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PYRIDINE-DERIVED HETEROCYCLES AS POTENTIAL PHOTOACYLATING REAGENTS

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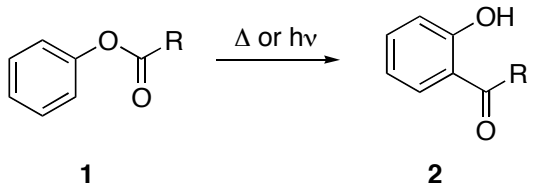
Abstract – We prepared several pyridine-derived heterocycles and investigated their photoacylating properties. Among representatives of 4 families of compounds (1-acetyl-7-azaindole, 1-acetyl-7-azaindoline, 2-acetamindpyridine and 2-amidopyrimidines), the 2-aminopyrimidine derivatives were the most promising candidates. Photoacylation of dodecylamine yields up to 47% were obtained, upon irradiation with UV light at 254 nm.

INTRODUCTION

Acyl-transfer reactions are processes of crucial importance in life (*e.g.* in the biosynthesis of peptides and proteins) and in organic synthesis (*e.g.* in the esterification reaction).[1] Photoacylation is an attractive subset of this larger family, not only because it allows for a precise control in the timing, a key parameter in one-pot and/or cascade reactions, but also because it operates under very mild conditions and no other reagents (such as acids or bases) are required. In the past few years, we have studied the photoacylating properties of nitroindoline derivatives.[2,3] Photoacyl transfer was also used to introduce the Cbz and Fmoc groups in very mild conditions.[4] However, the vast majority of the existing photoacylating agents is based on the nitroindoline skeleton,[5] and they suffer from the following drawbacks: a) they are (so far) limited to nitrogen nucleophiles; oxygen nucleophiles such as water and methanol have been used, but only with a large excess; b) they operate in a limited light energy range (300-400 nm); c) they frequently suffer from poor solubility in organic solvents. As a consequence, there is a need for new types of photoacylating reagents, and we therefore initiated a program aiming at rationally designing new potential candidates.

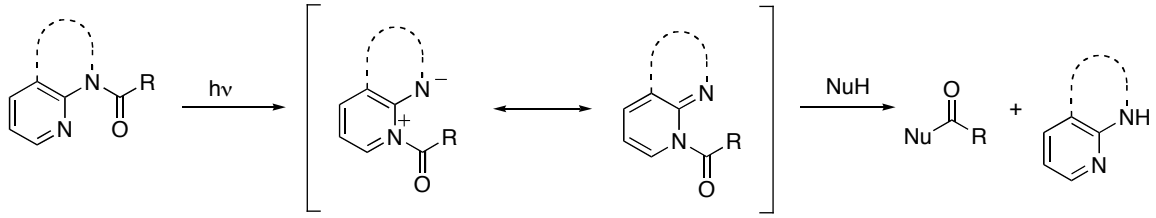
The Fries rearrangement (**1** → **2**, *Scheme 1*) is a thermal process, which can be considerably accelerated photochemically.[6] Although the commonly accepted mechanism is based on the radical scission of the

acyl-phenol bond, we considered the overall transfer as very promising in the nitrogen-containing analogue (**3**). In this case, the rearranged product (**4**) would be a powerful acyl transfer intermediate, resembling the putative intermediate in the DMAP-accelerated acylation of nucleophiles (*Scheme 2*).[7]



1 **2**

Scheme 1. The thermal and photochemical Fries rearrangement.



3 **4** **5**

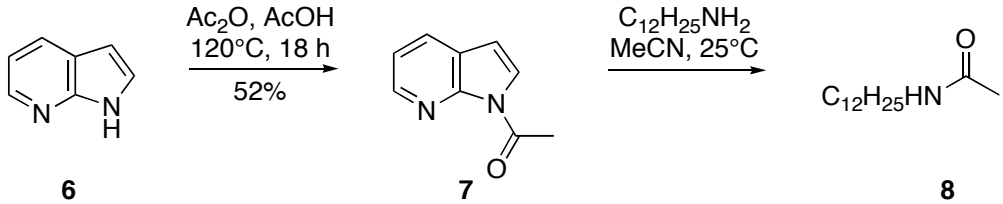
Scheme 2. Design of new photoacylation reagents.

We discuss below our investigations on the potential photoacylation properties of various derivatives of (**3**).

RESULTS AND DISCUSSION

a) 1-Acetyl-7-Azaindole

We first considered one of the simplest candidates for our purpose: the 1-acetyl-7-azaindole (**7**), which was readily prepared by acetylation of commercially available 7-azaindole (**6**), with acetic anhydride in acetic acid at reflux temperature for 18 h (52%, *Scheme 3*).[8] We then carried out the standard negative test for photoacylations, *i.e.* mixing the reagents in the absence of light, and observed a complete acylation after 15 min at room temperature. Hence, despite being an efficient and mild acylating reagent in non-photochemical conditions, **7** was abandoned.



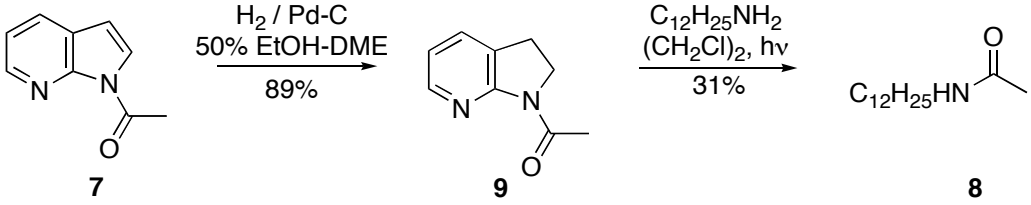
6 **7** **8**

Scheme 3. Acylation with 1-acetyl-7-azaindole

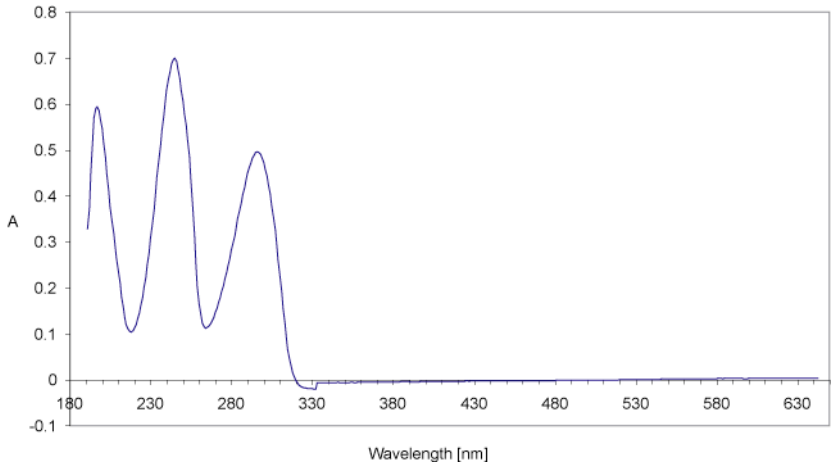
b) 1-Acetyl-7-Azaindoline

The aromaticity of the pyrrolic part of **6** being most probably the cause of its increased reactivity, we prepared the saturated analogue (**9**), by hydrogenation of **7** in the presence of palladium on charcoal, in

a 1:1 mixture of dimethoxyethane and ethanol (89%, *Scheme 4*). Negative control (18 h at 40°C in 1,2-dichloroethane) confirmed the absence of reaction of **9** in the dark. On the other hand, irradiation at 254 nm of an equimolar mixture of **9** and *n*-dodecylamine in 1,2-dichloroethane gave small amounts of amide (**8**) after 1 h.



Scheme 4. Photoacylation with 1-acetyl-7-azaindoline.



Scheme 5. Absorption spectrum of **9**

entry	*solvent*	*time*	λ	*yield*[a]
1	$(CH_2Cl)_2$	1 h	254 nm	31%
2	$(CH_2Cl)_2$	3 h	300 nm	28%
3	MeCN	1 h	254 nm	18%[b]
4	MeCN	3 h	300 nm	12%
5	EtOAc	3 h	300 nm	16%
6	THF	3 h	300 nm	14%
7	Et_2O	3 h	300 nm	8%
8	PhH	3 h	300 nm	14%
9	dioxane	4.5 h	300 nm	10%[b]
10	$CHCl_3$	4.5 h	300 nm	8%

[a]Determined by ^{1}H-NMR spectrum, using dodecylamine as an integration reference; [b]Isolated yield

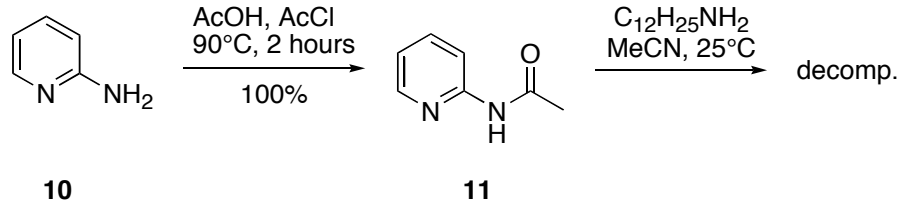
Table 1

Analysis of the side products revealed however the presence of 7-azaindole instead of the expected

7-azaindoline. There is hence the possibility of prior photochemically induced oxidation of **9** into (**7**), which *then* thermally reacts. We attempted to carry out the reaction under milder conditions, by photolysis at a longer wavelength, since the absorption spectrum of **9** suggests that 300 nm might be suitable for such a reaction. As expected from the UV-VIS spectrum (*Scheme 5*), **9** was unreactive under irradiation at 350 nm. On the other hand, reaction occurred at 300 nm, with yields comparable with those obtained at 254 nm (*Table 1*). The yields could not be improved by changing the solvent.

c) 2-Acetamidopyridine

We then turned our attention to the acyclic analogue of **9**, namely the 2-acetamidopyridine (**11**), which would not be subject to oxidation to the indole derivative as observed with the azaindoline compound. It was prepared by acetylation of the commercially available 2-aminopyridine (**10**) (acetyl chloride in acetic acid, 90°C, 2 h, 100%). Unfortunately, a solution of **11** in the presence of dodecylamine yielded only decomposition products even before irradiation (*Scheme 6*).

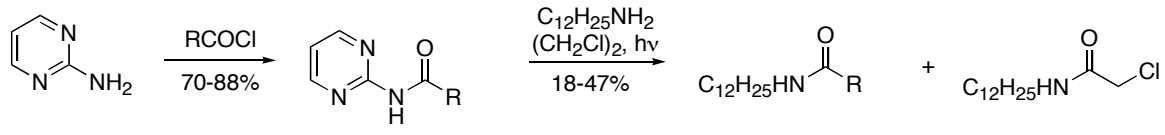


10 **11**

Scheme 6. Reactivity of 2-acetamidopyridine

d) 2-Amidopyrimidine derivatives

Reasoning that acyl migration could occur in both directions (*i.e.* either to the nitrogen atom of the pyridine ring or to the carbon on the other side), we turned our attention to the symmetrical 2-aminopyrimidine system (**13**). Preparation was straightforward; the commercially available 2-aminopyrimidine (**12**) was acylated either with acetyl chloride (acetic acid, 90°C, 24 h, 88%) or lauroyl chloride (pyridine/chloroform, 0°C, 70%).[9] In this case, the photolysis at 254 nm of **13** gave an initial encouraging 18% of **8** in 1,2-dichloroethane (*Scheme 7)*, while no reaction was observed in the absence of irradiation.



12 **13**: R=Me; **14**: R=$C_{11}H_{23}$ **8**: R=Me; **15**: R=$C_{11}H_{23}$ **16**

Scheme 7. Photoacylation with 2-amidopyridine derivatives

Switching to a longer wavelength was not beneficial (11%), whereas the use of 3 equivalents of **13** raised the yield to 26%. When **14** was used instead, 47% of **15** was observed by NMR spectrum.

Noteworthy, a significant side product was the chlorinated acetamide (**16**) (up to 32%), suggesting participation of the solvent in the reaction.

In conclusion, we prepared several pyridine-derived heterocycles and investigated their photoacylating properties. Among representatives of 4 families of compounds, the 2-aminopyrimidine derivatives were the most promising candidates, with a photoacylation yield up to 47%. The Fries rearrangement was our initial source of inspiration, but despite the fact that the photoacylation proceeded as expected, there is no evidence of a similarity in the mechanisms.

EXPERIMENTAL

General. ^{1}H and ^{13}C NMR spectra were recorded on Fourier transform *Bruker-DRX-500* (500 MHz) or *Bruker-DRX-400* (400 MHz) spectrometer with solvent used as a reference. For ^{13}C NMR, the number of hydrogen was determined by a DEPT sequence. IR spectra were recorded on Fourier transform *Perkin-Elmer 1600 FT-IR* spectrophotometer, neat, in $CHCl_3$ (NaCl cell) or in KBr; absorption bands are in cm^{-1}. UV spectra were recorded on a *UV Kontron Uvikon 860* spectrophotometer; absorption bands are in nm. MS were recorded on *Varian CH 4* or *SM 1* spectrometer, with electronic impact (70 eV). Photochemical irradiations were made in a *Srinivasan-Griffin* (Rayonet-RPR-100) photoreactor, in a quartz vessel, with 16 lamps of 254, 300, 350 or 420 nm. All melting points are uncorrected. Unless otherwise indicated, all commercial reagents were used without further purification.

General procedure for the photoacylation: A solution of acylating agent and nucleophile in 1,2-dichloroethane was flushed with argon for 10 min. It was then irradiated at 254 nm for 1 to 7.5 h, under argon, with stirring and cooling by water. The volatiles were then evaporated and the solid was purified by FC.

1-Acetyl-7-azaindole (*7*): A solution of 7-azaindole (**6**) (1.20 g, 10 mmol) in acetic anhydride (12 mL) and acetic acid (1.2 mL) was heated at reflux (*ca*. 150°C) for 22 h. The reaction mixture was then poured into water, giving a solid, which was filtered and dried in vacuo, to give 849 mg (52%) of the product as pale pink crystals (mp 63-65°C). ^{1}H NMR ($CDCl_3$) δ 8.37 (dd, J = 4.8, 1.5 Hz, 1H), 7.99 (d, J = 4.0 Hz, 1H), 7.88 (dd, J = 7.8, 1.8 Hz, 1H), 7.20 (dd, J = 7.8, 4.8 Hz, 1H), 6.59 (d, J = 4.3 Hz, 1H), 3.07 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 169.1 (C), 147.8 (C), 143.8 (CH), 129.3 (CH), 125.4 (CH), 123.7 (C), 118.6 (CH), 105.7 (CH), 25.8 (CH_3). IR (neat) 3148.4, 3111.7, 1688.0, 1581.0, 1530.4, 1379.1, 1312.6, 1261.0, 1239.4. UV (52 μM soln in MeCN) λ_{max} (ε) 194 (0.61), 237 (1.11), 268 (0.56). MS *m/z* (%) 160 (13, $M^{+\bullet}$), 118 (100), 91 (18); HR-MS 160.0643 ($C_9H_8N_2O$ calcd 160.0637). Anal. Calcd for $C_9H_8N_2O$: C, 67.49; H, 5.03;

N, 17.49. Found: C, 67.42; H, 4.97; N, 17.52.

N-Dodecylacetamide (***8***): 2-Acetylaminopyrimidine (60 mg, 0.44 mmol) and dodecylamine (28 mg, 0.15 mmol) in 15 mL of 1,2-dichloroethane were irradiated for 6 h as described in the general photoacylation procedure, giving 8.8 mg (26%) of the product as a white solid (mp 49-52°C), TLC R_f 0.17 (cyclohexane:EtOAc 1:2). ^{1}H NMR ($CDCl_3$) δ 5.40 (br s, 1H); 3.24 (q, J = 6.7 Hz, 2H), 1.98 (s, 3H), 1.50 (quint, J = 7.2 Hz, 2H), 1.33-1.24 (18H), 0.89 (t, J = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 169.9 (C), 39.7 (CH_2), 31.9 (CH_2), 29.62 (CH_2), 29.57 (CH_2), 29.53 (CH_2), 29.33 (CH_2), 29.29 (CH_2), 26.9 (CH_2), 23.4 (CH_3), 22.7 (CH_2), 14.1 (CH_3). IR (neat) 3306.9, 3278.5, 2915.4, 2850.2, 1637.2, 1554.4, 1467.4, 1370.3, 1291.0, 720.6. MS *m/z* (%) 227 (19, $M^{+\bullet}$), 212 (7), 198 (4), 184 (7), 170 (8), 156 (9), 142 (10), 128 (12), 114 (29), 100 (32), 86 (41), 73 (100), 72 (85), 60 (40); HR-MS 227.2247 ($C_{14}H_{29}NO$ calcd 227.2249).

1-Acetyl-7-azaindoline (***9***): A mixture of 1-acetyl-7-azaindole (**7**) (400 mg, 2.50 mmol) and 10% palladium on charcoal in 30 mL of EtOH:DME (1:1) was stirred at rt under H_2 for 5 h, then it was filtered on celite and evaporated, to give 362 mg (89%) of the product as a white solid (mp 122-124°C). ^{1}H NMR ($CDCl_3$) δ 8.11 (d, J = 5.1 Hz, 1H), 7.46 (dq, J = 7.4, 1.4 Hz, 1H), 6.87 (dd, J = 7.3, 5.1 Hz, 1H), 4.11 (t, J = 8.6 Hz, 2H), 3.06 (t, J = 8.6 Hz, 2H), 2.69 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 170.1 (C), 156.1 (C), 146.1 (CH), 133.3 (CH), 125.9 (C), 117.9 (CH), 45.5 (CH_2), 24.8 (CH_3), 24.2 (CH_2). IR (neat) 2965.2, 2933.5, 2911.3, 1645.6, 1584.9, 1411.8, 1384.4, 1322.4, 1238.8, 789.5. UV (51 μM soln in MeCN) λ_{max} (ε) 197 (0.59), 245 (0.64), 296 (0.50). MS *m/z* (%) 162 (22, $M^{+\bullet}$), 120 (100), 119 (91), 93 (80), 65 (14); HR-MS 162.0782 ($C_9H_{10}N_2O$ calcd 162.0793).

7-Azaindole: A solution of 1-acetyl-7-azaindoline (11.4 mg, 70 μmol) and dodecylamine (13.0 mg, 70 μmol) in 7.5 mL of 1,2-dichloroethane was irradiated for 1 h as described in the general photoacylation procedure, giving 2.1 mg (25%) of the product as a pale brown solid (mp 92-98°C), TLC R_f 0.21 (cyclohexane:EtOAc 1:1). ^{1}H NMR ($CDCl_3$) δ 9.78 (br s, 1H), 8.34 (dd, J = 4.7, 1.6 Hz, 1H), 7.97 (dd, J = 7.8, 1.5 Hz, 1H), 7.36 (dd, J = 3.3, 2.1 Hz, 1H), 7.11 (dd, J = 7.9, 4.7 Hz, 1H), 6.53 (dd, J = 3.5, 1.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 148.5 (C), 143.0 (CH), 128.9 (CH), 124.8 (CH), 120.2 (C), 116.0 (CH), 101.0 (CH). IR (neat) 3066.4, 2970.3, 2919.4, 2852.2, 2751.7, 1600.0, 1583.6, 1497.6, 1420.2, 1335.5, 1278.5, 1106.9, 901.1, 883.1. MS *m/z* (%) 118 (100, $M^{+\bullet}$), 91 (56), 64 (24), 63 (23); HR-MS 118.0533 ($C_7H_6N_2$ calcd 118.0531).

2-Acetylaminopyridine (***11***): A solution of 2-aminopyridine (**10**) (130 mg, 1.38 mmol) in acetic acid (4 mL) and acetyl chloride (1 mL) was stirred at reflux (*ca*. 90°C) for 2 h. An evaporation of the volatiles

gave 233 mg (quantitative) of the product as a white solid (decomp. 145-155°C). ^{1}H NMR ($CDCl_3$) δ 11.97 (br s, 1H), 8.67 (d, J = 8.8 Hz, 1H), 8.19 (m, 2H), 7.36 (t, J = 6.3 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 170.8 (C), 149.6 (C), 145.3 (CH), 137.8 (CH), 119.3 (CH), 116.9 (CH), 24.9 (CH_3). IR (neat) 3038.0, 2782.5, 1698.4, 1641.3, 1628.2, 1609.4, 1557.4, 1440.5, 1423.5, 1235.1, 1200.8, 1163.8, 935.5, 822.7, 783.0. UV (53 μM soln in MeCN) λ_{max} (ε) 198 (0.64), 232 (0.44), 286 (0.25). MS m/z (%) 136 (20, $M^{+\bullet}$), 94 (100), 67 (61); HR-MS 136.0641 ($C_7H_8N_2O$ calcd 136.0637).

2-Acetylaminopyrimidine (***13***): A solution of 2-aminopyrimidine (**12**) (1.00 g, 10.5 mmol) in a mixture of acetyl chloride (5 mL) and acetic acid (20 mL) was stirred at 90°C for 24 h. Addition of EtOAc to the cooled mixture lead to a precipitate, which was filtered and dried under vacuum to give 1.29 g (88%) of the product as a white solid (mp 125-130°C, then 180-185°C). ^{1}H NMR ($CDCl_3$) δ 9.68 (br s, 1H), 8.65 (d, J = 4.8 Hz, 2H), 7.01 (t, J = 4.8 Hz, 1H), 2.52 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 171.4 (C), 158.3 (CH), 157.7 (C), 116.0 (CH), 25.3 (CH_3). IR (neat) 3143.8, 2993.0, 1674.3, 1578.5, 1520.0, 1448.7, 1396.2, 1371.9, 1302.6, 1247.8, 1012.3, 860.6, 805.5. UV (50 μM soln in MeCN) λ_{max} (ε) 232 (0.96), 268 (0.13). MS m/z (%) 137 (28, $M^{+\bullet}$), 95 (100), 68 (57); HR-MS 137.0587 ($C_6H_7N_3O$ calcd 137.0589).

2-Lauroylaminopyrimidine (***14***): A mixture of 2-aminopyrimidine (**12**) (1.00 g, 11 μmol) and pyridine (0.85 mL, 0.83 g, 11 μmol) in 5 mL of $CHCl_3$ was stirred in an ice bath. Lauroyl chloride (2.5 mL, 2.3 g, 11 μmol) in 5 mL of $CHCl_3$ was slowly added dropwise at 0 °C, and the mixture was stirred at rt overnight. It was diluted with $CHCl_3$ to about 25 mL; this organic layer was washed with 5% aqueous K_2CO_3, which was extracted 3 times with $CHCl_3$. The combined organic layer was dried on $MgSO_4$ and evaporated. Recrystallisation from EtOAc afforded 2.06 g (70%) of a white solid (mp 86-90°C). ^{1}H NMR ($CDCl_3$) δ 8.60 (d, J = 4.8 Hz, 2H), 8.12 (br s, 1H), 7.01 (t, J = 4.9 Hz, 1H), 2.70 (t, J = 7.3 Hz, 2H), 1.74 (quint, J = 7.5 Hz, 2H), 1.45-1.22 (16H), 0.89 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 173.0 (C), 158.3 (CH), 157.5 (C), 116.2 (CH), 37.6 (CH_2), 31.9 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 25.0 (CH_2), 22.7 (CH_2), 14.1 (CH_3). IR (neat) 3140.2, 3096.7, 2920.6, 2849.9, 1683.9, 1581.6, 1523.3, 1469.7, 1448.4, 1385.6, 1299.5, 1274.9, 1209.2, 1185.2, 867.6, 812.6. UV (49 μM soln in MeCN) λ_{max} (ε) 233 (1.01), 267 (0.13). MS m/z (%) 277 (<1, $M^{+\bullet}$), 234 (1), 220 (<1), 206 (2), 192 (3), 164 (5), 150 (39), 137 (100), 96 (85), 95 (52); HR-MS 277.2154 ($C_{16}H_{27}N_3O$ calcd 277.2154). Anal. Calcd for $C_9H_8N_2O$: C, 69.27; H, 9.81; N, 15.15. Found: C, 69.27; H, 9.75; N, 15.24.

N-Lauroyl-dodecylamine (***15***): A solution of 2-lauroylaminopyrimidine (12.9 mg, 47 μmol) and dodecylamine (8.6 mg, 47 μmol) in 5 mL of 1,2-dichloroethane was irradiated for 7.5 h as described in the general photoacylation procedure, giving 3.0 mg (*ca.* 17%) of product (contaminated with some

2-chloro-*N*-dodecyl-acetamide and lauroic acid) as a brown solid (mp 76-79°C), TLC R_f 0.39 (cyclohexane:EtOAc 2:1). ^{1}H NMR ($CDCl_3$) δ 5.41 (br s, 1H), 3.24 (q, J = 6.7 Hz, 2H), 2.15 (t, J = 7.6 Hz, 2H), 1.62 (quint, J = 7.3 Hz, 2H), 1.49 (quint, J = 6.8 Hz, 2H), 1.34-1.22 (m, 34H), 0.88 (t, J = 6.8 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 173.1 (C), 39.5 (CH_2), 37.0 (CH_2), 31.9 (CH_2), 29.69 (CH_2), 29.65 (CH_2), 29.63 (CH_2), 29.62 (CH_2), 29.59 (CH_2), 29.55 (CH_2), 29.51 (CH_2), 29.37 (CH_2), 29.33 (CH_2), 29.31 (CH_2), 26.9 (CH_2), 25.9 (CH_2), 22.7 (CH_2), 14.1 (CH_3). IR ($CHCl_3$) 3448.6, 2927.3, 2855.1, 1660.2, 1518.4, 1466.3. MS *m/z* (%) 367 (11, $M^{+\bullet}$), 338 (4), 324 (6), 310 (4), 296 (9), 282 (8), 268 (6), 254 (11), 240 (43), 227 (56), 212 (25), 184 (15), 114 (42), 100 (29), 86 (45), 73 (77), 57 (100); HR-MS 367.3849 ($C_{24}H_{49}NO$ calcd 367.3814).

2-Chloro-N-dodecylacetamide (***16***): In the preparation of (**8**) described above, another chromatographic fraction (TLC R_f 0.68, cyclohexane:EtOAc 1:2) gave 5.3 mg (14%) of the product as a pale yellow solid (mp 54-59°C). ^{1}H NMR ($CDCl_3$) δ 6.57 (br s, 1H), 4.06 (s, 2H), 3.31 (q, J = 6.8 Hz, 2H), 1.55 (quint, J = 7.2 Hz, 2H), 1.38-1.22 (18H), 0.89 (t, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 165.7 (C), 42.7 (CH_2), 39.9 (CH_2), 31.9 (CH_2), 29.61 (CH_2), 29.55 (CH_2), 29.48 (CH_2), 29.33 (CH_2), 29.30 (CH_2), 29.2 (CH_2), 26.8 (CH_2), 22.7 (CH_2), 14.1 (CH_3). IR (neat) 3292.3, 2915.2, 2847.6, 1667.9, 1643.0, 1546.9, 1464.3, 1416.8, 1375.9, 1265.0, 1234.0. MS *m/z* (%) 261 (2, $M^{+\bullet}$), 226 (99), 212 (97), 184 (11), 148 (14), 120 (26), 107 (100), 94 (52), 72 (62), 69 (52), 57 (89), 55 (89); HR-MS 261.1857 ($C_{14}H_{28}NO^{35}Cl$ calcd 261.1859).

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REFERENCES

1. J. Otera, *Chem. Rev.,* 1993, **93**, 1449 and references therein.
2. C. Helgen and C. G. Bochet, *Synlett,* 2001, 1968.
3. a) B. Amit, D. A. Ben-Efraim, and A. Patchornik, *J. Am. Chem. Soc.,* 1976, **98**, 843. b) S. Pass, B. Amit, and A. Patchornik, *J. Am. Chem. Soc.,* 1981, **103**, 7674. c) For a recent application in solid-phase synthesis, see: K. C. Nicolaou, B. S. Safina, and N. Winssinger, *Synlett,* 2001, 900. d) For recent mechanistic studies, see: G. Papageorgiou, A. Barth, and J. E. T. Corrie, *Photochem. Photobiol. Sci.,* 2005, **4**, 216. A. D. Cohen, C. Helgen, C. G. Bochet, and J. P. Toscano, *Org. Lett.,* 2005, **7**, 2845.

4. C. Helgen and C. G. Bochet, *J. Org. Chem.,* 2003, **68**, 2483.

5. C. G. Bochet, *J. Chem. Soc., Perkin Trans. 1,* 2002, 125.

6. a) A. H. Blatt, *Organic Reactions,* 1942, **1**, 342. b) R. Martin, *Org. Prep. Proced. Int.,* 1992, 369. c) W. Kantlehner, *Eur. J. Org. Chem.,* 2003, 2530. d) D. Bellus, *Adv. Photochem.,* 1971, **8**, 109.

7. G. Höfle, W. Steglich, and H. Vorbrüggen, *Angew. Chem., Int. Ed.,* 1978, **17**, 569. E. F. V. Scriven, *Chem. Soc. Rev.,* 1983, **12**, 129. R. Murugan and E. F. V. Scriven, *Aldrichimica Acta,* 2003, **36**, 21.

8. C. Gálvez and P. Viladoms, *J. Heterocycl. Chem.,* 1982, **19**, 665.

9. C. V. Greco and J. F. Warchol, *J. Org. Chem.,* 1971, **36**, 604.