolactums in moderate to good yield. The compound obtained is 1.1-(4-methoxyphenyl)-3-(1-phenyl-(E)-methylidene)-2, 3, 3a, 4, 5, 7a-hexahydro-1H-2-indoone.



Mol. F : $C_{22}H_{21}O_2N$

M.P : 135 - 137^{0}C

IR (Nujol) : 3018, 2935, 1681, 1645, 1608, 1290, 1247, 1033, 692,cm-1

1 H NMR (200 MHz, $CDCL_3$) : δ 7.6 (d,J = 4.0 Hz, 1H), 7.55 - 7.4 (m, 5H), 7.3 (δ, J = 8.0 Hz,2H), 6.95 (d, J= 8.0 Hz, 2H), 6.15 – 6.05 (m, 1H) 3.8 (s,3H), 3.65-3.50 (m,1H), 2.25 – 2.0 (m, 3H), 1.6 1.45 (m, 1H)

^{13} C MNR (50.32 MHz, $CDCl_3$) : δ 168.65, 158.19, 136.52, 135.60, 133.25, 130.00, 129.77, 129.13, 126.63, 123.27, 114.64, 55.76, 54.77, 36.51, 24.45, 23.93.

Mass (m/z) : 331 (M+, 100), 302 (15), 212(18), 179 (12), 165 (22), 134 9), 115 (37) , 91 (24),

3.Conclusions

A new and novel methodology was developed towards the synthesis of a, b-unsaturated butyrolactums by the chromium catalyzed reaction of a-bromo acrylic amides with 1,3 dines and alkynes.

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