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Combination of Pyridinium and Isoquinolinium Ylides with Phenylisocyanate and Isothiocyanates: Synthesis, Characterisation, and X-Ray Crystal Structures of Mesoionic Monosubstituted 3-Oxo-Propanamides or Thioamides

Mohammad Seifi,[A] *S. Yousef Ebrahimipour,*[B] *Jim Simpson,*[C] *Michal Dusek,*[D] *Vaclav Eigner,*[D] *and Hassan Sheibani*[B,E]

[A]Department of Chemistry, Faculty of Science Najafabad Branch, Islamic Azad University, Najafabad, Esfahan, Iran.
[B]Department of Chemistry, Shahid Bahonar University of Kerman, Kerman 76169, Iran.
[C]Department of Chemistry, University of Otago, PO Box 56, Dunedin 9054, New Zealand.
[D]Institute of Physics of the ASCR, v.v.i., Na Slovance 2, 182 21 Prague 8, Czech Republic.
[E]Corresponding author. Email: hsheibani@mail.uk.ac.ir

Pyridinium ylides derived from 2-bromoacetophenone or methyl bromoacetate have been reacted with phenylisocyanate, phenyl- or methylisothiocyanate to afford mesoionic monosubstituted 3-oxo-propanamides or thioamides, via self-protonation of the intermediate *N*-anion. A similar reaction under the same conditions of isoquinolinium ylides with phenylisocyanate or phenyisothiocyante also produced the corresponding mesoionic compounds. In order to establish the exact structure of the mesoionic compounds, single crystal X-ray structures were obtained for three of the pyridinium ylides.

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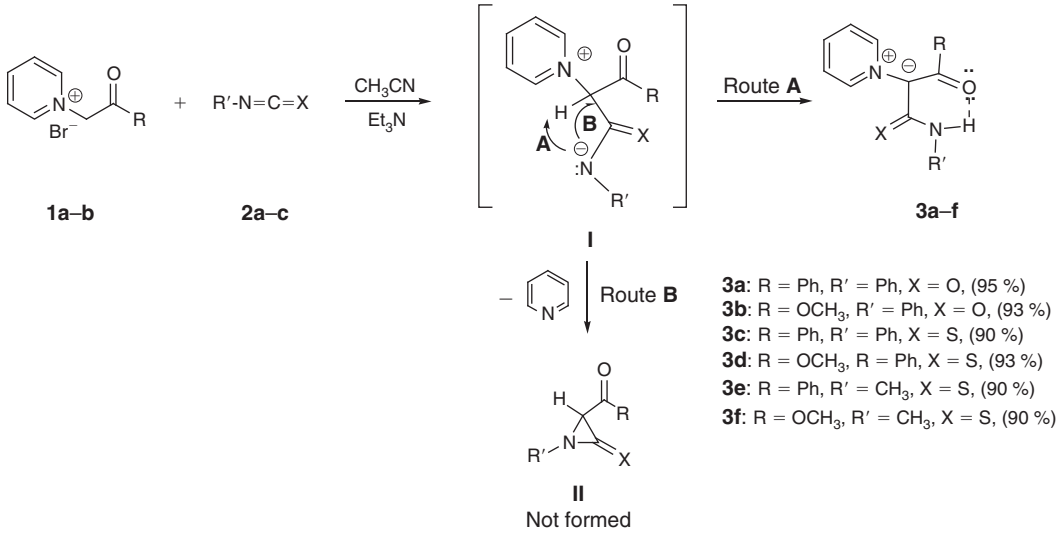
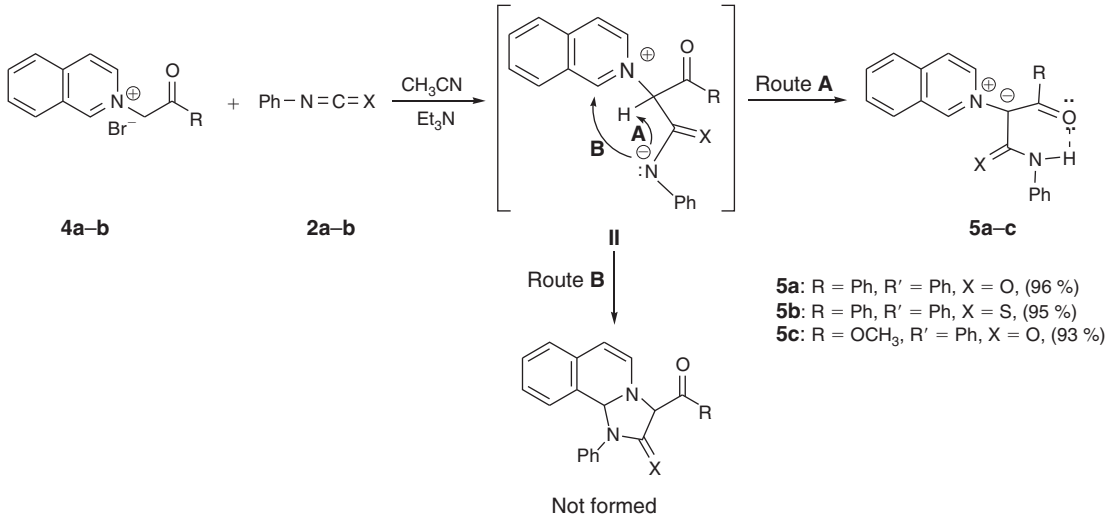
Introduction

Conjugated heterocyclic *N*-ylides are used as building blocks for a wide range of fused heterocyclic compounds due to their 1,3-dipolar character.[1–3] This character has been observed in many reactions such as cycloaddition reactions of (chlorocarbonyl) ketenes with 1,2- and 1,3-dinucleophiles.[4–6] In the preparation of heterocyclic compounds, cycloimmonium ylides such as pyridinium and isoquinolinium ylides have been used extensively. The positively charged nitrogen atom of an aza-heterocyclic compound can be covalently bonded to such zwitterionic ylides.[7] These ylides are zwitterions in which a carbanion is covalently bonded to a positively charged nitrogen atom from the azaheterocycle.[1] Generally, cycloimmonium ylides are unstable except when two electron-withdrawing groups are introduced on the carbanion. The negative charge at the ylidic carbanion centre is known to be the source of nucleophile behaviour by these ylides. This is also responsible for their ability to behave as mono- or bidentate ligands towards metal ions.[8–11] Pyridinium and isoquinolinium salts derived from α-halogenocarbonyl compounds are easily deprotonated to give the corresponding ylides, which find wide applications in the formation of three- and five-membered ring heterocycles such as cyclopropane and isoxazole, and 6-membered ring heterocyclic derivatives.[12–15] Combination of these ylides with Michael acceptors as electron-deficient reagents along with ring closure strategies (cyclisation) is the most useful methodology for preparing three- or five-membered rings.[16] Pyridinium ylides are a special variety of ammonium ylides, which can react with alkenes substituted with electron-withdrawing groups to give the corresponding cyclopropanes.[17,18] Also the pyridine group has been utilized as a leaving group in intermolecular reactions. However the 1,3-dipolar cycloaddition of heteroaromatic *N*-ylides, such as isoquinolinium ylides with electron-deficient alkynes and alkenes resulted in the formation of pyrrolo isoquinoline derivatives.[19–21] In addition these ylides have great potential for use as analytical reagents[3] and as semiconducting materials,[16]and some of them have also shown biological activity.[17] Cycloimmonium ylides are also used in the synthesis of ylidic polymers by interphase-transfer polycondensation reactions.[18] As a continuation of our interest in the synthesis of mesoionic compounds by the reactions of (chlorocarbonyl)ketenes with 1,3-dinucleophiles,[4–6] we wish to report the reactions of pyridinium and isoquinolinium ylides with phenylisocyanate and isothiocyanates leading to the synthesis of a variety of mesoionic compounds. These reactions produced the pyridinium or isoquinolinium methylides **3a**–**f** and



Scheme 1.



Scheme 2.

5a–**c** (Schemes 1 and 2) with two electron-withdrawing groups on the carbanion in excellent yields (90–96 %). Structures of **3a**–**f** and **5a**–**c** were confirmed by elemental analysis and spectroscopic data; structures of ylides **3b**–**d** were also established by X-ray crystallography.

Results and Discussion

We began our study by examining the reactivity of *N*-ylides derived from pyridinium and isoquinolinium bromides with activated double bonds. First we investigated the reaction of the pyridinium salts **1a**, **b** with phenylisocyanate **2a** and phenyl or methylisothiocyanates **2b** and **2c** in the presence of triethylamine, which yielded the 1,3-dioxo-2-(pyridin-1-ium-1-yl) propan-2-ide and 1-oxo-2-(pyridin-1-ium-1-yl)-3-thioxopropan-2-ide derivatives **3a**–**f**, respectively.

The mechanism of the reaction involves the base induced formation of an intermediate *N*-anion **I** (Scheme 1). This undergoes facile self-deprotonation (Route A) to yield the mesoionic products **3a**–**f** in excellent yields (Table 1). Interestingly, the alternative cyclisation reaction (Route B) resulting from loss of pyridine from the *N*-anion is not observed in this case.

Table 1. Solvent and base effects on the reaction of pyridinium or isoquinolinium bromides with phenylisocyanate

Comp. no.	Solvent	Base	Time [min]	Yield [%]
3a	Acetonitrile	Et_3N	15	95
3a	Acetonitrile	K_2CO_3	18	92
3a	Toluene	Et_3N	30	90
3a	Toluene	K_2CO_3	25	92
3a	CH_2Cl_2	Et_3N	20	90
3a	CH_2Cl_2	K_2CO_3	25	88
5a	Acetonitrile	Et_3N	12	96
5a	Acetonitrile	K_2CO_3	15	90
5a	Toluene	Et_3N	25	88
5a	Toluene	K_2CO_3	22	90
5a	CH_2Cl_2	Et_3N	18	87
5a	CH_2Cl_2	K_2CO_3	22	85

The corresponding reactions of isoquinolinium ylides (**4a**, **b**), prepared in situ from the reaction of isoquinolinium bromides, with phenylisocyanate or phenylisothiocyanate **2a**, **b** gave the analogous 2-(1,3-dioxo or 1-oxo-3-thiopropan-2-yl)

isoquinolin-2-ium derivatives **5a**–**c** again as mesoionic compounds and in high yields. A similar mechanism (Scheme 2) involving an intermediate isoquinolinium-*N*-anion is believed to be involved in the reaction with cyclisation to a dihydroimidazo [2,1-a]isoquinolin-2(3*H*)-one or thione disfavoured. Gololobov et al.[22] have reported that the reaction of pyridinium ylides derived from the reaction of a malonic ester with isocyanates leads to reversible C ⇆ N migration of the ethoxycarbonyl group with the formation of the corresponding carbamates in an unexpected way. In conjunction with our observations, it is interesting to note that reversible C ⇆ N migration of the benzoyl or methoxycarbonyl groups has not occurred in the reactions reported here. In order to optimise the reaction conditions, we used both polar and non-polar solvents in the reaction of pyridinium or isoquinolinium bromides with phenylisocyanate in the presence of either triethylamine or potassium carbonate as the base. The results are shown in Table 1. It is noteworthy that polar solvents such as acetonitrile and dichloromethane afford better yields with shorter reaction times than the less polar toluene. Acetonitrile and triethylamine are the most effective solvent and base, respectively.

According to the infra-red (IR) and ^{1}H NMR spectroscopic data, compounds **3a**–**f** and **5a**–**c** show an intramolecular hydrogen bond between the NH group of the amide acting as a donor and the oxygen atom of the ketone or ester acting as an acceptor. The IR spectra of compounds **3a**–**f** and **5a**–**c** showed the broad stretching bands of the NH groups in the range of 3450–3300 cm^{-1}. The carbonyl stretching bands of the ester, ketone, and amide groups are found in the region of 1690–1630 cm^{-1}. The ^{1}H NMR spectra of these compounds indicated the proton of the amide or thioamide groups (NH) appeared as a singlet and was well downfield (δ_H 14.61–10.62), which is consistent with literature precedents for closely related products.

X-Ray Crystal Structure

The molecular structures of the three compounds (Fig. 1) have similar features and they can be sufficiently discussed together. Each zwitterionic molecule comprises a central amide unit, **3b** (or thioamides **3c** or **3d**), that forms pyridinium ylides via the C2–N2 bonds to the pyridinium rings. The amide or thioamide N1 atoms carry phenyl substituents, while the C2 atoms that have a formal negative charge have pyridinium and either 1-oxo-1-methoxy, **3b** and **3d** or 1-oxo-1-phenyl, **3c**, substituents that combine with the C1 atoms of the amide or thioamide units to generate propan-2-ide functional groups. Compound **3b** crystallizes with a solvent water molecule in the asymmetric unit. The O atom of the solvent lies on a 2-fold axis and is linked to the main molecule by a very weak C15–H1c15···O1w hydrogen bond. The N1, C1, O1, C2, C3, O2, O3, C15 segment of **3b** is reasonably planar with a root-mean-square (rms) deviation of 0.0742 Å from the best fit plane through all eight atoms. The phenyl and pyridinium ring planes subtend dihedral angles of 24.08(4) and 79.07(4) °, respectively, to that plane. Similarly the C4, N1, C1, S1, C2, C3, O1, C15 segments of **3c** and **3d** are also almost planar with rms deviations for the eight atoms in the plane of 0.0573 and 0.0772 Å respectively. The corresponding dihedral angles between these planes and the phenyl and pyrimidine rings of the two molecules are 52.28(5) and 31.54(4)° for **3c** and 65.57(5) and 73.05(4)° for **3d**. A feature of all three compounds is the ready formation of strong intramolecular N1–H1n···O1 hydrogen bonds, that contribute to the planarity of the central portions of these molecules and form S(6) rings.[23] The pyridinium ylides reported here are unique,

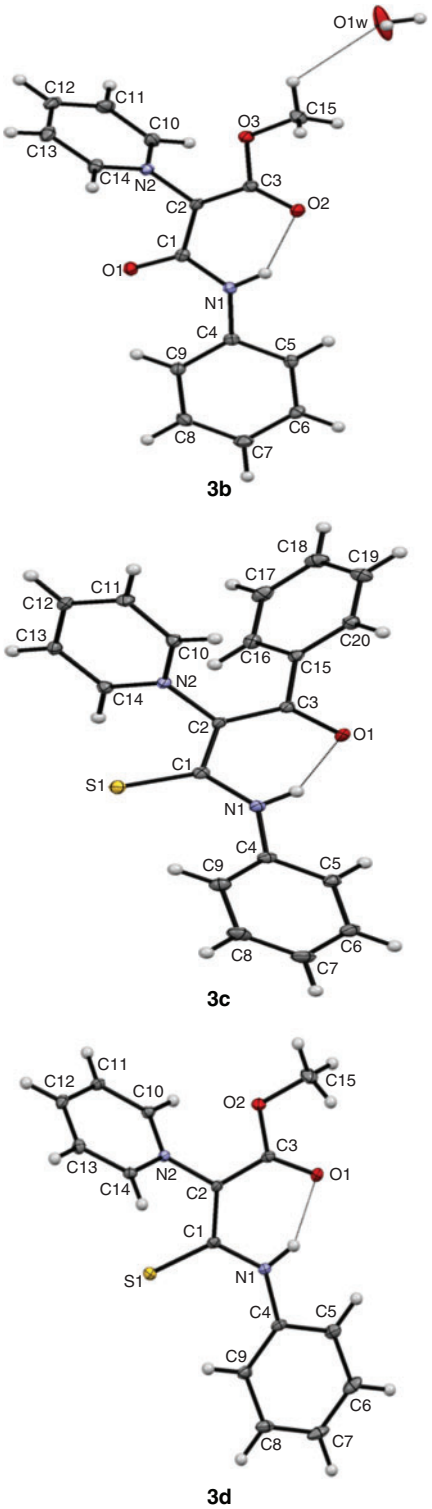


Fig. 1. The molecular structures of **3b**, **3c**, and **3d** with ellipsoids drawn at the 50 % probability level. Intramolecular hydrogen bonds and a C–H···O contact in the asymmetric unit of **3b** are drawn as dashed lines.

with no directly comparable compounds of their structures reported in the Cambridge Structural Database Version 5.35 (November 2013 plus three updates).[24] The database contains structures both of purely organic pyridinium ylides (ten examples) and of their transition metal complexes (four examples).[12] Of these, only the structure of 1-((4-bromophenyl)

Table 2. Crystallographic data for 3b–d

Compound	3b	3c	3d
Empirical formula	2 ($C_{15}H_{14}N_2O_3$)·H_2O	$C_{20}H_{16}N_2OS$	$C_{15}H_{14}N_2O_2S$
MW	558.6	332.4	286.3
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/*c*	*C*2/*c*	$P2_1/c$
a [Å]	11.7956 (11)	17.6133 (14)	8.9233 (7)
b [Å]	14.3714 (12)	8.8929 (6)	9.3219 (7)
c [Å]	16.0591 (15)	21.5344 (15)	17.0065 (13)
β [°]	100.089 (8)	101.973 (6)	93.618 (6)
Z	4	8	4
V [Å^3]	2680.2 (4)	3299.6 (4)	1411.82
D_{calc} [g cm^{-3}]	1.384	1.338	1.347
μ [mm^{-1}]	0.10	0.21	0.23
Reflections used	7692	8305	6633
Independent [R_{int}]	3172 (0.019)	3817 (0.022)	3241 (0.018)
Observed [$I > 3\sigma(I)$]	2573	3234	2756
Parameters refined	192	220	184
Max/min $\Delta\rho$ [e Å^{-3}]	0.22/−0.22	0.19/−0.22	0.21/−0.16
GOF	1.62	1.48	1.44
$R(F)/wR(F^2)$	0.039/0.111	0.035/0.101	0.031/0.096
CCDC number	1038675	1038676	1038677

carbamothioyl)-2-(4-methoxyphenyl)-2-oxo-1-(4-(pyridin-4-yl)-pyridineium-1-yl)ethanide displays the Ph–C(O)–C$^-$–C(S)–NH backbone comparable to those of **3c** and **3d**.

Crystal Structure Determination

Data were collected using Gemini Atlas CCD diffractometer with graphite monochromated $Mo_{K\alpha}$ radiation (λ 0.71073 Å) at 120 K. The structures were solved by charge flipping methods[25] and refined by full matrix least-squares on F^2 value using *Jana2006* suite of programs.[26] Electron density was visualised with *MCE*.[27] All hydrogen atoms were discernible in Fourier difference maps, but according to common practice the hydrogen atoms connected to carbon atoms were placed in ideal positions, while the hydrogen atoms connected to heteroatoms were refined with restrained geometry. In all cases U_{iso}(H) was set to 1.2U_{eq}(C,N,O). All non-hydrogen atoms were refined using harmonic refinement. For details of the crystallographic data see Table 2.

Conclusions

In summary, we have described herein the reaction of heteroaromatic *N*-ylides, particularly pyridinium and isoquinolinium ylides, with phenylisocyanate and isothiocyanates leading to the formation of mesoionic monosubstituted 3-oxo-propanamide or thioamide derivatives. The resulting compounds are stable at room temperature and the solid state structures of compounds **3b**–**d** were established using X-ray crystallography. Prominent among the advantages of these reactions are novelty, operational simplicity, and excellent yields. Further expansion of the synthesis scope and biological activity of similar compounds is in progress in our laboratory.

Experimental

General Information

Melting points were measured on an Electrothermal-9100 apparatus and are uncorrected. IR spectra were recorded on a Bruker FT-IR Tensor 27 infrared spectrophotometer. ^{1}H NMR and spectra were recorded on an Avance III 400 or 300 MHz Bruker spectrometer. ^{13}C NMR spectra were recorded on the same instruments at 100 or 75 MHz using TMS as an internal standard. Mass spectra were measured on a GCMS-QP1000 EX spectrometer at 70 eV. Elemental analyses were performed using a Heracus CHN-O-Rapid analyser. Pyridinium and isoquinolinium salts were prepared according to a literature procedure.[28]

*Typical Procedure for the Preparation of Compounds **3a–f** and **5a–c** in Acetonitrile*

A solution of the pyridinium salts (**1a**, **b**) or the isoquinolinium salts (**4a**, **b**) (2 mmol), phenylisocyanate or isothiocyanates (2 mmol) and triethylamine (0.2 mL) in acetonitrile (20 mL) was stirred at room temperature for ∼15 min (the progress of the reaction was monitored by TLC, using n-hexane/ethyl acetate as the eluent). The solvent was diluted with 50 mL of water and the resulting precipitate was collected by filtration. The crude product was recrystallised with dichloromethane/n-hexane (60/40) to give the pure solid sample for analysis.

*1,3-Dioxo-1-phenyl-3-(phenylamino)-2-(pyridin-1-ium-1-yl)propan-2-ide (**3a**)*

Greenish yellow crystals (95 % yield). mp 219°C; ν_{max} (KBr)/cm^{-1} 3444br (NH), 1639, 1619 (C=O), 1587, 1503 (C=C). δ_H (400 MHz, $CDCl_3$) 12.51 (1H, s, NH, amide), 8.52–7.01 (15H, m, Ar). δ_C (100 MHz, $CDCl_3$) 178.22, 163.58 (C=O), 149.12, 141.66, 140.46, 129.04, 128.82, 128.76, 128.43, 127.01, 119.85. *m/z* 316 (5 %, [M]$^+$), 235 (21), 196 (100), 167 (19), 119 (80), 105 (30), 91 (68), 77 (62), 65 (94), 51 (50). Anal. Calc. for $C_{20}H_{16}N_2O_2$: C 75.93, H 5.10, N 8.86 %. Found: C 75.79, H 5.01, N 8.52 %.

*1-Methoxy-1,3-dioxo-3-(phenylamino)-2-(pyridin-1-ium-1-yl)propan-2-ide (**3b**)*

Yellow crystals (93 % yield). mp 178–181°C. ν_{max} (KBr)/cm^{-1} 3411br (NH), 1627 (C=O), 1580, 1520, 1482 (C=C). δ_H (300 MHz, $CDCl_3$) 10.62 (1H, s, N^{1}H, amide), 8.57–6.95 (10H, m, C^{5}H, C^{6}H, C^{7}H, C^{8}H, C^{9}H, C^{10}H, C^{11}H, C^{12}H, C^{13}H, C^{14}H), 3.62 (3H, s, C^{15}H$_3$). δ_C (75 MHz, $CDCl_3$) 174.87 (C^3=O^2), 164.14 (C^1=O^1), 149.69, 141.21, 128.71, 125.69, 119.34, 50.14 (O^{3}C^{15}H$_3$). *m/z* 270 (6 %, [M]$^+$), 213(9), 178 (13), 152 (68), 119 (100), 101 (14), 91 (94), 86 (24), 79 (24), 64 (53), 52 (30). Anal. Calc. for $C_{15}H_{14}N_2O_3$: C 66.66, H 5.22, N 10.36 %. Found: C 66.57, H 5.19, N 10.15 %.

*1-Oxo-1-phenyl-3-(phenylamino)-2-(pyridin-1-ium-1-yl)-3-thioxopropan-2-ide (**3c**)*

Greenish yellow crystals (90 % yield). mp 179–180°C. ν_{max} (KBr)/cm^{-1} 3424br (NH), 1618 (C=O), 1595 (C=S), 1570 (C=C). δ_H (300 MHz, [D6]DMSO) 14.54 (1H, s, N1H, thioamide), 8.95–7.10 (15H, m, C^{5}H, C^{6}H, C^{7}H, C^{8}H, C^{9}H, C^{10}H, C^{11}H, C^{12}H, C^{13}H, C^{14}H, C^{16}H, C^{17}H, C^{18}H, C^{19}H, C^{20}H). δ_C (75 MHz, [D6]DMSO) 184.59 (C^1=S^1), 177.81 (C^3=O^1), 151.85, 145.61, 141.42, 141.29, 128.81, 128.61, 128.28, 126.88, 123.27. *m/z* 332 (6 %, [M]$^+$), 253 (7), 251 (10), 236 (5), 196 (12), 162 (57), 135 (100), 105 (61), 91 (12), 77 (98), 51 (44). Anal. Calc. for $C_{20}H_{16}N_2OS$: C 72.26, H 4.85, N 8.43 %. Found: C 72.01, H 4.75, N 8.22 %.

*1-Methoxy-1-oxo-3-(phenylamino)-2-(pyridin-1-ium-1-yl)-3-thioxopropan-2-ide (**3d**)*

Yellow crystals (93 % yield). mp 170°C. ν_{max} (KBr)/cm^{-1} 3444br (NH), 1640 (C=O), 1592 (C=S), 1564 (C=C).

δ_H (300 MHz, $CDCl_3$) 11.83 (1H, s, N^1H, thioamide), 8.61–7.09 (10H, m, C^5H, C^6H, C^7H, C^8H, C^9H, $C^{10}H$, $C^{11}H$, $C^{12}H$, $C^{13}H$, $C^{14}H$), 3.59 (3H, s, $C^{15}H_3$). δ_C (75 MHz, $CDCl_3$) 182.87 ($C^1{=}S^1$), 162.79 ($C^3{=}O^1$), 151.30, 143.47, 128.26, 126.23, 109.67, 50.49 ($O^2C^{15}H_3$). *m/z* 286 (4 %, $[M]^+$), 260 (6), 234 (12), 207 (7), 205 (13), 191 (12), 176 (13), 135 (100), 119 (32), 104 (11), 91 (28), 77 (87), 64 (18), 51 (58). Anal. Calc. for $C_{15}H_{14}N_2O_2S$: C 62.92, H 4.93, N 9.78 %. Found: C 62.75, H 4.85, N 9.67 %.

*1-(Methylamino)-3-oxo-3-phenyl-2-(pyridin-1-ium-1-yl)-1-thioxopropan-2-ide (**3e**)*

Russet brown crystals (90 % yield). mp 95°C. ν_{max} (KBr)/cm^{-1} 3493 (NH), 1639 (C=O), 1619 (C=N). δ_H (400 MHz, [D6]DMSO) 12.16 (1H, q, $^3J_{H-H}$ 4, NH), 8.83 (2H, d, $^3J_{H-H}$ 8, H_α-py), 8.32 (1H, t, $^3J_{H-H}$ 8, H_γ-py), 7.79 (2H, t, $^3J_{H-H}$ 8, H_β-py), 7.12–7.08 (5H, m, Ar), 3.10 (3H, d, $^3J_{H-H}$ 4, CH_3). δ_C (100 MHz, [D6]DMSO) 183.34 (C=S), 163.83 (C=O), 151.29 (C=N), 144.67, 141.49, 127.75, 127.68, 126.15, 126.06, 112.02 (C^-), 31.16 (NCH_3). *m/z* 270 (35 %, $[M]^+$), 269 (14), 237 (16), 191 (21), 163 (8), 118 (15), 105 (100), 77 (85), 51 (43). Anal. Calc. for $C_{15}H_{14}N_2OS$: C 66.64, H 5.22, N 10.36 %. Found: C 66.48, H 5.04, N 10.09 %.

*1-Methoxy-3-(methylamino)-1-oxo-2-(pyridin-1-ium-1-yl)-3-thioxopropan-2-ide (**3f**)*

Yellow crystals (90 %). mp 174–175°C. ν_{max} (KBr)/cm^{-1} 3493 (NH), 1695 (C=O), 1632 (C=N). δ_H (300 MHz, [D6]DMSO) 9.70 (1H, q, $^3J_{H-H}$ 6, NH), 8.74 (2H, d, $^3J_{H-H}$ 6, H_α-py), 8.47 (1H, t, $^3J_{H-H}$ 6, H_γ-py), 7.96 (2H, t, $^3J_{H-H}$ 6, H_β-py), 3.39 (3H, s, OCH_3), 3.02 (3H, d, $^3J_{H-H}$ 6, NCH_3). δ_C (75 MHz, [D6]DMSO) 185.71 (C=S), 164.14 (C=O), 151.91 (C=N), 144.96, 127.15, 107.45 (C^-), 50.11 (OCH_3), 31.51 (NCH_3). *m/z* 224 (100 %, $[M]^+$), 223 (66), 191 (49), 164 (13), 113 (11), 93 (10), 80 (93), 52 (34). Anal. Calc. for $C_{10}H_{12}N_2O_2S$: C 53.55, H 5.39, N 12.49 %. Found: C 51.08, H 5.19, N 12.22 %.

*2-(Isoquinolin-2-ium-2-yl)-1,3-dioxo-1-phenyl-3-(phenylamino)propan-2-ide (**5a**)*

Orange crystals (96 % yield). mp 191–193°C. ν_{max} (KBr)/cm^{-1} 3411br (NH), 1632, 1590 (C=O), 1536, 1501 (C=C). δ_H (300 MHz, $CDCl_3$) 12.57 (1H, s, NH), 9.20 (1H, s, HC_α=N), 8.19–6.99 (16H, m, Ar). δ_C (75 MHz, $CDCl_3$) 178.52, 164.03 (C=O), 152.21, 140.65, 140.47, 140.03, 136.01, 130.55, 129.65, 128.78, 128.73, 128.37, 127.16, 127.02, 126.82, 123.37, 122.43, 120.07, 119.06, 116.06. *m/z* 366 (2 %, $[M]^+$), 363 (59), 347 (8), 247 (41), 204 (12), 144 (10), 129 (60), 105 (100), 91 (10), 77 (93), 51 (35). Anal. Calc. for $C_{24}H_{18}N_2O_2$: C 78.67, H 4.95, N 7.65 %. Found: C 78.49, H 4.80, N 7.37 %.

*2-(Isoquinolin-2-ium-2-yl)-1-oxo-1-phenyl-3-(phenylamino)-3-thioxopropan-2-ide (**5b**)*

Brown crystals (95 % yield). mp 149–151°C. ν_{max} (KBr)/cm^{-1} 3444br (NH), 1635 (C=O), 1619, 1597 (C=C). δ_H (300 MHz, [D6]DMSO) 14.61 (1H, s, NH), 10.09 (1H, s, HC_α=N), 8.58–6.80 (16H, m, Ar). δ_C (75 MHz, [D6]DMSO) 184.80 (C=S), 178.14 (C=O), 156.64, 142.14, 141.53, 141.36, 137.28, 137.02, 130.93, 130.66, 129.94, 129.31, 128.83, 128.61, 128.24, 127.37, 127.24, 126.62, 124.05, 123.33. *m/z* 382 (5 %, $[M]^+$), 380 (18), 362 (12), 351 (17), 298 (13), 241 (9), 129 (15), 105 (100), 77 (94), 51 (23). Anal. Calc. for $C_{24}H_{18}N_2OS$: C 75.37, H 4.74, N 7.32 %. Found: C 75.14, H 4.55, N 7.01 %.

*2-(Isoquinolin-2-ium-2-yl)-1-methoxy-1,3-dioxo-3-(phenylamino)propan-2-ide (**5c**)*

Orange crystals (93 % yield). mp 135°C. ν_{max} (KBr)/cm^{-1} 3443br (NH), 1638, 1617 (C=O), 1581, 1526 (C=C). δ_H (300 MHz, $CDCl_3$) 10.72 (1H, s, NH), 9.28 (1H, s, HC_α=N), 8.30–6.94 (11H, m, Ar), 3.65 (3H, s, OCH_3). δ_C (75 MHz, $CDCl_3$) 177.53, 164.46 (C=O), 152.88, 141.04, 140.47, 136.13, 135.53, 130.16, 129.75, 128.72, 127.48, 126.74, 123.31, 121.72, 119.39, 98.20, 50.19 (OCH_3). *m/z* 320 (9 %, $[M]^+$), 260 (8), 228 (19), 201 (87), 170 (17), 143 (100), 130 (59), 119 (86), 102 (18), 91 (64), 77 (26), 64 (40), 51 (26). Anal. Calc. for $C_{19}H_{16}N_2O_3$: C 71.24, H 5.03, N 8.74 %. Found: C 70.94, H 4.88, N 8.46 %.

Crystallographic Data

CCDC 1038675–1038677 contain the supplementary crystallographic data for compounds **3b**, **3c**, and **3d** respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or email: deposit@ccdc.cam.ac.uk.

Supplementary Material

IR, ^1H, ^{13}C NMR, and mass spectral data for a representative set of compounds **3a**–**f** and **5a**–**d** are available on the Journal's website.

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