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# **Epoxidation of Vinyl Cyanides by Calcium Hypochlorite under Catalyst- and Solvent-free Conditions**

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#### ARTICLE INFO

ABSTRACT

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Keywords: Epoxidation Calcium hypochlorite Catalyst-free Solvent-free Crushing In this paper, epoxidation of a wide range of alkenes by calcium hypochlorite (Ca(OCl)<sub>2</sub>) was investigated under catalyst- and solvent-free conditions. It was noticed that the highest yield was achieved with crushing, when the reaction was between vinyl cyanides and Ca(OCl)<sub>2</sub>. The structure of the synthesized epoxides was confirmed by IR, <sup>1</sup>H- and <sup>13</sup>C-NMR and elemental analysis. Short reaction times, the use of a simple experimental procedure, and reducing of energy consumption are other important advantages of our work that could be mentioned too.

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Epoxides are an important class of organic compounds which are widely used in organic reactions due to their properties such as very useful balance between stability and reactivity resulting from high ring strain.<sup>1</sup> Epoxide derivatives have been found to be good raw material for epoxy resin, paints, surfactant, polymers and important intermediates for making valuable products in organic synthesis.<sup>2-4</sup> Furthermore, epoxides have been used as a precursor and highly useful building block for the synthesis of bioactive compounds in many reactions.<sup>5-8</sup> Based on foregoing, synthesis of epoxides from alkenes has attracted considerable attention. For this purpose several methods have been reported recently. For example, epoxidation of alkenes by tetrabutylammonium monopersulfat in the presence of Mn (III)salen,<sup>9</sup> by NaOCl and urea  $H_2O_2$  in the presence of chiral macrocyclicsalen Mn (III) complexes,<sup>10</sup> by tert-butyl hydroperoxide in the presence of oxidovanadium (IV) tetradentate schiff base complex,<sup>11</sup> by H<sub>2</sub>O<sub>2</sub> in the presence of manganese complex,<sup>12</sup> and by  $H_2O_2$  in the presence of Iron<sup>13</sup> have been reported. Epoxidation of alkenes were also carried out by using of other reagents such as peroxybenzoic acid, peracids, aldehyde/Oxone in the presence of appropriate catalyst.<sup>1422</sup> (TBHP) Epoxidation of 2-benzylidenemalononitrile was first reported in 1).<sup>23</sup> (Table 1, entry Epoxidation of 2-1967 benzylidenemalononitrile was also reported by Meninno, et al. in 2015 (Table 1, entry 2).<sup>24</sup> However, these methods for epoxidation of 2-benzylidenemalononitrile and its derivatives have not been entirely satisfactory and involve some disadvantages such as long reaction times, use of organic solvents and generally need expensive or non-available reagents

and catalysts. Thus, the introduction of new methods and /or further work on technical improvements to overcome these limitations is still needed.

 
 Table 1. Comparative methods for the epoxidation of 2benzylidenemalononitrile

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Entry	Oxidant	Conditions	Time	Yield	Ref
		Catalyst/Solvent//Temp		(70)	
		( <sup>0</sup> C)			
1	Hypochlorous acid	acetonitrile/0-80	-	-	[23]
2	CHP <sup>a</sup>	multifunctional	24(h)	78	[24]
3	Ca(OCl) <sub>2</sub>	cinchona derived thiourea/toluene/-20 catalyst-free/solvent- free/crushing	20(min)	90	this work

<sup>a</sup>cumyl hydroperoxide.

In conjunction with our ongoing research program involving the oxidation of 2-(methyl)malononitriles by  $Ca(OCl)_2$ ,<sup>25</sup> in this paper, we report an efficient, simple, green, facial and cost-effective method for the epoxidation of vinyl cyanide derivatives by  $Ca(OCl)_2$  under catalyst- and solvent-free conditions at room temperature.

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### Tetrahedron

In our initial study, the reaction of 2-benzylidenemalononitrile (1 mmol) and  $Ca(OCl)_2$  was considered as a model reaction to optimize the conditions. To find the best solvent, several solvents such as H<sub>2</sub>O, EtOH, MeCN, and n-hexane were employed as media. However, it was noticed that the highest yield was achieved under solvent-free conditions with crushing the mixture of 2-benzylidenemalononitrile and Ca(OCl)<sub>2</sub> (Table 2, entry 5). Similar reactions were then attempted in the presence of 0.5, 0.7,0.8 and 1.0 mmol of Ca(OCl)<sub>2</sub>. The results show that the use of 0.8 mmol of Ca(OCl)<sub>2</sub> under solvent-free conditions is sufficient to push the reaction forward. Greater amounts of the oxidant had no significant influence on the reaction time (Table 2, entry 6). To scale-up the reaction, epoxidation was performed on the 2, 4, and 6 mmol scales under solvent-free conditions. The obtained results indicate without changing reaction times producing similar yields. Other oxidation reagents such as anhydrous LiOCl, NaOCl, NaIO<sub>3</sub>, NaIO<sub>4</sub>, oxone and trichloromelamin, were also used. No reaction occurred with these oxidants under optimized conditions and only a 20 % yield was obtained by anhydrous LiOCl (Table 2 entries 9-14). Finally, we found that this reaction optimally proceeded by crushing 2benzylidenemalononitrile with Ca(OCl)<sub>2</sub> and completed within 20 min to afford the corresponding products (2a-o) in high yields.

 
 Table 2. Optimization of the epoxidation reaction of 2benzylidenemalononitrile under various conditions at room temperature

	CN CN		CN CN
Entry	Oxidant (mmol)	Conditions	Yield (%)
1	Ca(OCl) <sub>2</sub> (0.8)	H <sub>2</sub> O/r.t	Trace
2	Ca(OCl) <sub>2</sub> (0.8)	EtOH/r.t	Trace
3	Ca(OCl) <sub>2</sub> (0.8)	MeCN/r.t	20
4	Ca(OCl) <sub>2</sub> (0.8)	n-Hexane/r.t	35
5	Ca(OCl)2(0.8)	Solvent-free/crushing	90
6	Ca(OCl) <sub>2</sub> (1.0)	Solvent-free/crushing	90
7	Ca(OCl) <sub>2</sub> (0.7)	Solvent-free/crushing	85
8	Ca(OCl) <sub>2</sub> (0.7)	Solvent-free/crushing	60
9	LiOCl (anhydrous)	Solvent-free/crushing	20
10	NaOCl	Solvent-free/crushing	Trace
11	NaIO <sub>3</sub>	Solvent-free/crushing	-
12	NaIO <sub>4</sub>	Solvent-free/crushing	-
13	Oxone	Solvent-free/crushing	-
14	Tricholoromelamin	Solvent-free/crushing	-

The synthesized epoxide was characterized by IR, <sup>1</sup>H- and <sup>13</sup>C-NMR spectra, m.p. and elemental analysis. The IR spectrum of 3-phenyloxirane-2,2-dicarbonitrile (**2a**) showed a strong band at 1191 cm<sup>-1</sup> related to stretching vibration of C-O bond. The C=C stretching vibration of phenyl ring appeared at 1497 and 1605cm<sup>-1</sup>. The C=N stretching absorption band was also observed at 2260cm<sup>-1</sup>. <sup>1</sup>H-NMR spectrum of **2a** exhibited a sharp singlet ( $\delta = 4.74$  ppm) for 1H of the epoxide ring and a multiple ( $\delta = 7.45$ -7.57 ppm) for the 5H of phenyl group. The <sup>13</sup>C-NMR spectrum of **2a** consisted of the signals at 41.8 and 65.8 ppm for the C<sub>3</sub> and C<sub>2</sub> of the epoxide ring respectively, the signals at 110.3 and 111.7 ppm for the carbon atoms of the nitrile groups and finally the peaks at 126.8-131.4 ppm for the carbon atoms of phenyl ring. The elemental analysis of **2a** showed the existing of carbon (70.3%), hydrogen (3.4%) and nitrogen (16.5%) which it

was confirmed the synthesis of 3-phenyloxirane-2,2dicarbonitrile (Scheme 1).



Scheme 1. Structure of 3-phenyloxirane-2,2-dicarbonitrile (2a)

Under optimized conditions, 3-aryloxirane-2-carbonitriles (**2a-o**) were synthesized. In all cases, the reactions proceeded efficiently under solvent- and catalyst-free conditions to afford the corresponding products in high yields. The results are summarized in Table 3. It can be observed that the process tolerates both electron-donating and withdrawing substituent in benzaldehyde. All the products were characterized by FT-IR,<sup>1</sup>H- and <sup>13</sup>C-NMR spectra, m.p. and elemental analysis.

 Table 3. Epoxidation of vinyl cyanide by Ca(OCl)<sub>2</sub> under catalyst- and solvent-free conditions

	R <sup>1</sup>	$R^2$ –	Ca(OCl) <sub>2</sub> Crushing	<b>→</b>	$R^1 \xrightarrow{0} R^2$	
Entry	R <sup>1</sup>	$\mathbf{R}^2$	Product	Time (min)	Yield (%)	Mp (°C)
1	Ph	CN	2a	20	90	51
2	4-F C <sub>6</sub> H <sub>4</sub>	CN	2b	120	89	87-89
3	4-Cl C <sub>6</sub> H <sub>4</sub>	CN	2c	120	89	128
4	4-Br C <sub>6</sub> H <sub>4</sub>	CN	2d	120	86	129-130
5	4-CH3 C6H4	CN	2e	130	79	75
6	4-OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	CN	2f	150	75	79
7	4-NO2 C6H4	CN	2g	120	98	177
8	2-NO2 C6H4	CN	2h	120	99	128-129
9	Ph	CO <sub>2</sub> Et	2i	30	91	Oil
10	4-F C <sub>6</sub> H <sub>4</sub>	CO <sub>2</sub> Et	2j	40	93	Oil
11	4-Cl C <sub>6</sub> H <sub>4</sub>	CO <sub>2</sub> Et	2k	90	90	70-72
12	4-Br C <sub>6</sub> H <sub>4</sub>	CO <sub>2</sub> Et	21	100	87	94
13	4-CH3 C6H4	CO <sub>2</sub> Et	2m	60	81	63
14	$4-NO_2 C_6H_4$	$CO_2Et$	2n	120	99	128-130
15	$2\text{-NO}_2 C_6 H_4$	CO <sub>2</sub> Et	20	90	99	61
16	Ph	CONH <sub>2</sub>	-	150	30	-

Reaction conditions: vinyl cyanide (1 mmol),  $(Ca(OCl)_2 (0.8 \text{ mmol}), \text{ solvent-free}.$ 

It should be noted that the epoxidation reaction was also carried out with some other alkenes such as cyclohexene, ciscyclooctene, styrene,  $\alpha$ -methyl styrene,  $\beta$ -nitro styrene (E)-Stilbene and indene under optimized conditions. In all these cases, the product was not formed or formed in lower yields (Table 4). By a comparison of the results in Table 3 with Table 4, the reactions proceeded efficiently when the reaction was between vinyl cyanides and Ca(OCl)<sub>2</sub>.

**Table 4.** Epoxidation of various alkenes by  $Ca(OCl)_2$  under catalyst- and solvent-free conditions at room temperature

Entry	Alkenes	Yield (%)
1	Cyclohexene	Trace
2	cis-cyclooctene	Trace
3	Styrene	-
4	α-methyl styrene	-
5	$\beta$ -nitro styrene	Trace
5	(E)-Stilbene	Trace
6	Indene	Trace
<b>D</b> agation agndit	iona allega (1 mmal) Ca(OCI)	(0.9 mmal) solvant free

Reaction conditions: alkene (1 mmol), Ca(OCl)<sub>2</sub> (0.8 mmol), solvent-free, crushing.

Although the mechanism of the reaction has not been established experimentally, based on our experimental results

observed in Tables 3 and 4, the formation of the product can be rationalized as outlined in the Scheme 2



Scheme 2. The proposed mechanism for the epoxidation of vinyl cyanides by Ca(OCl)<sub>2</sub>

In summary, we have developed an improved and convenient procedure for the epoxidation of vinyl cyanide derivatives by  $Ca(OCl)_2$  under catalyst- and solvent-free conditions. The remarkable advantages of this method are simple experimental procedure, short reaction times, high yields, and the ease of product isolation.

# Typical procedure for the preparation of 3-phenyloxirane-2,2-dicarbonitrile

2-Benzylidenemalononitrile (1mmol) and Ca(OCl)<sub>2</sub> (0.8 mmol) were crushing in a mortar at room temperature for 20 min. After completion of the reaction, the mixture was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and filtered. The solvent of the resulting filtrate was evaporated and a pure product was obtained by recrystallization from ethanol with yield of 90%. The authenticity of the product was established by the data of IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and elemental analysis.

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### Tetrahedron

# Highlights

- The epoxidation of vinyl cyanides by Ca(OCl)<sub>2</sub> was investigated for the first time.
- Acceleration

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### **Graphical Abstract**

