# Phenylation Reaction of α-Acylnitromethanes To Give 1,2-Diketone Monooximes: Involvement of Carbon Electrophile at the Position α to the Nitro Group

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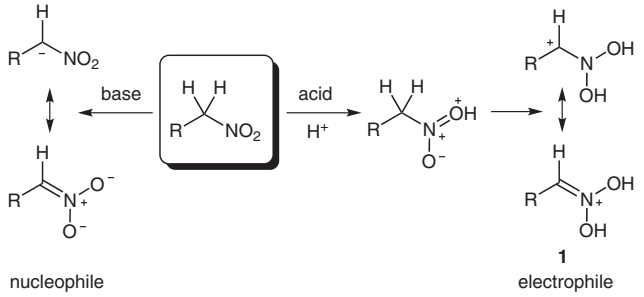
**Abstract:** The generality and the effects of substituents on phenylation reactions of α-acylnitromethanes catalyzed by trifluoromethanesulfonic acid have been studied. α-Aroylnitromethanes afforded benzil monooximes in good yield. In the case of aliphatic α-acylnitromethane, a similar phenylation reaction proceeded, but the yield of the phenylated 1,2-dione monooxime was low. These phenylation reactions represent examples of the generation of carbocation electrophiles at the α-position of a nitro group.

**Key words:** α-ketonitromethane, 1,2-dione monooxime, electrophilic aromatic substitutions, umpolung, protonation

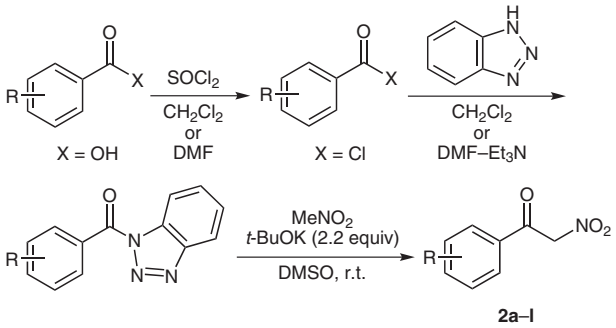
The generation of a cationic center at the α-position of a nitro group is a kind of umpolung (reverse polarity), because the protons at the α-position of the nitro group are acidic enough to be deprotonated, thereby generating a carbanion species that is able to act as a nucleophile (Scheme 1). The chemistry of carbanions derived from nitro compounds has been studied for a long time, and the synthetic usefulness of Henry-type reactions (nitroaldol reaction) and enhanced C-nucleophiles of α,α-doubly deprotonated primary nitroalkanes (nitroate dianions) is well established.[1] On the other hand, the chemistry of carbocations derived from nitro groups has not been extensively studied. The Nef and Meyer reactions in acidic media, which yield aldehydes/ketones and carboxylic acids, respectively, were among the earliest examples of the carbocation chemistry of nitro compounds.[2]

These named reactions involve a cationic carbon species at the α-position of the nitro group, i.e., an O-protonated *aci*-nitro species (**1**; Scheme 1), which is attacked by an oxygen nucleophile, such as water or sulfonate anion in sulfuric acid.[2] Friedel–Crafts type reaction of *aci*-nitro species **1** of nitroalkanes (R = alkyl group) with benzene, catalyzed by trifluoromethanesulfonic acid (TFSA), affords phenylated oximes in moderate to good yields.[3] While the substitution of an electron-withdrawing group (the R group), such as esters and ketones, facilitates the phenylation reaction, this reaction has been little explored.[3,4] In this paper we examine the generality and substituent effects of acid-catalyzed phenylation reactions of α-acylnitromethanes (**2**; Table 1), affording phenylated 1,2-diketone monooxime derivatives of type **3**.




**Scheme 1** Umpolung (reverse polarity) of a nitro group

A general synthetic method for generating α-acylnitromethanes was recently reported by Katritzky et al., involving the addition of a nitroate dianion, generated from nitromethane by the action of two equivalents of potassium *tert*-butoxide, to *N*-acylbenzotriazoles (Scheme 2).[5,6]




**Scheme 2** Preparation of α-acylnitromethanes

In the presence of TFSA, α-aroylnitromethanes reacted with benzene to give substituted benzil monooxime derivatives **3**. We optimized the reaction conditions (acid, co-solvent, reaction time, etc.) by using α-benzoylnitromethane **2a** as a representative example (Table 1). The reaction did not proceed even at reflux using trifluoroacetic acid (TFA; entries 1 and 2), whereas a large excess of TFSA (50 equiv with respect to the starting material **2a**) gave a low yield of the phenylated product (entry 7). The optimal reaction conditions involved the use of ten equivalents of TFSA and dichloromethane as a co-solvent; under these conditions, the reaction time was reduced to 20 minutes (entry 9).

The reaction showed apparent acidity dependence (Table 2). As the acidity of the acid medium increased, the

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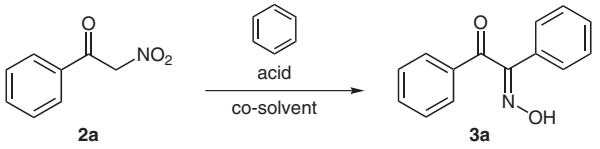
phenylation reaction started, and the yield of the product **3a** increased. Practically, however, the yield was maximized when the ratio of TFSA to TFA reached 45:55 (w/w) (entry 5), and slightly decreased in more acidic media (entries 6–8); this is probably due to formation of by-products arising from C–C bond cleavage: in neat TFSA, benzaldoxime (6%) and benzoic acid (5%) were formed.[3]

**Table 1** Optimization of Reaction Conditions[a]

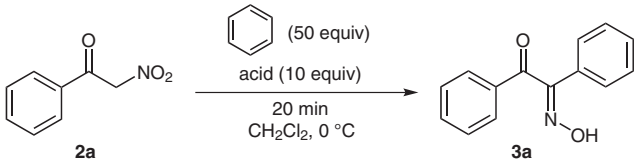



**2a** **3a**

| Entry | Acid (equiv) | Benzene (equiv) | Co-solvent | Temp (°C) | Time (min) | Yield of **3a** (%)[b] |
|---|---|---|---|---|---|---|
| 1 | TFA (100) | 10 | none | reflux (72 °C) | 96 h | 0 |
| 2 | TFA (100) | 10 | $CH_2Cl_2$ | 0 | 24 h | 0 |
| 3 | TFSA (10) | 10 | none | 0 | 60 | 52 |
| 4 | TFSA (10) | 50 | none | 0 | 60 | 59 |
| 5 | TFSA (10) | 10 | $CH_2Cl_2$ | 0 | 120 | 63 |
| 6 | TFSA (10) | 50 | $CH_2Cl_2$ | 0 | 60 | 72 |
| 7 | TFSA (50) | 10 | $CH_2Cl_2$ | 0 | 60 | 33 |
| 8 | TFSA (10) | 50 | $CH_2Cl_2$ | 0 | 60 | complex |
| 9 | TFSA (10) | 50 | $CH_2Cl_2$ | 0 | 20 | 73[c] |

[a] Reaction conditions: **2a** (1.5 mmol), co-solvent (1.5 mL), benzene, acid, 0 °C.
[b] Isolated yield after column chromatography.
[c] Ohwada et al. reported that a 71% yield of **3a** was obtained under similar reaction conditions [TFSA (10 equiv), benzene (30 equiv) and $CH_2Cl_2$ as a co-solvent].[3]

**Table 2** Acidity Dependence of the Reaction[a]

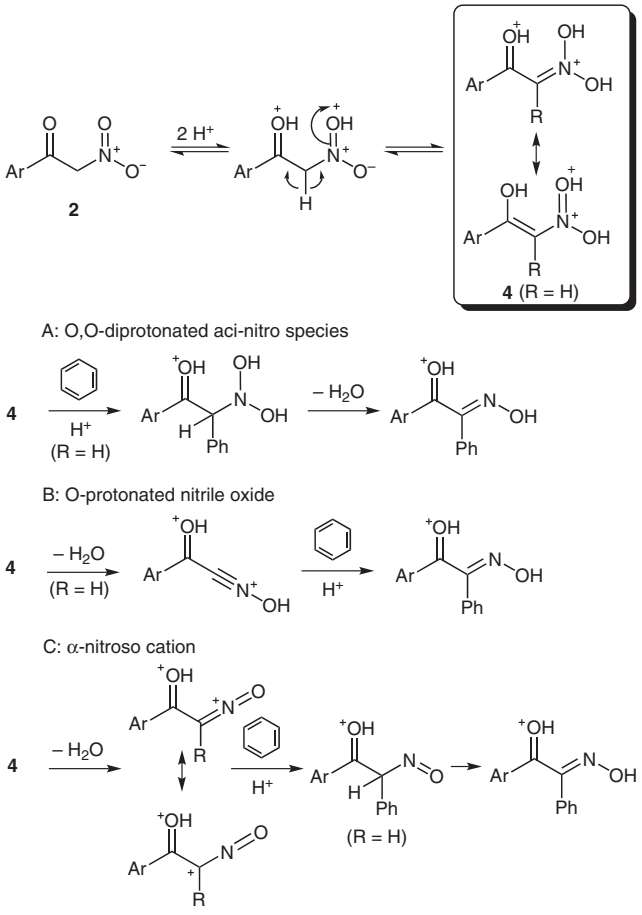



**2a** **3a**

| Entry | Ratio of TFSA/TFA (w/w) | Acidity ($-H_0$) | Yield of **3a** (%)[b] |
|---|---|---|---|
| 1 | 0:100 | 2.7 | 0 |
| 2 | 1:99 | 7.8 | 0 |
| 3 | 10:90 | 9.6 | 8 |
| 4 | 30:70 | 11.1 | 71 |
| 5 | 45:55 | 11.6 | 83 |
| 6 | 70:30 | 12.4 | 70 |
| 7 | 90:10 | 13.0 | 72 |
| 8 | 100:0 | 14.1 | 73 |

[a] Reaction conditions: α-nitroketone (1.5 mmol), acid (10 equiv), benzene (50 equiv), $CH_2Cl_2$ (1.5 mL).
[b] Isolated yield.

We studied the substituent effects in this reaction (Table 3). Aromatic electrophilic substituents (halogens and electron-withdrawing groups, **2b**–**h**) seemed to facilitate the reaction, whereas aromatic electron-donating substituents (**2i** or **2j**) reduced the reaction rate. In the case of TFSA, the yield was higher than those found in TFSA–TFA mixtures [45:55 (w/w)]. Probably, the remote electron-donating substituent decreases the electron-withdrawing ability of the whole aroyl group, thereby attenuating the electron-deficiency of the carbon electrophilic center of **4** (Scheme 3). On the other hand, an aliphatic keto-substituent (**2k** or **2l**) significantly reduced the yield of the phenylated product. Formation of by-products arising from C–C bond cleavage was enhanced [see Table 3, footnotes (c) and (d)]. We checked the stability of the phenylated oxime products in the acidic reaction medium (Table 4), in order to examine whether the reduction of the yields in TFSA may be due to the instability of the product oxime in the strongly acidic medium. However, as shown in Table 4, when the isolated oxime products were exposed to the reaction conditions, and then worked up in the usual manner, they were recovered in high yields, thus excluding involvement of degradation reac-




**Scheme 3** Proposed reaction mechanisms



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tions such as Beckmann rearrangement of the product oxime.

Several reaction mechanisms have been proposed for this reaction and, in view of the requirement for strongly acidic media, all of them involve dicationic species, i.e., O,O-diprotonated *aci*-nitro species (**A**),[3] O-protonated nitrile oxide (**B**),[7] and α-nitroso cation (**C**) (Scheme 3). Mechanism **C**, i.e., transformation of the nitro group into a nitroso group, is relevant to the mechanism of the Nef reaction under reducing conditions (e.g., catalyzed by $TiCl_3$).[8] These reaction mechanisms (**A**–**C**) differ from each other with respect to the order in which events such as elimination of water and removal of the α-proton take place. Furthermore, the formation of by-products (benzaldoxime and substituted benzoic acid) through C–C bond cleavage can be accounted for in terms of the involvement of the phenylated nitroso (or equivalent) intermediate (found in intermediates **A** and **C**, Scheme 4 and see below). However, mechanism **C** seems to be ruled out (see below), and so mechanism **A** is considered the most likely candidate.

**Table 3** Substituent Effect in the Phenylation Reaction

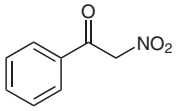
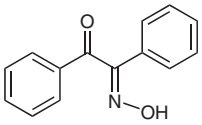
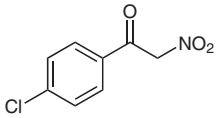
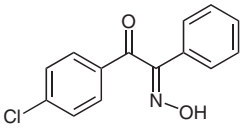
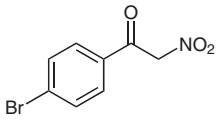
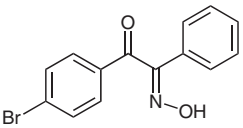
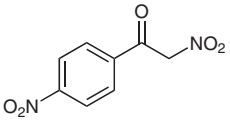
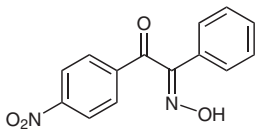
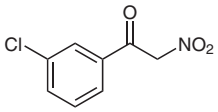
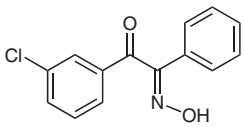
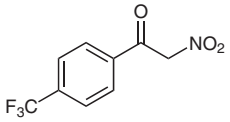
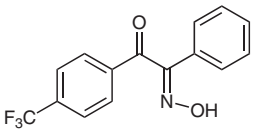
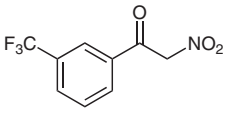
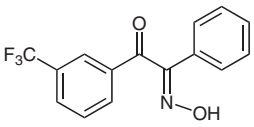
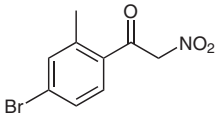
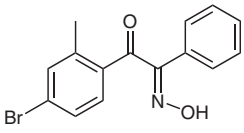
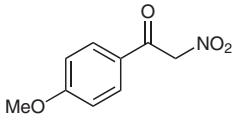
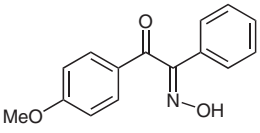
| Entry | Substrate **2** | Temp (°C) | Time (min) | Product **3**[a] | Yield (%) | |
|---|---|---|---|---|---|---|
| | | | | | TFSA | TSFA–TFA (45:55) |
| **a** |  | 0 | 20 |  | 73 | 83 |
| **b** |  | 0 | 20 |  | 67 | 80 |
| **c** |  | 0 | 20 |  | 66[b] | 83 |
| **d** |  | 0 | 20 |  | 70 | 74 |
| **e** |  | 0 | 20 |  | 67 | 81 |
| **f** |  | 0 | 20 |  | 65 | 76 |
| **g** |  | 0 | 20 |  | 86 | 90 |
| **h** |  | 0 | 20 |  | 75 | 78 |
| **i** |  | 0 | 110 |  | 68 | 41 |



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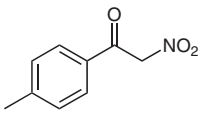
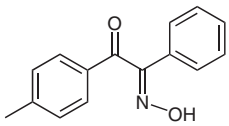
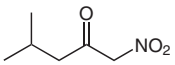
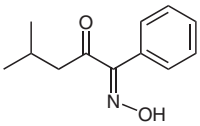
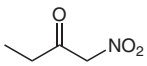
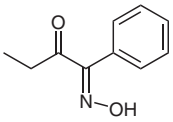
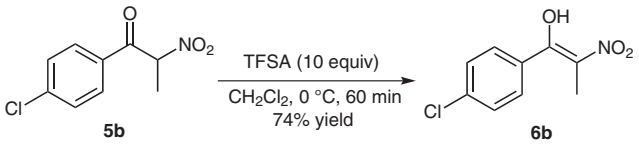
**Table 3** Substituent Effect in the Phenylation Reaction (continued)

| Entry | Substrate **2** | Temp (°C) | Time (min) | Product **3**[a] | Yield (%) | |
|---|---|---|---|---|---|---|
| | | | | | TFSA | TSFA–TFA (45:55) |
| **j** |  | 0 | 80 |  | 70 | 62 |
| **k** |  | 0 | 20 |  | 21[c] | 18[c] |
| **l** |  | 0 | 20 |  | 28[d] | 25[d] |

[a] A mixture of *anti*- and *syn*-oximes was obtained in some cases, e.g. in the case of **3b**, a mixture of oxime isomers (72:28) was obtained in the reaction using TFSA–TFA (45:55).
[b] Benzaldoxime (11%) and 4-bromobenzoic acid (13%) were obtained as by-products.
[c] Benzaldoxime was isolated in 21% yield in neat TFSA, or 10% yield in TFSA–TFA (45:55).
[d] Benzaldoxime was isolated in 55% yield in neat TFSA, or 19% yield in TFSA–TFA (45:55).

Finally, we carried out a similar phenylation reaction with α-aroylnitroethane (a secondary nitroalkane), such as **5b**, however, a complex mixture was formed. Interestingly, in the presence of TFSA, **5b** yielded the enol tautomer **6b** as a stable compound in 74% yield upon aqueous work-up (Scheme 5).[9]

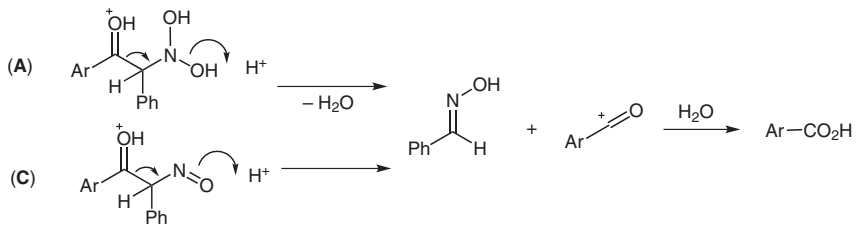



**Scheme 5**

This result is consistent with facile deprotonation of the α-proton of the nitro group in TFSA to generate **4** (R = $CH_3$, Scheme 3), which is a stabilized cation in this case. This observation may exclude mechanism **C** (Scheme 3) from further consideration in the present phenylation reaction.

In summary, we have established the generality and studied the substituent effects of phenylation reactions of α-acylnitromethane.[10] Aromatic α-aroylnitromethanes afforded benzil monooximes in good yield. Generally, in the case of aromatic electron-withdrawing substituents, regioselective synthesis of these monooximes from benzil (1,2-diketone) derivatives will be difficult, because the electrophilicity of the carbonyl group adjacent to the electron-deficient aromatic ring is enhanced.

In the case of aliphatic α-acylnitromethanes, a similar phenylation reaction occurs, although the yield of phenylated 1,2-dione monooxime is low. The present phenylation reactions represent examples of cationic electrophiles generated at the α-position of a nitro group.




**Scheme 4**

Melting points were determined with a Yanaco micro melting-point apparatus and are uncorrected. $^1$H- (400 MHz) and $^{13}$C NMR (100 MHz) spectra were recorded on a Bruker Avance 400 instrument. Chemical shifts were calibrated with 1% TMS as an internal standard or with the solvent peak, and are shown in ppm; coupling constants are shown in hertz (Hz). The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, dd = double doublet, dt = double triplet, m = multiplet, br s = broad singlet and br d = broad doublet. Low-resolution mass spectra (LRMS) and high-resolution mass spectra (HRMS) were recorded on a Bruker microTOF (ESI) instrument.

**Synthesis of *N*-Benzoylbenzotriazole from Acid Chloride; Typical Procedure**

To a solution of benzotriazole (2.62 g, 22 mmol) in anhydrous DMF (80 mL), $Et_3N$ (3.08 mL, 22 mmol) and benzoyl chloride (20 mmol) were added at 0 °C (ice-water bath) under an Ar atmosphere, and the reaction was stirred for 2 h at 0 °C. The mixture was poured into aq HCl (2 N, 160 mL) and extracted with EtOAc (3 × 200 mL). The organic layer was washed with brine (2 × 50 mL) and dried over



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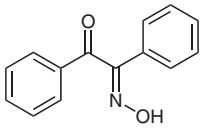
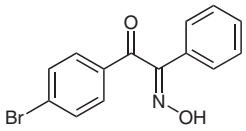
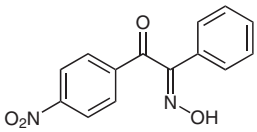
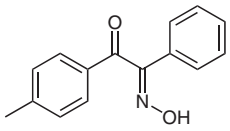
**Table 4** Recovery of Phenylated Oxime after Exposure to Acidic Reaction Conditions[a]

| Product | Recovery (%)[b] |
|---|---|
|  **3a** | 87 |
|  **3c** | 90 |
|  **3d** | 94 |
|  **3j** | 90 |

[a] Reaction conditions: oxime (0.2 mmol), TFSA (10 equiv), $CH_2Cl_2$ (2 mL) at 0 °C, 90 min.
[b] Isolation yield.

$Na_2SO_4$. The solvent was evaporated and the crude residue was purified by column chromatography (typically EtOAc–*n*-hexane, 1:5), to give *N*-benzoylbenzotriazole as a white solid (73% yield).

**Synthesis of *N*-(4-Trifluoromethyl)benzoylbenzotriazole from the Acid; Typical Procedure**

To a solution of benzotriazole (32 mmol, 4 equiv, 3.81 g) in anhydrous $CH_2Cl_2$ (30 mL), a solution of thionyl chloride (0.96 g, 8 mmol) in anhydrous $CH_2Cl_2$ (10 mL) was added dropwise at r.t. over 3 min. After 30 min stirring at r.t., 4-trifluoromethylbenzoic acid (8 mmol, 1.52 g) was added in one portion to the pale-yellow solution (white precipitates appeared immediately). After 4 h stirring at r.t., the solid was filtered off and washed with $CH_2Cl_2$. The combined organic layer (150 mL) was washed with aq NaOH (0.4 M, 2 × 50 mL) and $H_2O$ (100 mL), and dried over $MgSO_4$. The organic solvent was evaporated to give a pale-yellow solid, which was purified by column chromatography (silica gel; EtOAc–*n*-hexane, 1:8) to give *N*-(4-trifluoromethyl)benzoylbenzotriazole as a while solid (1.85 g, 80% yield).

**Synthesis of α-Acylnitromethanes 2a–l; Typical Procedure**

The synthesis of the α-acylnitromethanes was carried out as described in the literature.[5,6]

A mixture of $MeNO_2$ (11 mmol, 1.1 equiv) and *t*-BuOK (22 mmol, 2.2 equiv) in DMSO (50 mL) was stirred for 10 min under Ar at 16 °C (water bath). A solution of *N*-benzoylbenzotriazole (10 mmol, 1.0 equiv) in DMSO (50 mL) was added dropwise to the above solution at 16 °C (water bath), and the mixture was stirred at r.t. for 17 h. The mixture was poured into aq HCl (2 N, 100 mL), and then extracted with EtOAc (3 × 100 mL). The organic layer was washed with $H_2O$ (2 × 50 mL), dried over $Na_2SO_4$ and the solvent was evaporated to give a residue, which was purified by recrystallization (40% yield) to give **2a**.

**Benzoylnitromethane (2a)**

Recrystallized from $CH_2Cl_2$–*n*-hexane.

Colorless prisms; mp 103–105 °C.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 8.0 Hz, 2 H), 7.69 (t, *J* = 7.6 Hz, 1 H), 7.54 (t, *J* = 7.6 Hz, 2 H), 5.89 (s, 2 H).

$^{13}$C NMR (100 MHz, DMSO-$d_6$): δ = 188.9, 135.3, 133.9, 129.6, 128.9, 83.3.

Anal. Calcd for $C_8H_7NO_3 \cdot 1/12H_2O$: C, 57.66; H, 4.33; N, 8.40. Found: C, 57.74; H, 4.35; N, 8.38.

**4-Chlorobenzoylnitromethane (2b)**

Recrystallized from $CH_2Cl_2$–MeOH–*n*-hexane.

Colorless needles; mp 144–145 °C.

$^1$H NMR (400 MHz, DMSO-$d_6$): δ = 7.94 (d, *J* = 8.4 Hz, 2 H), 7.68 (d, *J* = 8.8 Hz, 2 H), 6.53 (s, 2 H).

$^{13}$C NMR (100 MHz, DMSO-$d_6$): δ = 188.0, 140.3, 132.6, 130.8, 129.7, 83.2.

Anal. Calcd for $C_8H_6ClNO_3 \cdot 1/4H_2O$: C, 47.08; H, 3.21; N, 6.86. Found: C, 47.07; H, 3.28; N, 6.82.

**4-Bromobenzoylnitromethane (2c)**

Recrystallized from EtOAc–*n*-hexane.

Colorless prisms; mp 142–143 °C.

$^1$H NMR (400 MHz, DMSO-$d_6$): δ = 7.87–7.81 (m, 4 H), 6.53 (s, 2 H).

$^{13}$C NMR (100 MHz, DMSO-$d_6$): δ = 188.3, 132.9, 132.7, 130.8, 129.6, 83.2.

Anal. Calcd for $C_8H_6BrNO_3 \cdot 1/4H_2O$: C, 38.66; H, 2.64; N, 5.64. Found: C, 38.76; H, 2.69; N, 5.73.

**4-Nitrobenzoylnitromethane (2d)**

Recrystallized from EtOH–*n*-hexane.

Yellow prisms; mp 148–149 °C.

$^1$H NMR (400 MHz, DMSO-$d_6$): δ = 8.39 (d, *J* = 8.4 Hz, 2 H), 8.12 (d, *J* = 8.4 Hz, 2 H), 6.61 (s, 2 H).

$^{13}$C NMR (100 MHz, DMSO-$d_6$): δ = 188.3, 151.2, 138.5, 130.4, 124.5, 83.4.

Anal. Calcd for $C_8H_6N_2O_5$: C, 45.72; H, 2.88; N, 13.33. Found: C, 45.65; H, 3.09; N, 13.35.

**3-Chlorobenzoylnitromethane (2e)**

Recrystallized from EtOH–*n*-hexane.

Colorless needles; mp 91–93 °C.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 2.0 Hz, 1 H), 7.89 (d, *J* = 7.6 Hz, 1 H), 7.82 (d, *J* = 8.4 Hz, 1 H), 7.62 (dt, *J* = 3.2, 8.0 Hz, 1 H), 6.56 (s, 2 H).

$^{13}$C NMR (100 MHz, DMSO-$d_6$): δ = 188.0, 135.7, 134.9, 134.4, 131.5, 128.7, 127.5, 83.3.

Anal. Calcd for $C_8H_6ClNO_3$: C, 48.14; H, 3.03; N, 7.02. Found: C, 48.11; H, 3.22; N, 7.06.

**4-Trifluoromethylbenzoylnitromethane (2f)**

The crude product was subjected to column chromatography (EtOAc–*n*-hexane, 2:3) then recrystallized from EtOAc–*n*-hexane.

Yield: 75%; colorless plates; mp 94–95 °C.

$^1$H NMR (400 MHz, DMSO-$d_6$): δ = 8.13 (d, *J* = 8.0 Hz, 2 H), 7.99 (d, *J* = 8.0 Hz, 2 H), 6.60 (s, 2 H).



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$^{13}$C NMR (100 MHz, DMSO-$d_6$): δ = 188.5, 137.1, 134.2, 128.8, 126.5, 125.4, 83.4.

Anal. Calcd for $C_9H_6F_3NO_3$: C, 46.36; H, 2.59; N, 6.01. Found: C, 46.37; H, 2.88; N, 5.99.

**3-Trifluoromethylbenzoylnitromethane (2g)**
Recrystallized from $CH_2Cl_2$–*n*-hexane.

Pale-yellow cubes; mp 79–80 °C.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 8.14 (br s, 1 H), 8.08 (d, *J* = 8.4 Hz, 1 H), 7.96 (d, *J* = 8.4 Hz, 1 H), 7.72 (t, *J* = 8.4 Hz, 1 H), 5.91 (s, 2 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 184.7, 134.1, 132.2, 131.5, 131.4, 131.4, 130.2, 125.1, 81.0.

Anal. Calcd for $C_9H_6F_3NO_3$: C, 46.36; H, 2.59; N, 6.01. Found: C, 46.33; H, 2.81; N, 6.11.

**4-Bromo-*o*-methylbenzoylnitromethane (2h)**
Recrystallized from EtOH–*n*-hexane.

Colorless plates; mp 108 °C.

$^1$H NMR (400 MHz, DMSO-$d_6$): δ = 7.75 (d, *J* = 8.4 Hz, 1 H), 7.66 (s, 1 H), 7.62 (d, *J* = 84 Hz, 1 H), 6.41 (s, 2 H), 2.46 (s, 3 H).

$^{13}$C NMR (100 MHz, DMSO-$d_6$): δ = 190.4, 142.3, 135.3, 132.5, 132.1, 129.6, 127.7, 84.4.

Anal. Calcd for $C_9H_8BrNO_3$: C, 41.17; H, 3.26; N, 5.33. Found: C, 41.26; H, 3.24; N, 5.12.

**4-Methoxybenzoylnitromethane (2i)**
Recrystallized from EtOH–*n*-hexane.

Colorless fine needles; mp 154–155 °C.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 7.2 Hz, 2 H), 7.00 (d, *J* = 8.8 Hz, 2 H), 5.83 (s, 2 H), 3.90 (s, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 183.9, 165.0, 130.7, 126.4, 114.5, 81.0, 55.7.

Anal. Calcd for $C_9H_9NO_4$: C, 55.39; H, 4.65; N, 7.18. Found: C, 55.38; H, 4.71; N, 7.40.

**4-Methylbenzoylnitromethane (2j)**
Recrystallized from EtOH–*n*-hexane.

Colorless needles; mp 139–140 °C.

$^1$H NMR (400 MHz, DMSO-$d_6$): δ = 7.83 (d, *J* = 8.0 Hz, 2 H), 7.40 (d, *J* = 8.4 Hz, 2 H), 6.50 (s, 2 H), 2.40 (s, 3 H).

$^{13}$C NMR (100 MHz, DMSO-$d_6$): δ = 188.3, 146.1, 131.4, 130.1, 129.0, 83.2, 21.8.

Anal. Calcd for $C_9H_9NO_3$: C, 60.33; H, 5.06; N, 7.82. Found: C, 60.36; H, 5.10; N, 7.83.

**1-Nitro-4-methylpenta-2-one (2k)**
Colorless oil.

$^1$H NMR (400 MHz, DMSO-$d_6$): δ = 5.80 (s, 2 H), 2.44 (d, *J* = 6.8 Hz, 2 H), 2.04 (hept, *J* = 6.8 Hz, 1 H), 0.87 (d, *J* = 6.4 Hz, 6 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 195.8, 83.6, 49.1, 24.5, 22.3.

HRMS (ESI): *m*/*z* [M – H]$^-$ calcd. for $C_6H_{10}NO_3^-$: 144.0661; found: 144.0664.

**1-Nitrobutan-2-one (2l)**
Colorless oil.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 5.30 (s, 2 H), 2.57 (q, *J* = 7.2 Hz, 2 H), 1.13 (t, *J* = 7.2 Hz, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 196.8, 83.0, 33.9, 7.0.

MS (ESI): *m*/*z* = 118.0 [M + H]$^+$.

Anal. Calcd for $C_4H_7NO_3$: C, 41.03; H, 6.83; N, 11.96. Found: C, 40.87; H, 5.91; N, 12.04.

**Reaction of α-Acylnitromethanes with Benzene in Acid; General Procedure**
To a solution of **2a–l** (1.5 mmol) and benzene (6.5 mL, 75 mmol, 50 equiv) in anhydrous $CH_2Cl_2$ (1.5 mL), TFSA (1.3 mL, 15 mmol, 10 equiv) was added at 0 °C (ice-water bath) under Ar, and the mixture was stirred for 20 min. The mixture was poured into ice-water (100 mL) and the mixture was extracted with $CHCl_3$ (3 × 100 mL). The organic layer was washed with brine (2 × 50 mL), and dried over $Na_2SO_4$. The solvent was evaporated and the resulting crude product was purified by flash column chromatography (typically with EtOAc–*n*-hexane, 1:10→2:3) to give **3a–l**. The reaction yields are shown in Table 3.

**Benzilmonooxime (3a)**
Colorless prisms; mp 137–138 °C.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 8.0 Hz, 1 H), 8.00 (d, *J* = 8.0 Hz, 2 H), 7.63–7.57 (m, 3 H), 7.49–7.43 (m, 5 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 191.4, 155.6, 136.4, 133.5, 130.4, 130.0, 129.4, 129.1, 128.4, 128.2.

Anal. Calcd for $C_{14}H_{11}NO_2$: C, 74.65; H, 4.92; N, 6.22. Found: C, 74.49; H, 5.17; N, 6.29.

**4-Chlorobenziloxime (3b)**
Colorless prisms; mp 125–126 °C.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 8.8 Hz, 2 H), 7.83 (br s, 1 H, OH), 7.58–7.56 (m, 2 H), 7.44–7.41 (m, 5 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 190.2, 155.6, 140.0, 134.8, 131.8, 130.1, 129.3, 128.9, 128.7, 128.3.

Anal. Calcd for $C_{14}H_{10}ClNO_2$: C, 64.75; H, 3.88; N, 5.39. Found: C, 64.60; H, 4.09; N, 5.39.

**4-Bromobenziloxime (3c)**
Colorless prisms; mp 134 °C.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 8.31 (br s, 1 H), 7.89 (d, *J* = 6.8 Hz, 2 H), 7.61 (d, *J* = 6.8 Hz, 2 H), 7.59–7.56 (m, 2 H), 7.46–7.44 (m, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 190.4, 155.6, 135.2, 131.9, 131.7, 130.1, 129.3, 128.8, 128.8, 128.3.

Anal. Calcd for $C_{14}H_{10}BrNO_2$: C, 55.29; H, 3.31; N, 4.61. Found: C, 55.39; H, 3.45; N, 4.67.

**4-Nitrobenziloxime (3d)**
Colorless prisms; mp 183–184 °C.

$^1$H NMR (400 MHz, $CD_3OD$): δ = 8.35 (d, *J* = 8.0 Hz, 2 H), 8.16 (d, *J* = 8.8 Hz, 2 H), 7.54–7.45 (m, 5 H).

$^{13}$C NMR (100 MHz, DMSO-$d_6$): δ = 191.6, 155.2, 149.7, 143.8, 131.5, 130.0, 129.9, 129.7, 128.3, 123.6.

Anal. Calcd for $C_{14}H_{10}N_2O_4$: C, 62.22; H, 3.73; N, 10.37. Found: C, 61.96; H, 3.91; N, 10.34.

**3-Chlorobenziloxime (3e)**
Colorless prisms; mp 137 °C.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 8.00 (br s, 1 H), 7.97 (br s, 1 H), 7.90 (d, *J* = 8.0 Hz, 1 H), 7.58–7.56 (m, 3 H), 7.47–7.42 (m, 4 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 190.1, 155.6, 138.1, 134.6, 133.2, 130.3, 130.1, 129.7, 129.4, 128.8, 128.5, 128.3.



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Anal. Calcd for $C_{14}H_{10}ClNO_2$: C, 64.75; H, 3.88; N, 5.39. Found: C, 64.73; H, 4.06; N, 5.36.

**4-Trifluoromethylbenziloxime (3f)**
Colorless prisms; mp 137–138 °C.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 8.10 (d, *J* = 8.4 Hz, 2 H), 8.05 (br s, 1 H), 7.74 (d, *J* = 8.4 Hz, 2 H), 7.58–7.55 (m, 2 H), 7.48–7.46 (m, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 190.5, 155.8, 139.6, 134.4, 130.6, 130.2, 129.3, 128.5, 128.3, 125.3, 125.2.

Anal. Calcd for $C_{15}H_{10}F_3NO_2$: C, 61.44; H, 3.44; N, 4.78. Found: C, 61.29; H, 3.49; N, 4.73.

**3-Trifluoromethylbenziloxime (3g)**
Recrystallized from *n*-hexane.

Colorless needles; mp 100–101 °C.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 8.28 (br s, 1 H), 8.24 (br s, 1 H, OH), 8.19 (br d, *J* = 7.6 Hz, 1 H), 7.84 (br d, *J* = 7.6 Hz, 1 H), 7.61 (t, *J* = 7.6 Hz, 1 H), 7.58–7.55 (m, 2 H), 7.48–7.45 (m, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 190.1, 155.7, 137.3, 133.6, 133.6, 131.0, 130.2, 129.6, 129.4, 129.0, 128.3, 127.3.

Anal. Calcd for $C_{15}H_{10}F_3NO_2$: C, 61.44; H, 3.44; N, 4.78. Found: C, 61.22; H, 3.52; N, 4.71.

**4-Bromo-*o*-methylbenziloxime (3h)**
Recrystallized from $CHCl_3$–*n*-hexane.

Colorless needles; mp 139 °C.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 8.01 (br s, 1 H), 7.55–7.42 (m, 8 H), 2.44 (s, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 193.8, 156.8, 139.9, 136.5, 134.1, 131.1, 130.2, 129.5, 128.6, 128.3, 128.2, 125.8, 20.3.

Anal. Calcd for $C_{15}H_{12}Br_3NO_2 \cdot 1/4H_2O$: C, 55.83; H, 3.90; N, 4.34. Found: C, 55.59; H, 3.86; N, 4.32.

**4-Methoxybenziloxime (3i)**
Colorless oil.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 9.24 (br s, 1 H), 8.01 (d, *J* = 8.8 Hz, 2 H), 7.61 (m, 2 H), 7.39 (m, 3 H), 6.91 (d, *J* = 8.4 Hz, 2 H), 3.83 (s, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 190.0, 164.1, 155.3, 132.9, 129.9, 129.5, 129.4, 129.1, 128.2, 113.8, 55.5.

Anal. Calcd for $C_{15}H_{13}NO_3 \cdot 1/4H_2O$: C, 69.35; H, 5.24; N, 5.39. Found: C, 69.08; H, 5.25; N, 5.38.

**4-Methylbenziloxime (3j)**
Recrystallized from $CH_2Cl_2$–*n*-hexane.

Colorless prisms; mp 108–109 °C.

$^1$H NMR (400 MHz, DMSO-$d_6$): δ = 12.37 (s, 1 H), 7.83 (d, *J* = 8.0 Hz, 2 H), 7.50–7.45 (m, 2 H), 7.44–7.43 (m, 3 H), 7.34 (d, *J* = 8.0 Hz, 2 H), 2.32 (s, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 191.0, 155.6, 144.6, 133.8, 130.5, 129.9, 129.4, 129.3, 129.2, 128.2, 21.7.

Anal. Calcd for $C_{15}H_{13}NO_2$: C, 75.30; H, 5.48; N, 5.85. Found: C, 75.06; H, 5.74; N, 5.87.

**4-Methyl-1-phenyl-1,2-pentanedione-1-oxime (3k)**
Recrystallized from *n*-hexane–$CH_2Cl_2$.

Colorless cubes; mp 126–126.5 °C.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.80 (br s, 1 H), 7.46–7.41 (m, 3 H), 7.33–7.31 (m, 2 H), 2.81 (d, *J* = 6.8 Hz, 2 H), 2.26 (hept, *J* = 6.8 Hz, 1 H), 0.98 (d, *J* = 6.4 Hz, 6 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 198.8, 156.7, 150.4, 129.1, 128.8, 127.9, 47.0, 25.2.

Anal. Calcd for $C_{12}H_{15}NO_2 \cdot 1/8H_2O$: C, 69.46; H, 7.41; N, 6.75. Found: C, 69.43; H, 7.10; N, 6.88.

**1-Phenyl-1,2-butanedione-1-oxime (3l)**
Colorless powder; mp 114–115 °C.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 8.23 (s, 1 H), 7.43–7.40 (m, 3 H), 7.34–7.31 (m, 2 H), 2.95 (q, *J* = 7.2 Hz, 2 H), 1.16 (t, *J* = 7.2 Hz, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 199.2, 156.5, 129.5, 129.1, 128.2, 127.9, 31.6, 8.0.

Anal. Calcd for $C_{10}H_{11}NO_2 \cdot 1/8H_2O$: C, 66.93; H, 6.32; N, 7.81. Found: C, 67.20; H, 6.30; N, 7.72.

**Acid-Catalyzed Tautomerization of α-Aroylnitroethane**
To a solution of **5b** (1.0 mmol, 213.6 mg) in anhydrous $CH_2Cl_2$ (1.0 mL), TFSA (0.87 mL, 10 mmol, 10 equiv) was added at 0 °C (ice-water bath) under Ar, and the mixture was stirred for 60 min. The mixture was poured into ice-water and the mixture was extracted with $CHCl_3$ (3 × 100 mL). The organic layer was washed with brine (2 × 50 mL), and dried over $Na_2SO_4$. The solvent was evaporated and the resulting crude product was purified by flash column chromatography (EtOAc–*n*-hexane, 1:1) to give **6b** (159 mg, 74% yield).

**α-(4-Chlorobenzoyl)nitroethane (5b)**
Colorless fine needles; mp 77–77.5 °C.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.90 (d, *J* = 8.8 Hz, 2 H), 7.51 (d, *J* = 8.8 Hz, 2 H), 6.09 (q, *J* = 7.2 Hz, 1 H), 1.84 (d, *J* = 7.2 Hz, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 188.5, 141.5, 131.9, 130.2, 129.6, 84.7, 16.0.

Anal. Calcd for $C_9H_8ClNO_3$: C, 50.60; H, 3.77; N, 6.56. Found: C, 50.32; H, 3.88; N, 6.43.

**1-(4-Chlorophenyl)-1-hydroxy-2-nitroprop-1-ene (6b)**
Recrystallized from *n*-hexane–$CH_2Cl_2$.

Colorless plates; mp 144–145 °C.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 9.46 (br s, 1 H), 8.00 (d, *J* = 8.8 Hz, 2 H), 7.44 (d, *J* = 8.4 Hz, 2 H), 2.12 (s, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 164.0, 140.9, 131.3, 129.1, 128.7, 124.9, 19.7.

Anal. Calcd for $C_9H_8ClNO_3 \cdot 1/8H_2O$: C, 50.07; H, 3.85; N, 6.49. Found: C, 50.18; H, 3.83; N, 6.29.

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(9) Detection of $^1$H-NOE between the $CH_3$ group and the aromatic *ortho*-protons supported the assignment of the *E*-geometry of the olefin of **6b**.
(10) The reaction of **2a** also proceeded with substituted benzenes, *p*-xylene and anisole, to give the corresponding oximes in comparable yields (see ref 3).

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