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The study of reaction mechanism for the transformation of nitronate into nitrile by phosphorus trichloride

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Abstract—Nitronate was generated using β-nitrostyrene and the anion of dimethyl malonate in THF at 0 °C. Subsequent treatment with PCl_3 in the presence/absence of DMAP either in THF or pyridine afforded nitroalkane, chloroxime, and nitrile. Pyridine, THF, and THF–pyridine co-solvent as solvents were investigated under different conditions. With different anions of malonates containing dipolarphiles, cyclic compounds were obtained as major products indicating nitrile oxides were generated during the reaction. Based on the results, compared to that of the one reported in literature, a plausible mechanism involving nitrile oxide intermediate was proposed.

1. Introduction

Nitrile oxides are the most important intermediates in the synthesis of heterocyclic compounds via 1,3-dipolar cycloaddition.[1] Two widely used methods to produce nitrile oxides are (i) reaction of aldoximes with oxidizing agents or halogenating species[2] and (ii) reaction of primary nitroalkanes with dehydrating agents such as PhNCO and Et_3N,[3] $POCl_3$,[4] diketene and Na,[5] H_2SO_4,[6] Me_3SiCl and Et_3N,[7] Ac_2O and AcONa,[8] AcCl and MeONa,[9] *p*-TsOH,[10] $PhSO_2$-Cl or ClCOOEt and Et_3N,[11] $SOCl_2$ and Et_3N,[12] $(BOC)_2O$ and DMAP,[13] BURGESS and DAST or $(COCl)_2$.[14]

Nitrile is also a valuable synthetic intermediate for organic chemistry including pharmaceuticals, agricultural chemicals, dyes and material science and is also a key constituent in many natural products.[15] Some of the useful methods for the preparation of alkylnitrile includes (i) the direct nucleophilic substitution of alkyl halides with inorganic cyanides;[16a,b] (ii) the exchange of alcohols into cyanides either by using HCN or acetone cyanohydrins under Mitsunobu conditions[16c] and (iii) the use of *n*-Bu_3P/KCN/18-crown-6 for the conversion of only primary alcohols to nitriles.[16d] However, these reactions are frequently accompanied by elimination of hydrogen halides especially when bulky alkyl halides were used and gives lower yields of the products with hindered primary and secondary alcohols. Recently, Iranpoor et al. have reported that alcohols, thiols, and trimethylsilyl ethers can be converted into their corresponding nitriles by using PPh_3/DDQ/*n*-Bu_4NCN in acetonitrile solution at rt.[16e] Usually, α,β-unsaturated nitriles can be obtained through a Wittig reaction of aldehyde with cyanoalkyl phosphonates. However, it always results in an unbiased form of *E*- and *Z*-isomeric nitriles.[17] Preparation of nitrile by means of dehydration of amides or aldoximes with an appropriate nonmetal dehydrating agent is an alternative method, which also suffers from disadvantages, such as inconvenient preparation of the reagents, limited substrate scope or incompatibility of sensitive groups to the reaction condition.[18] Several main or transition metal complexes were also used as dehydrating agents to affect this transformation.[19] The conversion of primary nitro compounds into nitrile were also reported by different electrophilic phosphorus derivatives[20a–c] such as $(EtO)_2PCl$, P_2I_4, and PCl_3, sulfur compounds[21a–d] such as SO_2, $Me_3SiSSSiMe_3$, and CS_2, silyl derivatives[22] such as Me_3SiI, radical chemistry,[23] or isocyanides.[24] Wehrli et al. used PCl_3 in pyridine to generate nitriles from primary nitro compounds in moderate yields and the following reaction mechanism (Scheme 1) has been proposed.[20c]

Our previous studies established that β-nitrostyrenes react with different nucleophiles to generate nitroalkanes, halooximes, nitrile oxides, and polycyclic compounds under different reaction conditions.[25] As part of our incessant research efforts with nitroolefin chemistry, we

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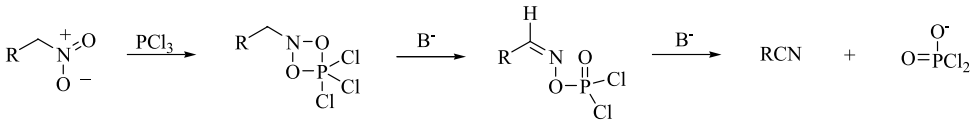


Scheme 1.

wish to report the reaction of *trans*-β-nitrostyrene **1** with different anions of malonate esters to generate nitronates and subsequent treatment with PCl_3 in the absence/presence of DMAP to afford nitroalkane **4** or **7**, chlorooxime **5**, nitrile **6**, **9** or **12**, and cyclic products **8** or **11** under different conditions and also to propose a plausible reaction mechanism.

2. Results and discussion

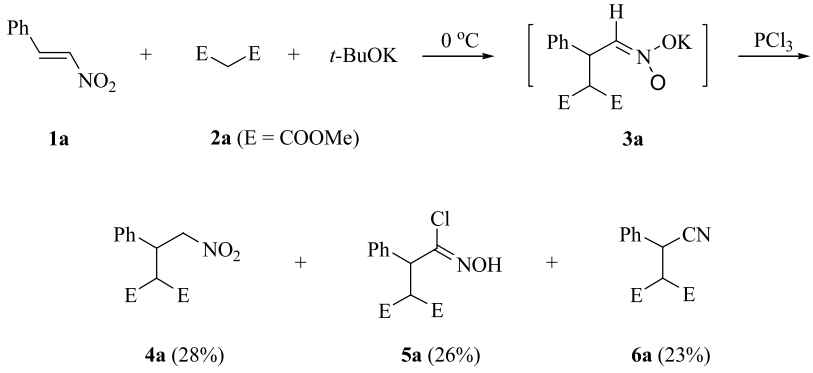
trans-β-Nitrostyrene **1a** reacts with the anion of dimethyl malonate to afford nitronate **3a**, and subsequent treatment with 3 equiv of PCl_3 for 1.5 h at rt afforded nitroalkane **4a** (28%), chlorooxime **5a** (26%), and nitrile **6a** (23%) (Scheme 2).

The compounds **4a**, **5a** and **6a** were characterized thoroughly using ^1H, ^{13}C NMR spectrums and the data is in consistent with the reported literature data.[21] Although parts of the ^1H NMR pattern of **5a** are similar to **6a**, these two products can be distinguished by the following characteristics. For example, the coupling constant of the vicinal proton of chlorooxime **5a** is 12.0 Hz and that of nitrile **6a** is only 9.6 Hz. In addition to this, the D_2O exchangeable proton of ClC═NOH was observed in product **5a**. Besides this, different IR absorptions were also observed for compound **5a** [3410 cm^{-1} (OH, broad) and 1639 cm^{-1} (C═N stretch, weak)] and **6a** [2248 cm^{-1} (CN stretch, weak)]. In the ^{13}C NMR spectrums of these compounds absorption at δ 141.24 ppm corresponds to ClC═NOH in **5a** and at δ 118.40 ppm to CN in **6a** and are also useful to distinguish between the two products.

Similar reactions were also conducted in different solvents with varying amounts of DMAP under different reaction conditions and all the experimental results were shown in Table 1. The result of entry 1 indicates that nitronate **3a** can be converted into **4a**, **5a** and **6a** by reacting with PCl_3 in THF solution. The increase in the amount of PCl_3 from 5 to 10 equiv did not improve the yields of **4a**, **5a** and **6a**. Literature studies revealed that DMAP is one of the most effective reagents to convert the nitronate into the final products.[21] A careful observation has led to identify two different reaction conditions during the addition of DMAP. Addition of 0.5 equiv of DMAP initially to the nitronate solution, followed by PCl_3 resulted in the formation of products **4a** (32%) with increased yield and **5a** (23%) and **6a** (25%) with decreased yield. In another variation, addition of PCl_3 followed by DMAP resulted in the increased yield of nitrile **6a** (38%) with reduced yields of **4a** (13%) and **5a** (15%). The decrease in the yields of **4a** and **5a** and the increase in the yield of **6a** clearly support the assumption that, DMAP plays an important role during reaction. Based on the above observation, increasing the amount of DMAP to 5 equiv afforded the nitrile product **6a** in 49% yield. Similarly, with further increase in the amount of DMAP to 10 equiv the yield of **6a** increased to 62%. These results clearly signify that the increase in the amount of DMAP increases the formation of nitrile product **6a** efficiently.

The effect of solvents and temperature were also investigated by employing different reaction conditions at different reaction times and proved that all the parameters play important roles and may have different effects to the same reaction. After observing the results of entries 1–7 in THF solution, pyridine was used as solvent for similar reactions by modifying the literature procedures and conditions. Only 13% of **4a** and 29% of **6a** were obtained and no product **5a** was observed when the reaction was carried out in pyridine at 95 °C for 2 h (entry 8). However, only 34% of **6a** was isolated when the same solution was stirred at rt for 9 h (entry 9). These results indicate that **4a** can be converted into **6a** slowly in pyridine solution and also consist with literature report.[21c]

Although the use of pyridine as solvent afforded the product **6a** only, the longer reaction times and formation of insoluble materials made the workup very difficult. In addition to this, lower yield of products, tedious workup procedures and longer reaction times limited the use of pyridine as a choice of solvent. In order to attain better yields of the nitrile, a

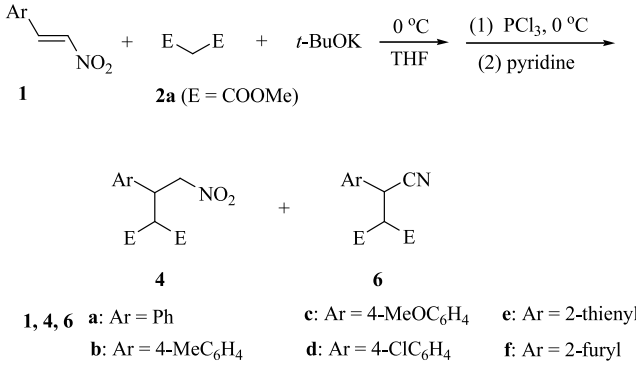


Scheme 2.

Table 1. Reaction of **1a** with anion of **2a** in presence of PCl_3 in different solvents to generate **4a**, **5a**, **6a**

Entry	PCl_3 (equiv)	Solvent	DMAP (equiv)	Condition	Time (h)	**4a** (%)[a]	**5a** (%)[a]	**6a** (%)[a]
1	3	THF	—	rt	1.5	28	26	23
2	5	THF	—	rt	1.5	10	29	24
3	10	THF	—	rt	1.5	12	29	29
4	5	THF	0.5[b]	rt	1.5	32	23	25
5	5	THF	0.5[c]	rt	48	13	15	38
6	5	THF	5[c]	rt	48	10	15	49
7	5	THF	10[c]	rt	48	10	—	62
8	5	Pyridine	—	95 °C	2	13	—	29
9	5	Pyridine	—	rt	9	—	—	34

[a] All compounds were purified by silica gel column chromatography and yields are for pure isolated products, relative to **1a**.
[b] DMAP was initially added to the nitronate solution followed by PCl_3.
[c] PCl_3 was initially added to the nitronate solution followed by DMAP.



Scheme 3.

combination of THF and pyridine were used as solvent. After the generation of nitronate in THF, pyridine was added to form the co-solvent of THF–pyridine solution (Scheme 3).

To our surprise, only 7% of **4a** and 43% of **6a** were isolated and no **5a** was detected by the crude ^1H NMR and GCMS analysis. Increasing the reaction time from 7.5 to 48 h dramatically increased the yield of nitrile **6a** to 60%, without accompanying any other products. To prove the efficiency of the reaction we have subjected various substituted nitroolefins to obtain the products **6b–f** in 17–59% yield under identical reaction conditions (Table 2).

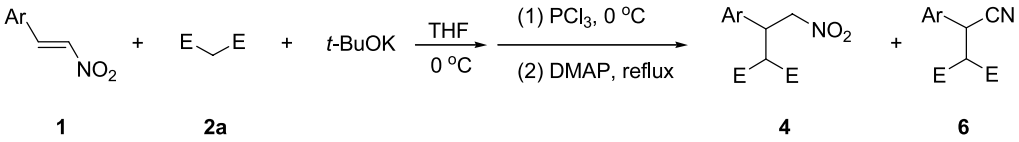
The use of THF–pyridine as co-solvent though yielded **6** only in most cases, similar disadvantages were observed due to formation of insoluble materials. The reaction at higher temperature (95 °C) in the presence of 1 equiv of DMAP under similar conditions resulted the product **6a** in 62% with 27% of **4a** (Scheme 4).

The increase in the amount of DMAP neither improved reaction rate nor the nitrile product formation. In the

Table 2. Reaction of **1** with anion of **2a** PCl_3 in the co-solvent of THF–pyridine solution

Entry	**1**	Solvent[a]	Condition	Time (h)	**4** (%)[b]	**6** (%)[b]
1	**1a**	THF–pyridine	rt	7.5	**4a** (7)	**6a** (43)
2	**1a**	THF–pyridine	rt	48	—	**6a** (60)
3	**1b**	THF–pyridine	rt	48	—	**6b** (59)
4	**1c**	THF–pyridine	rt	48	**4c** (10)	**6c** (31)
5	**1d**	THF–pyridine	rt	48	—	**6d** (51)
6	**1e**	THF–pyridine	rt	48	—	**6e** (34)
7	**1f**	THF–pyridine	rt	48	—	**6f** (17)

[a] After adding PCl_3 to the nitronate in 5 mL THF solution, 10 mL of pyridine was added to form the co-solvent of THF–pyridine solution.
[b] All compounds were purified by using silica gel column chromatography and yields are for pure isolated products, relative to **1**.



Scheme 4.

Table 3. Reaction of **1** with anion of **2a** in presence of PCl_3 and DMAP in THF under refluxing condition

Entry	1	Solvent	DMAP[a]	Time (h)	4 (%)[b]	6 (%)[b]
1	**1a**	THF	—	2	**4a** (7)	**6a** (44)
2	**1a**	THF	1	2	**4a** (27)	**6a** (62)
3	**1a**	THF	2	2	**4a** (10)	**6a** (61)
4	**1a**	THF	10	2	**4a** (11)	**6a** (57)
5	**1a**	THF	10	48	**4a** (11)	**6a** (62)
6	**1b**	THF	1	2	**4b** (31)	**6b** (59)
7	**1c**	THF	1	2	**4c** (19)	**6c** (58)
8	**1d**	THF	1	2	**4d** (27)	**6d** (55)
9	**1e**	THF	1	2	**4e** (35)	**6e** (41)
10	**1f**	THF	1	2	**4f** (26)	**6f** (33)

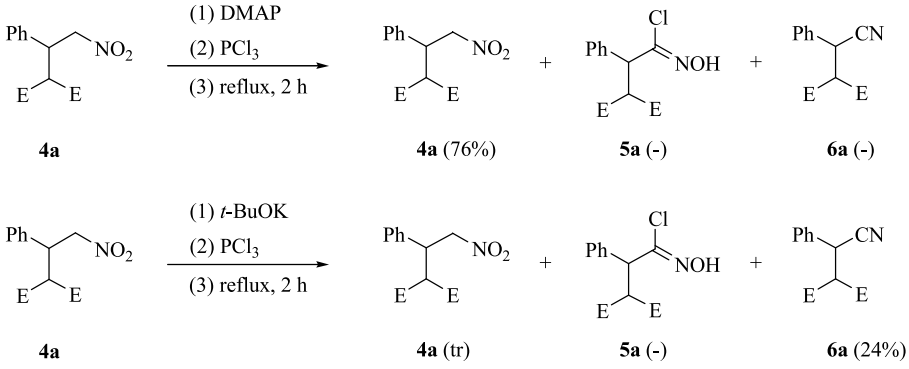
[a] After adding 5 equiv of PCl_3 to the nitronate solution, different amounts of DMAP were added and then the solution was refluxed for 2 h.
[b] All compounds were purified by silica gel column chromatography and yields are for pure isolated products, relative to **1**.

presence of 10 equiv of DMAP under refluxing conditions for 48 h yielded 11% of **4a** and 62% of **6a**. Similarly, substituted nitroolefins afforded products **4b–f** and **6b–f** by subjecting **1b–f** as substrates (Table 3).

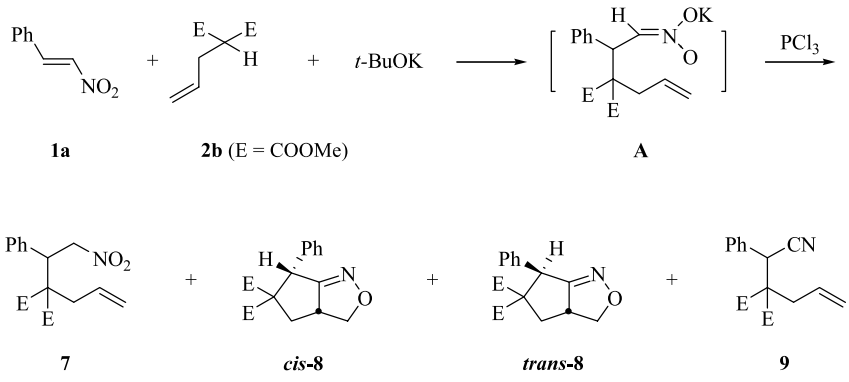
These results clearly indicate that using 1 equiv of DMAP under refluxing conditions for a time period of 2 h not only facilitates the reaction efficiently, but also increased the yield of **6a**. It is also revealed that **4a** is always present in the solution even when excess amounts of DMAP were used under refluxing conditions. To verify this observation, **4a** was first treated with 2 equiv of DMAP and subsequently treated with 5 equiv of PCl_3 in THF solution and the solution was refluxed for 2 h. To our surprise, 76% of unreacted **4a** was recovered and only traces of unidentified products were observed in the crude NMR. On the other hand, traces of **4a** and 24% of **6a** were isolated when **4a** was treated with *t*-BuOK followed by PCl_3 under similar conditions (Scheme 5). These results signify that *t*-BuOK can efficiently acts as a base rather than DMAP to deprotonate **4a** to generate nitronate and to convert it into the final products.

Other than dimethyl malonate **2a**, dimethyl allylmalonate **2b** was also used to react with **1a** and PCl_3 under similar conditions. A trace of nitroalkane **7** along with low to medium yields of bicyclic product **8** and nitrile **9** were obtained (Scheme 6).

It is interesting to find that higher yields (50–58%) of *cis*-**8** and *trans*-**8** (the NMR ratio is from 4.0:1.0 to 4.5:1.0) with better selectivity were observed, when the reaction was



Scheme 5.



Scheme 6.

Table 4. Reaction of **1a** with anion of **2b** in presence of PCl_3 and DMAP to generate **7**, **8**, and **9**

Entry	PCl_3 (equiv)	DMAP (equiv)	Temperature	Time (h)	**7**[a]	**8** (%)[a]	Cis/trans[b]	**9** (%)[a]
1	1.5	—	−78 °C	2	tr	50	4.0:1.0	27
2	2	—	−78 °C	2	tr	56	4.5:1.0	16
3	2	0.5[c]	−78 °C	2	tr	35	3.5:1.0	19
4	5	—	rt	2	3	31	1.0:1.1	16
5	5	—	−0 °C	2	7	32	2.0:1.0	13
6	5	1[c]	−0 °C	2	6	42	1.6:1.0	18
7	5	—	−10 °C	2	8	39	3.2:1.0	25
8	5	—	−78 °C	2	tr	45	4.2:1.0	22
9	5	1[c]	−78 °C	2	tr	53	3.7:1.0	20
10	5	1[d]	−78 °C	2	tr	58	3.8:1.0	26

[a] All compounds were purified by silica gel column chromatography and yields are for pure isolated products relative to **1**.
[b] The cis/trans ratio was measured by ^{1}H NMR.
[c] PCl_3 was added to the nitronate solution followed by DMAP.
[d] DMAP was added initially to the nitronate solution followed by PCl_3.

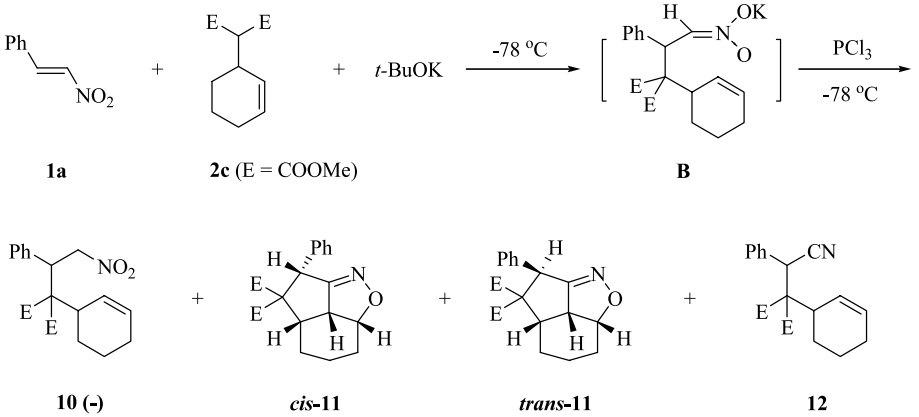
carried out at −78 °C using different equivalents of PCl_3. On the other hand, it was observed that either increase in the amount of PCl_3 or DMAP have no effect on the product yields as well as on the stereoselectivity of **8**. A decrease in the temperature from 25 to 0 °C, and further to −78 °C, reduced the nitroalkane **7** yields and increased the formation of **8** and **9**. A trace of the nitronate was observed at little elevated temperatures (i.e., at 25, 0, −10 °C) and in most cases the nitronate reacts readily with PCl_3 to generate **8** and **9** at −78 °C. Possible explanation is that the presence of the dimethoxycarbonyl group increases the steric hindrance of nitronate (**A**), which facilitates to react with PCl_3 to generate nitrile oxide. This undergoes intramolecular 1,3-dipolar cycloaddition with the vinyl group to produce **8** and little amount of nitrile oxide further reacts with PCl_3 to undergo deoxygenation reaction to yield **9**. Two diastereomers of bicyclic product were isolated and assigned to be *cis*-**8** and *trans*-**8**. Compound *cis*-**8** has been proposed as kinetically controlled product and *trans*-**8** to be thermodynamically controlled product, because the formation of these two products always favors the former at lower temperature and the later at higher temperature (Table 4).

In order to explore further, a different malonate ester such as dimethyl 3-(cyclohexen-1-yl)malonate **2c** also used to react with **1a**, under similar reaction conditions using PCl_3 at −78 °C. As expected, only 49% of tricyclic product **11** (cis/trans =3.8:1) and 9% of nitrile **12** were isolated without a small amount of nitroalkane **10**. The increase in the amount of PCl_3 from 2 to 5 equiv considerably increased the yield of the tricyclic product **11** (cis/trans=3.3:1) to 55%, along with nitrile product **12** (8%). A further increase in the amount of PCl_3 (10 equiv) did not improve the formation of tricyclic product (Table 5). Based on the steric effect in the 1,4-adduct (**B**) one can explain the formation of the products **11** and **12** from **1a** and **2c**. Compared to the results obtained with dimethyl allylmalonate **2b** (Table 4) the complete absence of nitroalkane product **10** implies the role of steric hindrance associated with the intermediate nitronate. The higher steric hindrance of the intermediate nitronate (**B**)

Table 5. Reaction of **1a** with anion of **2c** in presence of PCl_3 to generate **11** and **12**

Entry	PCl_3 (equiv)	Temperature (°C)	Time (h)	**11**[a]	Cis/trans[b]	**12** (%)[a]
1	2	−78	2	49	3.8:1.0	9
2	5	−78	2	55	3.3:1.0	8
3	10	−78	2	45	3.7:1.0	8

[a] All compounds were purified by silica gel column chromatography and yields are for pure isolated products, relative to **1a**.
[b] The cis/trans ratio was measured by ^{1}H NMR.



Scheme 7.

over (**A**) facilitates the formation of **11** and **12** from (**B**) than the formation of **8** and **9** from (**A**) at the same temperature (−78 °C) and the results obtained were also consistent with this assumption (Scheme 7).

The generation of different products can be controlled by changing several parameters such as, use of different solvent systems, conducting the reaction at different temperatures, varying the amounts of reagents and substrates and by using different nucleophiles. Based on these observations, we proposed a stepwise mechanism (Scheme 8) for the formation of different products involving nitronate and nitrile oxide intermediates. The mechanism is different from those reported by Wehrli et al.[20c] in which the generation of nitrile product exclusively proceeds through different steps. The anion generated from malonate ester and *t*-BuOK reacts with nitroolefin to form a nitronate intermediate **C**. The nitronate **C** under mild acidic conditions furnishes the product nitroalkane **4**, from which the nitronate can be regenerated using pyridine as a base. The reaction of PCl_3 on the nitronate generates a nitroso intermediate **E** via **D**. The nitroso compound either rearranges to form chloroxime **5** or to form nitrile oxide intermediate **F**. A clear evidence for the formation of nitrile oxide **F** can be explained on the basis of bicyclic product with dimethyl allylmalonate **2b** and the tricyclic product with 3-(cyclohexen-1-yl)malonate **2c**. We also concluded an important result that either from chloroxime **5** or from nitrile oxide **F**, the nitrile product **6** can be obtained by the reaction of PCl_3.

In conclusion, we have successfully developed a methodology using PCl_3 for the preparation of nitroalkanes, chloroximes, and nitriles using nitronates. We have also tested various parameters such as solvent, temperature and additives to achieve maximum yields of the nitrile compounds. With different anions of malonates containing dipolarphiles, cyclic compounds were obtained as major products indicating, nitrile oxides were generated during the reaction. A plausible reaction mechanism has been proposed involving a nitrile oxide intermediate for the formation of nitrile compounds, which is little different from the one reported in the literature.

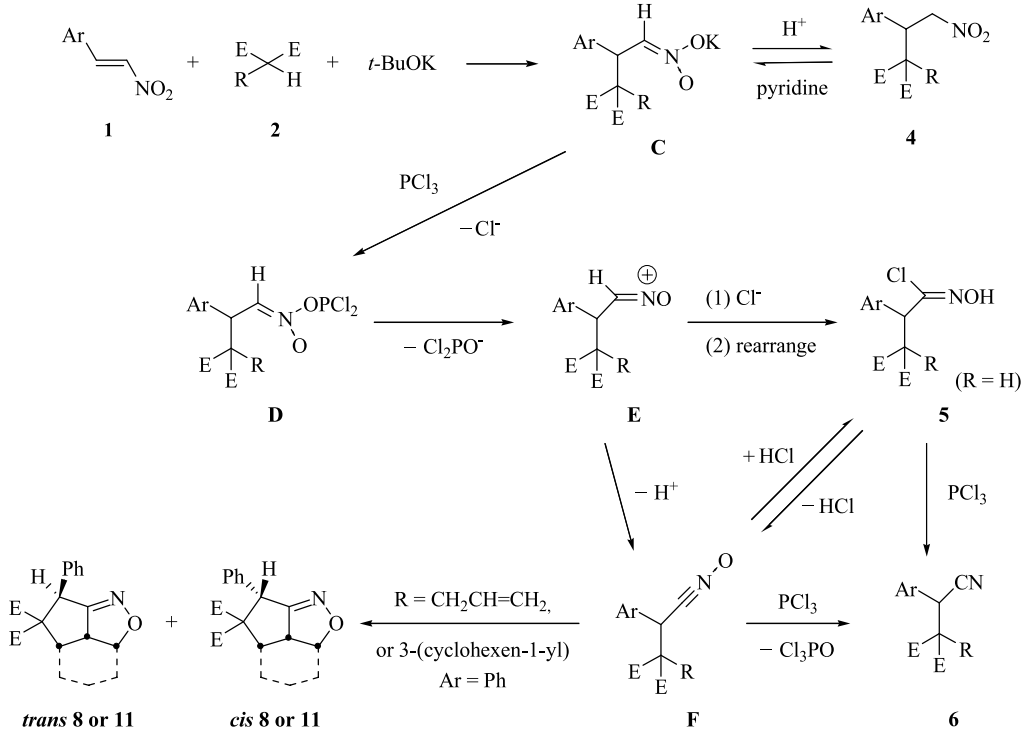
3. Experimental

3.1. General

All reactions were performed in flame or oven-dried glassware under a positive pressure of nitrogen. Analytical thin-layer chromatography was performed with E. Merck silica gel 60F glass plates and flash chromatography by use of E. Merck silica gel 60 (230–400 mesh). THF was distilled over sodium–benzophenone and pyridine was heated under reflux over calcium hydride before use. All melting points were determined on a MEL-TEMP II melting point apparatus and were uncorrected. ^1H and ^{13}C NMR spectra were recorded with a Bruker EX 400 FT NMR. All NMR data were obtained in $CDCl_3$ solution and chemical shift (δ) were given in ppm relative to TMS. MS or HRMS were measured by JEOL JMS-D300 or JEOL JMS-HX110 spectrometer. Elemental analyses were analyzed by HERAEUS VarioEL-III (for CHN).

3.2. Starting materials

trans-β-Nitrostyrene **1a** and analogues **1b**, **1c**, *trans*-2-(2-nitrovinyl)thiophene **1e**, 2-(2-nitrovinyl)furan **1f**, and other starting materials such as dimethyl malonate **2a**, dimethyl allylmalonate **2b**, *t*-BuOK, DMAP, pyridine, and PCl_3 were



Scheme 8.

purchased from Aldrich Chemical Co., and other commercially available reagents were used with or without further purification. The compounds such as *trans*-4-chloro-β-nitrostyrene **1d**[26] and dimethyl 3-(cyclohexen-1-yl)malonate **2c**[27] were prepared according to literature procedures with slight modifications.

3.3. Typical experimental procedures for the synthesis of nitroalkane 4a, chloroxime 5a, and nitrile 6a using PCl_3 at 0 °C in THF

Typical experimental procedure of entry 1 in Table 1 is representative.

To a 3 mL THF solution of *t*-BuOK (168 mg, 1.5 mmol) added a THF solution of dimethyl malonate **2a** (159 mg, 1.2 mmol) slowly at 0 °C. After stirring the reaction mixture at the same temperature for 30 min, a 5 mL solution of *trans*-β-nitrostyrene **1a** (149 mg, 1.0 mmol) in THF was added dropwise, and stirred for another 30 min. Followed by the addition of PCl_3 (0.26 mL, 3.0 mmol) to the nitronate solution at 0 °C and allowed to stir at rt for 1.5 h. The reaction mixture was poured into the ice cold dil HCl and extracted with CH_2Cl_2 (3×25 mL). The combined CH_2Cl_2 layers were washed with brine, distilled H_2O and dried over $MgSO_4$. Evaporation of the organic solvent, the crude product was purified by flash column chromatography using silica gel (eluent; hexane/ethylacetate; 100:1) to yield nitroalkane **4a** (79 mg, 28% Y), chloroxime **5a** (78 mg, 26% Y), and nitrile **6a** (57 mg, 23% Y).

3.4. Typical experimental procedure for the synthesis of nitrile 6 in a co-solvent of THF–pyridine

Typical experimental procedure of entry 1 in Table 2 is representative.

To a stirred solution of *t*-BuOK (168 mg, 1.5 mmol) in THF (5 mL) added dimethyl malonate **2a** (159 mg, 1.2 mmol) at 0 °C. After stirring the reaction mixture at the same temperature for 30 min, *trans*-β-nitrostyrene **1a** (149 mg, 1.0 mmol) was added to obtain a orange color nitronate **3a** solution. To this, PCl_3 (0.43 mL, 5 mmol) was added and stirred for another 30 min followed by the addition of 10 mL of pyridine to form THF–pyridine co-solvent system. The obtained reaction mixture was further stirred at rt for 7.5 h, and poured the contents into the ice cold dil HCl. The insoluble materials were filtered through a Celite pad and the aq layer was extracted with CH_2Cl_2 (3×25 mL). The combined CH_2Cl_2 layers were washed with ice cold brine solution, distilled water and dried over anhyd $MgSO_4$. After evaporation of the solvent, the crude mixture was purified by flash column chromatography using silica gel (eluent; hexane/ethylacetate; 100:1) to obtain **4a** (20 mg, 7% Y) and **6a** (106 mg, 43% Y).

3.4.1. 3,3-Dimethoxycarbonyl-1-nitro-2-phenylpropane (4a). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.21 (m, 5H), 4.93 (dd, J=13.2, 5.3 Hz, 1H), 4.86 (dd, J=13.2, 8.8 Hz, 1H), 4.24 (ddd, J=9.2, 8.8, 5.3 Hz, 1H), 3.86 (d, J=9.2 Hz, 1H), 3.76 (s, 3H), 3.56 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 167.2, 136.1, 129.0, 128.4, 127.8, 77.4, 54.7, 53.0, 52.8, 42.9. IR ($CHCl_3$) ν 3034, 2957 (CH stretch, strong), 1738 (C=O stretch, strong), 1604, 1558 (N=O stretch, strong), 1497, 1456, 1436, 1380, 1292, 1259, 1199, 1158, 1020 cm^{-1}. HRMS (CI) m/z calcd for $C_{13}H_{15}NO_6$ (M^+) 281.0899, found 281.0905. Anal. Calcd for $C_{13}H_{15}NO_6$ C, 55.51; H, 5.38; N, 4.98. Found C, 55.08; H, 5.26; N, 5.26.

3.4.2. 3,3-Dimethoxycarbonyl-1-nitro-2-(4-methylphenyl)propane (4b). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (s, 4H), 6.83 (dt, J=8.8, 2.0 Hz, 2H), 4.90 (dd, J=13.0, 5.2 Hz, 1H), 4.84 (dd, J=13.0, 9.0 Hz, 1H), 4.20 (td, J=9.0, 5.2 Hz, 1H), 3.84 (d, J=9.2 Hz, 1H), 3.75 (s, 3H), 3.56 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 167.2, 138.1, 133.0, 130.0, 127.6, 77.5, 54.7, 52.9, 52.7, 42.5, 21.0. IR ($CHCl_3$) ν 3028, 2956 (CH stretch, strong), 1737 (C=O stretch, strong), 1614, 1556 (N=O stretch, strong), 1516, 1436, 1380, 1291, 1259, 1198, 1159, 1022 cm^{-1}. HRMS (CI) m/z calcd for $C_{14}H_{17}NO_6$ (M^+) 295.1056, found 295.1056. Anal. Calcd for $C_{14}H_{17}NO_6$ C, 56.94; H, 5.80; N, 4.74. Found C, 57.02; H, 5.93; N, 4.69.

3.4.3. 3,3-Dimethoxycarbonyl-1-nitro-2-(4-methoxyphenyl)propane (4c). Mp 100 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (dt, J=8.8, 2.0 Hz, 2H), 6.83 (dt, J=8.8, 2.0 Hz, 2H), 4.89 (dd, J=13.0, 5.0 Hz, 1H), 4.82 (dd, J=13.0, 9.2 Hz, 1H), 4.19 (td, J=9.2, 5.0 Hz, 1H), 3.83 (d, J=9.2 Hz, 1H), 3.77 (s, 3H), 3.75 (s, 3H), 3.56 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 167.3, 159.5, 129.0, 127.9, 114.4, 77.7, 55.2, 54.9, 53.0, 52.8, 42.3. IR ($CHCl_3$) ν 3006, 2957 (CH stretch, strong), 2841, 1737 (C=O stretch, strong), 1612, 1556 (N=O stretch, strong), 1516, 1436, 1380, 1296, 1255, 1182, 1032 cm^{-1}. HRMS (CI) m/z calcd for $C_{14}H_{17}NO_7$ (M^+) 311.1005, found 311.1000. Anal. Calcd for $C_{14}H_{17}NO_6$: C, 54.02; H, 5.50; N, 4.50. Found C, 53.89; H, 5.44; N, 4.54.

3.4.4. 3,3-Dimethoxycarbonyl-1-nitro-2-(4-chlorophenyl)propane (4d). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (dt, J=8.4, 2.0 Hz, 2H), 7.17 (dt, J=8.4, 2.0 Hz, 2H), 4.90 (dd, J=13.2, 5.0 Hz, 1H), 4.82 (dd, J=13.2, 9.0 Hz, 1H), 4.23 (td, J=9.0, 5.0 Hz, 1H), 3.82 (d, J=9.0 Hz, 1H), 3.77 (s, 3H), 3.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 167.1, 134.7, 134.5, 129.4, 129.3, 77.2, 54.6, 53.1, 53.0, 42.4. IR ($CHCl_3$) ν 3028, 3006, 2957 (CH stretch, strong), 1737 (C=O stretch, strong), 1557 (N=O stretch, strong), 1493, 1436, 1379, 1259, 1199, 1159, 1015 cm^{-1}. HRMS (CI) m/z calcd for $C_{13}H_{14}ClNO_6$ (M^+) 315.0510, found 315.0510. Anal. Calcd for $C_{13}H_{14}ClNO_6$ C, 49.46; H, 4.47; N, 4.44. Found C, 49.35; H, 4.49; N, 4.58.

3.4.5. 3,3-Dimethoxycarbonyl-1-nitro-2-thienylpropane (4e). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (dd, J=4.8, 1.2 Hz, 1H), 6.95 (dd, J=3.6, 1.2 Hz, 1H), 6.93 (dd, J=4.8, 3.6 Hz, 1H), 4.95 (dd, J=13.6, 5.4 Hz, 1H), 4.90 (dd, J=13.6, 8.0 Hz, 1H), 4.24 (td, J=8.0, 5.4 Hz, 1H), 3.92 (d, J=7.8 Hz, 1H), 3.77 (s, 3H), 3.67 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 167.1, 138.5, 127.1, 126.8, 125.7, 77.9, 55.3, 53.2, 53.1, 38.4. IR ($CHCl_3$) ν 3113, 3010, 2957 (CH stretch, strong), 1732 (C=O stretch, strong), 1604, 1557 (N=O stretch, strong), 1436, 1380, 1265, 1162, 1018 cm^{-1}. HRMS (CI) m/z calcd for $C_{11}H_{13}NO_6S$ (M^+) 287.0464, found 287.0462. Anal. Calcd for $C_{11}H_{13}NO_6S$: C, 45.99; H, 4.56; N, 4.88; S, 11.16. Found C, 45.78; H, 4.29; N, 4.71; S, 10.52.

3.4.6. 3,3-Dimethoxycarbonyl-1-nitro-2-furylpropane (4f). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (dd, J=1.8, 0.8 Hz, 1H), 6.29 (dd, J=3.2, 1.8 Hz, 1H), 6.22 (dd, J=3.2, 1.8 Hz, 1H), 4.92 (dd, J=13.6, 8.2 Hz, 1H), 4.89 (dd, J=13.6, 5.0 Hz, 1H), 4.39 (td, J=8.0, 5.2 Hz, 1H), 3.94 (d, J=8.0 Hz, 1H), 3.77 (s, 3H), 3.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 167.3, 149.4, 142.9, 110.6, 108.5, 75.3, 53.1, 53.0, 52.7, 36.9. IR ($CHCl_3$) ν 3154, 3121, 3011, 2958 (CH stretch, strong), 2852, 1739 (C=O stretch, strong), 1559 (N=O stretch, strong), 1505, 1437, 1379, 1343, 1293, 1264, 1242, 1197, 1163, 1014 cm^{-1}. HRMS (CI) *m/z* calcd for $C_{11}H_{13}NO_7$ (M^+) 271.0692, found 271.0693. Anal. Calcd for $C_{11}H_{13}NO_7$ C, 48.71; H, 4.83; N, 5.16. Found C, 48.92; H, 4.71; N, 5.06.

3.4.7. 3,3-Dimethoxycarbonyl-2-phenylpropanohydroximoyl chloride (5a). Mp 149 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (br, 1H, D_2O exchangeable), 7.34–7.27 (m, 5H), 4.50 (d, J=12.0 Hz, 1H), 4.27 (d, J=12.0 Hz, 1H), 3.78 (s, 3H), 3.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 167.2, 141.2, 134.9, 128.8, 128.6, 128.5, 55.7, 53.0, 52.6, 52.5. IR ($CHCl_3$) ν 3410 (OH, broad), 2956 (CH stretch, weak), 1743 (C=O stretch, strong), 1639 (C=N stretch, weak), 1496, 1456, 1436, 1281, 1199, 1156, 1120, 1025 cm^{-1}. HRMS (CI) *m/z* calcd for $C_{13}H_{14}ClNO_5$ (M^+) 299.0561, found 299.0570. Anal. Calcd for $C_{13}H_{14}ClNO_5$ C, 52.10; H, 4.71; N, 4.67. Found C, 52.18; H, 4.67; N, 4.65.

3.4.8. 3,3-Dimethoxycarbonyl-2-(4-methylphenyl)propanohydroximoyl chloride (5b). Mp 144–144.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (br, 1H), 7.17 (d, J=8.2 Hz, 2H), 7.12 (d, J=8.2 Hz, 2H), 4.83 (d, J=12.0 Hz, 1H), 4.32 (d, J=12.0 Hz, 1H), 3.78 (s, 3H), 3.47 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 167.5, 140.9, 138.2, 131.8, 129.5, 128.4, 55.7, 53.1, 52.7, 52.0, 21.1. IR ($CHCl_3$) ν 3410 (OH, broad), 2956 (CH stretch, weak), 1744 (C=O stretch, strong), 1639 (C=N stretch, weak), 1514, 1436, 1280, 1246, 1156, 1120, 1027 cm^{-1}. HRMS (CI) *m/z* calcd for $C_{14}H_{16}^{37}ClNO_5$ ($(M+2)^+$) 315.0682, found 315.0675; (M^+) 313.0712, found 313.0690. Anal. Calcd for $C_{14}H_{16}ClNO_5$ C, 53.60; H, 5.14; N, 4.46. Found C, 53.90; H, 5.17; N, 4.36.

3.4.9. 3,3-Dimethoxycarbonyl-2-(4-methoxyphenyl)propanohydroximoyl chloride (5c). Mp 113–114 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (br, 1H), 7.21 (dt, J=8.8, 2.0 Hz, 2H), 6.85 (dt, J=8.8, 2.0 Hz, 2H), 4.44 (d, J=12.0 Hz, 1H), 4.31 (d, J=12.0 Hz, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 3.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 167.6, 159.5, 140.9, 129.7, 126.8, 114.2, 55.8, 55.2, 53.0, 52.7, 51.7. IR ($CHCl_3$) ν 3400 (OH, broad), 2957 (CH stretch, weak), 1742 (C=O stretch, strong), 1638 (C=N stretch, weak), 1611, 1513, 1437, 1305, 1256, 1199, 1179, 1119, 1031 cm^{-1}. HRMS (CI) *m/z* calcd for $C_{14}H_{16}^{37}ClNO_6$ ($(M+2)^+$) 331.0631, found 331.0635; (M^+) 329.0661, found 329.0662. Anal. Calcd for $C_{14}H_{16}ClNO_6$ C, 51.00; H, 4.89; N, 4.25. Found C, 51.06; H, 4.84; N, 4.10.

3.4.10. 3,3-Dimethoxycarbonyl-2-(4-chlorophenyl)propanohydroximoyl chloride (5d). Mp 129 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (br, 1H), 7.31 (dt, J=8.4, 2.0 Hz, 2H), 7.23 (dt, J=8.4, 2.0 Hz, 2H), 4.49 (d, J=11.8 Hz, 1H), 4.26 (d, J=11.8 Hz, 1H), 3.77 (s, 3H), 3.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 167.2, 140.4, 134.5, 133.5, 129.7, 129.1, 55.5, 53.2, 52.9, 51.7. IR ($CHCl_3$) ν 3402 (OH, broad), 2956 (CH stretch, weak), 1743 (C=O stretch, strong), 1639 (C=N stretch, weak), 1595, 1492, 1436, 1361, 1281, 1199, 1156, 1093, 1016 cm^{-1}. HRMS (CI) *m/z* calcd for $C_{13}H_{13}Cl_2NO_5$ (M^+) 333.0171, found 333.0175. Anal. Calcd for $C_{13}H_{13}Cl_2NO_5$ C, 46.73; H, 3.92; N, 4.19. Found C, 47.02; H, 3.89; N, 4.04.

3.4.11. 3,3-Dimethoxycarbonyl-2-thienylpropanohydroximoyl chloride (5e). Mp 157 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (br, 1H), 7.27 (dd, J=4.8, 1.0 Hz, 1H), 7.01 (dd, J=2.4, 1.0 Hz, 1H), 6.95 (dd, J=4.8, 2.4 Hz, 1H), 4.83 (d, J=12.0 Hz, 1H), 4.30 (d, J=12.0 Hz, 1H), 3.78 (s, 3H), 3.57 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 167.0, 140.6, 137.4, 127.6, 127.0, 126.2, 56.4, 53.10, 52.91, 47.50. IR ($CHCl_3$) ν 3305 (OH, broad), 2956 (CH stretch, weak), 1752 (C=O stretch, strong), 1639 (C=N stretch, weak), 1435, 1315, 1267, 1210, 1177, 1118, 1027 cm^{-1}. HRMS (CI) *m/z* calcd for $C_{11}H_{12}ClNO_5S$ (M^+) 305.0125, found 305.0122. Anal. Calcd for $C_{11}H_{12}ClNO_5S$ C, 43.21; H, 3.96; N, 4.58; S, 10.49. Found C, 43.22; H, 3.76; N, 4.53; S, 9.78.

3.4.12. 3,3-Dimethoxycarbonyl-2-furylpropanohydroximoyl chloride (5f). Mp 113–114 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (br, 1H), 7.37 (dd, J=1.6, 1.0 Hz, 1H), 6.33 (dd, J=3.2, 1.8 Hz, 1H), 6.22 (dd, J=3.2, 1.8 Hz, 1H), 4.70 (d, J=12.0 Hz, 1H), 4.32 (d, J=12.0 Hz, 1H), 3.77 (s, 3H), 3.61 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 148.1, 143.2, 138.5, 110.6, 109.5, 53.6, 53.1, 53.0, 46.1. IR ($CHCl_3$) ν 3410 (OH, broad), 2958 (CH stretch, weak), 1743 (C=O stretch, strong), 1639 (C=N stretch, weak), 1563, 1503, 1437, 1272, 1209, 1151, 1118, 1075, 1014 cm^{-1}. HRMS (CI) *m/z* calcd for $C_{11}H_{12}^{37}ClNO_6$ ($(M+2)^+$) 291.0318, found 291.0309; (M^+) 289.0348, found 289.0344. Anal. Calcd for $C_{11}H_{12}ClNO_6$ C, 45.61; H, 4.18; N, 4.84. Found C, 45.78; H, 4.20; N, 4.70.

3.4.13. 2,2-Dimethoxycarbonyl-1-cyano-1-phenylethane (6a). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 5H), 4.53 (d, J=9.6 Hz, 1H), 3.92 (d, J=9.6 Hz, 1H), 3.82 (s, 3H), 3.61 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 165.8, 132.0, 129.2, 129.1, 128.1, 118.4, 56.3, 53.3, 53.1, 36.7. IR ($CHCl_3$) ν 2957 (CH stretch, medium), 2248 (CN stretch, weak), 1740 (C=O stretch, strong), 1497, 1436, 1273, 1199, 1158, 1022 cm^{-1}. HRMS (CI) *m/z* calcd for $C_{13}H_{13}NO_4$ (M^+) 247.0845, found 247.0847. Anal. Calcd for $C_{13}H_{13}NO_4$ C, 63.15; H, 5.30; N, 5.67. Found C, 63.19; H, 5.32; N, 5.60.

3.4.14. 2,2-Dimethoxycarbonyl-1-cyano-1-(4-methylphenyl)ethane (6b). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, J=8.0 Hz, 2H), 7.17 (d, J=8.0 Hz, 2H), 4.49 (d, J=9.6 Hz, 1H), 3.90 (d, J=9.6 Hz, 1H), 3.82 (s, 3H), 3.62 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 165.9, 139.1, 129.9, 129.0, 128.0, 118.6, 56.4, 53.5, 53.1, 36.4, 21.1. IR ($CHCl_3$) ν 2957 (CH stretch, medium), 2247 (CN stretch, weak), 1739 (C=O stretch, strong), 1436, 1260, 1198, 1159, 1023 cm^{-1}. HRMS (CI) *m/z* calcd for $C_{14}H_{15}NO_4$ (M^+) 261.1001, found 261.1009. Anal. Calcd for $C_{14}H_{15}NO_4$ C, 64.36; H, 5.79; N, 5.36. Found C, 64.27; H, 5.83; N, 5.39.

3.4.15. 2,2-Dimethoxycarbonyl-1-cyano-1-(4-methoxyphenyl)ethane (6c). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, J=8.4 Hz, 2H), 6.88 (d, J=8.4 Hz, 2H), 4.48 (d, J=9.6 Hz, 1H), 3.89 (d, J=9.6 Hz, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 3.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 165.8, 159.9, 129.3, 123.7, 118.6, 114.5, 56.4, 55.3, 53.3, 53.1, 35.9. IR ($CHCl_3$) ν 2958 (CH stretch, medium), 2247 (CN stretch, weak), 1739 (C=O stretch, strong), 1436, 1255, 1200, 1182, 1158, 1032 cm^{-1}. HRMS (CI) m/z calcd for $C_{14}H_{14}NO_5$ (M^+) 277.0945, found 277.0948. Anal. Calcd for $C_{14}H_{14}NO_5$ C, 60.64; H, 5.45; N, 5.05. Found C, 60.82; H, 5.35; N, 5.17.

3.4.16. 2,2-Dimethoxycarbonyl-1-cyano-1-(4-chlorophenyl)ethane (6d). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (dt, J=8.8, 2.2 Hz, 2H), 7.32 (dt, J=8.8, 2.2 Hz, 2H), 4.52 (d, J=9.6 Hz, 1H), 3.89 (d, J=9.6 Hz, 1H), 3.83 (s, 3H), 3.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 165.6, 135.3, 130.5, 129.6, 129.5, 118.0, 56.1, 53.4, 53.3, 36.1. IR ($CHCl_3$) ν 2957 (CH stretch, medium), 2249 (CN stretch, weak), 1743 (C=O stretch, strong), 1494, 1436, 1271, 1199, 1155, 1094, 1017 cm^{-1}. HRMS (CI) m/z calcd for $C_{13}H_{12}ClNO_4$ (M^+) 281.0455, found 281.0456. Anal. Calcd for $C_{13}H_{12}ClNO_4$ C, 46.73; H, 3.92; N, 4.19. Found C, 46.55; H, 3.98; N, 4.16.

3.4.17. 2,2-Dimethoxycarbonyl-1-cyano-1-thienylethane (6e). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (dd, J=5.2, 1.2 Hz, 1H), 7.12 (dd, J=3.6, 1.2 Hz, 1H), 6.98 (dd, J=5.2, 3.6 Hz, 1H), 4.84 (d, J=9.2 Hz, 1H), 3.97 (d, J=9.2 Hz, 1H), 3.84 (s, 3H), 3.71 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 165.6, 133.3, 128.2, 127.3, 126.9, 117.5, 56.6, 53.5, 53.4, 31.9. IR ($CHCl_3$) ν 2957 (CH stretch, medium), 2249 (CN stretch, weak), 1741 (C=O stretch, strong), 1436, 1266, 1161, 1021 cm^{-1}. HRMS (CI) m/z calcd for $C_{11}H_{12}ClNO_5S$ (M^+) 305.0125, found 305.0122. Anal. Calcd for $C_{11}H_{12}ClNO_5S$ C, 43.21; H, 3.96; N, 4.58. Found C, 43.43; H, 3.89; N, 4.55.

3.4.18. 2,2-Dimethoxycarbonyl-1-cyano-1-furylethane (6f). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, J=1.8, 1.0 Hz, 1H), 6.33 (dd, J=3.2, 1.8 Hz, 1H), 6.22 (dd, J=3.2, 1.8 Hz, 1H), 4.70 (d, J=9.0 Hz, 1H), 4.06 (d, J=9.0 Hz, 1H), 3.84 (s, 3H), 3.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 165.6, 144.1, 143.7, 116.0, 110.9, 109.7, 53.5, 53.4, 53.3, 30.7. IR ($CHCl_3$) ν 2958 (CH stretch, medium), 2249 (CN stretch, weak), 1742 (C=O stretch, strong), 1503, 1437, 1267, 1208, 1162, 1015 cm^{-1}. HRMS (CI) m/z calcd for $C_{11}H_{11}NO_5$ (M^+) 237.0632, found 237.0641. Anal. Calcd for $C_{11}H_{11}NO_5$ C, 55.70; H, 4.67; N, 5.90. Found C, 55.94; H, 4.56; N, 5.83.

3.5. Typical experimental procedures for the synthesis of nitroalkane 4 and nitrile 6 using PCl_3 and DMAP in THF

Typical experimental procedure of entry 2 in Table 3 is representative.

To a stirred solution of *t*-BuOK (168 mg, 1.5 mmol) in 3 mL THF was added a THF solution of dimethyl malonate **2a** (159 mg, 1.2 mmol) at 0 °C. After stirring the reaction mixture at 0 °C for 30 min, *trans*-β-nitrostyrene **1a** (149 mg, 1.0 mmol) in 5 mL of THF was added dropwise to generate nitronate **3a** solution. To this, PCl_3 (0.43 mL, 5 mmol) followed by DMAP (122 mg, 1.0 mmol) were added sequentially at 0 °C and the resultant solution was refluxed for 30 min. The reaction mixture was then poured into ice cold dil HCl and extracted with CH_2Cl_2 (3×25 mL). The combined CH_2Cl_2 layers were washed with brine, distilled H_2O and dried over anhyd $MgSO_4$. After evaporation of the organic solvent, the crude mixture as purified by flash column chromatography using silica gel (eluent; hexane/ethyl acetate; 100:1) to obtain nitroalkane **4a** (76 mg, 27% Y) and nitrile **6a** (153 mg, 62% Y).

3.5.1. 3,3-Dimethoxycarbonyl-1-nitro-2-phenylhex-5-ene (7). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.29 (m, 3H), 7.13–7.10 (m, 2H), 5.79–5.70 (m, 1H), 5.15–4.96 (m, 4H), 4.20 (dd, J=10.8, 7.4 Hz, 1H), 3.81 (s, 3H), 3.75 (s, 3H), 2.58 (dd, J=14.4, 6.7 Hz, 1H), 2.28 (dd, J=14.4, 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 169.9, 134.8, 131.8, 128.8, 128.5, 119.8, 78.3, 60.8, 52.8, 52.7, 46.8, 38.5. IR ($CHCl_3$) ν 3034, 2955 (CH stretch, weak), 1735 (C=O stretch, strong), 1640 (C=C stretch, weak), 1556 (N=O stretch, strong), 1497, 1456, 1436, 1379, 1297, 1285, 1222, 1140, 1088 cm^{-1}. HRMS (CI) m/z calcd for $C_{16}H_{19}NO_6$ (M^+) 321.1212, found 321.1205. Anal. Calcd for $C_{16}H_{17}NO_5$ C, 59.81; H, 5.96; N, 4.36. Found C, 59.70; H, 5.86; N, 4.46.

3.5.2. *cis*-5,5-Dimethoxycarbonyl-6-phenyl-3a,4-dihydro-3*H*,6*H*-cyclopenta[*c*]isoxazole (*cis*-8). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29–7.24 (m, 5H), 5.02 (d, J=1.2 Hz, 1H), 4.64 (dd, J=9.7, 8.2 Hz, 1H), 4.10 (dd, J=12.3, 8.2 Hz, 1H), 3.81 (s, 3H), 2.70 (dd, J=13.6, 11.2 Hz, 1H), 2.56 (dd, J=13.6, 8.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 170.5, 168.4, 135.4, 129.8, 128.1, 127.9, 75.1, 70.2, 53.4, 52.2, 51.9, 46.7, 35.1. IR ($CHCl_3$) ν 3033, 2954 (CH stretch, medium), 2873, 1732 (C=O stretch, strong), 1648 (C=N stretch, weak), 1603, 1497, 1456, 1435, 1274, 1212, 1167, 1100, 1080, 1010 cm^{-1}. HRMS (CI) m/z calcd for $C_{16}H_{17}NO_5$ (M^+) 303.1107, found 303.1109. Anal. Calcd for $C_{16}H_{17}NO_5$ C, 63.36; H, 5.65; N, 4.62. Found C, 63.16; H, 5.49; N, 4.22.

3.5.3. *trans*-5,5-Dimethoxycarbonyl-6-phenyl-3a,4-dihydro-3*H*,6*H*-cyclopenta[*c*]isoxazole (*trans*-8). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.20 (m, 5H), 5.01 (d, J=1.4 Hz, 1H), 4.68 (dd, J=9.6, 7.7 Hz, 1H), 4.62–4.56 (m, 1H), 3.91 (dd, J=12.0, 7.7 Hz, 1H), 3.81 (s, 3H), 3.04 (s, 3H), 2.87 (dd, J=12.8, 7.6 Hz, 1H), 1.80 (dd, J=12.8, 11.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 170.7, 169.6, 135.6, 128.7, 128.2, 127.6, 75.7, 71.4, 55.3, 53.1, 52.1, 45.9, 36.5. IR ($CHCl_3$) ν 3004, 2954 (CH stretch, medium), 2870, 1732 (C=O stretch, strong), 1649 (C=N stretch, weak), 1604, 1497, 1455, 1435, 1280, 1259, 1208, 1176, 1102, 1078, 1009 cm^{-1}. HRMS (CI) m/z calcd for $C_{16}H_{17}NO_5$ (M^+) 303.1107, found 303.1111. Anal. Calcd for $C_{16}H_{17}NO_5$ C, 63.36; H, 5.65; N, 4.62. Found C, 63.16; H, 5.14; N, 4.06.

3.5.4. 2,2-Dimethoxycarbonyl-1-cyano-1-phenylpent-4-ene (9). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.33 (m, 3H), 7.31–7.28 (m, 2H), 5.82–5.71 (m, 1H), 5.23–5.19 (m, 2H), 4.49 (s, 1H), 3.82 (s, 3H), 3.73 (s, 3H), 2.78 (dd, J=14.8, 6.9 Hz, 1H), 2.57 (dd, J=14.8, 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 168.3, 131.1, 131.0, 129.2,

129.1, 128.9, 120.6, 118.8, 61.1, 52.9, 52.8, 40.5, 36.9. IR ($CHCl_3$) ν 3034, 2955 (CH stretch, medium), 2246 (CN stretch, weak), 1739 (C=O stretch, strong), 1640 (C=C stretch, weak), 1602, 1495, 1456, 1436, 1300, 1255, 1218, 1141, 1083 cm^{-1}. HRMS (CI) *m/z* calcd for $C_{16}H_{17}NO_4$ (M^+) 287.1158, found 287.1162. Anal. Calcd for $C_{16}H_{17}NO_4$ C, 66.89; H, 5.96; N, 4.88. Found C, 66.81; H, 5.79; N, 4.76.

3.5.5. *cis*-4,4-Dimethoxycarbonyl-3-phenyl-4a,5,6,7,7a,7b-hexahydro-3*H*-indeno[1,7-*cd*]isoxazole (*cis*-11). Mp 189–190 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.38–7.23 (m, 5H), 5.02 (s, 1H), 4.81 (dd, $J=17.2$, 8.8 Hz, 1H), 3.84 (s, 3H), 3.77 (dd, $J=9.2$, 8.2 Hz, 1H), 3.26 (s, 3H), 2.99–2.92 (m, 1H), 2.27–2.24 (m, 1H), 2.18–2.13 (m, 1H), 1.74–1.70 (m, 1H), 1.61–1.41 (m, 2H), 1.02–0.92 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 169.8, 166.7, 135.7, 129.9, 128.0, 127.6, 78.7, 74.2, 54.2, 53.5, 51.5, 46.6, 41.9, 29.0, 25.4, 19.8. IR ($CHCl_3$) ν 3032, 2952 (CH stretch, medium), 2864, 1729 (C=O stretch, strong), 1645 (C=N stretch, weak), 1497, 1455, 1435, 1355, 1313, 1280, 1254, 1205, 1180, 1079, 1044 cm^{-1}. HRMS (CI) *m/z* calcd for $C_{19}H_{21}NO_5$ (M^+) 343.1420, found 343.1429. Anal. Calcd for $C_{19}H_{21}NO_5$ C, 66.46; H, 6.16; N, 4.08. Found C, 66.40; H, 6.15; N, 3.93.

3.5.6. *trans*-4,4-Dimethoxycarbonyl-3-phenyl-4a,5,6,7,7a,7b-hexahydro-3*H*-indeno[1,7-*cd*]isoxazole (*trans*-11). Mp 154 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.29–7.21 (m, 5H), 5.05 (d, $J=2.0$ Hz, 1H), 4.85 (dd, $J=17.2$, 8.8 Hz, 1H), 4.60 (dd, $J=8.6$, 8.2 Hz, 1H), 3.79 (s, 3H), 3.00 (s, 3H), 2.95–2.90 (m, 1H), 2.11–2.06 (m, 1H), 1.69–1.63 (m, 2H), 1.39–1.29 (m, 1H), 1.08–0.90 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 169.8, 169.4, 135.6, 128.8, 128.3, 127.6, 77.0, 57.0, 52.6, 52.0, 44.7, 40.5, 28.5, 24.3, 20.3. IR ($CHCl_3$) ν 3032, 2954 (CH stretch, medium), 1730 (C=O stretch, strong), 1644 (C=N stretch, weak), 1601, 1497, 1456, 1435, 1280, 1254, 1207, 1078 cm^{-1}. HRMS (CI) *m/z* calcd for $C_{19}H_{21}NO_5$ (M^+) 343.1420, found 343.1428. Anal. Calcd for $C_{19}H_{21}NO_5$ C, 66.46; H, 6.16; N, 4.08. Found C, 66.41; H, 6.15; N, 3.93.

3.5.7. 2,2-Dimethoxycarbonyl-2-(cyclohex-2-enyl)-1-cyano-1-phenylethane (12). Mp 132 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.40–7.36 (m, 3H), 7.34–7.32 (m, 2H), 5.78–5.75 (m, 1H), 5.60–5.56 (m, 1H), 4.93 (s, 1H), 3.71 (s, 3H), 3.60 (s, 3H), 3.38–3.30 (m, 1H), 2.08–1.92 (m, 2H), 1.87–1.18 (m, 1H), 1.68–1.55 (m, 1H), 1.36–1.26 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 131.8, 129.3, 129.1, 128.8, 128.5, 126.5, 118.5, 65.6, 52.4, 40.9, 40.1, 24.7, 24.3, 22.0. IR ($CHCl_3$) ν 3030, 2952 (CH stretch, strong), 2240 (CN stretch, weak), 1736 (C=O stretch, strong), 1638 (C=C stretch, weak), 1435, 1326, 1293, 1246, 1230, 1152, 1092, 1047, 1022 cm^{-1}. HRMS (CI) *m/z* calcd for $C_{19}H_{21}NO_4$ (M^+) 327.1471, found 327.1479. Anal. Calcd for $C_{19}H_{21}NO_4$ C, 69.71; H, 6.47; N, 4.28. Found C, 69.04; H, 6.33; N, 3.98.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2005.08.041. The spectrums including ^1H, ^{13}C NMR and IR for all important compounds and for some compounds XRD information are available.

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