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Synthesis and Photochemistry of Novel 3,5-Diacetyl-1,4-dihydropyridines

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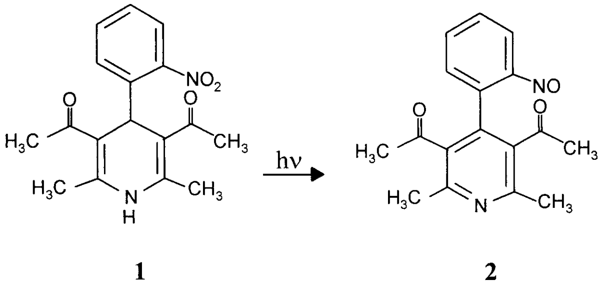
Summary. Some novel 3,5-diacetyl-1,4-dihydropyridine derivatives were synthesized; their photochemical behaviour was studied under oxygen or argon atmosphere. Irradiation of these compounds resulted in the aromatization of the ring and formation of 3,5-diacetylpyridine derivatives. The presence of oxygen plays an important role in the type, rate, or failure of oxidation. Irradiation of these compounds with of 2-furyl or 5-methyl-2-furyl substituents in position 4 under argon resulted in the formation of a pyridine ring with retention of these substituents, whereas loss of these substituents and ring aromatization was observed upon irradiation under oxygen.

Keywords. 1,4-Dihydropyridines; Heterocycles; Photochemistry; Photooxidation.

Introduction

In the course of our studies on the chemistry of 1,4-dihydropyridine-3,5-diesters, also known as *Hantzsch* esters [1], especially their photochemical behaviour, we were interested to investigate the effect of an acetyl group instead of an ester group in positions 3 and 5 on the rate and type of oxidation.

Recent results have indicated that not only the type and nature of the 4-substituent plays an important role in the photooxidation, but also the presence or absence of oxygen has an effect on the rate or failure of the reaction [2, 3]. *Berson* and *Brown* [4] have shown that upon irradiation of dihydropyridine **1** disproportionation with loss of a molecule of water and formation of **2** occurs.



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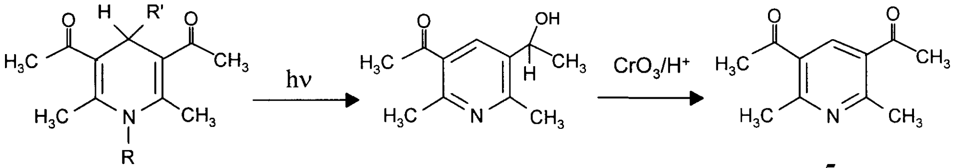
Further investigations [5] on the photoreactivity of 3,5-diacetyl-1,4-dihydropyridines **3a**–**c** (*t*-butanol, medium pressure mercury lamp, N_2 atmosphere) have shown that only in the case of **3a** the product **4** has been obtained; in all other cases, irradiation resulted in the recovery of unchanged starting material. Chromic acid oxidation of the photoproduct led to the known diacetyl pyridine **5** [6].



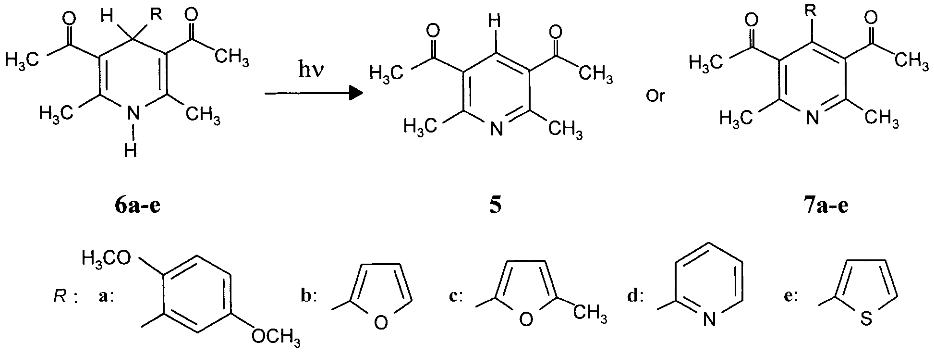
3 **4** **5**

a: $R = R' = H$
b: $R = H, R' = CH_3$
c: $R = CH_3, R' = H$

In continuation of our work, we synthesized the novel 3,5-diacetyl-1,4-dihydropyridines **6a**–**e** and investigated their photochemical behaviour under oxygen or argon atmosphere.

Results and Discussion

A 15×10^{-3} *M* solution of **3a** or **6a**–**e** in $CHCl_3$ was irradiated under oxygen and argon atmosphere until all starting material had disappeared. The results are summarized in Table 1.



6a-e **5** **7a-e**

It is interesting to compare the results of the reactions under oxygen or argon atmosphere in the following aspects:

i) Whereas in the presence of oxygen the irradiation time, can be shortened, oxidation of **6d** does not occur in the absence of oxygen.
ii) Whereas irradiation of **6a** and **6e** under both atmospheres yields **7a** and **7e** with retention of the substituent in position 4, loss of this substituent and formation of **5** were observed only upon irradiation of **6b** and **6c** under oxygen.

The observed fast reaction under oxygen atmosphere indicates the involvement of the singlet state of **3a** and **6a**–**e** in the reaction, since it could not be quenched by

Table 1. Irradiation of dihydropyridines **3a** and **6a–e** under O_2 and Ar

	O_2		Ar	
	Product (%)[a]	Time (h)[b]	Product (%)[a]	Time (h)[b]
3a	**5** (85)	4	**5** (81)	9.5
6a	**7a** (81)	12.5	**7a** (77)	19
6b	**5** (85)	7	**7b** (75)	22
6c	**5** (88)	6	**7c** (79)	19.5
6d	**7d** (80)	11.5	**6d** (–)	12
6e	**7e** (78)	14	**7e** (80)	17

[a] Isolated yield; [b] Irradiation times refer to disappearance of the starting material

triplet oxygen (oxygen in its ground state). This suggestion is also supported by the fact that in the case of **6d** the photooxidation did not occur under argon. Another possibility that singlet oxygen formed by energy transfer from excited **3a** and **6a**–**e** to oxygen in the ground state is involved in the reaction can be ruled out since dihydropyridines are not suitable triplet sensitizers for the formation of singlet oxygen. Recently, we have reported on the photosensitized oxidation of *Hantzsch* esters using rose bengal, methylene blue, and tetraphenylporphine under oxygen [7]. The results indicated that photooxidation in the presence of these triplet sensitizers is faster in comparison to the reaction in their absence. Additional studies have shown that photooxidation of **3a** and **6a**–**e** proceeds fast in the presence of these sensitizers [8].

The loss of the substituent in position 4 has been observed earlier in photochemical reactions of *Hantzsch* esters only in the cases of carboxy groups [9], some heterocyclic groups [3], and secondary alkyl and benzyl groups [3]. Thermal oxidation of *Hantzsch* esters with expulsion of benzylic and secondary substituents in position 4 by various oxidants such as pyridinium chlorochromate (*PCC*) [10], ceric ammonium nitrate (*CAN*) [11], bismuth nitrate pentahydrate [12], manganese(III) acetate [13], *tetrakis*-pyridine cobalt(II) dichromate (*TPCD*) [14], 3-carboxypyridinium chlorochromate (*CPCC*) [15], nicotinium dichromate (*NDC*) [16], sodium nitrite/oxalic acid [17], sodium nitrite/sodium hydrogen sulfate [18], sodium nitrite/magnesium hydrogen sulfate [19], sodium nitrate in the presence of wet SiO_2 [20], barium manganate [21], and potassium peroxodisulfate [22] has been reported.

IR, ^1H NMR (Table 2), and UV data gave useful information on the structural assignment of the photoproducts **5** and **7a**–**e**. A comparison of the IR spectra showed the disappearance of the NH band and a shift of the CO vibration to higher frequency due to oxidation and aromatization of the ring, which cause a decrease in the conjugation of the CO groups with the C–C double bonds. Comparison of the ^1H NMR spectra indicated the loss of the NH signal and of characteristic peaks of the substituent in position 4 in the case of **5** because of the expulsion of the substituent upon photooxidation of **6b** and **6c**. In this case, H–C_4 appears in the aromatic region at 8.25 ppm. In the ^1H NMR spectra of photoproducts containing the 4-substitunt, the loss of NH and H–C_4 resonances was observed. Owing to conjugation of the C–C double bond of dihydropyridine with the carbonyl double

Table 2. Comparison of the IR and ^{1}H NMR spectra of **3a**, **6a–e** with those of **5**, **7a–e**

	IR (γ/cm^{-1})		^{1}H NMR (δ/ppm)					IR (γ/cm^{-1})	^{1}H NMR (δ/ppm)		
	NH	CO	2,6-CH$_3$	3,5-COCH$_3$	4-H	NH		CO	2,6-CH$_3$	3,5-COCH$_3$	4-H
3a	3400	1670	2.18	2.23	3.43	5.26	**5**	1680	2.64	2.77	8.25
6a	3260	1665	2.24	2.28	5.29	6.15	**7a**	1683, 1700	1.90	2.40	–
6b	3250	1665	2.32	2.36	5.15	6.71	**7b**	1690, 1700	2.15	2.51	–
6c	3280	1668	2.32	2.37	5.07	6.83	**7c**	1690	2.19	2.49	–
6d	3200	1655	2.25	2.32	5.31	8.09	**7d**	1700	2.08	2.56	–
6e	3320	1670	2.33	2.34	5.38	6.72	**7e**	1690	2.03	2.51	–

bond, the methyl groups in positions 2 and 6 are shifted downfield and the protons of the acetyl groups are shifted upfield in comparison with these resonances in the photoproduct (pyridine ring). Also, the UV spectra did not show any strong absorption above 300 nm, which is characteristic for the pyridine ring.

Experimental

All melting points were determined with a Stuart Scientific SMP2 and are uncorrected. IR: Shimadzu IR-435; UV: Shimadzu UV-160; ^{1}H NMR: Bruker AW80 (80 MHz), Bruker WM 300 (300 MHz); mass spectra: AMD 604; EI mode (70 eV): temperature of inlet system given; FD mode: high voltage applied given, no additional heating of the emitter filament. Elemental analyses: Carlo Erba 1106 CHN-analyzer; the results agreed favourably with the calculated values. Preparative thin layer chromatography (PLC) was carried out on $20 \times 20\,\text{cm}^2$ plates coated with a 1 mm layer of Merk silica gel PF$_{254}$ prepared by applying the silica as a slurry and drying in air.

All irradiations were performed using a 400 W high-pressure Hg-vapour lamp from NARVA with cooling of samples in Duran glass ($\lambda \geq 280\,\text{nm}$) by running cold water. Argon (99.99%) or oxygen (99.99%) was bubbled through the solutions during irradiation.

General procedure for the preparation of compound **3a**, **6a–e**

A mixture of 0.02 mol of appropriated aldehyde and 0.04 mol of acetylacetone in 20 cm^3 EtOH was saturated with NH$_3$ gas (**3a**) or treated with 3 cm^3 of NH$_3$ solution (**6a–e**) and refluxed for the time given. The solvent was evaporated, and the residue was cooled in refrigerator. The solid material was purified by recrystallization.

3,5-Diacetyl-2,6-dimethyl-1,4-dihydropyridine (**3a**; $C_{11}H_{15}NO_2$)

8 h refluxed, recrystallized from ethanol/petroleum ether (5 : 1); m.p.: 197°C (Ref. [6]: 198°C); IR (KBr): $\nu = 3400$ (NH), 1670 (CO) cm^{-1}; ^{1}H NMR (CDCl$_3$): $\delta = 2.18$ (s, 6H, 2- and 6-CH$_3$), 2.23 (s, 6H, 3- and 5-COCH$_3$), 3.43 (s, 2H, 4-H), 5.26 (s, 1H, NH) ppm; EI-MS (170°C): m/z (%) = 193 [M$^+$] (93), 192 [M$^+$-H] (100), 178 [M$^+$-CH$_3$] (81), 150 [M$^+$-COCH$_3$] (37), 107 [M$^+$-2 × COCH$_3$] (10); UV (CHCl$_3$): $\lambda_{\max}$ (lg ε) = 393 (3.92), 275 (3.90), 249 (3.97) nm; UV (CH$_3$OH): $\lambda_{\max}$ (lg ε) = 408 (3.63), 276 (3.62), 251 (3.88) nm.

3,5-Diacetyl-4-(2′,5′-dimethoxyphenyl)-2,6-dimethyl-1,4-dihydropyridine (**6a**; $C_{19}H_{23}NO_4$)

6 h refluxed, recrystallized from EtOH; m.p.: 192°C; IR (KBr): $\nu = 3260$ (NH), 1665 (CO) cm^{-1}; ^{1}H NMR (CDCl$_3$): $\delta = 2.24$ (s, 6H, 2- and 6-CH$_3$), 2.28 (s, 6H, 3- and 5-COCH$_3$), 3,69 (s, 3H,

5′-OCH$_3$), 3.77 (s, 3H, 2′-OCH$_3$), 5.29 (s, 1H, 4-H), 6.15 (s, 1H, NH), 6.61 (d, $J = 2.98$ Hz, 1H, 6′-H), 6.65 (dd, $J = 8.73$ Hz and 3.04 Hz, 1H, 4′-H), 6.74 (d, $J = 8.73$ Hz, 1H, 3′-H) ppm; EI-MS (160°C): m/z (%) = 329 [M$^+$] (13), 298 [M$^+$-OCH$_3$] (78), 283 [M$^+$-OCH$_3$, -CH$_3$] (11), 192 [M$^+$-4-substituent] (100), 150 (21); UV (CHCl$_3$): λ_{max} (lg ε) = 367 (3.62), 341 (3.7), 298 (3.5), 258 (3.5) nm; UV (CH$_3$OH): λ_{max} (lg ε) = 373 (3.65), 240 (3.55) nm.

3,5-Diacetyl-4-(2′-furyl)-2,6-dimethyl-1,4-dihydropyridine (**6b**; $C_{15}H_{17}NO_3$)

8 h refluxed, recrystallized from ethanol/petroleum ether (5 : 1); m.p.: 167°C; IR (KBr): $\nu = 3250$ (NH), 1665 (CO) cm^{-1}; ^{1}H NMR (CDCl$_3$): $\delta = 2.32$ (s, 6H, 2- and 6-CH$_3$), 2.36 (s, 6H, 3- and 5-COCH$_3$), 5.15 (s, 1H, 4-H), 5.89 (dd, $J = 3.18$ Hz and 0.63 Hz, 1H, 3′-H), 6.21 (dd, $J = 3.18$ Hz and 1.87 Hz, 1H, 4′-H), 6.71 (s, 1H, NH), 7.24 (dd, $J = 1.60$ Hz and 0.66 Hz, 1H, 5′-H) ppm; EI-MS (130°C): m/z (%) = 259 [M$^+$] (51), 244 [M$^+$-CH$_3$] (10), 216 [M$^+$-COCH$_3$] (100), 192 [M$^+$-furyl] (25), 174 (47), 149 [M$^+$-furyl, -COCH$_3$] (8); UV (CHCl$_3$): λ_{max} (lg ε) = 368 (3.77), 343 (3.79), 255 (3.60) nm; UV (CH$_3$OH): λ_{max} (lg ε) = 391 (3.68), 342 (3.66), 238 (3.48) nm.

3,5-Diacetyl-2,6-dimethyl-4-(5′-methyl-2′-furyl)-1,4-dihydropyridine (**6c**; $C_{16}H_{19}NO_3$)

7 h refluxed, recrystallized from ethanol/cyclohexane (4 : 1); m.p.: 175°C; IR (KBr): $\nu = 3280$ (NH), 1668 (CO) cm^{-1}; ^{1}H NMR (CDCl$_3$): $\delta = 2.19$ (s, 3H, 5′-CH$_3$), 2.32 (s, 6H, 2- and 6-CH$_3$), 2.37 (s, 6H, 3- and 5-COCH$_3$), 5.07 (s, 1H, 4-H), 5.73 (d, $J = 3.01$ Hz, 1H, 3′-H), 5.77 (dd, $J =$ 3.04 Hz and 0.88 Hz, 4′-H), 6.83 (s, 1H, NH) ppm; EI-MS (60°C): m/z (%) 192 [M$^+$-4-substituent]; FD-MS (0.005V): m/z (%) = 273 [M$^+$] (31), 192 [M$^+$-4-substituent] (100), 134 (17); UV (CHCl$_3$): λ_{max} (lg ε) = 347 (3.97), 249 (4.07) nm; UV (CH$_3$OH): λ_{max} (lg ε) = 362 (3.81), 252 (3.99), 222 (3.92) nm.

3,5-Diacetyl-2,6-dimethyl-4-(2′-pyridyl)-1,4-dihydropyridine (**6d**; $C_{16}H_{18}N_2O_2$)

10 h refluxed, recrystallized from ethanol/petroleum ether (5 : 1); m.p.: 178°C. IR (KBr): $\nu = 3200$ (NH), 1655 (CO) cm^{-1}; ^{1}H NMR (CDCl$_3$): $\delta = 2.25$ (s, 6H, 2- and 6-CH$_3$), 2.32 (s, 6H, 3- and 5-COCH$_3$), 5.31 (s, 1H, 4-H), 7.12 (ddd, $J_{5',4'} = 6$ Hz, $J_{5',6'} = 4.9$ Hz, $J_{5',3'} = 1.1$ Hz, 1H, 5′-H), 7.34 (dd, $J_{3',4'} = 7.8$ Hz, $J_{3',5'} = 0.9$ Hz, 1H, 3′-H), 7.60 (ddd, $J_{4',3'}$ or $J_{4',5'} = 7.8$ Hz, $J_{4',6'} = 1.8$ Hz, 1H, 4′-H), 8.09 (s, 1H, NH), 8.45 (ddd, $J_{6',5'} = 4.8$ Hz, $J_{6',4'} = 1.8$ Hz, $J_{6',3'} = 0.9$ Hz, 1H, 6′-H) ppm; EI-MS (145°C): m/z (%) = 270 [M$^+$] (5), 192 [M$^+$-pyridyl] (100); FD-MS (0.01 V): m/z = (%) 270 [M$^+$] (100), 227 [M$^+$-COCH$_3$] (13); UV (CHCl$_3$): λ_{max} (lg ε) = 371 (3.74), 255 (4.0) nm; UV (CH$_3$OH): λ_{max} (lg ε) = 386 (3.74), 250 (4.25), 210 (3.8) nm.

3,5-Diacetyl-2,6-dimethyl-4-(2′-thienyl)-1,4-dihydropyridine (**6e**; $C_{15}H_{17}NO_2S$)

8 h refluxed, recrystallized from ethanol; m.p.: 171°C; IR (KBr): $\nu = 3320$ (NH), 1670 (CO) cm^{-1}; ^{1}H NMR (CDCl$_3$): $\delta = 2.33$ (s, 6H, 2- and 6-CH$_3$), 2.34 (s, 6H, 3- and 5-COCH$_3$), 5.38 (s, 1H, 4-H), 6.72 (s, 1H, NH), 6.76 and 6.77 (2 bt, 1H, 3′-H), 6.84 (dd, $J = 5.1$ Hz and 3.5 Hz, 1H, 4′-H), 7.07 (dd, $J = 5.1$ Hz and 1.19 Hz, 1H, 5′-H) ppm; EI-MS (145°C): m/z (%) = 275 [M$^+$] (70), 260 [M$^+$-CH$_3$] (17), 232 [M$^+$-COCH$_3$] (100), 192 [M$^+$-thienyl] (72); UV (CHCl$_3$): λ_{max} (lg ε) = 365 (4.02), 248 (4.1) nm; UV (CH$_3$OH): λ_{max} (lg ε) = 377 (3.86), 241 (4.17) nm.

General procedure for the irradiation of dihydropyridines

A solution of 0.3 mmol **3a** or **6a–e** in 20 cm^3 CHCl$_3$ under Ar or O$_2$ was irradiated until all starting material had disappeared (TLC; the corresponding times are given in Table 1). When the reaction was complete, the solvent was evaporated and the product was isolated by PLC.

3,5-Diacetyl-2,6-dimethylpyridine (**5**; $C_{11}H_{13}NO_2$)

PLC, ethyl acetate/cyclohexane (3 : 2), $R_f = 0.50$, recrystallized from *n*-hexane; m.p.: 66°C; IR (KBr): $\nu = 1680$ (CO) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 2.64$ (s, 6H, 2- and 6-CH_3), 2.77 (s, 6H, 3- and 5-$COCH_3$), 8.25 (s, 1H, 4-H) ppm; EI-MS (45°C): m/z (%) = 191 [M^+] (3), 176 [M^+-CH_3] (52), 148 [M^+-$COCH_3$] (5), 106 [M^+-$COCH_3$, -H_2CCO] (34), 105 [M^+-2 × $COCH_3$] (5); UV ($CHCl_3$): λ_{max} (lg ε) = 256 (4.20) nm; UV (CH_3OH): λ_{max} (lg ε) = 277 (3.88), 245 (4.12) nm.

3,5-Diacetyl-4-(2′,5′-dimethoxyphenyl)-2,6-dimethylpyridine (**7a**; $C_{19}H_{21}NO_4$)

PLC, ethyl acetate/cyclohexane (3 : 2), $R_f = 0.67$, recrystallized from *n*-hexane; m.p. 106°C; IR (KBr): $\nu = 1700$, 1683 (CO) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 1.9$ (s, 6H, 2- and 6-CH_3), 2.4 (s, 6H, 3- and 5-$COCH_3$), 3.7 (s, 6H, 2′- and 5′-OCH_3), 6.6 (s, 1H, 6′-H), 6.9 (s, 2H, 3′- and 4′-H) ppm; EI-MS (100°C): m/z (%) = 327 [M^+] (89), 312 [M^+-CH_3] (6), 297 [M^+-2 × CH_3] (21), 296 [M^+-OCH_3] (100), 253 [M^+-OCH_3, -$COCH_3$] (4), 226 (10), 127 (9), 115 (9), 43 [$COCH_3$] (65); UV ($CHCl_3$): λ_{max} (lg ε) = 258 (3.40) nm; UV (CH_3OH): λ_{max} (lg ε) = 241 (3.40) nm.

3,5-Diacetyl-4-(2′-furyl)-2,6-dimethylpyridine (**7b**; $C_{15}H_{15}NO_3$)

PLC, ethyl acetate/cyclohexane (1 : 2), $R_f = 0.61$, recrystallized from *n*-hexane; m.p.: 86°C; IR (KBr): $\nu = 1700$ (sh), 1690 (CO) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 2.15$ (s, 6H, 2- and 6-CH_3), 2.51 (s, 6H, 3- and 5-$COCH_3$), 6.54 (dd, $J = 1.7$ Hz and 3.4 Hz, 1H, 4′-H), 6.59 (dd, $J = 0.7$ Hz and 3.5 Hz, 1H, 3′-H), 7.58 (dd, $J = 0.7$ Hz and 1.6 Hz, 5′-H) ppm; EI-MS (70°C): m/z (%) = 257 [M^+] (49), 242 [M^+-CH_3] (3), 214 [M^+-$COCH_3$] (63), 200 [M^+-H_2CCO, -CH_3] (60), 199 [M^+-$COCH_3$, -CH_3] (4), 173 [M^+-2 × H_2CCO] (7), 43 ($COCH_3$); UV ($CHCl_3$): λ_{max} (lg ε) = 260 (3.70) nm; UV (CH_3OH): λ_{max} (lg ε) = 237 (3.80) nm.

3,5-Diacetyl-4-(5′-methyl-2′-furyl)-2,6-dimethylpyridine (**7c**; $C_{16}H_{17}NO_3$)

PLC, ethyl acetate/cyclohexane (1 : 2), $R_f = 0.56$, recrystallized from ethyl acetate/petroleum ether (2 : 7); m.p.: 91°C; IR (KBr): $\nu = 1690$ (CO) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 2.19$ (s, 6H, 2- and 6-CH_3), 2.34 (d, $J = 0.47$, 3H, 5′-CH_3), 2.49 (s, 6H, 3- and 5-$COCH_3$), 6.13 (dd, $J = 0.84$ Hz and 3.48 Hz, 1H, 4′-H), 6.47 (d, $J = 3.42$ Hz, 1H, 3′-H) ppm; EI-MS (60°C): m/z (%) = 271 [M^+] (55), 256 [M^+-CH_3] (10), 228 [M^+-$COCH_3$] (39), 214 [M^+-H_2CCO, -CH_3] (100); UV ($CHCl_3$): λ_{max} (lg ε) = 252 (3.10) nm; UV (CH_3OH): λ_{max} (lg ε) = 250 (3.18) nm.

3,5-Diacetyl-4-(2′-pyridyl)-2,6-dimethylpyridine (**7d**; $C_{16}H_{16}N_2O_2$)

PLC, ethyl acetate/cyclohexane (3 : 1), $R_f = 0.42$, recrystallized from petroleum ether; m.p.: 112°C; IR (KBr): $\nu = 1700$ (CO) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 2.08$ (s, 6H, 2- and 6-CH_3), 2.56 (s, 6H, 3- and 5-$COCH_3$), 7.36 (ddd, $J = 7.78$ Hz, 4.59 Hz and 1.17 Hz, 2H, 3′- and 5′-H), 7.76 (ddd, $J =$ 7.74 Hz and 1.7 Hz, 1H, 4′-H), 8.68 (ddd, $J = 4.2$ Hz, 1.6 Hz and 1.2 Hz, 1H, 6′-H) ppm; EI-MS (85°C): m/z = (%) 253 [M^+-CH_3] (71), 211 [M^+-H_2CCO, -CH_3] (29), 210 [M^+-$COCH_3$, -CH_3] (14), 182 [M^+-2 × $COCH_3$] (7), 134 (25), 120 (49), 91 (100); FD-MS (0.005 V): m/z (%) = 268 [M^+] (11), 253 [M^+-CH_3] (100), 210 [M^+-$COCH_3$, -CH_3] (10); UV ($CHCl_3$): λ_{max} (lg ε) = 237 (3.80) nm; UV (CH_3OH): λ_{max} (lg ε) = 241 (3.40) nm.

3,5-Diacetyl-4-(2′-thienyl)-2,6-dimethylpyridine (**7e**; $C_{15}H_{15}NO_2S$)

PLC, ethyl acetate/cyclohexane (3 : 2), $R_f = 0.53$, recrystallized from ethyl acetate/*n*-hexane (1 : 5); m.p. 130°C; IR (KBr): $\nu = 1690$ (CO) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 2.03$ (s, 6H, 2- and 6-CH_3), 2.51

(s, 6H, 3- and 5-$COCH_3$), 7.03 (dd, $J = 3.57$ Hz and 1.19 Hz, 1H, 3′-H), 7.11 (dd, $J = 5.1$ Hz and 3.57 Hz, 1H, 4′-H), 7.51 (dd, $J = 5.03$ Hz and 1.19 Hz, 1H, 5′-H) ppm; EI-MS (85°C): $m/z = (\%)$ 273 [M^+] (58), 258 [M^+-CH_3] (57), 230 [M^+-$COCH_3$] (100), 216 (37), 198 (11), 189 (49); UV ($CHCl_3$): λ_{max} (lg ε) = 281 (3.90), 249 (3.97) nm; UV (CH_3OH): λ_{max} (lg ε) = 281 (3.95), 239 (4.04) nm.

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