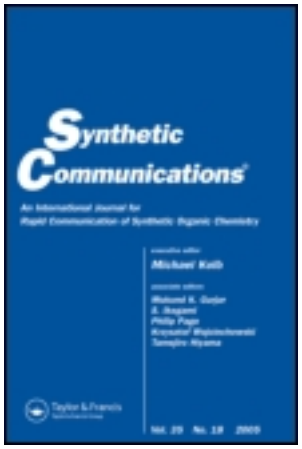

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New Preparation of (Z)-1-Phenyl-3-cyano-2-propen-1-ones

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NEW PREPARATION OF (*Z*)-1-PHENYL-3-CYANO-2-PROPEN-1-ONES

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GRAPHICAL ABSTRACT

R_1 = Ph, alkyl, CH_2CO_2Me

Abstract *Reaction of γ-phenyl-β,γ-unsaturated hydroxamates with bis(collidine)-bromine(I) hexafluorophosphate led to the formation of cyclic bromo imidates. Reaction of these with triethylamine led to the formation of 3-cyano-2-propen-1-ones with good yields by a fragmentation reaction.*

Keywords Aryl compound; bromonium; 5-endo cyclization; enone; nitrile

INTRODUCTION

We are engaged in a program concerning the study of the reactivity of bis (collidine)bromine(I) hexafluorophosphate as an electrophile.[1] Recently, we examined the reaction of β,γ-unsaturated hydroxamates with this bromo reagent. The reactivity of unsaturated hydroxamates with electrophiles has been only briefly reported in the literature. Formation of lactams was observed using bromine or *N*-bromosuccinimide.[2] On the other hand, a mixture of γ-butyrolactams and immonium salts was generally obtained with selenium reagents.[3]

RESULTS

The hydroxamate **3** was prepared in two steps in good yield from the commercially available *trans*-styrilacetic acid **1**, by reaction of the acid chloride with hydroxylamine followed by acetylation. Reaction of this compound with bis(collidine)

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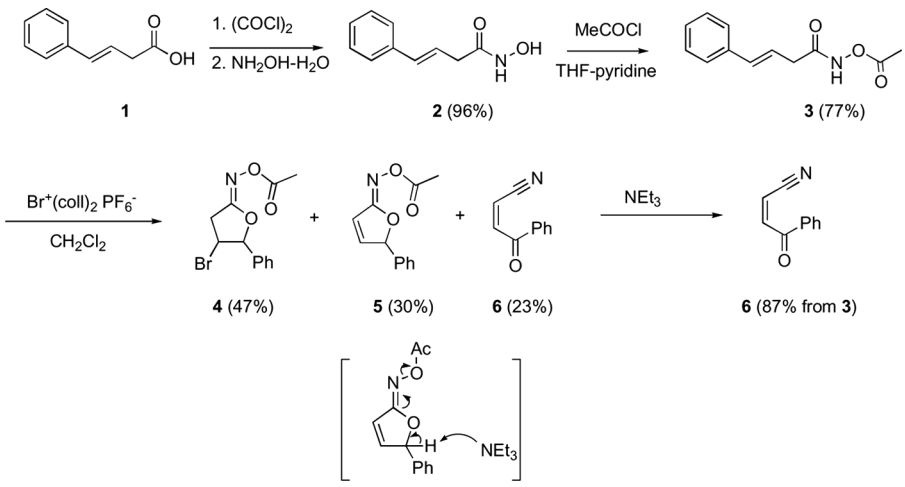
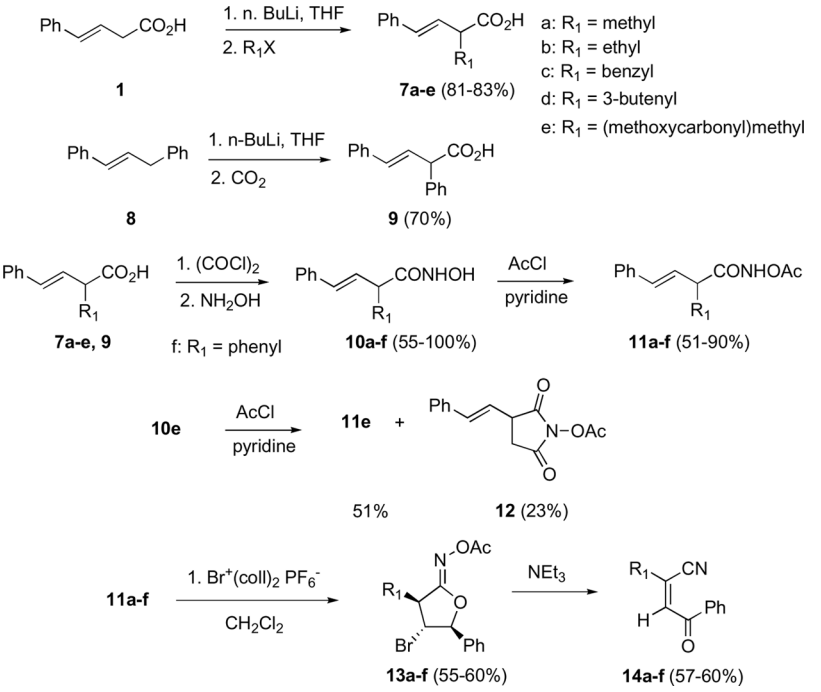


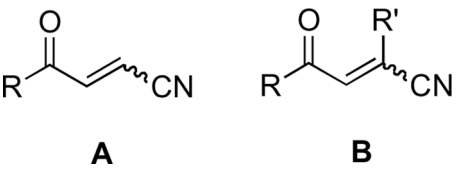
Scheme 1. Preparation of 4-oxo-4-phenylbut-2-enenitrile **6**.

bromine(I) hexafluorophosphate in dichloromethane at room temperature led to the formation of a mixture of the cyclic bromo imine **4**, the corresponding HBr elimination product **5**, and the unsaturated nitrile **6** (Scheme 1). Large degradation of these products was observed during their purification over silica gel. To avoid the yield loss during their purification, the crude reaction product was reacted with 1 equivalent of triethylamine: (*Z*)-4-oxo-4-phenylbut-2-enenitrile **6** was obtained in good yield as a unique product. This compound was characterized from its NMR and infrared (IR) spectra and by comparison of its spectra with those reported in the literature.[4,5] The formation of compound **6** can probably be explained by a Beckmann fragmentation,[6] initiated by abstraction of the hydrogen in α of the oxygen atom as indicated in Scheme 1.

Then, we decided to examine the case of 2-substituted styrilacetic acids. These different compounds have been prepared as reported in Scheme 2. 2-Subtituted derivatives **7a–e** were obtained by alkylation of styryl acid, and (*E*)-2,4-diphenylbut-3-enoic acid **9** has been obtained by carbonation of (*E*)-1,3-diphenylprop-1-ene. The hydroxamates were then obtained by reaction of the corresponding acid chlorides with hydroxylamine, followed by acetylation. In the case of the formation of the hydroxamate **11e**, a side reaction was observed, leading to the minor formation of the succinimide **12**. Reaction of these compounds with bis(collidine)bromine(I) hexafluorophosphate in dichloromethane at room temperature led to the formation of the few stable cyclic bromo imidates. In all cases, only one diastereoisomer was formed, and its stereochemistry was deduced from our previous results concerning the cyclization of the corresponding acids.[7] After reaction with triethylamine, these cyclic bromo imidates led to the formation of 3-cyano-2-propen-1-ones. The structures of these compounds were easily established from their spectra data. Only one isomer was formed. In the case of compound **14f** (R_1 = phenyl), the stereochemistry was clearly established by comparison of its spectra with those reported in the literature. The stereochemistries observed in the formation of **6** and **14f** led us to



Scheme 2. Preparation of 1-phenyl-3-cyano-2-propen-1-ones **14a–f**.



Scheme 3. Substituted *β*-cyano enones.

propose also a *Z* stereochemistry for compounds **14a–e**. This family of compounds is already reported in the literature (see the experimental section). Formation of β-cyano disubstituted[4,8] (type A, Scheme 3) and trisubstituted[9] enones (type B) has been reported. Because enones have an important place in organic synthesis,[10] we think this new formation of these highly functionalized compounds can be interesting in synthesis.

EXPERIMENTAL

All reactions were carried out under argon. Purification of products was carried out by normal-phase flash chromatography.

(*E*)-*N*-Hydroxy-4-phenylbut-3-enamide 2

Oxalyl chloride (0.2 mL, 2.275 mmol, 1.75 eq.) was added dropwise to a CH_2Cl_2 solution (5 mL) of commercial (*E*)-4-phenylbut-3-enoic acid **1** (0.210 g, 1.3 mmol) cooled at 0 °C. The solution was stirred one night at rt and then concentrated under vacuum. An aqueous solution of hydroxyamine (4.5 mL of a 2.5 M solution prepared from an equimolar mixture of $N^+H_3OH\ Cl^-$ and NaOH, 7 eq.) was added to the acid chloride. There was formation of a white solid, which was isolated by filtration. The filtrate was extracted twice with CH_2Cl_2(10 mL). The organic phases were dried ($MgSO_4$) and concentrated under vacuum. The residue was added to the previous solid. Yield: 0.221 g, 96%. Mp 135–137 °C. ^{1}H NMR (MeOH-d^4, 250 MHz) δ: 7.33–7.11 (m, 5H), 6.47 (d, $J = 16.0$ Hz, 1H), 6.23 (dt, $J = 7.0$ and 16.0 Hz, 1H), 2.97 (d, $J = 7.0$ Hz, 2H). ^{13}C NMR (MeOH-d^4, 62.9 MHz) δ: 169.6, 136.9, 133.4, 128.4, 127.2, 126.0, 122.0, 36.6. IR (MeOH-d^4, cm^{-1}): 3344, 3031, 1650. HR MS: calculated for $C_{10}H_{11}NNaO_2$ ($M + Na^+$): 200.0687. Found: 200.0690.

(3*E*)-*N*-(Acetoxy)-4-phenylbut-3-enamide 3

Pyridine (30 μL, 1.06 eq.) was added to a tetrahydrofuran (THF) solution (10 mL) of hydroxamic acid **2** (69 mg, 0.39 mmol) cooled at 0 °C in 10 min. The solution was stirred 20 min at rt, and acetyl chloride (40 μL, 1.06 eq.) was added dropwise. After 2 h at rt, ether (5 mL) was added, and the homogenous organic solution was washed successively with water (5 mL), aqueous 0.5 M HCl solution (5 mL), and saturated NaCl solution (5 mL). The organic phase was dried ($MgSO_4$) and concentrated under vacuum to give a white solid, which was used without further purification for the next step. Yield: 66 mg, 77%. Mp 131–133 °C. ^{1}H NMR ($CDCl_3$, 360 MHz) δ: 9.0 (br. s, 1H), 7.38–7.25 (m, 5H), 6.59 (d, $J = 15.8$ Hz, 1H), 6.29 (dt, $J = 15.8$ and 7.4 Hz, 1H), 3.25 (d, $J = 7.3$ Hz, 2H), 2.22 (s, 3H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 169.3, 168.7, 136.3, 135.0, 128.6, 127.9, 126.3, 120.4, 37.5, 18.2. IR (CH_2Cl_2, cm^{-1}): 3148, 2964, 1792, 1662. HR MS: calculated for $C_{12}H_{13}NNaO_3$ ($M + Na^+$): 242.0793. Found: 242.0803.

Reaction of Hydroxamate 3 with Bis(collidine)bromine(I) Hexafluorophosphate

Bis(collidine)bromine(I) hexafluorophosphate[11] (307 mg, 0.66 mmol) was added to a dichloromethane solution (10 mL) of hydroxamate **3** (131 mg, 0.6 mmol). After 2 h at rt, the solvent was removed under vacuum. The ^{1}H NMR of the crude reaction mixture showed the presence of three products: the bromo imidate **4** (47%), the unsaturated imidate **5** (30%), and the nitrile **6** (23%). Purification of this mixture by liquid chromatography over silica gel led to intensive degradations. Only small amounts of these compounds were isolated.

(2*Z*)-4-Bromo-5-phenyldihydrofuran-2(3*H*)-one *O*-Acetyloxime 4

Oil. ^{1}H NMR ($CDCl_3$, 250 MHz) δ: 7.37–7.20 (m, 5H), 5.66 (d, $J = 4.8$ Hz, 1H), 4.29 (ddd, $J = 4.8$, 5.8 and 7.0 Hz, 1H), 3.40 (dd, $J = 17.5$ and 7.0 Hz, 1H), 3.12 (dd,

$J = 17.5$ and 5.8 Hz, 1H), 2.17 (s, 3H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 168.0, 162.2, 135.1, 129.5, 129.1, 125.4, 92.3, 46.1, 37.0, 19.3. IR (film, cm^{-1}): 2902, 1767, 1679. HR MS: calculated for $C_{12}H_{12}BrNNaO_3$ ($M + Na^+$): 319.9898. Found: 319.9899.

(2*Z*)-5-Phenyl-2(5*H*)-furanone *O*-Acetyloxime 5

^1H NMR ($CDCl_3$, 250 MHz) δ: 7.37–7.20 (m, 5H), 7.04 (d, $J = 5.7$ Hz, 1H), 6.34 (d, $J = 5.7$ Hz, 1H), 6.29 (br. s, 1H), 2.15 (s, 3H).

(*Z*)-4-Oxo-4-phenylbut-2-enenitrile 6

After reaction of hydroxamate **3** with bis(collidine)bromine(I) hexafluorophosphate, triethylamine (2 eq.) was added to the reaction mixture. After stirring for 2 h at rt, the mixture was concentrated under vacuum, and the residue was purified by liquid chromatography over silica gel to give compound **6**[4,5] as a white solid (mp 77 °C, 87%). ^1H NMR ($CDCl_3$, 360 MHz) δ: 7.97 (d, $J = 7.2$ Hz, 2H), 7.64 (d, $J = 11.5$ Hz, 1H), 7.63 (m, 1H), 7.54 (dd, $J = 7.2$ and 7.2 Hz, 2H), 6.00 (d, $J = 11.5$, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 186.6, 141.7, 135.4, 134.2, 128.9, 128.6, 115.4, 108.8. IR (CH_2Cl_2, cm^{-1}): 3084, 3054, 2965, 2928, 1671, 1603, 1579, 908, 732. HR MS: calculated for $C_{10}H_7NNaO$ ($M + Na^+$): 180.0425. Found: 180.0427.

Preparation of Acids 7a–e

These compounds have been prepared by alkylation of the anion formed by reaction of (*E*)-4-phenylbut-3-enoic acid **1** with butyl lithium.[12]

(*E*)-2-Methyl-4-phenylbut-3-enoic acid 7a[13]. Yield: 61%. ^1H NMR ($CDCl_3$, 250 MHz) δ (ppm): 11.00 (bs, 1H), 7.27–7.42 (m, 5H), 6.63 (d, $J = 16.1$ Hz, 1H), 6.41 (dd, $J = 15.9$ and 7.75 Hz, 1H), 3.45 (dd, $J = 14.5$ and 7.4 Hz, 1H), 1.52 (d, $J = 6.9$ Hz, 3H). ^{13}C NMR ($CDCl_3$, 63 Hz) δ (ppm): 181.2, 136.6, 131.6, 128.4 (2C), 127.8, 127.5, 126.3 (2C), 42.9, 17.1. IR (CH_2Cl_2) υ (cm^{-1}): 3300, 3027, 2979, 2936, 1706, 1415, 1213, 965, 693. LR MS: 194.0 ($M + NH_4^+$, 100).

(*E*)-2-Ethyl-4-phenylbut-3-enoic acid 7b[12]. Yield: 81%. ^1H NMR ($CDCl_3$, 250 MHz) δ (ppm): 11.71 (bs, 1H), 7.55–7.17 (m, 5H), 6.59 (d, $J = 15.9$ Hz, 1H), 6.27 (dd, $J = 15.9$ and 8.9 Hz, 1H), 3.18 (dd, $J = 16.0$ and 7.3 Hz, 1H), 1.98 (septuplet, 7.3 Hz, 1H), 1.76 (septuplet, 7.4 Hz, 1H), 1.06 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR ($CDCl_3$, 63 Hz) δ (ppm): 180.0, 136.4, 132.5, 128.2 (2C), 127.3, 126.5, 126.1 (2C), 50.9, 25.4, 11.4. IR (CH_2Cl_2) υ (cm^{-1}): 3200, 2934, 1702, 1268, 966, 745, 692. LR MS: 208.0 ($M + NH_4^+$, 100).

(*E*)-2-Benzyl-4-phenylbut-3-enoic acid 7c[14]. Yield: 81%. ^1H NMR ($CDCl_3$, 250 MHz) δ (ppm): 11.35 (bs, 1H), 7.64–7.18 (m, 10H), 6.52 (d, $J = 15.9$ Hz, 1H), 6.31 (dd, $J = 15.9$ and 8.7 Hz, 1H), 3.59 (dd, $J = 15.7$ and 7.6 Hz, 1H), 3.30 (dd, $J = 13.7$ and 7.5 Hz, 1H), 3.05 (dd, $J = 13.7$ and 7.3 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75.5 Hz) δ (ppm): 179.9, 138.1, 136.4, 133.2, 129 (2C), 128.4 (2C), 127.7 (2C), 126.5, 126.3 (2C), 125.9 (2C), 51.1, 38.5. IR (CH_2Cl_2) υ (cm^{-1}): 3200, 2957, 1692, 1455, 1413, 1290, 965, 754, 696. LR MS: 270.0 ($M + NH_4^+$, 100).

(*E*)-2-Styrylhex-5-enoic acid 7d. Yield: 81%. ^{1}H NMR ($CDCl_3$, 250 MHz) δ (ppm): 12.09 (bs, 1H), 7.58–7.21 (m, 5H), 6.61 (d, $J = 15.9$ Hz, 1H), 6.27 (dd, $J = 15.8$, 9 Hz, 1H), 5.89 (m, 1H), 5.18 (t, $J = 12.4$ Hz, 2H), 3.32 (dd, $J = 15.5$ and 7.8 Hz, 1H), 2.35–2.16 (m, 2H), 2.16–1.85 (m, 2H). ^{13}C NMR ($CDCl_3$, 75.5 Hz) δ (ppm): 180.2, 137.2, 136.4, 132.8, 128.3 (2C), 127.5, 126.4, 126.2 (2C), 115.4, 48.7, 31.2, 30.9. IR (CH_2Cl_2) υ (cm^{-1}): 3200, 2977, 1706, 1641, 1450, 1416, 1287, 966, 914, 746, 693. LR MS: 234.0 ($M + NH_4^+$, 100).

(*E*)-2-((Methoxycarbonyl)methyl)-4-phenylbut-3-enoic acid 7e. Yield: 83%. ^{1}H NMR ($CDCl_3$, 250 MHz) δ (ppm): 10.9 (bs, 1H), 7.50–7.19 (m, 5H), 6.63 (d, $J = 15.9$ Hz, 1H), 6.24 (dd, $J = 15.9$ and 8.4 Hz, 1H), 3.84–3.64 (m, 4H), 2.99 (dd, $J = 16.7$ and 8.5 Hz, 1H), 2.71 (dd, $J = 16.7$ and 5.9 Hz, 1H). ^{13}C NMR ($CDCl_3$, 62.9 Hz) δ (ppm): 178.4, 171.6, 136.2, 133.7, 128.5 (2C), 127.9, 126.4 (2C), 124.5, 51.9, 44.7, 35.9. IR (CH_2Cl_2) υ (cm^{-1}): 3200, 3025, 2957, 2936, 1732, 1696, 1423, 1298, 1164, 968, 743, 693. LR MS: 235.0 ($M + H^+$, 20), 252.0 ($M + NH_4^+$, 100).

(*E*)-2,4-Diphenylbut-3-enoic Acid 9

This acid has been prepared, as previously reported,[15] by carbonation of the anion formed by reaction of 1,3-diphenyl-1-propene **8**[16] with *n*-butyl lithium using carbon dioxide (70%).

Preparation of *N*-Hydroxyamides 10a–f

These compounds were obtained by the procedure reported for the preparation of compound **2**.

(*E*)-*N*-Hydroxy-2-methyl-4-phenylbut-3-enamide 10a. Oil. Yield: 93%. ^{1}H NMR ($CDCl_3$, 250 MHz) δ (ppm): 8.41–8.15 (m, 2H), 7.52–7.09 (m, 5H), 6.57 (d, $J = 15.9$ Hz, 1H), 6.22 (dd, $J = 15.8$ and 8.0 Hz, 1H), 3.34–3.07 (m, 1H), 1.44 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR ($CDCl_3$, 62.9 Hz) δ (ppm): 171.2, 136.3, 132.6, 128.4 (2C), 127.7, 127.5, 126.3 (2C), 43.9, 17.2. IR (CH_2Cl_2) υ (cm^{-1}): 3179, 3020, 2902, 1634, 1536, 1353, 909, 734, 699. LR MS: 192.1 ($M + H^+$, 40), 209.1 ($M + NH_4^+$, 13).

(*E*)-2-Ethyl-*N*-hydroxy-4-phenylbut-3-enamide 10b. White solid, mp 107 °C. Yield: 99%. ^{1}H NMR ($CDCl_3$, 250 MHz) δ (ppm): 8.30 (m, 2H), 7.53–7.16 (m, 5H), 6.52 (d, $J = 15.8$ Hz, 1H), 6.16 (dd, $J = 15.8$ and 8.7 Hz, 1H), 2.80 (m, 1H), 1.60 (m, 2H), 0.90 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR ($CDCl_{3-}$, 62.9 Hz) δ (ppm): 171.8, 136.3, 133.6, 128.6 (2C), 127.9, 126.3 (3C), 49.5, 25.3, 11.6. IR (CH_2Cl_2) υ (cm^{-1}): 3669, 3024, 2928, 1623, 1496, 1096, 983, 737, 691. LR MS: 206.0 ($M + H^+$, 100), 223.0 ($M + NH_4^+$, 32).

(*E*)-2-Benzyl-*N*-hydroxy-4-phenylbut-3-enamide 10c. Yellow solid, mp 125.5 °C. Yield: 81%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 11.35 (s, 1H), 7.64–7.18 (m, 10H), 6.52 (d, $J = 15.9$ Hz, 1H), 6.31 (dd, $J = 15.9$ and 8.7 Hz, 1H), 3.59 (dd, $J = 15.9$ and 7.6 Hz, 1H), 3.30 (dd, $J = 13.7$ and 7.6 Hz, 1H), 3.05 (dd, $J = 13.7$ and 7.3 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75.5 Hz) δ (ppm): 179.9, 138.1,

136.4, 133.2, 129 (2C), 128.4 (2C), 127.7 (2C), 126.5, 126.3 (2C), 125.9 (2C), 51.1, 38.5. IR (CH_2Cl_2) υ (cm^{-1}): 2957, 1692, 1455, 1413, 1290, 965, 754, 696. LR MS: 270.0 ($M + NH_4^+$, 100).

(*E*)-*N*-Hydroxy-2-styrylhex-5-enamide 10d. White solid, mp 48–49 °C. Yield: 93%. ^{1}H NMR ($CDCl_3$, 360 MHz) δ (ppm): 9.00 (bs, 2H), 7.29 (m, 5H), 6.47 (d, $J = 15.6$ Hz, 1H), 6.13 (dd, $J = 15$, 8 Hz, 1H), 5.74 (m; 1H), 5.01 (dd, $J = 16.7$ and 8.3 Hz, 2H), 2.96 (bs, 1H), 2.15–1.86 (m, 3H), 1.70 (s, 1H). ^{13}C NMR ($CDCl_3$, 75.5 Hz) δ (ppm): 171.9, 137.3, 136.3, 133.5, 128.6 (2C), 127.8, 126.4, 126.3 (2C), 115.5, 46.8, 30.9 (2C). IR (CH_2Cl_2) υ (cm^{-1}): 3697, 3182, 2922, 1629, 1525, 1265, 965, 749, 693. LR MS: 232.0 ($M + H^+$, 100), 249.1 ($M + NH_4^+$, 13).

(*E*)-Methyl 3-(Hydroxycarbamoyl)-5-phenylpent-4-enoate 10e. Oil. Yield: 55%. ^{1}H NMR ($CDCl_3$, 250 MHz) δ (ppm): 9.60 (bs, 2H), 7.55–7.16 (m, 5H), 6.50 (bs, 1H), 6.10 (bs, 1H), 3.50 (m, 3H), 3.00–2.50 (m, 3H). ^{13}C NMR ($CDCl_3$, 62.9 Hz) δ (ppm): 173.8, 172.4, 136, 135.8, 128.5 (2C), 127.9, 126.6 (2C), 124.9, 52.0, 43.2, 35.8. IR (CH_2Cl_2) υ (cm^{-1}): 3182, 3024, 2921, 1656, 1545, 1369, 908, 765, 657. LR MS: 250.1 ($M + H^+$, 55), 267.1 ($M + NH_4^+$, 13).

(3*E*)-*N*-Hydroxy-2,4-diphenylbut-3-enamide 10f. White solid. Yield: 100%. ^{1}H NMR (MeOH-d^4, 360 MHz) δ: 7.40–7.20 (m, 10H), 6.70–6.20 (m, 2H), 4.51 (d, $J = 6.8$ Hz, 1H). ^{13}C NMR (MeOH-d^4, 62.9 MHz) δ: 169.1, 137.5, 136.2, 133.3, 130.0, 128.8, 128.6, 127.5, 127.2, 126.4, 122.8, 48.5. HR MS: calculated for $C_{16}H_{16}NO_2$ ($M + H^+$): 254.1181. Found: 254.1185.

Preparation of *N*-Acetoxyamides 11a–f

These compounds were obtained by the procedure reported for the preparation of compound **3**.

(3*E*)-*N*-(Acetoxy)-2-methyl-4-phenyl-3-butenamide 11a. Oil. Yield: 90%. ^{1}H NMR ($CDCl_3$, 250 MHz) δ (ppm): 8.99 (s, 1H), 7.49–7.22 (m, 5H), 6.62 (d, $J = 15.84$ Hz, 1H), 6.28 (dd, $J = 15.9$ and 8.3 Hz, 1H), 3.45–3.19 (m, 1H), 2.25 (s, 3H), 1.45 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR ($CDCl_3$, 62.9 Hz) δ (ppm): 168.7 (2C), 136.2, 132.7, 128.6 (2C), 127.9, 127.6, 126.3 (2C), 42.1, 18.2, 17.2. IR (CH_2Cl_2) υ (cm^{-1}): 3683, 3152, 2978, 1794, 1651, 1656, 1530, 1370, 1176, 976, 852. LR MS: 234.0 ($M + H^+$, 91), 251.1 ($M + NH_4^+$, 54).

(3*E*)-*N*-(Acetoxy)-2-ethyl-4-phenyl-3-butenamide 11b. White solid, mp 126 °C. Yield: 87%. ^{1}H NMR ($CDCl_3$, 250 MHz) δ (ppm): 9.16 (s, 1H), 7.51–7.12 (m, 5H), 6.58 (d, $J = 15.9$ Hz, 1H), 6.23 (dd, $J = 15.9$ and 8.8 Hz, 1H), 3.18 (dd, $J = 16.0$ and 7.3 Hz, 1H), 2.24 (s, 3H), 1.99 (septuplet, $J = 7.1$ Hz, Hz, 1H), 1.72 (septuplet, $J = 7.4$ Hz, 1H), 1(t, $J = 7.4$ Hz, 3H). ^{13}C NMR ($CDCl_3$, 62.9 Hz) δ (ppm): 168.7 (2C), 136.3, 133.5, 128.5 (2C), 127.8, 126.5, 126.3 (2C), 49.7, 25.3, 18.2, 11.5. IR (CH_2Cl_2) υ (cm^{-1}): 3685, 3159, 2932, 1792, 1651, 1526, 1449, 1189, 972, 734. LR MS: 248 ($M + H^+$, 51), 265.1 ($M + NH_4^+$, 89).

(3*E*)-*N*-(Acetoxy)-2-benzyl-4-phenyl-3-butenamide 11c. White solid, mp 128 °C. Yield: 90%. ^{1}H NMR ($CDCl_3$, 250 MHz) δ (ppm): 9.00 (s, 1H), 7.48–7.11 (m, 10H), 6.50 (d, $J = 15.9$ Hz, 1H), 6.27 (dd, $J = 15.9$ and 8.3 Hz, 1H), 3.57–3.18

(m, 2H), 3.16–2.84 (m, 1H), 2.20 (s, 3H). ^{13}C NMR ($CDCl_3$, 90.5 Hz) δ (ppm): 170.7, 168.4, 138.2, 136.2, 133.7, 129.1 (2C), 128.5 (2C), 127.8 (2C), 126.5, 126.3 (2C), 125.9 (2C), 50.0, 38.3, 18.2. IR (CH_2Cl_2) υ (cm^{-1}): 3682, 3155, 2978, 2885, 1794, 1665, 1522, 1495, 1179, 1042, 970, 908, 848, 734, 706. LR MS: 310.0 ($M+H^+$, 100), 327 ($M+NH_4^+$, 17).

(*E*)-*N*-Acetoxy-2-styrylhex-5-enamide 11d. Oil. Yield: 86%. ^{1}H NMR ($CDCl_3$, 250 MHz) δ (ppm): 9.51 (s, 1H), 7.57–7.11 (m, 5H), 6.57 (d, $J=15.9$ Hz, Hz, 1H), 6.23 (dd, $J=15.9$ and 8.9 Hz, 1H), 5.82 (m, 1H), 5.08 (dd, $J=20.6$ and 5.3 Hz, 2H), 3.16 (dd, $J=15.0$ and 7.5 Hz, 1H), 2.35–1.96 (m, 6H), 1.80 (m, 1H. ^{13}C NMR ($CDCl_3$, 75.5 Hz) δ (ppm): 171.5, 168.6, 137.5, 136.4, 133.5, 128.63 (2C), 127.9, 126.6, 126.4 (2C), 115.6, 47.1, 31.1, 30.9, 18.2. IR (CH_2Cl_2) υ (cm^{-1}): 3081, 3026, 2928, 2852, 1797, 1669, 1496, 1449, 1368, 1177, 1028, 968, 852, 745, 693. LR MS: 274.1 ($M+H^+$, 57), 291.1 ($M+NH_4^+$, 13).

Preparation of Hydroxamate 11e

In the conditions used for the preparation of compound **2**, a mixture of two products separable by liquid chromatography was obtained: the hydroxamate **11e** and the succinimide **12**.

(*E*)-Methyl 3-(Acetoxycarbamoyl)-5-phenylpent-4-enoate 11e

Oil. Yield: 51%. ^{1}H NMR ($CDCl_3$, 360 MHz) δ (ppm): 9.51 (bs, 1H), 7.55–7.21 (m, 5H), 6.66 (d, $J=15.9$ Hz, 1H), 6.26 (dd, $J=15.9$ and 8.8 Hz, 1H), 3.72(bs, 4H), 3.04 (dd, $J=16.9$ and 8.3 Hz, 1H), 2.69 (dd, $J=16.9$ and 5.7 Hz, 1H), 2.30–2.11 (bs, 3H). ^{13}C NMR ($CDCl_3$, 62.9 Hz) δ (ppm): 172.0 (2C), 168.4, 136, 134.2, 128.5 (2C), 128, 126.4 (2C), 124.8, 51.9, 43.5, 36.1, 18.1. IR (CH_2Cl_2) υ (cm^{-1}): 3790, 3232, 2789, 1794, 1694, 1665, 1660, 1420, 1375, 1150, 986, 865. LR MS: 292.1 ($M+H^+$, 85), 310.2 ($M+NH_4^+$, 100).

1-Acetoxy-3-(*E*)-2-styryl-2,5-pyrrolidinedione 12

Oil: 23%. ^{1}H NMR ($CDCl_3$, 360 MHz) δ (ppm): 7.51–7.22 (m, 5H), 6.66 (d, $J=15.9$ Hz, 1H), 6.19 (dd, $J=15.9$ and 7.4 Hz, 1H), 3.90–3.67 (bs, 1H), 3.14 (dd, $J=18.1$ and 9.1 Hz, 1H), 2.79 (dd, $J=18.1$ and 4.7 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR ($CDCl_3$, 62.9 Hz) δ (ppm): 169.8, 168.1, 165.4, 135.5, 134.7, 128.8 (2C), 128.5, 126.4 (2C), 122.4, 40.6, 32.3, 17.4. LR MS: 260.0 ($M+H^+$, 5), 277.0 ($M+NH_4^+$, 100).

(3*E*)-*N*-(Acetoxy)-2,4-phenylbut-3-enamide 11f

White solid, mp 117–118 °C. Yield: 85%. ^{1}H NMR ($CDCl_3$, 250 MHz) δ: 8.93 (br.s, 1H), 7.50–7.20 (m, 10H), 6.70–6.40 (m, 2H), 4.47 (d, $J=6.8$ Hz, 1H), 2.23 (s, 3H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 168.8, 168.7, 136.2, 135.2, 134.8, 130.1, 128.9, 128.7, 127.9, 127.4, 126.8, 120.5, 47.4, 18.4. HR MS: calculated for $C_{18}H_{18}NO_3$ ($M+H^+$): 296.1287. Found: 296.1287.

Reaction of Hydroxamates 11a–f with Bis(collidine)bromine(I) Hexafluorophosphate

Bis(collidine)bromine(I) hexafluorophosphate[11] (307 mg, 0.66 mmol) was added to a dichloromethane solution (10 mL) of hydroxamate (0.6 mmol). After 2 h at rt, the solvent was removed under vacuum. The residue was purified by liquid chromatography over silica gel (except for **13e–f)**.

(2*Z*,3*R**,4*S**,5*R**)-4-Bromo-3-methyl-5-phenyl-dihydro-2(3*H*)-furanone *O*-Acetyloxime 13a

Oil: 60%. ^{1}H NMR ($CDCl_3$, 360 MHz) δ (ppm): 7.53–7.37 (m, 5H), 5.42 (d, $J = 9.21$ Hz, 1H), 3.84 (dd, $J = 10.6$ and 9.3 Hz, 1H), 3.34 (m, 1H), 2.17 (s, 3H), 1.51 (d, $J = 6.75$ Hz, 3H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 167.9, 164.3, 134.5, 129.6, 128.8, 126.7, 126.5 (2C), 89.1, 53.4, 45, 19.3, 13.3. LR MS: 312.0 ($M + H^+$, 100).

(2*Z*,3*R**,4*S**,5*R**)-4-Bromo-3-ethyl-5-phenyl-dihydro-2(3*H*)-furanone *O*-Acetyloxime 13b

Oil. ^{1}H NMR ($CDCl_3$, 360 MHz) δ (ppm): 7.60–7.25 (m, 5H), 5.44 (d, $J = 8.60$ Hz, 1H), 4.00 (dd, $J = 9.8$ and 8.7 Hz, 1H), 3.34 (td, $J = 9.8$ and 5.8 Hz, 1H), 2.17 (s, 3H), 2.12–1.78 (m, 2H), 1.14 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 169.9, 166.6, 138.3, 129 (2C), 128.8, 126.3 (2C), 89.4, 55.3, 50.4, 21.2, 19.3, 11.6. LR MS: 325.9 ($M + H^+$, 100).

(2*Z*,3*R**,4*S**,5*R**)-4-Bromo-3-benzyl-5-phenyl-dihydro-2(3*H*)-furanone *O*-acetyloxime 13c

Oil: 57%. ^{1}H NMR ($CDCl_3$, 250 MHz) δ: 7.50–7 (m, 10H), 6.69 (d, $J = 7.6$ Hz, 1H), 4.62 (t, $J = 10.8$ Hz, 1H), 3.6–3.4 (m, 1H), 3.34–3.1 (m, 2H), 2.26 (s, 3H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 168.4, 164.2, 137, 133, 129.6 (4C), 129.4 (4C), 126.7, 126.2, 89.7, 55.7, 48.0, 34.2, 18.3. LR MS: 388 ($M + H^+$, 20), 405 ($M + NH_4^+$, 100).

(2*Z*,3*R**,4*S**,5*R**)-4-Bromo-3-(3-buten-1-yl)-5-phenyl-dihydro-2(3*H*)-furanone *O*-Acetyloxime 13d

Oil: 55%. ^{1}H NMR ($CDCl_3$, 360 MHz) δ (ppm): 7.64–7.18 (m, 5H), 5.93–5.77 (m, 1H), 5.45 (d, $J = 8.5$ Hz, 1H), 5.20–4.98 (m, 2H), 4.02 (dd, $J = 9.5$ and 8.5 Hz, 1H), 3.65–3.31 (m, 1H), 2.17 (s, 3H), 1.77–1.71 (m, 3H), 1.28 (m, 1H). LR MS: 352 ($M + H^+$, 100).

The (3*H*)-furanones **13e** and **13f** were unstable and could not be isolated by liquid chromatography. The subsequent reactions with triethylamine were carried out on the crude reaction products.

Preparation of (*Z*)-1-Phenyl-3-cyano-2-propen-1-ones 14a–f

The reactions were carried out using the procedure reported for the preparation of compound **6**, starting from either the crude reaction products or the purified (3*H*)-furanones.

(*Z*)-2-Methyl-4-oxo-4-phenylbut-2-enenitrile 14a. Oil: 60%. ^{1}H NMR ($CDCl_3$, 360 MHz) δ (ppm): 8.09–7.19 (m, 6H), 2.33 (d, $J = 1.7$ Hz, 3H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 189.4, 136.7, 136.6, 129.9 (2C), 129.5 (3C), 123.8, 119.2, 17.6. IR (CH_2Cl_2) υ (cm^{-1}): 3063, 2928, 2221, 1667, 1600, 1597, 1449, 1241, 985, 695. HR MS: calculated for $C_{11}H_{10}NO$ ($M + H^+$): 172.0762. Found: 172.0762.

(*Z*)-2-Ethyl-4-oxo-4-phenylbut-2-enenitrile 14b. Oil: 65%. ^{1}H NMR ($CDCl_3$, 360 MHz) δ (ppm): 7.57–7.15 (m, 6H), 3.30 (q, $J = 7.1$ Hz, 2H), 1.48 (s, 3H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 193.5, 147.0, 133.8, 129.6, 128.8 (2C), 128.2 (2C), 126.3, 108.5, 38.1, 14.8. IR (CH_2Cl_2) υ (cm^{-1}): 3289, 2923, 2218, 1763, 1689, 1597, 1449, 1329, 1212, 988, 754. HR MS: calculated for $C_{12}H_{12}NO$ ($M + H^+$): 186.0919. Found: 186.0921.

(*Z*)-2-Benzyl-4-oxo-4-phenylbut-2-enenitrile 14c. Oil: 57%. ^{1}H NMR ($CDCl_3$, 250 MHz) δ (ppm): 7.27–8.05 (m, 11H), 4.11 (s, 2H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 194.3, 147.1, 133.7 (2C), 130.3 (2C), 128.7 (4C), 128.5 (4C), 128.4, 116.2, 44.5. IR (CH_2Cl_2) υ (cm^{-1}): 2923, 2852, 2211, 1767, 1687, 1580, 1449, 1334, 1213, 997, 754. HR MS: calculated for $C_{17}H_{14}NO$ ($M + H^+$): 248.1075. Found: 248.1079.

(*Z*)-2-(2-Oxo-2-phenylethylidene)hex-5-enenitrile 14d. Oil: 55%. ^{1}H NMR ($CDCl_3$, 360 MHz) δ (ppm): 7.53–7.17 (m, 6H), 6.00–5.71 (m, 1H), 5.16–4.90 (m, 2H), 2.31–2.00 (m, 3H), 1.84–1.58 (m, 1H). ^{13}C NMR ($CDCl_3$, 75.5 Hz) δ (ppm): 195.9, 147.3, 138.2, 131.2, 129.9 (2C), 128.7, 128.4 (2C), 126.3, 114.9, 100.0, 30.3 (2C). IR (CH_2Cl_2) υ (cm^{-1}): 2832, 2756, 2321, 1770, 1696, 1610, 1355, 1336, 1115, 969, 760. HR MS: calculated for $C_{14}H_{17}N_2O$ ($M + NH_4^+$): 229.1341. Found: 229.1343.

(*Z*)-Methyl 3-cyano-5-oxo-5-phenylpent-3-enoate 14e. Oil: 55%. ^{1}H NMR ($CDCl_3$, 250 MHz) δ (ppm): 7.90–7.40 (m, 6H), 3.70 (s, 3H), 3.25 (m, 2H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 191.2, 170.5, 145.1, 140.2, 128.5 (2C), 128.8, 128.1 (2C), 125.2, 113.8, 52.4, 36.8. HR MS: calculated for $C_{13}H_{15}N_2O_3$ ($M + NH_4^+$): 247.1083. Found: 247.1087.

(*Z*)-4-Oxo-2,4-diphenylbut-2-enenitrile 14f[17]. Yield 90%. White solid, mp 94–96 °C (lit.[17a] mp 95–96 °C). ^{1}H NMR ($CDCl_3$, 360 MHz) δ: 8.18–8.04 (m, 2H), 7.94 (s, 1H), 7.86–7.82 (m, 2H), 7.70–7.65 (m, 1H), 7.60–7.50 (m, 5H).

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