Synthesis of Unsymmetrical Bis(imidoyl)dichlorides of Oxalic Acid

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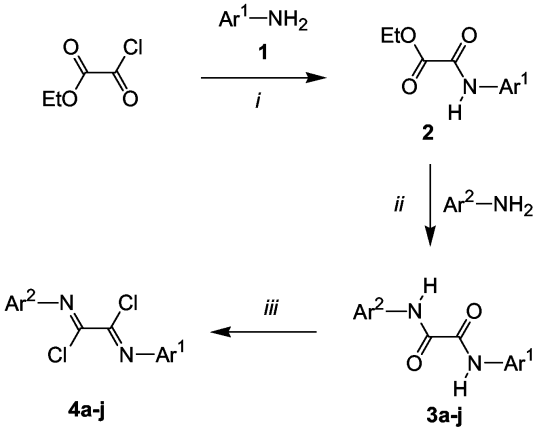
Z. Naturforsch. **60b,** 1192 – 1196 (2005); received July 20, 2005

Unsymmetrical oxalic acid-bis(imidoyl)dichlorides were prepared from ethyl 2-chloro-2-oxoacetate in three steps.

Key words: Imidoyl Chlorides, Oxalyl Derivatives, Pigments

Oxalic acid bis(imidoyl)dichlorides have been first reported by Wallach in 1879 [1]. After initial studies of the reactivity of these compounds [2, 3], Beckert and coworkers reported on the synthesis of a great variety of symmetrical, aryl-substituted derivatives based on the work of Wallach [4]. The synthesis of alkyl-substituted bis(imidoyl)chlorides is problematic, due to their unstable nature. Beckert and our group reported on cyclization reactions of symmetrical bis(imidoyl)dichlorides with a variety of bis(nucleophiles) [5]. Recently, the first examples of *unsymmetrical* oxalic acid bis(imidoyl)dichlorides have been reported by Beckert [6] and by our group [7]. Herein, we wish to report full details of our approach to unsymmetrical bis(imidoyl)dichlorides based on a three-step synthesis starting with ethyl 2-chloro-2-oxoacetate.



Scheme 1. Synthesis of unsymmetrical oxalic acid bis(imidoyl)dichlorides **4a** – **j**: *i*, NEt_3, THF, 0 → 20 °C; *ii*, toluene, reflux, 6 – 8 h; *iii*, PCl_5, toluene, reflux, 1 h.

Table 1. Products and yields.

3,4	Ar^1	Ar^2	% (**3**)[a]	% (**4**)[a]
a	C_6H_5	2-(MeO)C_6H_4	78[b], 70[c]	60
b	,,	4-(MeO)C_6H_4	85[d], 85[e]	56
c	,,	2,4-$Me_2C_6H_3$	63	65
d	,,	3,5-$Me_2C_6H_3$	56	65
e	,,	1-Naphthyl	65	56
f	4-MeC_6H_4	4-(MeO)C_6H_4	42	59
g	,,	3,5-$Me_2C_6H_3$	51	77
h	4-(MeO)C_6H_4	2,4-$Me_2C_6H_3$	60	65
i	,,	3,5-$Me_2C_6H_3$	50	57
j	4-(O_2N)C_6H_4	4-(MeO)C_6H_4	83	23

[a] Yields of isolated products; [b] prepared from ethyl 2-oxo-2-(phenylamino)acetate and *o*-anisidine; [c] prepared from ethyl 2-oxo-2-(*o*-methoxyphenyl)acetate and aniline; [d] prepared from ethyl 2-oxo-2-(phenylamino)acetate and *p*-anisidine; [e] prepared from ethyl 2-oxo-2-(*p*-methoxyphenyl)acetate and aniline.

The reaction of ethyl 2-chloro-2-oxoacetate with a number of anilines **1** gave the ethyl 2-oxo-2-(arylamino)acetates **2** (Scheme 1) [8]. The reaction of **2** with a variety of anilines afforded the novel unsymmetrical oxalamides **3a** – **j** (42 – 83%). Reflux of a toluene solution of oxalamides **3** with phosphorus pentachloride (PCl_5) afforded, after recrystallization from *n*-heptane, the unsymmetrical oxalic acid bis(imidoyl) dichlorides **4a** – **j** (23 – 77%). During the optimization of this transformation, the quality of PCl_5, the reaction time (1 h, reflux), the absence of water and the conditions for recrystallization (*n*-heptane) proved to play an important role.

Experimental Section

General procedure for the synthesis of oxalamides

To a toluene solution (10 ml) of the corresponding amine (10 mmol) was added the ethyl 2-oxo-2-(arylamino)acetate **2** (10 mmol) and the mixture was refluxed for 6 – 8 h. The product was isolated by filtration and washing with ethanol.

N-(*o*-Methoxyphenyl)-N'-phenyl-oxayl-amide (**3a**)

Starting with ethyl 2-oxo-2-(*o*-methoxyphenylamino)acetate (2.23 g, 10 mmol) and aniline (0.93 g, 10 mmol), **3a** (1.90 g, 70%) was isolated as a colourless solid, m. p. 179 °C. Starting with ethyl 2-oxo-2-(phenyl)acetate (1.93 g, 10 mmol) and *o*-anisidine (1.32 g, 10 mmol), **3a** (2.10 g, 78%) was isolated. M. p. 178 °C. – IR (KBr): $\tilde{\nu}$ = 495 (w), 691 (m), 759 (s), 865 (w), 1256 (s), 1430 (m), 1445 (s), 1484 (s), 1599 (s), 1679 (s), 3330 (m) cm^{-1}. – ^1H NMR (200 HMz, [D_6]DMSO): δ = 3.92 (s, 3 H, OCH_3), 7.00 – 7.05 (t, 1 H, Ar), 7.13 – 7.22 (m, 3 H, Ar), 7.35 – 7.41 (t, 2 H, Ar), 7.85 – 7.88 (d, 2 H, Ar), 8.19 – 8.22, (d, 1 H, Ar), 9.91 (s, 1 H, NH), 10.94 (s, 1 H, NH). – ^{13}C NMR (50 MHz, [D_6]DMSO): δ = 55.94, 111.16, 119.49, 120.58, 124.55, 124.75, 125.37, 125.63, 128.65, 137.36, 137.58, 148.91, 157.23, 158.16, 158.52. – MS (EI, 70 eV): m/z (%) = 270 ([M]$^+$, 100), 240 (15), 123 (16), 93 (78), 77 (15). – $C_{15}H_{14}N_2O_3$ (270.28): calcd. C 66.68, H 5.18; found C 66.47, H 5.03.

N-(*p*-Methoxyphenyl)-N'-phenyl-oxalamide (**3b**)

Starting with ethyl 2-oxo-2-(*p*-methoxyphenylamino) acetate (2.23 g, 10 mmol) and aniline (0.93 g, 10 mmol), **3b** (2.30 g, 85%) was isolated as a colourless solid, m. p. 191 °C. Starting with ethyl 2-oxo-2-(phenyl)acetate (10 mmol) and *p*-anisidine (10 mmol) **3b** (2.3 g, 85%) was isolated as a colourless solid. M. p. 210 °C. IR (KBr): $\tilde{\nu}$ = 494 (w), 754 (m), 825 (s), 1033 (m), 1244 (m), 1303 (w), 1445 (s), 1528 (s), 1597 (s), 1656 (s), 3297 (s) cm^{-1}. – ^1H NMR (200 MHz, [D_6]DMSO): δ = 3.75 (s, 3 H, OCH_3), 6.94 – 6.97 (d, 2 H, Ar), 7.13 – 7.18 (t, 1 H, Ar), 7.35 – 7.40 (t, 2 H, Ar), 7.76 – 7.87 (m, 4 H, Ar), 10.76 (s, 1 H, NH), 10.81 (s, 1 H, NH). – ^{13}C NMR (50 MHz, [D_6]DMSO): δ = 55.12, 113.78, 120.36, 121.85, 124.51, 128.66, 130.64, 137.57, 156.09, 158.04, 158.66. – MS (EI, 70 eV): m/z (%) = 270 ([M]$^+$, 100), 148 (49), 107 (40), 93 (75), 77 (30). – $C_{15}H_{14}N_2O_3$ (270.28): calcd. C 66.66, H 5.22, N 10.36; found C 66.93, H 5.47, N 10.28.

N-(2,4-Dimethylphenyl)-N'-phenyl-oxal-amide (**3c**)

Starting with ethyl 2-oxo-2-(phenylamino)acetate (1.90 g, 10 mmol) and 2,4-xylidine (1.20 g, 10 mmol)**, 3c** (1.70 g, 63%) was isolated as a colourless solid. M. p. 184 °C. – IR (KBr): $\tilde{\nu}$ = 487 (w), 751 (s), 821 (m), 1295 (m), 1442 (s), 1520 (s), 1598 (s), 1666 (s), 3283 (s) cm^{-1}. – ^1H NMR (200 MHz, [D_6]DMSO): δ = 2.21 (s, 3 H, CH_3), 2.27 (s, 3 H, CH_3), 7.02 – 7.05 (d, 1 H, Ar), 7.08 (s, 1 H, Ar), 7.13 – 7.18 (t, 1 H, Ar), 7.34 – 7.40 (m, 3 H, Ar), 7.86 – 7.88 (d, 2 H, Ar), 10.23 (s, 1 H, NH), 10.79 (s, 1 H, NH). – ^{13}C NMR (50 MHz, [D_6]DMSO): δ = 17.45, 20.43, 120.38, 124.56, 126.59, 128.64, 130.84, 130.90, 132.12, 132.37, 135.34, 137.50, 158.46, 158.55. – MS (EI, 70 eV): m/z (%) = 268 ([M]$^+$, 66), 147 (28), 120 (60), 93 (100), 77 (56). – $C_{16}H_{16}N_2O_2$ (268.30): calcd. C 71.65, H 5.96, N 10.44; found C 70.57, H 5.91, N 10.58.

N-(3,5-Dimethylphenyl),-N'-phenyl-oxal-amide (**3d**)

Starting with ethyl 2-oxo-2-(phenylamino)acetate (1.90 g, 10 mmol) and 3,50-xylidine (1.20 g, 10 mmol), **3d** (1.50 g, 56%) was isolated as a colourless solid. M. p. 180 °C. – IR (KBr): $\tilde{\nu}$ = 523 (m), 754 (s), 1443 (s), 1527 (s), 1598 (s) cm^{-1}. – ^1H NMR (200 MHz, [D_6]DMSO): δ = 2.27 (6 H, $2CH_3$), 6.81 (s, 1 H, Ar), 7.14 – 7.19 (t, 1 H, Ar) 7.36 – 7.41 (t, 2 H, Ar), 7.48 (s, 2 H, Ar), 7.84 – 7.87 (d, 2 H, Ar). – ^{13}C NMR (50 MHz, [D_6]DMSO): δ = 21.03, 118.12, 120.35, 124.56, 126.11, 128.67, 137.30, 137.50, 137.66, 158.38, 158.57. – MS (EI, 70 eV): m/z (%) = 268 ([M]$^+$, 100), 147 (42), 121 (94), 93 (96), 77 (74). – $C_{16}H_{16}N_2O_2$ (268.30): calcd. C 71.65, H 5.96, N 10.44; found C 71.38, H 5.77, N 10.59.

N-(1-Naphthyl)-N'-pheny l-oxalamide (**3e**)

Starting with ethyl 2-oxo-2-(naphth-1'-ylamino)acetate (2.43 g, 10 mmol) and aniline (0.93 g, 10 mmol), **3e** (1.90 g, 65%) was isolated as a colourless solid. – IR (KBr): $\tilde{\nu}$ = 491 (w), 690 (m), 757 (m), 1445 (s), 1501 (s), 1528 (s), 1599 (m), 1682 (s), 3326 (m). – ^1H NMR (200 MHz, [D_6]DMSO): δ = 7.13 – 7.16 (m, 1 H, Ar), 7.37 – 7.99 (m, 11 H, Ar), 10.86 (s, 1 H, NH), 10,97 (s, 1 H, NH). – ^{13}C NMR (50 MHz, [D_6]DMSO): δ = 120.45, 122.87, 124.55, 126.15, 126.67, 128.05, 128.31, 128.66, 132.41, 133.62, 137.61, 158.58, 159.57. – MS (EI, 70 eV): m/z (%) = 290 ([M]$^+$, 84), 240 (19), 169 (53), 143 (86), 93 (100). – $C_{18}H_{14}N_2O_2$ (290.31): calcd. C 74.49, H 4.82, N 9.64; found C 74.19, H 5.36, N 9.75.

N-(*p*-Methoxyphenyl)-N'-(p-tolyl)-oxal-amide (**3f**)

Starting with ethyl 2-oxo-2-(*p*-tolylamino)acetate (2.07 g, 10 mmol) and *p*-anisidine (1.23 g, 10 mmol), **3f** (1.20 g, 42%) was isolated as a colourless solid. M. p. 189 °C. – IR (KBr): $\tilde{\nu}$ = 498 (m), 742 (m), 822 (s), 1033 (m), 1262 (s), 1409 (m), 1532 (s), 1596 (s), 1660 (s), 3297 (s) cm^{-1}. – ^1H NMR (200 MHz, [D_6]DMSO): δ = 2.28 (s, 3 H, CH_3),

3.75 (s, 3 H, OCH_3), 6.93 – 6.96 (d, 2 H, Ar), 7.16 – 7.19 (d, 2 H, Ar), 7.73 – 7.80 (q, 4 H, Ar), 10.71 (s, 2 H, NH). – ^{13}C NMR (50 MHz, [D_6]DMSO): $\delta = 20.44$, 55.11, 113.78, 120.29, 121.80, 129.04, 130.67, 133.58, 135.07, 156.05, 158.12, 158.45. – MS (EI, 70 eV): m/z (%) = 284 ([M]$^+$, 80), 123 (41), 106 (100), 77 (15). – $C_{16}H_{16}N_2O_3$ (284.30): calcd. C 67.37, H 5.61, N 9.81; found C 67.55, H 5.83, N 9.76.

N-(3,5-Dimethylphenyl)-N'-(p-tolyl)-oxalamide (**3g**)

Starting with ethyl 2-oxo-2-(*p*-tolylamino)acetate (2.00 g, 10 mmol) and 3,5-xylidine (1.20 g, 10 mmol), **3g** (1.45 g, 51%) was isolated as a colourless solid. M. p. 193 °C. – IR (KBr): $\tilde{\nu} = 807$ (m), 1408 (m), 1527 (s), 1666 (s), 3281 (s) cm^{-1}. – ^1H NMR (200 MHz, [D_6]DMSO): $\delta = 2.26$ (s, 6 H, 2 × CH_3), 2.28 (s, 3 H, CH_3), 6.80 (s, 1 H, Ar), 7.16 – 7.19 (d, 2 H, Ar), 7.48 (s, 2 H, Ar), 7.73 – 7.76 (d, 2 H, Ar), 10.59 (s, 1 H, NH), 10.70 (s, 1 H, NH). – ^{13}C NMR (50 MHz, [D_6]DMSO): $\delta = 20.52$, 21, 11, 118.18, 120.37, 126.15, 129.13, 133.71, 134.97, 137.43, 137.71, 155.37, 158.45, 158.55, 160.78. MS (EI, 70 eV): m/z (%) = 282 ([M]$^+$, 100), 106 (80), 91 (27), 77 (26), 28 (66). – $C_{17}H_{18}N_2O_2$ (282.33): calcd. C 72.35, H 6.37, N 9.92; found C 71.53, H 6.25, N 9.76.

N-(2,4-Dimethylphenyl)-N'-(*p*-methoxyphenyl)-oxalamide (**3h**)

Starting with ethyl 2-oxo-2-(*p*-methoxyphenylamino)acetate (2.20 g, 10 mmol) and 2,40-xylidine (1.20 g, 10 mmol), **3h** (1.80 g, 60%) was isolated as a colourless solid. M. p. 183 °C. – IR (KBr): $\tilde{\nu} = 827$ (m), 1246 (s), 1523 (s), 1661 (s), 1693 (m), 3301 (s) cm^{-1}. – ^1H NMR (200 MHz, [D_6]DMSO): $\delta = 2.21$ (s, 3 H, CH_3), 2.27 (s, 3 H, CH_3), 3.75 (s, 3 H, OCH_3), 6.91 – 7.25 (m, 3 H, Ar), 7.35 – 7.38 (d, 1 H, Ar), 7.65 – 7.68 (d, 1 H, Ar), 7.77 – 7.82 (d, 2 H, Ar), 10.20 (s, 1 H, NH), 10.75 (s, 1 H, NH). – ^{13}C NMR (50 MHz, [D_6]DMSO): $\delta = 17.45$, 20.44, 55.11, 113.77, 121.86, 124.64, 126.61, 128.12, 128.82, 130.43, 130.63, 132.00, 132.44, 135.27, 156.08, 158.07, 158.58, 16.78. – MS (EI, 70 eV): m/z (%) = 298 ([M]$^+$, 100), 148 (37), 123 (91), 77 (25), 28 (43). – $C_{17}H_{18}N_2O_3$ (298.33): calcd. C 68.47, H 6.03, N 9.39; found C 67.93, H 5.87, N 8.91.

N-(3,5-Dimethylphenyl)-N'-(*p*-methoxyphenyl)-oxalamide (**3i**)

Starting with ethyl 2-oxo-2-(*p*-methoxyphenylamino)acetate (2.20 g, 10 mmol) and 3,50-xylidine (1.20 g, 10 mmol), **3i** (1.50 g, 50%) was isolated as a colourless solid. M. p. 212 °C. – IR (KBr): $\tilde{\nu} = 814$ (m), 1416 (s), 1528 (s), 1664 (s), 1692 (m) cm^{-1}. – ^1H NMR (200 MHz, [D_6]DMSO): $\delta = 2.26$ (s, 6 H, 2 x CH_3), 3.74 (s, 3 H, OCH_3), 6.79 (s, 1 H, Ar), 6.93 – 6.96 (d, 2 H, Ar), 7.47 (s, 2 H, Ar), 7.77 – 7.79 (d, 2 H, Ar), 10.57 (s, 1 H, NH), 10.69 (s, 1 H, NH). – ^{13}C NMR (50 MHz, [D_6]DMSO): $\delta = 21.12$, 55.19, 113.86, 118.16, 121.88, 126.10, 130.70, 137.44, 137.71, 156.14, 158.17, 158.60. MS (EI, 70 eV): m/z (%) = 298 ([M]$^+$, 100), 148 (36), 121 (85), 121 (100), 77 (15), 28 (50). – $C_{17}H_{18}N_2O_3$ (298.33): calcd. C 68.47, H 6.03, N 9.39; found C 67.32, H 5.59, N 9.32.

N-(*p*-Methoxyphenyl)-N'-(*p*-nitrophenyl)-oxalamide (**3j**)

Starting with ethyl 2-oxo-2-(*p*-nitrophenylamino)acetate (2.38 g, 10 mmol) and *p*-anisidine (1.23 g, 10 mmol), **3j** (2.60 g, 83%) was isolated as a colourless solid. M. p. 178 °C. – IR (KBr): $\tilde{\nu} = 744$ (w), 832 (w), 1243 (m), 1340 (s), 1410 (m), 1526 (s), 1603 (m), 1667 (s), 3295 (s) cm^{-1}. – ^1H NMR (200 MHz, [D_6]DMSO): $\delta = 3.76$ (s, 3 H, OCH_3), 6.92 – 6.98 (d, 2 H, Ar), 7.73 – 7.80 (d, 2 H, Ar), 8.12 – 8.32 (q, 4 H, Ar), 10.77 (s, 1 H, NH), 11.33 (s, 1 H, NH). – ^{13}C NMR (50 MHz, [D_6]DMSO): $\delta = 55.20$, 113.89, 120.39, 121.99, 124.75, 130.59, 143.21, 143.86, 156.23, 157.45, 159.55. – MS (EI, 70 eV): m/z (%) = 315 ([M]$^+$, 100), 300 (50), 149 (90), 108 (45). – $C_{15}H_{13}N_3O_5$ (315.27): calcd. C 57.16, H 4.12, N 13.32; found C 57.80, H 4.22, N 13.23.

General procedure for the synthesis of oxaldiimidoyl dichlorides

A toluene solution (60 ml) of oxamide **3** (10 mmol) and PCl_5 (20 mmol) was refluxed for 1 h under exclusion of moisture. The solution was concentrated (30 ml) *in vacuo* to give a precipitate upon standing at −20 °C. The solid was filtered off and recrystallized (*n*-heptane).

N-(*p*-Methoxyphenyl)-N'-phenyl-oxaldiimidolyl dichloride (**4b**)

Starting with **3b** (2.70 g, 10 mmol) and PCl_5 (4.16 g, 20 mmol), **4b** (1.70 g, 56%) was isolated as a yellow solid. M. p. 203 °C. – IR (KBr): $\tilde{\nu} = 751$ (w), 831 (w), 1030 (w), 1250 (s), 1445 (m), 1528 (s), 1662 (s), 3299 (s), 3414 (w) cm^{-1}. – ^1H NMR (200 MHz, $CDCl_3$): $\delta = 3.80$ (s, 3 H, OCH_3), 6.94 – 6.97 (d, 2 H, Ar), 7.06 – 7.09 (d, 1 H, Ar), 7.21 – 7.68 (m, 6 H, Ar). – ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 55.35$, 114.01, 114.04, 120.21, 123.69, 123.96, 126.29, 128.86, 129.12, 137.67, 137.99, 158.71, 158.94. – MS (EI, 70 eV): m/z (%) = 307 ([M]$^+$, 45) 271 (14), 168 (100), 138 (64), 77 (86), 28 (24). – $C_{15}H_{12}Cl_2N_2O$ (307.16): C 58.67, H 3.90, N 9.11; found C 58.70, H 4.12, N 8.97.

N-(2,4-Dimethylpheny)-N'-phenyl)-oxaldiimidoyl dichloride (**4c**)

Starting with **3c** (2.68 g, 10 mmol) and PCl_5 (4.16 g, 20 mmol), **4c** (2.0 g, 65%) was isolated as a yellow solid.

M. p. 148 °C. – IR (KBr): $\tilde{\nu}$ = 826 (m), 1443 (w9, 1521 (m), 1666 (s), 3282 (s) cm^{-1}. – ^1H NMR (200 MHz, $CDCl_3$): δ = 2.23 (s, 3 H, CH_3), 2.34 (s, 3 H, CH_3), 6.94 – 7.66 (m, 2 H, Ar). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 17.83, 21.03, 118.65, 120.12, 120.35, 126.51, 126.73, 128.95, 129.17, 129.74, 131.27, 136.47, 136.36, 142.01, 145.79. – MS (EI, 70 eV): m/z (%) = 305 ($[M]^+$, 15), 269 (7), 166 (33), 138 (36), 77 (44), 28 (100). – $C_{16}H_{14}Cl_2N_2$ (305.19): calcd. C 62.99, H 4.58, N 9.17; found C 63.08, H 4.96, N 9.09.

N-(3,5-Dimethylphenyl)-N'-phenyl-oxaldiimidoyl dichloride (**4d**)

Starting with **3d** (2.60 g, 10 mmol) and PCl_5 (4.16 g, 20 mmol), **4d** was isolated as a yellow solid. – ^1H NMR (200 MHz, $CDCl_3$): δ = 2.31 (s, 6 H, 2 × CH_3), 6.71 (s, 2 H, Ar), 6.86 (s, 1 H, Ar), 7.06 7.09 (d, 2 H, Ar), 7.19 – 7.24 (t, 1 H, Ar), 7.36 – 7.42 (t, 2 H, Ar). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.17, 22.56, 117.74, 119.58, 120.21, 126.48, 128.04, 128.83, 129.02, 138.55, 138.72, 145.53, 145.63. $C_{16}H_{14}Cl_2N_2$.

N-(1-Naphthyl)-N'-phenyl-oxaldiimidoyl chloride (**4e**)

Starting with **3e** (2.90 g, 10 mmol) and PCl_5 (4.16 g, 20 mmol), **4e** (1.85 g, 56%) was isolated as a yellow solid. – IR (KBr): $\tilde{\nu}$ = 492 (w), 793 (m), 1445 (s), 1501 (s), 1526 (s), 1682 (s), 3268 (s). – ^1H NMR (200 MHz, $CDCl_3$): δ = 7.15 – 7.17 (d, 1 H, Ar), 7.22 – 7.33 (m, 3 H, Ar), 7.43 – 7.45 (d, 1 H, Ar), 7.48 – 7.62 (m, 4 H, Ar), 7.76 – 7.78 (d, 1 H, Ar), 7.81 – 7.89 (m, 1 H, Ar), 7.96 – 8.05 (m, 1 H, Ar). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 115.03, 115.16, 120.34, 120.46, 123.25, 123.32, 125.27 126.47, 126.66, 127.05, 127.97, 129.00, 133.91, 133.94, 138.64, 138.97, 141.77, 145.72. – $C_{18}H_{12}Cl_2N_2$ (327.19): calcd. C 66.09, H 3.66, N 8.56; found C 65.52, H 3.83, N 8.49.

N-(*p*-Methoxyphenyl)-N'-(*p*-tolyl)-oxaldiimidoyl dichloride (**4f**)

Starting with **3f** (2.85 g, 10 mmol) and PCl_5 (4.16 g, 20 mmol), **4f** (1.90 g, 59%) was isolated as a yellow solid. M. p. 171 °C. – IR (KBr): $\tilde{\nu}$ = 695 (w), 779 (m), 847 (s), 1027 (m), 1248 (s), 1503 (s), 1657 (s), 3297 (m) cm^{-1}. – ^1H NMR (200 MHz, $CDCl_3$): δ = 2.38 (s, 3 H, CH_3), 3.84 (s, 3 H, OCH_3), 6.95 – 7.07 (m, 4 H, Ar), 7.22 – 7.31 (m, 4 H, Ar). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.11, 55.44, 114.09, 120.77, 120.82, 123.73, 123.85, 129.50, 129.74, 136.59, 137.92, 138.11, 143.19, 158.77, 158.89. – MS (EI, 70 eV): m/z (%) = 321 ($[M]^+$, 42), 285 (16), 168 (98), 151 (100), 91 (71). – $C_{16}H_{14}Cl_2N_2O$ (321.19): calcd. C 59.85, H 4.36, N 8.72; found: C 59.21, H 4.61, N 8.60.

N-(3,5-Dimethylphenyl)-N-(*p*-tolyl)-oxaldiimidoyl dichloride (**4g**)

Starting with **3g** (10 mmol) and PCl_5 (4.16 g, 20 mmol), **4g** was isolated as a yellow solid. – ^1H NMR (200 MHz, $CDCl_3$): δ = 2.42 (s, 3 H, CH_3), 2.44 (s, 3 H, CH_3), 2.48 (s, 3 H, CH_3), 6.82 (s, 2 H, Ar), 6.96 (s, 1 H, Ar), 7.16 – 7.19 (d, 2 H, Ar), 7.29 – 7.32 (d, 2 H, Ar). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 20.91, 21.12, 22.53, 117.68, 119.98, 120.77, 127.95, 129.34, 129.41, 136.58, 136.81, 137.83, 138.46, 142.75, 145.59. $C_{17}H_{16}Cl_2N_2$.

N-(2,4-Dimethylphenyl)-N'-(*p*-methoxyphenyl)-oxaldiimidoyl dichloride (**4h**)

Starting with **3h** (2.90 g, 10 mmol) and PCl_5 (4.16 g, 20 mmol), **4h** (2.20 g, 65%) was isolated as a yellow solid. M. p. 56 °C. – IR (KBr): $\tilde{\nu}$ = 830 (s), 1032 (m), 1249 (s), 1523 (s), 1597 (m), 1665 (s), 3302 (s) cm^{-1}. – ^1H NMR (200 MHz, $CDCl_3$): δ = 2.22 (s, 3 H, CH_3), 2.33 (s, 3 H, CH_3), 3.83 (s, 3 H, OCH_3), 6.90 – 7.08 (m, 5 H, Ar), 7.23 – 7.33 (d, 2 H, Ar). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 17.79, 20.98, 55.41, 114.06, 118.61, 123.92, 126.70, 129.41, 131.18, 136.25, 137.83, 137.95, 138.07, 142.28, 158.75, 158.89. – MS (EI, 70 eV): m/z (%) = 335 ($[M]^+$, 59), 300 (41), 168 (1009, 77 (81), 28 (89). – $C_{17}H_{16}Cl_2N_2O$ (335.22): calcd. C 60.93, H 4.77, N 8.35; found C 59.60, H 4.79, N 8.38.

N-(3,5-Dimethylphenyl)-N'-(*p*-methoxyphenyl)-oxaldiimidoyl dichloride (**4i**)

Starting with **3i** (2.90 g, 10 mmol) and PCl_5 (4.16 g, 20 mmol), **4i** (1.90 g, 57%) was isolated as a yellow solid. M. p. 67 °C. – IR (KBr): $\tilde{\nu}$ = 730 (m), 817 (w), 1038 (w), 1261 (m), 1531 (s), 1664 (s), 3293 (s) cm^{-1}. – ^1H NMR (200 MHz, $CDCl_3$): δ = 2.32 – 2.34 (s, 6 H, 2 × CH_3), 3.84 (s, 3 H, OCH_3), 6.70 (s, 2 H, Ar), 6.95 (s, 1 H, Ar), 6.97 – 6.98 (d, 2 H, Ar), 7.29 – 7.30 (d, 2 H, Ar). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 20.81, 21.30, 55.43, 114.08, 117.74, 120.19, 124.03, 127.98, 128.53, 128.69, 137.86, 138.66, 145.92, 158.91. – MS (EI, 70 eV): m/z (%) = 335 ($[M]^+$, 25), 299 (15), 168 (100), 77 (38). – $C_{17}H_{16}Cl_2N_2O$ (335.22): calcd. C 60.43, H 4.77, N 8.35; found C 60.09, H 4.44, N 8.01.

N-(*p*-Methoxypheynyl)-N'-(*p*-nitrophenyl)-oxaldiimidoyl dichloride (**4j**)

Starting with **3j** (3.15 g, 10 mmol) and PCl_5 (4.18 g, 20 mmol), **4j** (0.80 g, 23%) was isolated as a yellow solid. M. p. 132 °C. – IR (KBr): $\tilde{\nu}$ = 778 (m), 860 (m), 1110 (w), 1251 (s), 1345 (s), 1505 (s), 1665 (m) cm^{-1}. – ^1H NMR (200 MHz, $CDCl_3$): δ = 3.85 (s, 3 H, OCH_3), 6.98 – 7.00 (d, 2 H, Ar), 7.12 – 7.14 (d, 2 H, Ar), 7.39 – 7.40 (d, 2 H, Ar), 8.33 – 8.34 (d, 2 H, Ar). – ^{13}C NMR (50 MHz,

$CDCl_3$): $\delta = 55.45$, 114.02, 114.15, 120.17, 123.66, 124.68, 124.92, 125.54, 137.06, 142.53, 145.44, 151.74, 159.56.– $C_{15}H_{11}Cl_2N_3O_3$ (352.15): calcd. C 51.16, H 3.12, N 11.92; found C 50.12, H 4.22, N 11.24.

Acknowledgement

Financial support from the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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