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# Synthesis of 5-substituted-3H-[1, 3, 4]-oxadiazol-2-one derivatives: A carbon dioxide route (CDR)

M.Brahmayya, Shenghong. A.Dai, S.Y.Suen*

Department of Chemical Engineering, National Chung Hsing University, Kuo-Kuang road, Taichung-402, Taiwan, ROC.

*Corresponding author: Prof.Shing-Yi Suen, sysuen@dragon.nchu.edu.tw , Phone 886-4-2285 2590, Fax 886-4-2285 4734

The authors (co-first authors) contributed equally to this work

Abstract : A carbon dioxide route (CDR) of making biologically important 5-substituted-3H-[1,3,4]-oxadizole-2-one (SHOs) has been accomplished through synthesis and cyclization of varieties of hydrazides as their key intermediates. All these hydrazides were prepared readily in 95~98% by reacting acid chlorides with hydrazine monohydrate in the initial step. Then, SHOs were obtained in high yields from hydrazides by reacting them with carbon dioxide under basic conditions. More notable than high yields, the present CDR process for the first time has succeeded in straightforward cyclization reaction leading to SHOs formation with the simple reagents in ethanol solution.

**Keywords**: Carbon dioxide, Cyclization, 1, 3, 4-Oxadiazoles, Characterizations.

**1. Introduction.**1, 3, 4-Oxadiazole compounds represent a large family of biologically important 5-membered heterocyclic intermediates, which were interesting the superlative to the synthetic chemists all over the world [1-5]. A huge number of 2, 5-disubstituted-[1, 3, 4]-oxadiazole containing drugs have been covering their significant roles in medicinal chemistry [6]. In specific, the development of effective and practical organic synthesis of 5-(aryl or alkyl)-3H-[1, 3, 4]-oxadiazoles is a lively subject of organic research work. In the sequence of our current work we have been becoming to show an interest in preparation of 1, 3, 4-oxadiazoles due to their versatile building blocks with a wide scope of biological activities like, anti-inflammatory, antitubercular, antibacterial, antiviral, antipyretic, anticancer, central nervous system depressants, antischistosomal, analgesic, antiemetic and anticonvulsive properties[7]. The

famous use of heterocyclic intermediates is a scaffold in medicinal chemistry[8].A number of 2, 5 disubstituted-[1,3,4]-oxadiazoles have significant interest in polymer chemistry due to their luminescence properties[9].

Generally, synthetic procedures established on dehydrative cyclisation of semicarbazides, hydrazides are frequently used and curiously involved a corrosive reagents such as concentrated sulfuric acid or $POCl_3$, boron trifluoride diethyl etherate or Burgess reagent, phosphorus oxychloride, polyphosphoric acid, Thionyl chlorides where these conversely, results in an inflexible byproduct in the reaction and where the examinations were inadequate and has no experimental diversity[10-14]. To avoid undesirable reagents in the reaction, presently we have been focused our deep interest in the improvement in novel synthetic strategies to obtain attractive functionalized oxadiazoles. In a determination to chemically stitch up these biologically important heterocyclic molecules, we wanted to develop a modern synthetic route for the preparation of 5-substituted-3H-[1, 3, 4]-oxadiazole 2-one derivatives as a major chemical skeletons. We have paid an attention to this CDR process for the cheaper price of reagents and efficient reaction conditions without any by-products or any mishaps in handling of acidchlorides[15-18]. Moreover carbon dioxide ($CO_2$) is a nontoxic, an abundant, non-flammable, easily available chief greenhouse gas and a renewable carbon reservoir. To the best of our literature awareness, limited approaches existed for the synthesis of 1, 3, 4-oxadiazoles with the use of $CO_2$ gas. Conversion of $CO_2$ to useful organic and inorganic products and is of an unlimited prominence from a scientific field[16-19]. In spite of many efforts has been made to convert $CO_2$, the diversity of reactions is inadequate since $CO_2$ is thermodynamically grooming and kinetically inactive[20]. The Investigation of these innovative reactions to the conversion of carbon dioxide into an important organic product, which could support green and sustainability to this methodology and easier to use in the industries instead of restricted reagents like morpholine[21] and chloroform[22].The chemical fascination of carbondioxide through the cyclisation of several hydrazides with $CO_2$ to afford SHOs has been found to keep progress of various basic medium catalysts[23]. However, the synthesis of SHOs and their analogues of $CO_2$ and hydrazides have not been reported well. Herein, we

discovered for the first time that atmospheric carbondioxide could react with hydrazides to generate SHOs without any harsh conditions (Scheme-2) at atmospheric $CO_2$. Prepared samples were examined with $^{1}$HNMR, IR, $^{13}$ C NMR and UV-Visible spectroscopy.

**2. Materials and methods.** All commercially available reagents and solvents were obtained from the commercial suppliers and used without further purification. For the cyclisation reaction, all the experiments were conducted in a 100 mL round-bottomed Pyrex glass flask with continuous and constant stirring speed at 600 rpm. Thin layer chromatography (TLC) was applied on silica gel plates. Flash column chromatography was done by using 300-400 mesh type silica gels. Visualisation on TLC was attained by illumination under UV lamp (254nm). $^{1}$HNMR spectra were recorded on a 400 MHz spectrometer and $^{13}$C NMR was recorded on 100 MHz spectrometer using tetramethylsilane (TMS) served as an internal standard. Infrared (IR) spectra were recorded with Perkin Elmer Spectrum One FT-IR spectrometer. Samples were prepared as potassium bromide pellets for IR characterizations. High-resolution mass spectrometry, UV-visible spectrum was recorded on UV–vis spectrophotometer (UV-1601, Shimadzu, Australia). (HRMS) was recorded. All of the substrates were prepared for the known experimental procedures with minor modification.

**2.1 Preparation of butanoyl hydrazide (scheme-1).**

Some reports were well-established for the synthesis of hydrazides but still there was a problem of reaction handlings and experimental practices with those of highly reactive acid halides. Herewith, we provided a very useful experimental methods and procedures at extremely lower temperature -10 $^{0}$ C for this well established reactions, which could be practical and useful (fig.1).

**2.2 A careful experimental procedure for the preparation of hydrazides.**

A neat and well dried 100 ml, three-necked round-bottomed flask was fitted with a Teflon-coated thermocouple and containing magnetic beat inside the flask. 50ml of ethanol (98%) and sodium hydroxide (0.35 g, 0.0087 mol) were charged into the flask. The magnetic paddle was started to stir

continuously to mix the input chemical components to obtain a solution. An aqueous solution of hydrazine monohydrate (98%, 0.40 gm, 0.008 mole) was added into the flask with standard precautions in the fuming-cup board. This reaction mixture was cooled in an ice-methanol/salt bath to attain an internal cooling temperature of –10 to 0 °C. Before adding the butanoyl chloride to the reaction mixture, open one neck of the flask to make sure an outlet for the simultaneous generated HCl gas vapours to go out into cupboard. This can decrease higher pressure in the RBF, to avoid accidents. Then, start addition of a benzoyl chloride (0.43 gm, 0.0034 mol) with help of a long range synerge needle, and where the needle's tip should be dipped in the reaction mixture by using correctly fitted rubber-septum support from other neck of RBF to make a steady flow rate into the reaction mixture over a period of one hour, keeping the same cooling temperature (fig-1.a). A white solid suspended product has been formed within 5-10 minutes. This whole reaction mass is neutralised with 10% of sodium hydroxide (15 ml) solution only due to the generated HCl gas always passed out from the open end of the reactor. So that the less quantity of base is used. The reaction mixture was further taken into the ethyl acetate (20 ml) and then separated out as organic layer. This was transferred to a 100 ml, single necked flask and concentrated to a volume of ca.10 ml by rotary evaporation (at ca. 10mm) and finally the suspension was filtered and further concentrated to 5 ml and add 25 ml of toluene and the resulting liquid is taken in double-necked round bottom flask which was equipped with a dean-stalk liquid separator, thermometer to separate out the azeotropic mixtures at constant temperature $110^0$ C (fig-1.b). Finally, we found a shiny powder at the bottom of RBF, after the complete evaporation of aqueous and organic solvents in the flask. This solid product was recrystallized from 10mL of diethyl ether to obtain 0.38-0.395 gm (95-98%) of propyl hydrazide. The completion of reaction was monitored by thin layer chromatography, Infrared spectrum and $^1$HNMR. Compounds 3a-j were prepared with this method and then further used to synthesize SHOs. Spectral data was summarized at supporting information S1-S20.

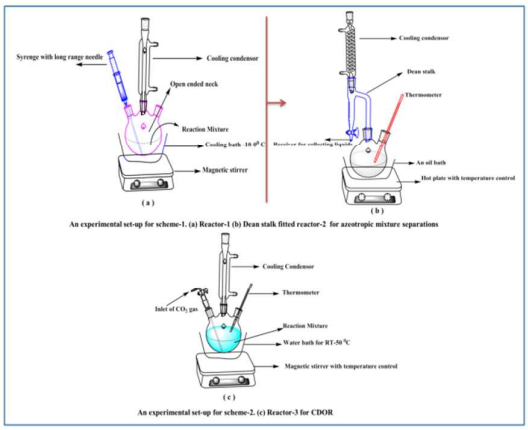
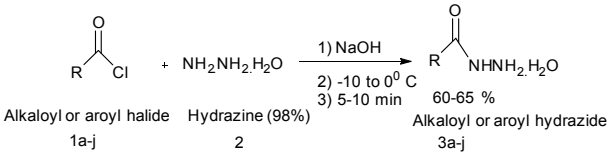



Figure 1.An experimental setup of scheme-1 and scheme-2 reactions

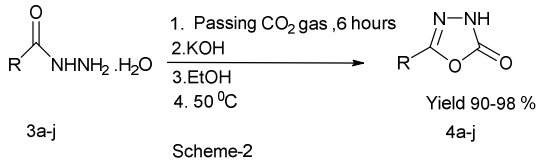



Scheme-1

**2.3 Preparation of 5-(p-methoxy)-3H-[1, 3, 4]-oxadiazol-2-one**

we had taken compound 3c (0.12 g, 0.0064 mol) was dissolved in the ethanol (10 ml) in a 100 ml three necked round bottom flask with a magnetic beat inside to mix the reaction mass. The solution was vigorously stirred. Then, further added a strong base KOH (0.37 g, 0.0044 mol), into the reactor and stirred for 15 minutes to obtain a homogeneous solution in the flask under the room temperature. Pass the carbon dioxide into the reactor through the other neck of the flask by using the help of gas purging glass tube while its tip was dipped in reaction mixture and maintain the temperature at 50 $^0$C for six hours (fig-1.c). Then remove the $CO_2$ inlet and close the reactor's neck and reflux the reaction mass for 30 minutes to obtain a crude product. This residual product was taken in 10-15 mL of water and quenched with dilute HCl (10%). The precipitate was filtered off, dried and the yield was 95% (m.p 110$^0$ C). It was further taken into the ethanol and recrystallized. The completion of reaction was monitored by thin layer chromatography and Infrared spectrophotometer.

The same procedure had been applied for the selected alkaloyl hydrazides (3j) or aroyl halides (3a-i) to attain 5-substituted-1,3,4-oxadiazole-2-ones (4j) or (4a-i).




Scheme-2

## 3. Results and discussion.

**3.1 Chemistry**. The titled molecules were synthesized by the ring closure reactions to various alkaloyl or aroylhydrazides (3a-j, scheme-1) with carbon dioxide in the presence of potassium hydroxide in excellence yields (4a-j,scheme-2). The substrate hydrazides (3a-j) were synthesized by dehydrochlorination of various aromatic and non-aromatic acid chlorides with hydrazine monohydrate under strong basic medium condition.

**3.2. Synthesis.** As a continuous effort in extent the application scope of 5-membered cyclisation reactions, we intend to use oxadiazole compounds rather than isoxazoles [24]. To our surprise, when the reaction against hydrazine hydrate (2), acidchlorides (1a-j) was carried out in the presence of sodium hydroxide at -10$^0$ C temperature instead of -5-0$^0$ C to afford hydrazide 3a-j within a 5-10 minutes. It demonstrated that petty modified procedure for the synthesis of hydrazides is more naturally approachable and useful than the known methods with our experimentally proved conditions (Table-1). It is obvious that the basic medium plays an important role in this process. Hence, the possibility and the limitation of this procedure explored for such a way of setting the temperature at -10$^0$ C and quantity of the base is 0.0087 mol. All the selected acidchlorides (1a-j), such as alkaloyl or aroyl acid chlorides, which were smoothly reacted with hydrazine hydrate and sodium hydroxide to afford the corresponding hydrazides in good to excellent yields (Table 2) under the mentioned optimization conditions in Table-1.The electron donating substituent groups on the aromatic acid chlorides did a slight influence on the reaction to afford higher yields (table-2. entries 1, 3, 5, 6, 8).Whereas the electron withdrawing groups of acid chlorides had been showed a slight decreasing yields on its corresponding final product (table-2, entries 2, 4, 7, 9).Where as in the case of entry 10 (table-2), there was a positve inductive effect (+I)

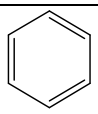
towards the nitrogen in its corresponding substrate (butanoyl chloride) resulted in the higher yield of product. A variation of the reaction temperature from –10 $^0$C to 0 $^0$ C shows a constructive influence on both reaction rates and yield. It was noteworthy, the yields were not improved when the reaction was carried out at 40 $^0$C, RT, 0 $^0$ C and -5$^0$ C, when it was compared at temperature -10 $^0$ C.

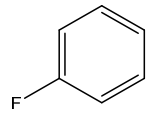
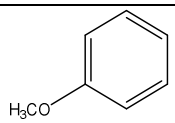
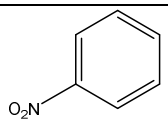
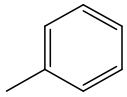
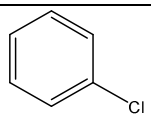
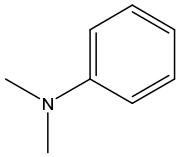
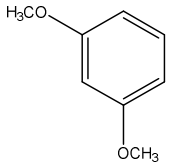
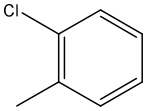
Table-1.An optimal condition for the reaction of (p-methyl)-benzoyl chloride and hydrazine monohydrate to afford 3e.

| Entry | NaOH [a] (mol) | Temperature ($^0$ C ) | Yield (%) |
|---|---|---|---|
| 1 | 0.001 | 40 | None |
| 2 | 0.001 | RT | 10 |
| 3 | 0.001 | 0 | 70 |
| 4 | 0.0011 | 0 | 74 |
| 5 | 0.0018 | -5 | 80 |
| 6 | 0.002 | -5 | 83 |
| 7 | 0.004 | -5 | 85 |
| 8 | 0.0060 | -10 | 90 |
| 9 | 0.0082 | -10 | 97 |
| 10 | 0.0087 | -10 | 98 |

[a] The reaction was used under anhydrous NaOH.

Table-2: Synthesis of 3a-j by using the hydrazinemonohydrate with alkaloyl or aroyl halides.

| **Entry** | **R** | **Product** | **Conversion[a] (%)** | **Yield (%)[b]** |
|---|---|---|---|---|
| 1 |  | 3a | 96 | 94 |

| | | | | |
|---|---|---|---|---|
| 2 |  | 3b | 90 | 90 |
| 3 |  | 3c | 98 | 96 |
| 4 |  | 3d | 93 | 89 |
| 5 |  | 3e | 98 | 96 |
| 6 |  | 3f | 96 | 92 |
| 7 |  | 3g | 95 | 91 |
| 8 |  | 3h | 99 | 97 |
| 9 |  | 3i | 96 | 93 |
| 10 | Propyl | 3j | 97 | 95 |

[a, b] Conversion and isolated yields were based on the NMR spsectroscopy.

The compound butanoyl hydrazide formation was confirmed by its IR spectra (Fig. 2), $^{1}$HNMR spectrum (fig.S19) and UV-anlaysis (Fig.4) monitoring. The same reaction conditions also have been applied fruitfully to the synthesis of other aroyl hydrazides. All hydrazides prepared for this series were compiled in Table 2.

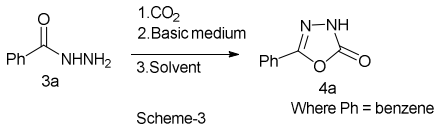
**3.3 Cyclisation of selected hydrazides into 1,3,4-oxadiazoles.**

In 1998, J.R.Young showed a cyclisation reaction to aryl iodides with amidoximes under carbon monoxide (CO) with palladium catalysts in tri ethylamine /organic solvent forming an oxadiazoles[25-27]. Nevertheless, the utilized reaction conditions and chemicals were not environmental benign and even more expensive.

In this study we had improved the preparation and procedures to carry out the cyclisation of hydrazides with greener carbon dioxide gas testing different reaction conditions to find the best way for the production of oxadiazoles with the lowest price and with a greener reaction condition.

Afterwards of the obtaining acceptable results from the synthesis of corresponding acid hydrazides, we then turned our attentions to the preparation of SHOs (4a-j).To do so, we have chosen a benzohydrazide to optimize the reaction conditions carefully (scheme-3). The effects of different reaction conditions were investigated and summarized below in Table-3. From the literature survey, we fixed the ethanol was an optimal solvent and potassium hydroxide as base. We were deeply focussed in quantity of potassium hydroxide and temperature in the study of optimized conditions for the benzohydrazide to 5-phenyl-3H-[1, 3, 4]-oxadiazol-2-one. We found that the conventional temperature is at 50 $^{0}$ C. The required quantity of potassium hydroxide is 0.0044 mol in the selected solvent ethanol under CDR procedure (Table-3).The cyclization was carried by purging carbondioxide gas into the reactor, which contains the hydrazide, potassium hydroxide and ethanol to obtain the title compounds at constant temperature 50$^{0}$ C with a maximum time period of 6 hours. The scope of this simple CDR process was explored for using a collection of structurally diverse organic acid chlorides and optimized with the benzohydrazide (scheme-

3) and table-3. Hydrazides reacted with carbon dioxide to form the organic intermediates 4a-j, which lost a mole ratio of potassium hydroxide to afford the closed-ring intermediate 4a-j.




Scheme-3

Table-3. Optimization of reaction conditions for the synthesis of 5-phenyl-3H-[1, 3, 4]- oxadiazole-2-one by using 3a.

| Entry | KOH [a] (mol) | Solvent | Temperature ($^0$C ) | Yield (%) |
|---|---|---|---|---|
| 1 | 0.001 | Ethanol | 0 | None |
| 2 | 0.001 | Ethanol | RT | 10 |
| 3 | 0.001 | Ethanol | 35 | 76 |
| 4 | 0.0044 | Ethanol | 40 | 73 |
| 5 | 0.0044 | Ethanol | 45 | 91 |
| 6 | 0.0044 | Ethanol | 50 | 96 |

[a] The reaction was monitored under anhydrous KOH.

Table-4.Syntheis of 5-substituted-1,3,4 oxadiazole-2-ones

| Entry | Corresponding hydrazides (3a-j of scheme-1) | product | Time (hours) | Yield (%) |
|---|---|---|---|---|
| 1 | 3a | 4a | 5 | 92 |
| 2 | 3b | 4b | 4 | 89 |

| | | | | |
|---|---|---|---|---|
| 3 | 3c | 4c | 5 | 95 |
| 4 | 3d | 4d | 6 | 95 |
| 5 | 3e | 4e | 6 | 93 |
| 6 | 3f | 4f | 6 | 90 |
| 7 | 3g | 4g | 6 | 87 |
| 8 | 3h | 4h | 6 | 93 |
| 9 | 3i | 4i | 6 | 90 |
| 10 | 3j | 4j | 6 | 95 |

Isolated yields were based proton NMR.

In all over the case studies, no difficulty was found whether the substrates are of active organic halides (table-4, entries 1,3,5,6,8), which contained methyl, methoxy groups or the substrates of inactive organic halides (table-4, entries 2, 4, 7), such as halo or nitro substituents on their corresponding phenyl rings were used, the reactions proceeded smoothly to afford the desired SHOs (4a-j) in good at excellent yields. All the resulting characterizations were completely matched with previous reports, and our technique is an efficient and environmentally benign. The plausible reaction mechanism for the formation of 5-susbstituted-3H-[1, 3, 4]-oxadiaozl-2-ones is proposed in Scheme-4 (fig-5).

**3.4. Characterizations.**

The FTIR-spectra (fig.2) of unmodified hydrazinemonohydrate absorption peaks that were refer to stretching of hydroxyl (-OH), amine (-NH) at wave numbers of 3400-3500 $cm^{-1}$, 3000 $cm^{-1}$(shifted to lower than hydroxy due to the nearby regions of amine and hydroxyl groups) respectively. These data are consistent with those of other studies[29-30]. Where as the one of our selected unmodified substrate butanoyl chloride (1j) shows its absorption peaks of acyl (-COCl), aliphatic ($-CH_2$) at 1725-1700, 2982 $cm^{-1}$ respectively. The product 3j shows its absorption peaks that refers to streching of amide (-CONH), amine ($-NH_2$), aliphatic ($CH_2$) at 1610 $cm^{-1}$, 3200 $cm^{-1}$, 2980-2990 $cm^{-1}$ respectively. The FTIR spectra (fig.3) of the product 4j absorption peaks was assigned to amide at (-CONH) 1625 $cm^{-1}$, aliphatic ($CH_2$ ) 2995

$cm^{-1}$, carbonyl (COONH) 1746 $cm^{-1}$ and 3267-3600 $cm^{-1}$ (mixed NH and any other hydroxy) respectively. On the other hand the comparative studies of UV spectrum (fig.4) of compound 4j (5mg/10 ml ethanol) showed a distinguished splitted wavelength range of the visible region (200-330nm) rather than the compounds hydrazinemonohydrate (2) (5mg in 10 mL in ethanol), butanoyl chloride (1j) (5mg in 10 mL of ethanol) , butyrohydrazide (3j) (5mg in 10 mL of ethanol) which shows their absorption at below 200 nm (5mg in 10 mL of ethanol) and were consistent with literature[30-31]. When we had observed the NMR results of 3a-j and 4a-j, those clearly indicating the significant chemical shift values of amidic (-CONH) was at above 10 ppm for $^{1}$HNMR and 150-170 ppm in $^{13}$CNMR respectively, in both cases of scheme-1 and scheme-2 analogues.We were summarized the all distinguished chemical shift values of both $^{1}$HNMR and $^{13}$CNMR in the individual figures at supporting information (fig.S1-S40) for all synthesized compounds.

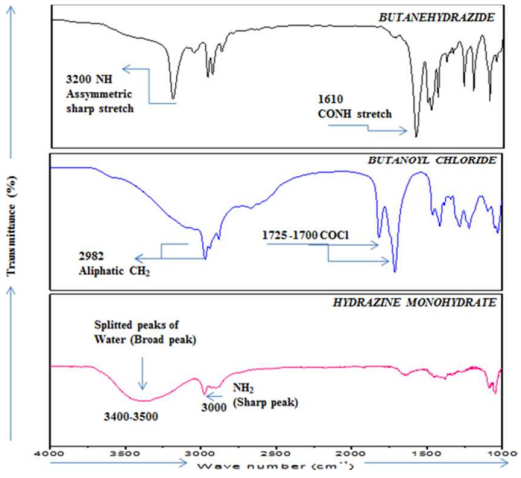



Figure 2.Comparative IR-Spectra of hydrazine monohydrate, butanoyl chloride and butanehydrazide.

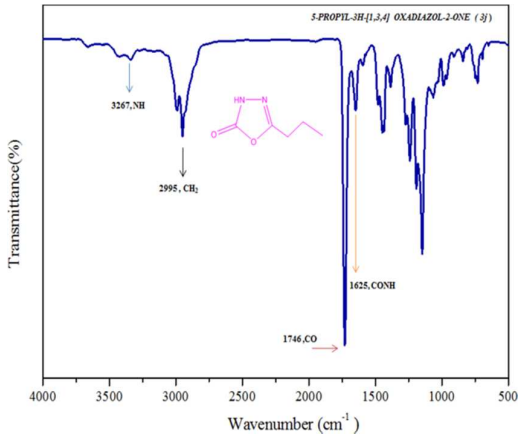



Figure 3.IR-spectrum of compound 4j.

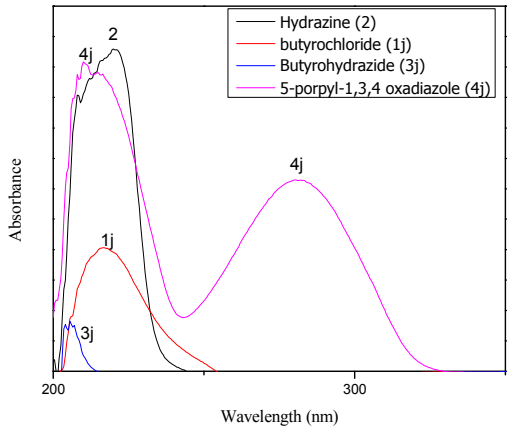



Figure 4. A Comparative UV-spectrum for hydrazinemonohydrate, butyrochloride, butyrohydrazide and 5-propyl-1,3,4-oxadiazole.

**3.5 Mechanism.**

Finally, we found that the acid chlorides could be converted completely in a shorter time (5-10 minutes) in each reaction (scheme-1, table-2 and step-1 in fig-5). But a very long time i.e 4-6 hours was essential to reach acceptable selectivity of the preferred product of (scheme-2, table-4 and step-2 in fig-5).The time (4-6 hours) required for the final product of 3a-j to 4a-j clearly indicating that the slower reaction. This characteristic phenomenon could clear that the reactant is converted into the product of an intermediate like potassium salt of 2-oxy-5-(aryl or alkyl)-1, 3, 4-oxadiazole-2-one as we proposed theoretical assumption (plausible mechanism, fig-5). In this work, we studied the reaction of $CO_2$ with hydrazides

(3a-j) in detail and were confirmed by the results of $^{1}$HNMR,$^{13}$C NMR (fig.S1-S40) analysis and consistency with all simulated and obtained data of some previous reports[32-33].

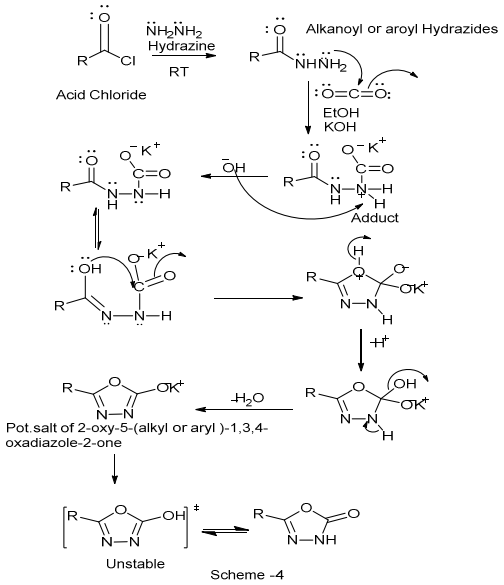



Figure 5.A plausible mechanism for the total sysnthesis.

## 4. Conclusions.

In summary, we have discovered a two-step synthetic process for the preparation of 5-alkyl-3H-[1,3,4]-oxadiazol-2ones (SHOs) by using a simple CDR process, where the carbon dioxide can smoothly react with hydrazides to form the targeted molecules at an atmospheric pressure under basic ethanol solution. The reaction condition is mild, isolation of products is easy and the yields of SHOs are consistently high. Hence, this novel CDR process might have great potentials for industrial applications.

## 5. Acknowledgements.

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