Mononitroalkylations of Butane-2,3-dione

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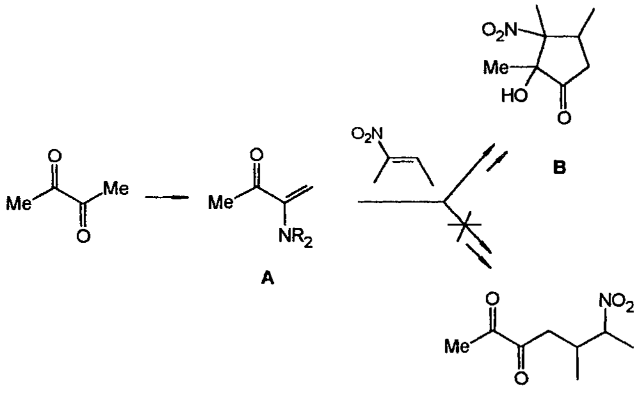
The morpholino enamine of monoprotected butane-2,3-dione reacts with cyclic and acyclic conjugated nitroalkenes in a Michael-type reaction to yield nitro-substituted α-diketones, after acidic hydrolysis of the mononitroalkylated enamine adducts. Cyclopentanone, hexahydro-1*H*-pentalen-2-one and octahydro-2*H*-inden-2-one derivatives are readily obtained by base-catalyzed intramolecular nitroaldol reaction of the acyclic hydrolysis products.

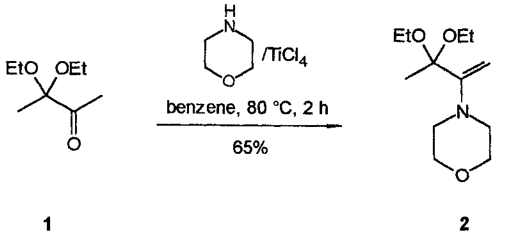
There has been some interest in the functionalization of α-diketones,[1] in view of their characteristic activity as inhibitors of enzymes containing arginyl residues in their catalytic center, such as, for instance, carboxypeptidase[2] and purine nucleoside phosphorylase.[3] In particular, the introduction of a nitro function might be promising, owing to its great synthetic versatility.[4]

Here we report on studies directed to the development of a synthetic route to the mononitroalkylation of butane-2,3-dione via Michael-type reaction between an enamine and a nitroolefin. However, if the α-oxoenamine **A** derived from butane-2,3-dione is employed, it participates in a [3 + 2] carbocyclization reaction to give polysubstituted cyclopentanones **B** with a high diastereomeric excess, rather than furnishing Michael-type products **C** (Scheme 1), after hydrolysis of the amine intermediates.[5]



Scheme 1

Therefore, in order to avoid the carbocyclization reaction, we have taken into account the synthetic approach involving the monoprotection of butane-2,3-dione to the diethyl ketal **1**[6] and its conversion to the corresponding enamine **2** (Scheme 2).



Scheme 2

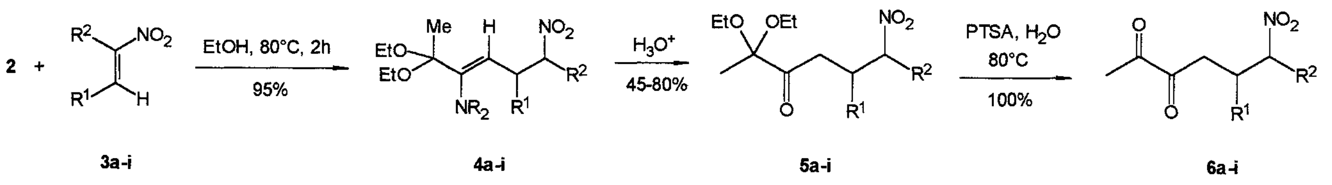
The resultant enamine **2** was reacted with the nitroolefins **3a–i** listed in Scheme 3, in refluxing anhydrous ethanol, under argon, for 2 hours. The crude reaction mixtures were clean and contained essentially the enamine intermediates **4**, as a mixture of *syn/anti* isomers, when R^1 and R^2 were different from hydrogen (**4e–g**), or a mixture of *cis/trans* isomers in the case of the cyclic nitroolefins (**4h, i**). The nitroalkylated enamines **4** could neither be distilled, owing to their thermal instability, nor chromatographed. However, their *Z* geometry was determined by NOE difference measurements, performed on the crude reaction mixtures. Irradiation of the methyl group of the quaternary carbon atom in fact produced an enhancement (7 % average value) on the vinyl proton. The only exception to this was the enamine **4a**, for which also the *E* isomer was present (40 %).

As a consequence of the *Z* configuration and the reduced *n*,π overlap due to steric hindrance, the vinyl protons resonated lowfield (δ = 5.20–5.90) (Table 1). The vinyl proton of the *E* isomer of **4a** resonated at δ = 4.46. A further consequence was that hydrolyzes of the *Z* isomers were slow, requiring longer times than ordinary trisubstituted enamines, owing to the presence of a severe 1,3-allylic strain.[7]

The enamines **4a–i** were hydrolyzed with aqueous AcOH/AcONa (pH = 4.6) to yield the corresponding protected γ-nitro ketones **5a–i**. Deprotection of the carbonyl group, carried out in refluxing benzene with 4-toluenesulfonic acid as a catalyst and a few drops of water, furnished the desired nitro-substituted α-diketones **6a–i** in moderate to good yield (Scheme 3).

Like the enamines, the hydrolysis products also possessing two chiral centers were mixtures of diastereomers. The NMR spectra indicate a predominance of the *anti* isomers in the linear systems (**e–g**) and that of the *trans* isomers in the systems derived from cyclic nitroolefins (**h, i**). The relative configurations were established by comparing the values of the vicinal coupling constants of their respective nitromethine protons. For the diastereomers derived from cyclic nitroolefins, the geometry was determined from some ^{13}C chemical shift differences, with the support of 2D-heteronuclear experiments. In the *cis* isomers, notably, C-1 of the chain and the nitro-bearing carbon are shifted upfield relative to the *trans* isomers, due to γ-gauche steric effect (Table 2). In the case of the compounds derived from 1-nitrocyclohexene, also the chemical shift and coupling constants of the nitromethine proton are consistent with the assignments. In the *trans* derivatives it resonated at higher field with larger *J* than in the corresponding *cis* isomers.

It was found that in some cases changing the solvent and the temperature of the reaction allowed the identification of different amine intermediates. In particular when the



R_2NH = morpholine

	a	b	c	d	e	f	g	h	i
R^1	H	Me	H	Ph	Ph	Me	Ph	$-(CH_2)_3-$	$-(CH_2)_4-$
R^2	H	H	Me	H	Me	Ph	Ph		

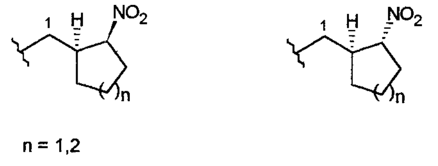
Scheme 3

Table 1. Chemical Shifts and Coupling Constants for the Vinyl Proton of **4**

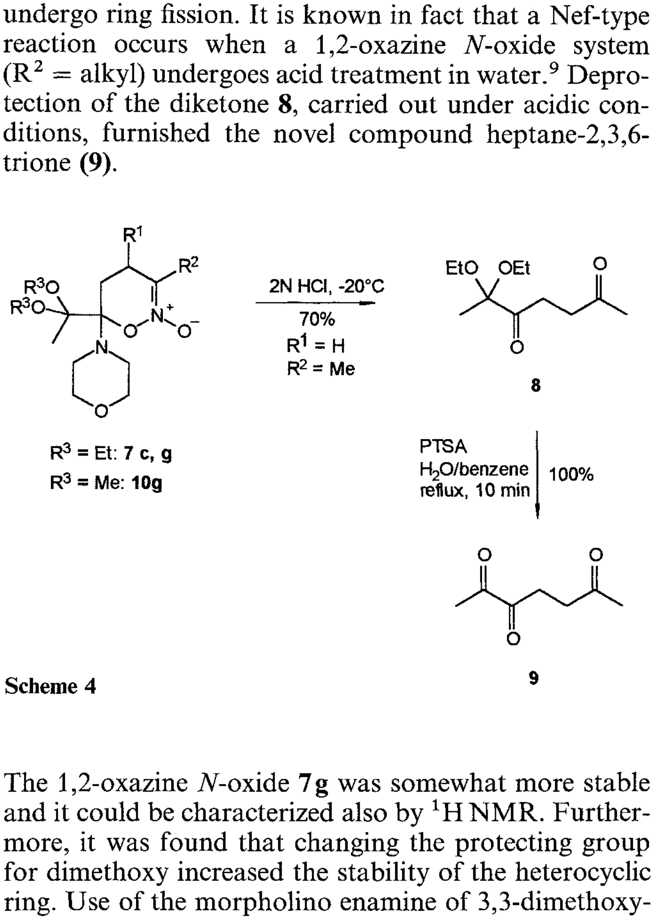
Enamine **4**	C=C*H*, δ, *J* (Hz)
(*Z*)-**4a**	5.42 (t, *J* = 6.8)
(*E*)-**4a**	4.46 (t, *J* = 6.0)
4b	5.40 (d, *J* = 8.3)
4c	5.48 (dd, *J* = 7.0, 7.5)
4d	5.90 (d, *J* = 9.0)
4e	5.86 (d, *J* = 10.0), 5.80 (d, *J* = 10.0)
4f	5.49 (d, *J* = 9.7), 5.05 (d, *J* = 10.7)
4g	5.81 (d, *J* = 10.1), 5.33 (d, *J* = 10.4)
4h	5.46 (d, *J* = 9.5), 5.22 (d, *J* = 8.6)
4i	5.73 (d, *J* = 9.8), 5.38 (d, *J* = 9.8)

reactions involving 2-nitropropene (**3c**) and α-nitrostilbene (**3g**) were carried out in anhydrous diethyl ether, at − 20 °C, cyclic nitronic esters **7c** and **7g** were formed. (Scheme 4). Differently from other 1,2-oxazine *N*-oxide systems,[8] the heterocycle **7c** was unstable and only its IR spectrum could be registered in Nujol mull. It showed a strong $C=N^+-O^-$ stretching band at 1610 cm^{-1}, while the NO_2 stretching bands were absent. When it was dissolved in $CDCl_3$, it immediately opened to the nitroalkylated enamine **4c**. Formation of **7c**, however, was also shown by the isolation of the protected dicarbonyl compound **8**, when the hydrolysis of the crude reaction mixture was performed immediately on completion of the reaction before the heterocycle could undergo ring fission. It is known in fact that a Nef-type reaction occurs when a 1,2-oxazine *N*-oxide system (R^2 = alkyl) undergoes acid treatment in water.[9] Deprotection of the diketone **8**, carried out under acidic conditions, furnished the novel compound heptane-2,3,6-trione (**9**).

Table 2. Selected ^{13}C NMR Data of Compounds **4–6**



Compound	C-1	C-NO_2	Compound	C-1	C-NO_2
cis-**4h**	122.4	91.1	*trans*-**4h**	125.4	92.1
cis-**4i**	115.4	87.9	*trans*-**4i**	125.3	90.5
cis-**5h**	38.4	89.6	*trans*-**5h**	41.5	90.8
cis-**5i**	39.1	85.1	*trans*-**5i**	40.5	89.7
cis-**6h**	37.6	89.1	*trans*-**6h**	39.2	90.3
cis-**6i**	36.2	84.9	*trans*-**6i**	38.7	89.6



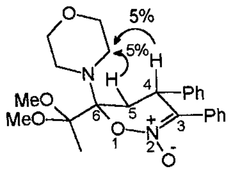
Scheme 4

The 1,2-oxazine *N*-oxide **7g** was somewhat more stable and it could be characterized also by ^1H NMR. Furthermore, it was found that changing the protecting group for dimethoxy increased the stability of the heterocyclic ring. Use of the morpholino enamine of 3,3-dimethoxybutan-2-one in the reaction with α-nitrostilbene in fact afforded the 1,2-oxazine *N*-oxide **10g**, as a single stable diastereomer. Its configuration was established by ^1H NMR and by NOE difference experiments (Table 3). Irradiation of H-4 and H-5_{eq} produced an enhancement on the methylene adjacent to nitrogen at δ = 3.06.

For **7g** the stereostructure can be established by analogy with the respective chemical shift and vicinal couplings of **10g**, as shown in Table 3.

Some of the nitro-substituted α-diketones **6** could be converted into the corresponding five-membered ring α-

Table 3. Chemical Shift and Coupling Constants for **7g** and **10g**

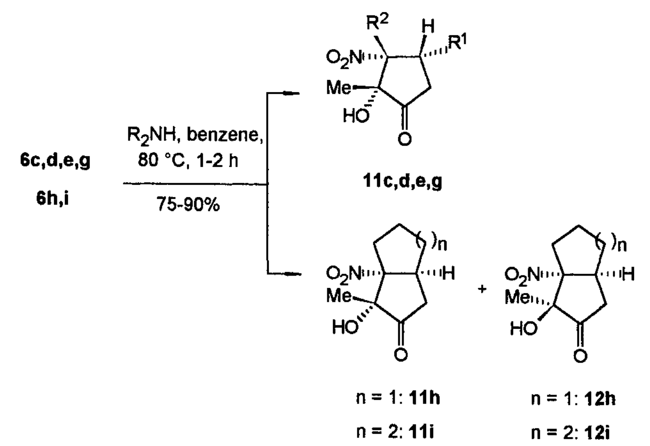


10g

Compound	δ, J (Hz)				
	H-4	CH_2N	CH_2N	H-5_{eq}	H-5_{ax}
7g	4.17 (dd, J = 10.4, 8.2)	3.28 (m)	3.03 (m)	2.64 (dd, J = 8.2, 15.0)	2.38 (dd, J = 10.4, 15.0)
10g	4.16 (dd, J = 10.4, 8.4)	3.30 (m)	3.06 (m)	2.67 (dd, J = 8.4, 15.0)	2.38 (dd, J = 10.4, 15.0)

ketols, by an intramolecular Henry reaction, under basic conditions (Scheme 5).

Interestingly, while for **6c, d, e, g** the cyclization was highly diastereoselective, as a single cyclopentanone **11c, d, e, g** was obtained in each case, a 3:2 mixture of hexahydro-1*H*-pentalen-2-ones was obtained from **6h**, namely **11h** and **12h**, and a 1:1 mixture of octahydro-2*H*-inden-2-ones, **11i** and **12i**, was isolated from **6i**.



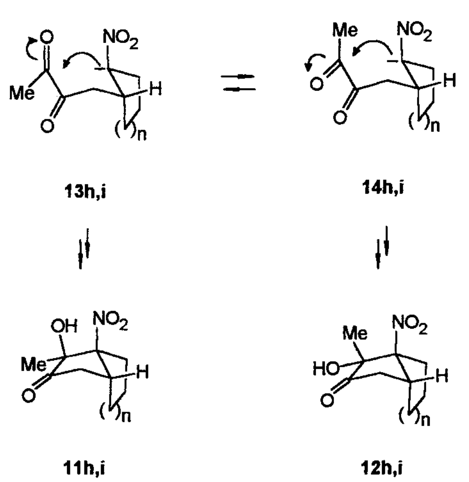
Scheme 5

For the monocyclic compounds **11c, d, e, g**, the stereostructure was tentatively assigned as shown in Scheme 5, on the basis of NOE difference measurements. The enhancements observed were too low (2–4%) to assign the structure with certainty.

The bicyclic compounds **11i** and **12i** are already known, their stereochemistry being established by X-ray analysis.[5b] They differed for the configuration of C-1. A distinction between the two diastereomers **11h** and **12h** can be made by a comparison of the chemical shift of their methyl groups with that of the corresponding **11i** and **12i**. The highfield methyl group is *cis* to the nitro group (δ = 1.28 for **12h** vs δ = 1.22 for **12i**; δ = 1.45 for **11h** vs δ = 1.39 for **11i**), as confirmed by NOE difference experiments performed on **12h**. When irradiating the methyl group, an enhancement (6%) was observed on the proton at the bridge carbon atom.

It should be noted that no pentalenone derivatives had been obtained from the [3 + 2] carbocyclization reaction between 1-nitrocyclopentene and the α-oxoenamine **A** (Scheme 1), as the aminocyclopentene intermediate did not undergo hydrolysis to the expected system **B**.

The formation of the bicyclic compounds **11h, i** and **12h, i** can be understood considering the intermediacy of the carbanion rotamers **13** and **14**, generated by the base (Scheme 6).



Scheme 6

Collapse of the carbanion onto the carbonyl carbon atom occurs from both the diastereotopic faces and in fact no diastereoselectivity was observed.

Mps were taken on a Büchi apparatus and are uncorrected. IR spectra were recorded in Nujol mulls, unless otherwise stated, on a Perkin-Elmer 1320 spectrometer. ^1H NMR and ^{13}C NMR spectra were obtained on a JEOL EX400 (400 MHz for proton and 100.4 MHz for carbon). NMR spectra were recorded in $CDCl_3$ and chemical shifts are given relative to TMS (δ 0.0, ^1H) or $CDCl_3$ (δ = 77.0, ^{13}C). Coupling constants are given in Hz. Electron impact mass spectra were obtained on a VG 7070 spectrometer at 70 eV. TLC were performed on Merck silica gel 60 F_{254} plates. Flash column chromatography was run on Merck Kieselgel 60 (230–400 mesh) (eluant: EtOAc light petroleum 1:4). Light petroleum refers to the fraction with bp 40–70 °C. Stable compounds were separated by flash chromatography and purified by preparative layer chromatography (Merck silica gel 60, 0.5 mm thick) using a mixture of

EtOAc and light petroleum (1:4) as eluant. The solvents were purified by distillation. For the parent enamine **2** the elemental analysis was not satisfactory, owing to the partial loss of ethanol during repeated distillations. Elemental analyses were performed on a Carlo Erba 1106 elemental analyzer. Compounds **5a–i**, **6a–g**, **8**, **9**, **11h** and **12h** gave C, H, N analysis ± 0.30%.

β-Nitrostyrene **(3d)** was purchased from Aldrich Chemicals, 1-nitroethene **(3a)**,[10] 1-nitropropene **(3b)**,[10] 2-nitropropene **(3c)**,[10] 1-nitro-2-phenylpropene **(3e)**,[11] 1-nitro-1-phenylpropene **(3f)**,[12] α-nitrostilbene **(3g)**,[13] 1-nitrocyclopentene **(3h)**,[14] and 1-nitrocyclohexene **(3i)**[14] were prepared by literature procedures.

3,3-Diethoxy-2-morpholinobut-1-ene (2):

A three-neck flask was charged with morpholine (20 mL, 0.23 mol) in dry benzene (100 mL), under Ar, at 10 °C. $TiCl_4$ (2.5 mL, 0.023 mol) in benzene (10 mL) was then added followed by a solution of the ketal **1**[6] (3.7 g, 0.023 mol), under stirring. The solution was then heated to reflux for 2 h, filtered through Celite (4.0 g) and the solvent was removed under reduced pressure. The oil was distilled to give **2**; yield: 3.4 g (65%); bp 76–78 °C/0.2 Torr.

IR (film): $\nu = 3040$ (=CH), 1610 (C=C), 1125 cm^{-1} (C–O–C).

^1H NMR: $\delta = 4.78$ (s, 1 H, C=CH *trans*[15] to morpholine), 4.23 (s, 1 H, C=CH *cis*[15] to morpholine), 3.72 (m, 4 H, CH_2OCH_2), 3.47 (q, $J = 7.1$ Hz, 4 H, $2CH_2CH_3$), 2.95 (m, 4 H, CH_2NCH_2), 1.49 (s, 3 H, CH_3), 1.17 (t, $J = 7.1$ Hz, 6 H, $2CH_2CH_3$).

^{13}C NMR: $\delta = 155.0$ (s), 100.3 (s), 92.8 (t), 66.8 (2 t), 56.3 (2 t), 49.9 (2 t), 24.3 (q), 15.0 (2 q).

MS: m/z (%) = 229.16752 ($M^{+\cdot}$, 3%) ($C_{12}H_{23}NO_3$ requires: 229.16779), 214 (M – CH_3, 1.7), 200 (M – Et, 1), 185 (M – 44, 22), 184 (28), 156 (184 – C_2H_4, 34), 154 (10), 118 (9), 117 ($CH_3C(OEt)_2^+$, 87), 113 (6), 112 (25), 100 (24), 89 (117 – C_2H_4, 50), 86 (6), 70 (14), 61 (89 – C_2H_4, 100).

Nitroalkylation; General Procedure:

To a solution of the enamine **2** (0.65 g, 2.83 mmol) in anhyd EtOH (20 mL), under Ar was added the nitroolefin **3** (2.83 mmol) and the reaction mixture was heated to reflux for 2 h. Evaporation of the solvent furnished the crude nitroalkylated enamine **4** as a yellow oil. The crude reaction mixture was dissolved in $CHCl_3$ (10 mL) and hydrolyzed at pH 4.6 (acetate buffer), at r.t. The organic phase was separated, washed with aq $NaHCO_3$, water and dried (Na_2SO_4). Purification by silica gel chromatography (light petroleum/EtOAc 4:1) afforded the protected γ-nitro ketone **5**. This latter compound was dissolved in benzene (15 mL) and heated at 80 °C for 2 h in the presence of a few drops of water and PTSA as a catalyst. Evaporation of the solvent gave the diketone **6**.

In the reactions involving nitroethene **(3a)** and 1-nitropropene **(3b)**, the nitroolefin (2.8 mmol), dissolved in anhyd Et_2O (20 mL), was added dropwise to a solution of the enamine **2** (2.8 mmol) in the same solvent (15 mL), at –20 °C, under Ar and allowed to react at r.t. for 24 h.

Reaction with Nitroethene:

2,2-Diethoxy-6-nitrohexan-3-one **(5a)**; purification by column chromatography gave **5a** (oil, 50% yield).

IR (film): $\nu = 1720$ (C=O), 1545, 1380 (NO_2), 1150 cm^{-1} (C–O–C).

^1H NMR: $\delta = 4.37$ (t, $J = 6.6$ Hz, 2 H, CH_2NO_2), 3.43 (q, $J = 7.1$ Hz, 2 H, CH_2CH_3), 3.35 (q, 2 H, CH_2CH_3), 2.71 (t, $J = 6.6$ Hz, 2 H, CH_2CO), 2.19 (quintet, $J = 6.6$ Hz, 2 H, $CH_2CH_2NO_2$), 1.30 [s, 3 H, $CH_3C(OEt)_2$], 1.14 (t, 6 H, $2CH_2CH_3$).

^{13}C NMR: $\delta = 208.2$ (s), 102.2 (s), 74.6 (t), 57.7 (2 t), 34.1 (t), 21.1 (t), 20.7 (q), 15.3 (2 q).

MS: m/z (%) = 188 ($M^{+\cdot}$ – OEt, 14), 160 (McLafferty, $M^{+\cdot}$ – 73, nitroethene, 8), 118 (8), 117 (63), 113 (28), 89 (117 – 28, C_2H_4, 41), 61 (89 – C_2H_4, 100), 43 (61 – H_2O, 86).

6-Nitrohexane-2,3-dione **(6a)**:

IR (film): $\nu = 1710$ (C=O), 1550, 1380 cm^{-1} (NO_2).

^1H NMR: $\delta = 4.39$ (t, $J = 7.0$ Hz, 2 H, CH_2NO_2), 2.86 (t, $J = 7.0$ Hz, 2 H, CH_2CO), 2.29 (s, 3 H, CH_3), 2.24 (quintet, $J = 7.0$ Hz, 2 H, $CH_2CH_2NO_2$).

^{13}C NMR: $\delta = 197.0$ (s), 196.6 (s), 74.1 (t), 32.2 (t), 23.5 (q), 20.6 (t).

MS: m/z (%) = 115 ($M^{+\cdot}$ – 44, 10), 88 (10), 85 (10), 71 (9), 69 (15), 55 (19), 45 (50), 44 (20), 43 (CH_3CO^+, 100).

Reaction with 1-Nitropropene:

2,2-Diethoxy-5-methyl-6-nitrohexan-3-one **(5b)**; purification by column chromatography gave **5b** (oil, 60% yield).

IR (film): $\nu = 1725$ (C=O), 1550, 1380 (NO_2), 1100 cm^{-1} (C–O–C).

^1H NMR: $\delta = 4.39$ (pseudo q, A part of an ABX system, $J_{AB} = 11.9$ Hz, 1 H, $CHNO_2$), 4.37 (pseudo q, B part of an ABX system, $J_{AB} = 11.9$ Hz, 1 H, $CHNO_2$), 3.50 (2 m, 4 H, $2CH_2CH_3$), 2.75 (m, 3 H, CH_2CHCH_3), 1.36 [*s*, 3 H, $CH_3C(OEt)_2$], 1.20 (t, 6 H, $2CH_2CH_3$), 1.06 (d, $J = 6.4$ Hz, 3 H, $CHCH_3$).

^{13}C NMR: $\delta = 208.2$ (s), 102.6 (s), 80.7 (t), 58.1 (2 t), 41.7 (t), 28.5 (d), 21.1 (q), 17.9 (q), 15.7 (2 q).

MS: m/z (%) = 202 ($M^{+\cdot}$ – OEt, 7), 127 ($M^{+\cdot}$ – NO_2, 10), 117 [$CH_3(OEt)_2^+$, 63], 89 (117 – C_2H_4, 39), 61 (89 – C_2H_4, 100), 43 (61 – H_2O, 74).

5-Methyl-6-nitrohexane-2,3-dione **(6b)**:

IR (film): $\nu = 1710$ (C=O), 1540, 1350 cm^{-1} (NO_2).

^1H NMR: $\delta = 4.30$ (m, 2 H, CH_2NO_2), 2.80 (m, 3 H, CH_2CHCH_3), 2.29 (s, 3 H, CH_3), 1.02 (d, $J = 7.0$ Hz, 3 H, $CHCH_3$).

^{13}C NMR: $\delta = 196.8$ (s), 196.7 (s), 80.0 (t), 39.1 (t), 28.0 (q), 23.4 (d), 17.5 (q).

MS: m/z (%) = 130 ($M^{+\cdot}$ – 43, 10), 102 (5), 83 (7), 69 (15), 55 (15), 43 (CH_3CO^+, 100).

Reaction with 2-Nitropropene:

2,2-Diethoxy-6-nitroheptan-3-one **(5c)**; purification by column chromatography gave **5c** (oil, 52% yield).

IR (film): $\nu = 1720$ (C=O), 1542, 1385 (NO_2), 1160, 1135 cm^{-1} (C–O–C).

^1H NMR: $\delta = 4.55$ (ddq, $J_1 = 6.6$ Hz, $J_2 = 9.3$ Hz, $J_3 = 4.4$ Hz, 1 H, $CHNO_2$), 3.42, 3.32 (2 m, 4 H, $2CH_2CH_3$), 2.67 (dd, $J_1 = 7.7$ Hz, $J_2 = 6.6$ Hz, 2 H, CH_2CH_2CO), 2.05 (m, 2 H, CH_2CO), 1.52 (d, $J = 6.6$ Hz, 3 H, CH_3CHNO_2), 1.33 [s, 3 H, $CH_3C(OEt)_2$], 1.17 (t, $J = 7.0$ Hz, 6 H, $2CHCH_3$).

^{13}C NMR: $\delta = 208.1$ (s), 102.1 (s), 82.5 (d), 57.5 (2 t), 33.6 (t), 28.5 (t), 20.6 (q), 19.3 (q), 15.3 (2 q).

MS: m/z (%) = 202 ($M^{+\cdot}$ – OEt, 13), 155 (10), 127 ($M^{+\cdot}$ – NO_2, 27), 118 (8), 117 [$CH_3C(OEt)_2^+$, 74], 89 (117 – C_2H_4, 43), 61 (89 – C_2H_4, 100), 43 (61 – H_2O, 90).

6-Nitroheptane-2,3-dione **(6c)**:

IR (film): $\nu = 1710$ (C=O), 1540, 1350 cm^{-1} (NO_2).

^1H NMR: $\delta = 4.53$ (m, 1 H, $CHNO_2$), 2.78 (t, $J = 7.0$ Hz, 2 H, CH_2CO), 2.27 (s, 3 H, CH_3CO), 2.16, 2.02 (2 m, 2 H, CH_2CHNO_2), 1.51 (d, $J = 6.6$ Hz, 2 H, $CHCH_3$).

^{13}C NMR: $\delta = 197.0$ (s), 196.5 (s), 82.2 (d), 31.6 (t), 27.9 (t), 23.3 (q), 19.1 (q).

MS: m/z (%) = 145 ($M^{+\cdot}$ – 28, 10), 118 (27), 117 (100), 104 (30), 91 (19), 89 (117 – C_2H_4, 26), 77 (16), 61 (89 – C_2H_4, 52), 43 (CH_3CO^+, 52).

6,6-Diethoxyheptane-2,5-dione **(8)**:

IR (film): $\nu = 1720$ (C=O), 1150, 1130 cm^{-1} (C–O–C).

^1H NMR: $\delta = 3.46$ (dq, 2 H, CH_2CH_3), 3.36 (dq, 2 H, CH_2CH_3), 2.84, 2.63 (2 t, 4 H, CH_2CH_2CO), 2.13 (s, 3 H, CH_3CO), 1.33 (s, 3 H, CH_3), 1.14 (t, 6 H, $2CH_2CH_3$).

^{13}C NMR: $\delta = 208.6$ (s), 207.2 (s), 102.2 (s), 57.5 (2 t), 36.3 (t), 32.2 (t), 29.9 (q), 20.9 (q), 15.2 (2 q).

MS: m/z (%) = 171 ($M^{+\cdot}$ – OEt, 14), 117 [$CH_3(OEt)_2^+$, 69], 89 (117 – C_2H_4, 29), 61 (89 – C_2H_4, 100), 43 (61 – H_2O, 100).

Heptane-2,3,6-trione **(9)**:

IR (film): $\nu = 1710$ cm^{-1} (C=O).

^{1}H NMR: $\delta = 2.70$ (m, 2H, CH_2COCO), 2.57 (m, 2H, CH_2), 2.27 (s, 3H, CH_3COCO), 2.13 (s, 3H, CH_3CO).

^{13}C NMR: $\delta = 206.7$ (s), 198.0 (s), 197.2 (s), 37.4 (t), 29.6 (t), 23.6 (2q).

MS: m/z (%) = 99 ($M^{+\bullet} - CH_3CO$, 100), 71 (75), 57 (20).

[2R-(2α,3α)]-2-Hydroxy-2,3-dimethyl-3-nitrocyclopentanone* (**11c**):
IR (film): ν = 3400 (OH), 1760 (C=O), 1540, 1385 cm^{-1} (NO_2).

^{1}H NMR: $\delta = 2.68$ (ddd, $J_1 = 8.6$ Hz, $J_2 = 11.0$ Hz, $J_3 = 19.6$ Hz, 1H, H-5α), 2.66 (bs, 1H, OH), 2.54–2.35 (m, 2H, H-4α, H-5β), 2.06 (ddd, $J_1 = 8.0$ Hz, $J_2 = 11.1$ Hz, $J_3 = 15.3$ Hz, 1H, H-4β), 1.64 [s, 3H, $CH_3C(NO_2)$], 1.20 (s, 3H, $CH_3C(OH)$].

^{13}C NMR: $\delta = 214.0$ (s), 94.3 (s), 81.0 (s), 30.8 (t), 30.5 (t), 21.0 (q), 17.6 (q).

Reaction with β-Nitrostyrene:
2,2-Diethoxy-6-nitro-5-phenylhexan-3-one (**5d**); purification by column chromatography gave **5d** (oil, 59% yield).

IR (film): ν = 1725 (C=O), 1600, 1585, 780, 700 (Ph), 1545, 1375 (NO_2), 1150 cm^{-1} (C−O−C).

^{1}H NMR: $\delta = 7.27$ (m, 5H, Ph), 4.70 (m, 2H, CH_2NO_2), 4.06 (m, 1H, $C\mathit{H}Ph$), 3.37 (m, 4H, $2C\mathit{H}_2CH_3$), 3.20 (dd, $^3J = 7.3$ Hz, $^2J = 18.5$ Hz, 1H, CHCO), 2.98 (dd, $^3J = 6.8$ Hz, $^2J = 18.5$ Hz, 1H, CHCO), 1.25 [s, 3H, $C\mathit{H}_3C(OEt)_2$], 1.15, 1.10 (2t, 6H, $2CH_2C\mathit{H}_3$).

^{13}C NMR: $\delta = 206.8$ (s), 139.1 (s), 128.2 (d), 127.6 (d), 127.5 (d), 102.2 (s), 79.5 (t), 57.7 (t), 41.1 (t), 38.9 (d), 20.3 (q), 15.3 (2q).

MS: m/z (%) = 264 ($M^{+\bullet}$ − OEt, 2), 118 (8), 117 [$CH_3(OEt)_2^+$, 100], 104 (10), 91 (4), 89 (117 − C_2H_4, 38), 61 (89 − C_2H_4, 95), 43 (61 − H_2O, 57).

6-Nitro-5-phenylhexane-2,3-dione (**6d**):
IR (film): ν = 1710 (C=O), 1605, 1500, 745, 710 (Ph), 1550, 1375 cm^{-1} (NO_2).

^{1}H NMR: $\delta = 7.35$–7.20 (m, 5H, Ph), 4.63 (2 pseudo q, $J_{AB} = 12.5$ Hz, 2H, CH_2NO_2), 4.04 (m, 1H, $C\mathit{H}Ph$), 3.35 (pseudo q, A part of an ABX system, $J_{AB} = 18.0$ Hz, 1H, $CHNO_2$), 3.15 (pseudo q, B part of an ABX system, $J_{AB} = 18.0$ Hz, 1H, $CHNO_2$), 2.25 (s, 3H, CH_3).

^{13}C NMR: $\delta = 196.6$ (s), 195.9 (s), 138.2 (s), 129.2 (d), 128.2 (d), 127.4 (d), 79.5 (t), 38.9 (t), 38.8 (d), 23.4 (q).

MS: m/z (%) = 192 ($M^{+\bullet}$ − 43, 10), 145 (28), 117 (28), 104 (45), 91 (14), 77 (17), 51 (10), 43 (CH_3CO^+, 100).

Reaction with 2-Nitro-1-phenylpropene:
2,2-Diethoxy-6-nitro-5-phenylheptan-3-one (**5e**); the hydrolysis of the crude reaction mixture gave **5e**, as a 1:3 mixture of *syn/anti* isomers (70% yield), which were separated by column chromatography.

syn-**5e**:
IR (film): ν = 1720 (C=O), 1600, 1580, 780, 700 (Ph), 1545, 1385 (NO_2), 1150 cm^{-1} (C−O−C).

^{1}H NMR: $\delta = 7.21$ (m, 3H, *m*- and *p*-Ar−H), 7.15 (m, 2H, *o*-Ar−H), 4.82 (quintet, $J = 6.7$ Hz, 1H, $CHNO_2$), 3.69 (ddd, $J_1 = 6.7$ Hz, $J_2 = 9.1$ Hz, $J_3 = 5.2$ Hz, 1H, $C\mathit{H}Ph$), 3.41 (m, 1H, $C\mathit{H}CH_3$), 3.28 (m, 2H, $C\mathit{H}_2CH_3$), 3.16 (m, 1H, $C\mathit{H}CH_3$), 3.13 (dd, $J_1 = 18.5$ Hz, $J_2 = 9.1$ Hz, 1H, CHCO), 3.03 (dd, $J_1 = 18.5$ Hz, $J_2 = 5.2$ Hz, 1H, CHCO), 1.45 (d, $J = 6.7$ Hz, 3H, $CHC\mathit{H}_3$), 1.17 (s, 3H, CH_3), 1.11, 1.07 (2t, 6H, $2CH_2C\mathit{H}_3$).

^{13}C NMR: $\delta = 207.0$ (s), 138.2 (s), 128.7 (d), 128.3 (d), 127.8 (d), 102.3 (s), 86.2 (d), 57.6 (t), 44.4 (d), 39.7 (t), 20.4 (q), 17.0 (q), 15.3 (q).

MS: m/z (%) = 278 ($M^{+\bullet}$ − OEt, 2), 231 (1), 203 (3), 185 (3), 175 (2), 157 (2), 131 (3), 118 (9), 117 [$CH_3C(OEt)_2^+$, 100], 89 (117 − C_2H_4, 42), 77 (3), 61 (89 − C_2H_4, 79), 43 (61 − H_2O, 63).

anti-**5e**:
IR (film): ν = 1720 (C=O), 1600, 1580, 780, 700 (Ph), 1540, 1385 (NO_2), 1180 cm^{-1} (C−O−C).

^{1}H NMR: $\delta = 7.21$ (m, 3H, *m*- and *p*-Ar−H), 7.15 (m, 2H, *o*-Ar−H), 4.74 (dq, $J_1 = 10.2$ Hz, $J_2 = 6.7$ Hz, 1H, $CHNO_2$), 3.69 (dt, $J_1 = J_2 = 10.2$ Hz, $J_3 = 3.8$ Hz, 1H, $C\mathit{H}Ph$), 3.32 (m, 1H, $C\mathit{H}CH_3$), 3.27 (dd, $J_1 = 18.0$ Hz, $J_2 = 10.0$ Hz, 1H, CHCO), 3.19 (m, 2H, $C\mathit{H}_2CH_3$), 3.05 (m, 1H, $C\mathit{H}CH_3$), 2.65 (dd, $J_1 = 18.0$ Hz, $J_2 = 3.8$ Hz, 1H, CHCO), 1.26 (d, $J = 6.7$ Hz, 3H, CH_3), 1.07 (t, 3H, $CH_2C\mathit{H}_3$), 1.05 (s, 3H, CH_3), 1.02 (t, 3H, $CH_2C\mathit{H}_3$).

^{13}C NMR: 206.0 (s), 138.4 (s), 128.8 (d), 128.7 (d), 128.5 (d), 102.1 (s), 87.1 (d), 57.6 (t), 57.4 (t), 45.1 (d), 41.1 (t), 20.2 (q), 18.0 (q), 15.3 (q).

MS: m/z (%) = 278 ($M^{+\bullet}$ − OEt, 3), 231 (1), 203 (4), 185 (4), 175 (3), 157 (3), 131 (6), 118 (15), 117 [$CH_3C(OEt)_2^+$, 100], 89 (117 − C_2H_4, 45), 77 (7), 61 (89 − C_2H_4, 78), 43 (61 − H_2O, 54).

6-Nitro-5-phenylheptane-2,3-dione (**6e**):
syn-**6e**:
IR (film): ν = 1710 (C=O), 1600, 1580, 780, 700 (Ph), 1545, 1370 cm^{-1} (NO_2).

^{1}H NMR: $\delta = 7.20$ (m, 3H, *m*- and *p*-Ar−H), 7.10 (m, 2H, *o*-Ar−H), 4.77 (quintet, $J = 6.9$ Hz, 1H, $CHNO_2$), 3.58 (ddd, $J_1 = 6.9$ Hz, $J_2 = 9.1$ Hz, $J_3 = 5.9$ Hz, 1H, $C\mathit{H}Ph$), 3.29 (dd, $J_1 = 17.9$ Hz, $J_2 = 9.1$ Hz, 1H, CHCO), 3.11 (dd, $J_1 = 17.9$ Hz, $J_2 = 5.9$ Hz, 1H, CHCO), 2.13 (s, 3H, CH_3CO), 1.45 (d, $J = 6.9$ Hz, 3H, CH_3).

^{13}C NMR: $\delta = 196.6$ (s), 196.2 (s), 137.6 (s), 128.7 (d), 128.3 (d), 128.1 (d), 86.4 (d), 44.3 (d), 36.9 (t), 23.4 (q), 16.5 (q).

MS: m/z (%) = 221 ($M^{+\bullet} - C_2H_4$, 22), 207 (10), 206 ($M^{+\bullet} - CH_3CO^+$, 13), 159 (23), 147 (19), 131 (28), 118 (23), 117 (31), 115 (17), 105 (17), 104 (26), 91 (32), 77 (17), 73 (30), 43 (CH_3CO^+, 100).

anti-**6e**:
IR (film): ν = 1710 (C=O), 1600, 1585 (Ph), 1545, 1385 cm^{-1} (NO_2).

^{1}H NMR: $\delta = 7.34$–7.05 (m, 5H, Ar−H), 4.68 (dq, $J_1 = 9.9$ Hz, $J_2 = 6.7$ Hz, 1H, $CHNO_2$), 3.64 (ddd, $J_1 = 9.9$ Hz, $J_2 = 9.6$ Hz, $J_3 = 4.6$ Hz, 1H, $C\mathit{H}Ph$), 3.34 (dd, $J_1 = 17.7$ Hz, $J_2 = 9.6$ Hz, 1H, CHCO), 2.85 (dd, $J_1 = 17.7$ Hz, $J_2 = 4.6$ Hz, 1H, CHCO), 2.04 (s, 3H, CH_3CO), 1.22 (d, $J = 6.7$ Hz, 3H, CH_3).

^{13}C NMR: $\delta = 196.4$ (s), 195.6 (s), 140.5 (s), 128.7 (d), 128.3 (d), 128.1 (d), 86.9 (d), 44.8 (d), 38.7 (t), 23.1 (q), 17.6 (q).

MS: m/z (%) = 221 ($M^{+\bullet} - C_2H_4$, 30), 206 ($M^{+\bullet} - CH_3CO^+$, 17), 159 (25), 147 (31), 131 (39), 118 (35), 117 (44), 115 (24), 105 (43), 104 (62), 91 (39), 77 (30), 73 (49), 43 (CH_3CO^+, 100).

Reaction with 1-Nitro-1-phenylpropene:
2,2-Diethoxy-5-methyl-6-nitro-6-phenylhexan-3-one (**5f**); the hydrolysis of the crude reaction mixture gave **5f** as a 2:3 mixture of *syn/anti* isomers (45% yield), which were separated by column chromatography.

syn-**5f**:
IR (film): ν = 1720 (C=O), 1600, 1490, 730, 700 (Ph), 1550, 1380 (NO_2), 1150 cm^{-1} (C−O−C).

^{1}H NMR: $\delta = 7.49$ (m, 2H, *o*-Ar−H), 7.41 (m, 3H, *m*- and *p*-Ar−H), 5.39 (d, $J = 9.4$ Hz, 1H, $CHNO_2$), 3.54–3.38 (m, 4H, $2C\mathit{H}_2CH_3$), 3.18 (m, 1H, $C\mathit{H}CH_3$), 2.67 (2 pseudo q, $J_{AB} = 18.6$ Hz, 2H, CH_2CO), 1.36 (s, 3H, CH_3), 1.21, 1.20 (2t, 6H, $2CH_2C\mathit{H}_3$), 0.78 (d, $J = 6.9$ Hz, 3H, $CHC\mathit{H}_3$).

^{13}C NMR: $\delta = 207.6$ (s), 133.4 (s), 129.9 (d), 129.0 (d), 128.2 (d), 102.3 (s), 95.9 (d), 57.7 (t), 57.6 (t), 41.3 (t), 32.9 (d), 20.6 (q), 16.0 (q), 15.3 (q).

MS: m/z (%) = 278 ($M^{+\bullet}$ − OEt, 1), 231 (278 − NO_2, 5), 205 (4), 203 (4), 185 (4), 149 (4), 118 (16), 117 [$CH_3C(OEt)_2^+$, 100], 105 (8), 91 (25), 89 (117 − C_2H_4, 30), 61 (89 − C_2H_4, 70), 43 (61 − H_2O, 65).

anti-**5f**:
IR (film): ν = 1720 (C=O), 1600, 1490, 730, 700 (Ph), 1540, 1370 (NO_2), 1150 cm^{-1} (C−O−C).

^{1}H NMR: $\delta = 7.48$ (m, 2H, *o*-Ar−H), 7.37 (m, 3H, *m*- and *p*-Ar−H), 5.49 (d, $J = 11.3$ Hz, 1H, $CHNO_2$), 3.34 (m, 2H, $C\mathit{H}_2CH_3$), 3.20 (m, 3H, $C\mathit{H}CH_3$, $C\mathit{H}_2CH_3$), 2.43 (2 pseudo q,

J_{AB} = 18.8 Hz, 2H, CH_2CO), 1.16 (s, 3H, CH_3), 1.12 (d, J = 6.4 Hz, 3H, $CHCH_3$), 1.11, 1.10 (2t, 6H, $2CH_2CH_3$).

^{13}C NMR: δ = 207.4 (s), 133.3 (s), 130.0 (d), 129.0 (d), 128.4 (d), 102.1 (s), 96.3 (d), 57.5 (2t), 40.2 (t), 32.9 (d), 20.4 (q), 17.1 (q), 15.2 (q).

MS: m/z (%) = 278 ($M^{+\cdot}$ – OEt, 1), 231 (278 – NO_2, 11), 118 (17), 117 [$CH_3C(OEt)_2^+$, 100], 105 (17), 91 (25), 89 (117 – C_2H_4, 44), 61 (89 – C_2H_4, 87), 43 (61 – H_2O, 75).

5-Methyl-6-nitro-6-phenylhexane-2,3-dione (**6f**):

syn-**6f**:

IR ($CHCl_3$): ν = 1710 (C=O), 1600 (Ph), 1550, 1380 cm^{-1} (NO_2).

^{1}H NMR: δ = 7.50–7.40 (m, 5H, Ar–H), 5.36 (d, J = 9.4 Hz, 1H, $CHNO_2$), 3.19 (m, 1H, $CHCH_3$), 2.88 (2 pseudo q, J_{AB} = 18.1, 2H, CH_2CO), 2.36 (s, 3H, CH_3CO), 0.79 (d, J = 6.8 Hz, 3H, $CHCH_3$).

^{13}C NMR: δ = 196.8 (s), 196.6 (s), 133.0 (s), 130.1 (d), 129.1 (d), 128.1 (d), 95.7 (d), 39.2 (t), 32.9 (q), 23.5 (d), 16.2 (q).

MS: m/z (%) = 159 ($M^{+\cdot}$ – 90, 11), 131 (25), 115 (20), 105 (50), 91 (47), 77 (33), 43 (CH_3CO^+, 100).

anti-**6f**:

IR ($CHCl_3$): ν = 1710 (C=O), 1600 (Ph), 1550, 1380 cm^{-1} (NO_2).

^{1}H NMR: δ = 7.50–7.40 (m, 5H, Ph), 5.34 (d, J = 11.2 Hz, 1H, $CHNO_2$), 3.24 (m, 1H, $CHCH_3$), 2.54 (2 pseudo q, J_{AB} = 18.1 Hz, 2H, CH_2CO), 2.21 (s, 3H, CH_3CO), 1.12 (d, J = 6.8 Hz, 3H, $CHCH_3$).

^{13}C NMR: δ = 196.6 (s), 196.5 (s), 132.8 (s), 130.3 (d), 129.2 (d), 128.3 (d), 96.4 (d), 38.0 (t), 33.2 (q), 23.3 (d), 17.3 (q).

MS: m/z (%) = 159 ($M^{+\cdot}$ – 90, 15), 154 (35), 131 (33), 117 (33), 115 (33), 105 (58), 91 (44), 77 (48), 43 (CH_3CO^+, 100).

Reaction with α-Nitrostilbene:

2,2-Diethoxy-6-nitro-5,6-diphenylhexan-3-one (**5g**); the hydrolysis of the crude reaction mixture gave **5g** as a 1:1 mixture of *syn*/*anti* isomers (80% yield), which were separated by column chromatography.

syn-**5g**; mp 130–131 °C.

IR (Nujol): ν = 1725 (C=O), 1600, 1585, 800, 730 (Ph), 1550, 1360 (NO_2), 1100 cm^{-1} (C–O–C).

^{1}H NMR: δ = 7.70–7.20 (m, 10H, Ar–H), 5.88 (d, J = 12.2 Hz, 1H, $CHNO_2$), 4.44 (ddd, J_1 = 12.2 Hz, J_2 = 9.8 Hz, J_3 = 3.4 Hz, 1H, C*H*Ph), 3.23 (dq, 1H, $CHCH_3$), 3.16 (dq, 1H, $CHCH_3$), 3.06 (dd, ^3J = 9.8 Hz, ^2J = 18.1 Hz, 1H, CHCO), 3.05 (dq, 1H, $CHCH_3$), 2.98 (dq, 1H, $CHCH_3$), 2.80 (dd, ^3J = 3.4 Hz, ^2J = 18.1 Hz, 1H, CHCO), 1.06 (t, 3H, CH_2CH_3), 1.01 (t, 3H, CH_2CH_3), 0.93 (s, 3H, CH_3).

^{13}C NMR: δ = 206.3 (s), 138.9 (s), 132.7 (s), 130.3 (d), 129.2 (d), 128.7 (d), 128.5 (d), 128.2 (d), 127.7 (d), 102.0 (s), 95.5 (d), 57.5, 57.4 (t), 44.0 (d), 40.7 (t), 19.8 (q), 15.1 (2q).

MS: m/z (%) = 180 (7), 179 (6), 178 (7), 117 [$CH_3C(OEt)_2^+$, 100], 89 (117 – C_2H_4, 27), 61 (89 – C_2H_4, 50), 43 (61 – H_2O, 58).

anti-**5g**; mp 107–108 °C.

IR (film): ν = 1725 (C=O), 1600, 1585, 800, 730 (Ph), 1550, 1360 (NO_2), 1100 cm^{-1} (C–O–C).

^{1}H NMR: δ = 7.41–7.01 (m, 5H, Ar–H), 5.74 (d, J = 11.2 Hz, 1H, $CHNO_2$), 4.40 (dt, $J_1 = J_2$ = 11.2 Hz, J_3 = 2.9 Hz, 1H, C*H*Ph), 3.49 (dd, J_1 = 11.2 Hz, J_2 = 18.1 Hz, 1H, CHCO), 3.40 (dq, 1H, $CHCH_3$), 3.26 (dq, 2H, CH_2CH_3), 3.10 (dq, 1H, $CHCH_3$), 2.80 (dd, J_1 = 2.9 Hz, J_2 = 18.1 Hz, 1H, CHCO), 1.16 (t, 3H, $CHCH_3$), 1.11 (s, 3H, CH_3), 1.09 (t, 3H, CH_2CH_3).

^{13}C NMR: δ = 206.3 (s), 137.7 (s), 132.8 (s), 129.6 (d), 128.6 (d), 128.4 (d), 128.3 (d), 127.2 (d), 102.1 (s), 95.1 (d), 57.7, 57.4 (t), 44.6 (d), 41.5 (t), 20.1 (q), 15.3 (q), 15.2 (q).

MS: m/z (%) = 340 ($M^{+\cdot}$ – OEt, 0.1), 193 (3), 180 (3), 179 (4), 178 (3), 117 [$CH_3C(OEt)_2^+$, 100], 104 (6), 89 (117 – C_2H_4, 22), 61 (89 – C_2H_4, 43), 43 (61 – H_2O, 35).

6-Nitro-5,6-diphenylhexane-2,3-dione (**6g**):

syn-**6g**:

IR (film): ν = 1710 (C=O), 1600, 1585, 780, 700 (Ph), 1550, 1350 cm^{-1} (NO_2).

^{1}H NMR: δ = 7.62 (m, 2H, Ar–H), 7.45–7.20 (m, 6H, Ar–H), 7.05 (m, 2H, Ar–H), 5.74 (d, J = 11.8 Hz, 1H, $CHNO_2$), 4.38 (ddd, J_1 = 11.8 Hz, J_2 = 10.1 Hz, J_3 = 4.3 Hz, 1H, C*H*Ph), 3.15 (dd, ^2J = 17.4 Hz, ^3J = 4.3 Hz, 1H, CHCO), 2.02 (s, 3H, CH_3).

^{13}C NMR: δ = 196.3 (s), 195.6 (s), 138.0 (s), 132.3 (s), 130.5 (d), 129.4 (d), 129.0 (d), 128.4 (d), 128.1 (2d), 95.8 (d), 44.4 (t), 38.4 (d), 23.2 (q).

anti-**6g**:

IR (film): ν = 1710 (C=O), 1600, 1585, 780, 700 (Ph), 1550, 1350 cm^{-1} (NO_2).

^{1}H NMR: δ = 7.60 (m, 2H, Ar–H), 7.45–7.20 (m, 6H, Ar–H), 7.05 (m, 2H, Ar–H), 5.75 (d, J = 11.8 Hz, 1H, $CHNO_2$), 4.39 (ddd, J_1 = 11.8 Hz, J_2 = 10.0 Hz, J_3 = 4.4 Hz, 1H, C*H*Ph), 3.15 (dd, ^2J = 17.4 Hz, ^3J = 10.0 Hz, 1H, CHCO), 2.64 (dd, ^2J = 17.4 Hz, ^3J = 4.4 Hz, 1H, CHCO), 2.01 (s, 3H, CH_3).

^{13}C NMR: δ = 196.5 (s), 195.8 (s), 138.2 (s), 132.4 (s), 129.7 (d), 129.4 (d), 128.7 (d), 128.4 (d), 127.6 (d), 126.3 (d), 95.2 (d), 44.7 (t), 39.3 (d), 23.3 (q).

[4R-(4α,6β)]-6-(1,1-Diethoxyethyl)-6-morpholino-3,4-diphenyl-5,6-dihydro-4H-1,2-oxazine N-Oxide* (**7g**); mp 123–124 °C (45% yield).

IR (Nujol): ν = 1595 ($C{=}\overset{+}{N}$), 1580, 1565, 770 (Ph), 1110 cm^{-1} (C–O–C).

^{1}H NMR: δ = 7.68 (d, 2H, *o*-Ar–H), 7.15 (m, 8H, Ar–H), 4.16 (dd, $^3J_{ea}$ = 8.4 Hz, $^3J_{aa}$ = 10.4 Hz, 1H, C*H*Ph), 3.63 (m, 8H, $2CH_2CH_3$, CH_2OCH_2), 3.30 (m, 2H, CH_2NCH_2), 3.06 (m, 2H, CH_2NCH_2), 2.67 (dd, $^3J_{ea}$ = 8.4 Hz, ^2J = 15.0 Hz, 1H, C*H*CHPh), 2.38 (dd, $^3J_{aa}$ = 10.4 Hz, ^2J = 15.0 Hz, 1H, C*H*CHPh), 1.44 (s, 3H, CH_3), 1.18, 1.16 (2t, 6H, $2CH_2CH_3$).

[4R-(4α,6β)]-6-(1,1-Dimethoxyethyl)-6-morpholino-3,4-diphenyl-5,6-dihydro-4H-1,2-oxazine N-Oxide* (**10g**); mp 119–120 °C.

IR (Nujol): ν = 1590 ($C{=}\overset{+}{N}$), 1600, 1580 (Ph), 1105 cm^{-1} (C–O–C).

^{1}H NMR: δ = 7.68 (d, 2H, *o*-Ar–H), 7.28–7.20 (m, 8H, Ar–H), 4.17 (dd, $^3J_{ea}$ = 8.2 Hz, $^3J_{aa}$ = 10.4 Hz, 1H, C*H*Ph), 3.62 (m, 4H, CH_2OCH_2), 3.35, 3.34 (2s, 6H, $2OCH_3$), 3.28 (m, 2H, CH_2NCH_2), 3.03 (m, 2H, CH_2NCH_2), 2.64 (dd, ^3J = 8.2 Hz, ^2J = 15.0 Hz, 1H, C*H*CHPh), 2.38 (dd, ^3J = 10.4 Hz, ^2J = 15.0 Hz, 1H, C*H*CHPh), 1.40 (s, 3H, CH_3).

^{13}C NMR: δ = 141.6 (s), 131.6 (s), 129.0 (d), 128.7 (d), 128.4 (d), 128.1 (d), 127.7 (d), 127.0 (d), 104.6 (s), 99.9 (s), 68.6 (t), 50.1 (q), 48.4 (q), 47.7 (t), 41.5 (d), 33.9 (t), 18.6 (q).

Reaction with 1-Nitrocyclopentene:

cis- and trans-2-(3,3-Diethoxy-2-oxobutyl)-1-nitrocyclopentane (**5h**); purification by column chromatography gave **5h** as a 1:4 mixture of *cis*/*trans* isomers (oil, 65% yield).

IR (film): ν = 1725 (C=O), 1545, 1370 (NO_2), 1150 cm^{-1} (C–O–C).

^{1}H NMR: δ = 4.98 (dt, J_1 = 6.2 Hz, J_2 = 1.7 Hz, 0.2H, $CHNO_2$), 4.46 (dt, J_1 = 5.7 Hz, J_2 = 8.3 Hz, 0.8H, $CHNO_2$), 3.37 (dq, 2H, CH_2CH_3), 3.28 (m, 2H, CH_2CH_3), 2.80–2.50 (m, 3H, $CHCH_2CO$), 2.20–2.0 (m, 3H, ring CH_2), 1.8–1.6 (m, 3H, ring CH_2), 1.23, 1.22 (2 s, 3H, CH_3), 1.07, 1.06 (2 t, 6H, CH_2CH_3).

cis-**5h**:

^{13}C NMR: δ = 208.2 (s), 102.3 (s), 89.6 (d), 57.5 (2t), 40.6 (d), 38.4 (t), 30.8 (t), 29.6 (t), 22.8 (t), 20.9 (q), 15.3 (2q).

trans-**5h**:

^{13}C NMR: δ = 207.9 (s), 102.2 (s), 90.8 (d), 57.7 (2t), 41.5 (d), 41.5 (t), 31.9 (t), 31.5 (t), 23.8 (t), 20.6 (q), 15.3 (2q).

MS: m/z (%) = 228 ($M^{+\cdot}$ – OEt, 8), 181 (228 – HNO_2, 13), 153

(13), 135 (11), 125 (5), 118 (11), 117 [$CH_3C(OEt)_2^+$, 87], 89 (117 – C_2H_4, 50), 67 (28), 61 (89 – C_2H_4, 100), 43 (61 – H_2O, 69).

cis- and trans-2-(2,3-Dioxobutyl)-1-nitrocyclopentane (**6h**); mp 156–157 °C (dioxime; $MeOH/H_2O$).

$C_9H_{15}N_3O_4$	calc.	C 47.2	H 6.60	N 18.33
(229)	found	47.5	6.71	18.19

IR (film): $\nu = 1710$ (C=O), 1545, 1370 cm^{-1} (NO_2).

^{1}H NMR: $\delta = 5.07$ (dt, $J_1 = 2.0$ Hz, $J_2 = 6.6$ Hz, 0.2 H, $CHNO_2$), 4.58 (dt, $J_1 = J_2 = 6.2$ Hz, $J_3 = 7.8$ Hz, 0.8 H, $CHNO_2$), 2.95 (m, 2 H, CH_2CO), 2.90 (m, 0.8 H, $C\mathit{H}CH_2CO$), 2.83 (m, 0.2 H, $C\mathit{H}CH_2CO$), 2.35, 2.34 (2 s, 3 H, CH_3CO), 2.32–2.15 (m, 3 H, ring CH_2), 2.00–1.70 (m, 2 H, ring, CH_2), 1.40–1.20 (m, 1 H, ring CH).

cis-**6h**:

^{13}C NMR: $\delta = 196.7$ (s), 196.6 (s), 89.1 (d), 40.2 (d), 37.6 (t), 30.1 (t), 29.4 (t), 23.2 (q), 22.6 (t).

trans-**6h**:

^{13}C NMR: $\delta = 197.0$ (s), 196.7 (s), 90.3 (d), 41.0 (d), 39.2 (t), 31.7 (t), 31.6 (t), 23.5 (t), 23.2 (q).

MS: m/z (%) = 156 ($M^{+\cdot} - COCH_3$, 10), 109 ($M^{+\cdot} - COCH_3 - HNO_2$, 15), 81 (109 – 28, 27), 67 (18), 43 (100).

[*1R*-(1α,3aα,6aα)*]*-1-Hydroxy-1-methyl-6a-nitrohexahydro-1H-pentalen-2-one* (**11h**).

IR (film): $\nu = 3500$ (OH), 1755 (C=O), 1540, 1380 cm^{-1} (NO_2).

^{1}H NMR: $\delta = 3.47$ (m, W_H 21.6, 1 H, H-3a), 3.09 (dd, $J_{3\alpha 3\beta} = 19.0$ Hz, $J_{3\beta 3a} = 11.0$ Hz, 1 H, H-3β), 2.64 (m, 1 H, H-6β), 2.55 (bs, 1 H, OH), 2.29 (m, 1 H, H-5α), 2.08 (dd, $J_{3\alpha 3\beta} = 19.0$ Hz, $J_{3a3\alpha} = 6.8$ Hz, 1 H, H-3α), 1.92–1.70 (m, 3 H, 2 H-4, H-6α), 1.68–1.52 (m, 1 H, H-5β), 1.45 (s, 3 H, CH_3).

^{13}C NMR: $\delta = 212.0$ (s, C-2), 104.8 (s, C-6a), 79.1 (s, C-1), 41.1 (d, C-3a), 40.8 (t, C-3), 32.6 (t, C-6), 32.0 (t, C-4), 24.1 (t, C-5), 19.1 (q, CH_3).

[*1R*-(1α,3aβ,6aβ)*]*-1-Hydroxy-1-methyl-6a-nitrohexahydro-1H-pentalen-2-one* (**12h**).

IR (film): $\nu = 3500$ (OH), 1755 (C=O), 1540, 1380 cm^{-1} (NO_2).

^{1}H NMR: $\delta = 3.60$ (m, W_H 28.8, 1 H, H-3a), 3.04 (dd, $J_{3\alpha 3\beta} = 19.7$ Hz, $J_{3\beta 3a} = 11.7$ Hz, 1 H, H-3β), 2.91 (bs, 1 H, OH), 2.47 (dt, $J_{6\alpha 6\beta} = 15.5$ Hz, $^3J = 5.7$ Hz, 1 H, H-6β), 2.20 (m, 1 H, H-5β), 2.16 (dt, $J_{6\alpha 6\beta} = 15.5$ Hz, $^3J = 8.6$ Hz, 1 H, H-6α), 2.04 (dd, $J_{3\alpha 3\beta} = 19.7$ Hz, $J_{3\alpha 3\alpha} = 5.9$ Hz, 1 H, H-3α), 1.78–1.70 (m, 2 H, 2 H-4), 1.68–1.52 (m, 1 H, H-5α), 1.28 (s, 3 H, CH_3).

^{13}C NMR: $\delta = 212.3$ (s, C-2), 105.7 (s, C-6a), 81.0 (s, C-1), 39.8 (t, C-3), 39.0 (d, C-3a), 33.4 (t, C-6), 32.8 (t, C-4), 23.6 (t, C-5), 21.7 (q, CH_3).

MS of the mixture **11h, 12h**: m/z (%) = 111 ($M^{+\cdot} - NO_2 - CH_2CO$, 36), 81 (11), 67 (13), 43 (100).

Reaction with 1-Nitrocyclohexene

cis- and trans-3,3-Diethoxy-1-(2-nitrocyclohexyl)butan-2-one (**5i**):

IR (film): $\nu = 1725$ (C=O), 1540, 1360 (NO_2), 1150 cm^{-1} (C–O–C).

^{1}H NMR: $\delta = 4.67$ (quintet, $J = 5.1$ Hz, 0.1 H, $CHNO_2$), 4.30 (dt, $J_1 = J_2 = 11.3$ Hz, $J_3 = 3.8$ Hz, 0.9 H, $CHNO_2$), 3.43, 3.40 (2 m, 4 H, $C\mathit{H}_2CH_3$), 2.63–2.25 (m, 3 H, $CHCH_2CO$), 1.85–1.43 (m, 8 H, ring CH_2), 1.28 (s 0.3 H, CH_3), 1.25 (s, 2.7 H, CH_3), 1.13, 1.12 (2 t, 0.3 H, $CH_2C\mathit{H}_3$), 1.11, 1.10 (2 t, 2.7 H, $CH_2C\mathit{H}_3$).

cis-**5i**: ^{13}C NMR: $\delta = 207.8$ (s), 102.2 (s), 85.1 (d), 57.5 (2 t), 39.1 (t), 33.8 (d), 28.3 (t), 27.1 (t), 23.3 (t), 21.1 (t), 20.7 (q), 15.2 (q).

trans-**5i**: ^{13}C NMR: $\delta = 207.4$ (s), 102.1 (s), 89.7 (d), 57.6 (2 t), 40.5 (t), 36.5 (d), 31.8 (t), 30.3 (t), 24.6 (t), 24.3 (t), 20.5 (q), 15.2 (q).

MS: m/z (%) = 242 ($M^{+\cdot}$ – OEt, 7), 195 (242 – HNO_2, 5), 167 (7), 149 (11), 118 (11), 117 [$CH_3C(OEt)_2^+$, 88], 89 (117 – C_2H_4, 46), 67 (13), 61 (89 – C_2H_4, 100), 43 (61 – H_2O, 77).

cis- and trans-1-(2-Nitrocyclohexyl)butane-2,3-dione (**6i**); mp 151–152 °C (dioxime; $MeOH/H_2O$).

$C_{10}H_{17}N_3O_4$	calc.	C 49.4	H 7.04	N 17.27
(243)	found	49.5	7.06	17.08

IR (film): $\nu = 1710$ (C=O), 1545, 1370 cm^{-1} (NO_2).

^{1}H NMR: $\delta = 4.70$ (dt, $J_1 = J_2 = 4.1$ Hz, $J_3 = 6.8$ Hz, 0.1 H, $CHNO_2$), 4.33 (dt, $J_1 = J_2 = 11.2$ Hz, $J_3 = 3.9$ Hz, 0.9 H, $CHNO_2$), 2.75 (2 pseudo q, AB part of an ABX system, $J_{AB} = 18.1$ Hz, 2 H, CH_2CO), 2.52 (m, 1 H, $C\mathit{H}CH_2CO$), 2.34, 2.33 (2 s, 3 H, CH_3CO), 2.29–2.23 (m, 1 H, ring CH), 2.00–1.80 (m, 3 H, ring CH, CH_2), 1.75–1.69 (m, 1 H, ring CH), 1.49–1.28 (m, 2 H, ring CH_2), 1.26–1.08 (m, 1 H, ring CH).

cis-**6i**: ^{13}C NMR: $\delta = 196.9$ (s), 84.9 (d), 36.2 (t), 27.8 (t), 27.6 (t), 22.5 (t), 23.4 (q), 21.6 (t).

trans-**6i**: ^{13}C NMR: $\delta = 196.8$ (s), 196.7 (s), 89.6 (d), 38.7 (t), 36.6 (d), 31.7 (t), 30.7 (t), 24.5 (t), 24.1 (t), 23.4 (q).

MS: m/z (%) = 170 ($M^{+\cdot} - COCH_3$, 18), 123 ($M^{+\cdot} - COCH_3 - HNO_2$, 27), 95 (123 – 28, 45), 81 (86), 67 (27), 55 (14), 43 (100).

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