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A Convenient Preparative Method of Nitrile Oxides by the Dehydration of Primary Nitro Compounds with Ethyl Chloroformate or Benzenesulfonyl Chloride in the Presence of Triethylamine

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Three nitrile oxides ($MeOCOC{\equiv}N{\rightarrow}O$, $PhC{\equiv}N{\rightarrow}O$, and $EtC{\equiv}N{\rightarrow}O$) were effectively generated in situ by dehydration of the corresponding primary nitro compounds (RCH_2NO_2) with $PhSO_2Cl$ or ClCOOEt in the presence of triethylamine. Various cycloadducts were prepared by the reaction of them with dipolarophiles. Some advantages of these methods are described in comparison with other known methods.

1,3-Dipolar cycloaddition reaction using nitrile oxides is one of the versatile methods for the preparation of five-membered heterocycles.[1] Preparation of nitrile oxides by the dehydration of primary nitro compounds has been known so far.[2–8] Following combinations of reagents have been known to be effective for the dehydration; (a) PhNCO and Et_3N,[3] (b) Ac_2O and AcONa,[4] (c) AcCl and MeONa,[5] (d) *p*-TsOH,[6] (e) $POCl_3$,[3d] (f) Diketene and Na,[7] and (g) H_2SO_4.[8] The most widely used one among these methods is (a). Though the method has been known to be sufficiently effective for the preparation of a variety of heterocycles, an equimolar amount of *N,N′*-diphenylurea is formed as a by-product during the reaction. In many cases, separation of the by-product from the reaction mixture can be accompilshed easily by filtration because diphenylurea shows very low solubilities towards many organic solvents. But, in some cases, the desired heterocyclic compounds also show solubilities similar to that of diphenylurea towards organic solvents, thus, the separation is often tedious. Recently, we reported the cycloaddition reactions of dipolarophiles with nitrile oxides prepared by the action of a catalytic amount of *p*-TsOH on primary nitro compounds [method (d)].[6a] Though this reaction gave no such by-products and the yields of the desired heterocycles are also comparable to those by the method (a), good results could not be attained in some cases where the primary nitro compounds bear thermally labile functional groups because of the necessity of the high reaction temperature (>140 °C).

Hydrolysis of ethyl chloroformate or benzenesulfonyl chloride gives water soluble products, ($EtOH+HCl+CO_2$) or ($PhSO_3H+HCl$). The use of these reagents for the dehydration of primary nitro compounds has the advantage that the by-products can be removed easily by washing the reaction mixture with water. We report here the usefulnes of the combination of reagents such as $ClCOOEt/Et_3N$ and $PhSO_2Cl/Et_3N$ for the dehydration of primary nitro compounds.

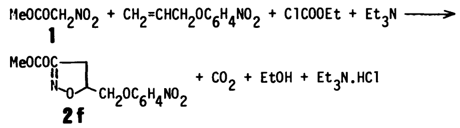
Results and Discussion

The reaction of methyl nitroacetate (**1**) with allyl *p*-nitrophenyl ether in the presence of various amounts of ClCOOEt and Et_3N in several kinds of solvents was examined in order to search the optimum reaction conditions. Table 1 summarizes the results along with yields of the cycloadduct, methyl 5-(*p*-nitrophenoxymethyl)-2-isoxazoline-3-carboxylate (**2f**). Table 1 suggests that the maximum yield of the cyclo-

Table 1. Reaction of Methyl Nitroacctate (**1**) with Allyl *p*-Nitrophenyl Ether under Various Conditions

Run	Molar ratio of				Solv.	Reaction time/h	Temp/°C	Yield of **2f**/%
	1	: $CH_2{=}CHCH_2OAr$	: ClCOOEt	: Et_3N				
1	1	1	1	1	C_6H_6	20	80	30
2	1	1	2	2	C_6H_6	20	r.t.*	30
3	1	1	3	3	—	6	80	41
4	1	1	2	2	C_6H_6	6	80	43
5	1	1	2	2	$CHCl_3$	6	60	34
6	1	1	2	2	THF	6	67	34
7	1	1	2	2	CH_3CN	6	82	21
8	1	1	2	2	Et_2O	6	34	10
9	1	1	2	2	DMF	6	50	5
10	1	1	3	3	C_6H_6	6	80	34

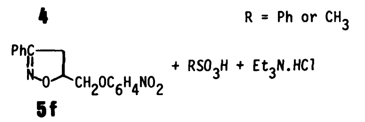
* Room temperature.



(1)

adduct was obtained by the treatment of the substrates with two molar amount of the dehydrating agents in benzene at the refluxing temperature (Method A). As expected, evolution of CO_2 gas and formation of ethanol were observed.

We also examined the reactions of (nitromethyl)benzene (**4**) with allyl *p*-nitrophenyl ether in the presence of benzenesulfonyl chloride (or methanesulfonyl chloride) and Et_3N under various conditions (Table 2). In this case, the optimum conditions for the cycloadduct, 3-phenyl-5-(*p*-nitrophenoxymethyl)-2-isoxazoline (**5f**), were as follows; the use of two molar amounts of benzenesulfonyl chloride and Et_3N, and chloroform as a solvent at room temperature (Method B). Reactions of some primary nitro compounds (**1**, **4**, and **7**) with a number of dipolarophiles were carried out under these conditions (Method A and B). Table 3 summarized the results. The yields obtained in the reaction by use of another dehydrating agents are also shown for convenience of comparison.



(2)

$$RCH_2NO_2 + \text{dipolarophile} + \left\{\begin{array}{c} ClCOOEt/Et_3N \\ \text{or} \\ PhSO_2Cl/Et_3N \end{array}\right\} \longrightarrow \text{isoxazoline or isoxazole} \qquad (3)$$

$$\begin{array}{lll} \mathbf{1};\ R = COOMe & \mathbf{2};\ R = COOMe & \mathbf{3};\ R = COOMe \\ \mathbf{4};\ R = Ph & \mathbf{5};\ R = Ph & \mathbf{6};\ R = Ph \\ \mathbf{7};\ R = Et & \mathbf{8};\ R = Et & \mathbf{9};\ R = Et \end{array}$$

The structure of the cycloadducts, 2-isoxazolines (**2**, **5**, and **8**) and isoxazoles (**3**, **6**, and **9**), were established by the comparison of the spectral and physical proper-

Table 2. Reaction of (Nitromethyl)benzene (**4**) with Allyl *p*-Nitrophenyl Ether under Various Conditions

Run	**4** :	CH_2=$CHCH_2OAr$:	RSO_2Cl :	Et_3N	Solv.	Reaction time/h	Temp °C	Yield of **5f**
1	1	1	1.2(R=CH_3)	1.2	C_6H_6	6	80	12%
2	1	1	1.2(R=CH_3)	1.2	CCl_4	6	77	16%
3	1	1	1.2(R=CH_3)	1.2	$CHCl_3$	6	60	10%
4	1	1	1.2(R=Ph)	1.2	C_6H_6	6	80	40%
5	1	1	1.2(R=Ph)	1.2	CCl_4	6	77	39%
6	1	1	1.2(R=Ph)	1.2	$CHCl_3$	6	60	48%
7	1	1	1.2(R=Ph)	1.2	C_6H_6	15	r.t.	41%
8	1	1	1.2(R=Ph)	1.2	$CHCl_3$	15	r.t.	47%
9	1	1	2 (R=Ph)	2	C_6H_6	15	r.t.	40%
10	1	1	2 (R=Ph)	2	$CHCl_3$	15	r.t.	73%
11	1	1	3 (R=Ph)	3	$CHCl_3$	15	r.t.	68%

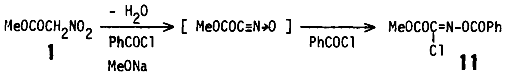
Table 3. Yields of Cycloadducts[a] by Method A, B, and Other Known Methods

Dipolarophile		Method A	Method B	Other Method		Method A	Method B	Other Method		Method A	Method B	Other Method
Norbornene	**2a**	45%	50%		**5a**	83%	64%		**8a**	10%	72%	
CH_2=$CHOC_4H_9$-*n*	**2b**	74%	40%		**5b**	80%	45%		**8b**	6%	34%	62%[b]
CH_2=$CHOCOCH_3$	**2c**	27%			**5c**	20%	43%	84%[c]	**8c**		57%	89%[b]
CH_2=$CHC_{12}H_{25}$-*n*	**2d**	33%	2%	25%[d]	**5d**	31%	78%	45%[d]	**8d**		49%	
CH_2=$CHCH_2Ph$	**2e**	21%		15%[d]	**5e**	24%	60%	29%[d]	**8e**	17%	46%	
CH_2=$CHCH_2O$-$C_6H_4NO_2$-*p*	**2f**	43%	5%	22%[d]	**5f**	53%	73%	42%[d]	**8f**		42%	
CH_2=$CHPh$	**2g**	47%	19%		**5g**	22%	75%		**8g**	6%	58%	58%[b]
CH_2=$CHCN$	**2h**	40%			**5h**	30%	59%		**8h**	3%	30%	92%[b]
CH_2=$CHCOOCH_3$	**2i**	5%			**5i**	64%	50%		**8i**		45%	45%[e]
Methyl methacrylate	**2j**	6%			**5j**	49%	75%		**8j**	4%	65%	
Dimethyl fumarate	**2k**	24%	3%	36%[d]	**5k**	46%	83%	76%[f]	**8k**		37%	58%[d]
N-Phenylmaleimide	**2l**	6%		70%[d]	**5l**	57%	73%	54%[d]	**8l**		42%	58%[d]
Phenylacetylene	**3a**	26%			**6a**	25%	70%	47%[f]	**9a**	6%	31%	30%[g]
MeOCOC≡CCOOMe	**3b**	30%	32%	20%[f]	**6b**	35%	80%	82%[h]	**9b**	13%	29%	30%[h]

a) The cycloadduct obtained from monosubstituted olefins, methyl methacrylate, and phenylacetylene is found to be 5-substituted regioisomer. b) Lit, 3a. c) Lit, 3b. d) Lit, 6a. e) Lit, 3d. f) Lit, 5a. g) Lit, 3e. h) Lit, 4a.

ties of the cycloadducts with those of anthentic specimens (see Experimental Section).

Almost cycloadducts can be easily isolated from the reaction mixtures after washing the reaction mixtures with water followed by usual work-up. However, in some cases by Method A, formation of an unexpected product made the isolation of desired cycloadducts difficult. The structre of the unexpected product was found to be R-C(Cl)=NOCO$_2$Et (**10a**: R=COOMe, **10b**: R=Ph, **10c**: R=Et) on the basis of elemental and spectral analyses, In fact, a considerable amount of **10** was obtained along with furazan 2-oxide, dimer of the nitrile oxide, in the rections of primary nitro compounds with ClCOOEt/Et$_3$N in the absence of dipolarophile. The formation of methyl 2-chloro-2-(benzoyloxyimino)acetate (**11**), MeOCOC(Cl)=NOCOPh, which has a structure similar to **10a**, has been reported in the dehydration reaction of **1** with benzoyl chloride and MeONa, and explained on the basis of 1,3-addition of benzoyl chloride to nitrile



$$\underset{\mathbf{1}}{\mathrm{MeOCOCH_2NO_2}} \xrightarrow[\substack{\mathrm{PhCOCl}\\ \mathrm{MeONa}}]{-\mathrm{H_2O}} [\,\mathrm{MeOCOC{\equiv}N{\to}O}\,] \xrightarrow[\mathrm{PhCOCl}]{} \underset{\mathbf{11}}{\mathrm{MeOC\underset{\displaystyle Cl}{\underset{|}{O}C}{=}N\text{-}OCOPh}} \tag{4}$$

oxide.[5a] The formation of **10** in the present reaction may also be explained by a similar mechanism. The mechanism for the formation of nitrile oxide from primary nitro compounds by both Method A and B can be explained as shown in Scheme 1; i) abstraction of α-hydrogen of the primary nitro compounds by triethylamine gives its nitronate anion (**12**), ii) substitution reaction of ClCOOEt or PhSO$_2$Cl with the nitronate anion gives ethoxycarbonyl or benzenesulfonyl nitronate (**13** or **14**), respectively, and iii) elimination of EtOCO$_2$H or PhSO$_3$H from the nitronates via a cyclic transition state gives the nitrile oxides.

The present two methods for generation of nitrile oxides were found to be usefull ones for the preparation of 2-isoxazolines and isoxazoles because of the easiness of the operation and of the use of low-priced dehydrating agents.

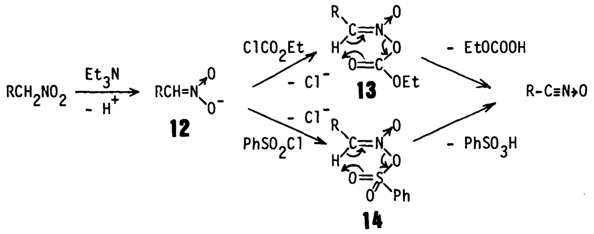
Experimental

Measurements. All melting and boiling points are uncorrected. The ^{1}H NMR spectra were measured on a Varian T-60A instrument with Me$_4$Si as an internal standard; chemical shifts are given in δ units and coupling constants (J) are in herz units: s=singlet; d=doublet; t=triplet; q=quartet; m=multiplet br=broad singlet. The IR spectra were recorded on a Hitachi 215 Infrared Spectrophotometer. All new products gave satisfactory elemental analyses (±0.3% for C, H, and N).

Materials. Methyl nitroacetate (**1**)[9] and (nitromethyl) benzene (**4**)[10] were prepared according to the method described in the literatures. Chloroform was used after passing through column chromatography on almina for the purpose of removal of contaminant ethanol which exists in the solvent as a stabilizer. The other chemicals were of commercial origin and were used without further purification.

Reation of Primary Nitro Compounds with Dipolarophiles in the Presence of Ethyl Chloroformate and Triethylamine (Method A). General Procedure. To a stirred benzene solution (50 ml) of primary nitro compound (0.01 mol), dipolarophile (0.01 mol), and ethyl chloroformate (2.17 g, 0.02 mol) was added a benzene solution (10 ml) of triethylamine (2.02 g, 0.02 mol) at room temperature. Gradual evolution of CO$_2$ (trapped as CaCO$_3$) and ethanol was observed in the course of the reaction. (Sometimes evolution of a small amount of ethyl chloride was also observed). After refluxing the benzene solution for 6 h, the reaction mixture was cooled and washed with water several times. The benzene solution was dried over sodium sulfate and evaporated in a rotary evaporator to give crude products. Crystalline crude products were recrystallized from the solvents and oily crude products were purified by the fractional distillation. In some cases, a small amount of R-C(Cl)=NOCOEt (R=CO$_2$Me, Ph, and Et) or Et$_2$NCO$_2$Et was also isolated by the fractional distillation. Yields of the cycloadducts are shown in Table 3. Similar yields of the cycloadducts were attained from the reaction using ClCOOMe instead of ClCOOEt.

Reaction of Primary Nitro Compounds with Dipolarophiles in the Presence of Benzenesulfonyl Chloride and Triethylamine (Method B). General Procedure. To a stirred chloroform solution (50 ml) of primary nitro compound (0.01 mol), dipolarophile (0.01 mol), and benzenesulfonyl chloride (3.53 g, 0.02 mol) was added triethylamine (2.02 g, 0.02 mol) below 10 °C. The mixture was stirred for 15 h at room temperature and then washed with water several times. The chloroform solution was dried over sodium sulfate and evaporated in a rotary evaporator. Distillation of PhSO$_2$Cl in vacuo from the residue gave crude products. Crystalline or oily products were purified according to the Method A. Complete elimination of PhSO$_2$Cl from the crude products can be easily attained by stirring them with aqueous 2-aminoethanol, though this operation can not be used for the compounds bearing ester functional group. Yields of the cycloadducts are shown in Table 3. Similar yields of the cycloadducts were obtained from the reaction using *p*-toluenesulfonyl chloride instead of PhSO$_2$Cl. Compounds (**2d—f**,[6a] **2g**,[12] **2l**,[6a] **3a**,[12] **3b**,[5a] **5a**,[11] **5c**,[3b] **5d—f**,[6a] **5g**,[13] **5h**,[14] **5i—j**,[15] **5k**,[5a] **5l**,[6a] **6a**,[5a] **6b**,[4a] **8b—c**,[3a] **8g—h**,[3a] **8i**,[3d] **8k—l**,[6a] **9a**,[3e] and **9b**[4a]) obtained by the Methods (A and/or B) were identified on the basis of the melting (or boilig) points and the spectral data. Melting (or boiling) points, NMR spectral data, and analytical data of the other cycloadducts were as follows; **2a**: Bp 115 °C/1.1 mmHg(1 mmHg=133.322 Pa); ^{1}H NMR (CDCl$_3$)



Scheme 1.

0.9—1.8 (m, 6H), 2.6 (br, 2H), 3.3 (d, 1H, J=8), 3.83 (s, 3H), 4.7 (d, 1H, J=8). Found: C, 61.49; H, 6.68; N 7.22%. Calcd for $C_{10}H_{13}NO_3$: C, 61.52; H, 6.71; N, 7.18%. **2b**: Bp 137 °C/5 mmHg; ^{1}H NMR ($CDCl_3$) δ=0.9 (t, 3H, J=7), 1.1—1.9 (m, 4H), 2.97 (dd, 1H, J=3 and 18), 3.33 (dd, 1H, J=6 and 18), 3.3—4.0 (m, 2H), 3.9 (s, 3H), 5.73 (dd, 1H, J= 3 and 6). Found: C, 53.85; H, 7.50; N, 7.02%. Calcd for $C_9H_{15}NO_4$: C, 53.72; H, 7.51; N, 6.96%. **2c**: Bp 115 °C/1 mmHg; ^{1}H NMR ($CDCl_3$) δ=2.1 (s, 3H), 3.13 (dd, 1H, J=3 and 19), 3.53 (dd, 1H, J=6 and 19), 3.93 (s, 3H), 6.8 (dd, 1H, J=3 and 6). Found: C, 44.90; H, 5.04; N, 7.44%. Calcd for $C_7H_9NO_5$: C, 44.92; H, 4.85; N, 7.48%. **2h**: Bp 116 °C/1 mmHg; ^{1}H NMR ($CDCl_3$) δ=3.6 (d, 2H, J=9), 3.93 (s, 3H), 5.47 (t, 1H, J=9). Found: C, 46.90; H, 3.95; N, 18.42%. Calcd for $C_6H_6N_2O_3$: C, 46.76; H, 3.92; N, 18.18%. **2i**: Bp 130 °C/4 mmHg; ^{1}H NMR ($CDCl_3$) δ=3.5 (d, 2H, J=9), 3.8 (s, 3H), 3.9 (s, 3H), 4.22 (dd, 1H, J=9 and 11). Found: C, 44.99; H, 4.73; N, 7.55%. Calcd for $C_7H_9NO_5$: C, 44.92; H, 4.85; N, 7.48%. **2j**: Bp 122 °C/1.7 mmHg; ^{1}H NMR ($CDCl_3$) δ=1.67 (s, 3H), 3.03 (d, 1H, J=18), 3.75 (d, 1H, J=18), 3.8 (s, 3H), 3.9 (s, 3H). Found: C, 47.75; H, 5.49; N, 7.00%. Calcd for $C_8H_{11}NO_5$: C, 47.76; H, 5.51; N, 6.96%. **5b**: Bp 141 °C/1 mmHg; ^{1}H NMR ($CDCl_3$) δ=0.9 (t, 3H, J=7), 1.1—1.9 (m, 4H), 3.1 (dd, 1H, J=3 and 18) 3.45 (dd, 1H, J=6 and 18), 3.4—4.0 (m, 2H), 5.67 (dd, 1H, J=3 and 6), 7.2—7.6 (m, 3H), 7.6—7.8 (m, 2H). Found: C, 71.07; H, 7.69; N, 6.54%. Calcd for $C_{13}H_{17}NO_2$: C, 71.20; 7.82; 6.39%. **8a**: Bp 88 °C/1 mmHg; ^{1}H NMR ($CDCl_3$) δ=0.9—1.8 (m, 9H), 2.0—2.6 (m, 4H), 3.0 (d, 1H, J=8), 4.4 (d, 1H, J=8). Found: C, 72.88; H, 9.01; N, 8.51%. Calcd for $C_{10}H_{15}NO$: C, 72.69; H, 9.15; N, 8.48%. **8d**: Mp 35—36 °C (from methanol), bp 163 °C/1 mmHg: ^{1}H NMR ($CDCl_3$) δ=0.7—1.7 (m, 28H), 2.35 (q, 2H, J=7), 2.5 (dd, 1H, J=9 and 18), 3.0 (dd, 1H, J=11 and 18), 4.3—4.8 (m, 1H). Found: C, 76.30; H, 12.44; N, 5.21%. Calcd for $C_{17}H_{33}NO$: C, 76.33; H, 12.44; N, 5.24%. **8e**: Bp 144 °C/3.4 mmHg; ^{1}H NMR ($CDCl_3$) δ=1.1 (t, 3H, J=7), 2.3 (q, 2H, J=7), 2.55—3.3 (m, 4H), 4.5—5.1 (m, 1H), 7.27 (s, 5H). Found: C, 76.34; H, 8.22; N, 7.45%. Calcd for $C_{12}H_{15}NO$: C, 76.15: H, 7.99; N, 7.40%. **8f**: Mp 83—85 °C (from ethanol); ^{1}H NMR ($CDCl_3$) δ=1.2 (t, 3H, J=7), 2.4 (q, 2H, J=7), 2.9—3.2 (m, 2H), 4.1 (d, 2H, J=6), 4.6—5.2 (m, 1H), 6.97 (d, 2H, J=8), 8.2 (d, 2H, J=8). Found: C, 57.61; H, 5.63; N, 11.10%. Calcd for $C_{12}H_{14}N_2O_4$: C, 57.59; H, 5.64; N, 11.20%. **8j**: Bp 83 °C/1.7 mmHg; ^{1}H NMR ($CDCl_3$) δ=1.15 (t, 3H, J=7), 1.6 (s, 3H), 2.35 (q, 2H, J=7), 2.77 (d, 1H, J=18), 3.47 (d, 1H, J=18), 3.75 (s, 3H). Found: C, 56.08; H, 7.66; N, 8.11%. Calcd for $C_8H_{13}NO_3$: C, 56.12; H, 7.65; N, 8.18%.

An Equimolar Reaction of Primary Nitro Compounds with ClCOOEt in the Presence of Triethylamine. An equimolar (0.02 mol) mixture of primary nitro compound (**1**, **4**, or **7**), ClCOOEt, and triethylamine in benzene (50 ml) was refluxed for 6 h. The reaction mixture was washed with water several times, and then evaporated in a rotary evaporator. In the case of $PhCH_2NO_2$ (**4**), residual crystals were recrystallized from ethanol to give pure 3,4-diphenylfurazan 2-oxide in 60% yield; mp 112—114 °C (lit,[16] 114 °C). In the case of $MeOCOCH_2NO_2$ (**1**), residual oil was distilled in vacuo to give pure dimethyl 3,4-furazan-dicarboxylate 2-oxide in 25% yield; bp 115 °C/2 mmHg (lit,[16] 151 °C/10 mmHg). In the case of 1-nitropropane, distillation of residual oil gave recovered nitropropane (30%) and ethyl diethylcarbamate (20%) [bp 73 °C/25 mmHg (lit,[17] bp 165 °C)].

Reaction of Primary Nitro Compounds with Double the Molar Quantity of ClCOOEt and Triethylamine. To a benzene solution (50 ml) of primary nitro compound (0.02 mol) and ClCOOEt (0.04 mol) was added triethylamine (0.04 mol) and then the mixture was refluxed for 6 h. After filtration of triethylamine hydrochloride the filtrate was evaporated to give oily residue, which was distilled in vacuo to give esters of chloroximes; **methyl 2-chloro-2-(ethoxycarbonyldioxyimino)acetate (10a)**: 25% Yield, bp 100 °C/1 mmHg; ^{1}H NMR (δ) in $CDCl_3$; 1.4 (t, 3H, J=7), 4.0 (s, 3H), and 4.2 (q, 2H, J=7). Found: C, 34.64; H, 3.96; N, 6.69; Cl, 16.72%. Calcd for $C_6H_8NO_3Cl$: C, 34.37; H, 3.82; N, 6.68; Cl, 16.95%.

α-Chloro-α-(ethoxycarbonyloxyimino)toluene (10b): 70% Yield, bp 110—115 °C/0.3 mmHg, mp 32—34 °C (from hexane), ^{1}H NMR (δ) in $CDCl_3$: 1.4 (t, 3H, J=7), 4.3 (q, 2H, J=7), 7.3—7.6 (m, 3H), and 7.8—8.1 (m, 2H). IR (nujol): 1780 cm^{-1} (-OCOO-). Found: C, 52.96; H, 4.38; N, 6.27; Cl, 15.50%. Calcd for $C_{10}H_{10}NO_3Cl$; C, 52.75; H, 4.40; N, 6.15; Cl, 15.57%.

1-Chloro-1-(ethoxycarbonyldioxyimino)propane (10c): 3% Yield, bp 70—74 °C/1.3 mmHg, ^{1}H NMR (δ) in $CDCl_3$: 1.25 (t, 3H, J=7), 1.37 (t, 3H, J=7), 2.7 (q, 2 H, J=7), and 4.33 (q, 2H, J=7).

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