Acetylenic Chemistry. Part 24 [1]. *N*-Vinylation of N-H Acid Heterocycles

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The vinylation of 9*H*-carbazole (**1**), 1*H*-indole (**3a**), and 1*H*-pyrrolo[2,3-*b*]pyridine (**3b**) with propiolic acid ethyl ester resulting in *N*-acrylic esters is reported here.

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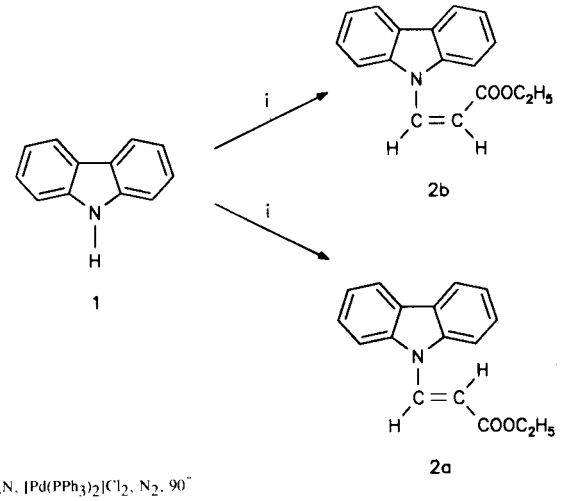
In a previous paper we described the reaction of 9(10*H*)-acridinone with propiolic acid ethyl ester which resulted in a vinylation [3]. This reaction has been extended to other N-H acid compounds. At first 9*H*-carbazole (**1**) was treated with propiolic acid ethyl ester in triethylamine. After the reaction two products could be isolated with a yield of 58% and 10%.

The spectroscopic data revealed that the product with the higher yield is ethyl *E*-3-(9*H*-carbazol-9-yl)acrylate (**2a**). The by-product is the *Z*-isomer **2b** (Scheme 1).

Scheme 1

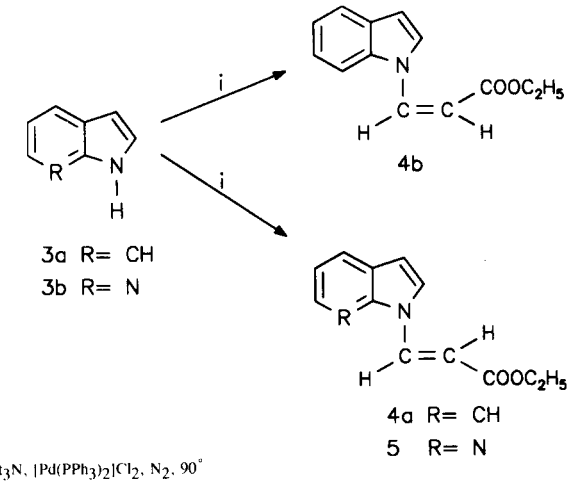


This is in contrast to the reaction of acridinone with propiolic acid ethyl ester [3], from which a *Z*-isomer could not be isolated. Due to the smaller 5-membered ring between the two phenyl rings, the angle between the nitrogen atom and the bridged carbon atom is changed. With the aid of a computer program, these angles were calculated and determined theoretically. Concerning the acridinone compounds described in [3] an angle of 120.50° and concerning the carbazole compound an angle of 129.70° were calculated. This difference could be responsible for the preference of a vinylation and hence the isolation of *E*- as well as *Z*-vinylation products.

In a further attempt 1*H*-indole (**3a**) was used and also in this case besides the *E*- **4a** a *Z*-acryl acid ethyl ester **4b** could be isolated. All the other proton signals of the indole are between the flanked vinyl proton doublets. In the ^{1}H-nmr spectrum of the *Z*-isomer **4b** the resonance signal of the 2-H proton could be observed shifted with about 1.2 ppm to the lower field by the anisotropic effect of the carbonyl oxygen. Both products are however sensitive to light.

In the third trial, using 1*H*-pyrrolo[2,3-*b*]pyridine (**3b**) under the same conditions, only ethyl E-3-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)acrylate (**5**) could be isolated (Scheme 2). In this case no *Z*-compound was found.

Scheme 2



EXPERIMENTAL

Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. The ir and electronic absorption spectra were measured with a Zeiss DMR 21 and Pye-Unicam Sp3-200 respectively. The ^{1}H- and ^{13}C-nmr were recorded on a Varian Gemini 200 (200 MHz) spectrometer, using tetramethylsilane as the internal standard. The mass spectra were obtained on a Varian MAT 44S and MAT 312 instrument at 70 eV. E. Merck (Darmstadt) silica gel 60 (grain size: 0.063-0.2 mm) was used for "flash chromatography".

General Procedure for the Synthesis of Acrylic Acid Esters.

To a suspension of a heterocyclic compound (5 mmoles) and 30

mg of $[Pd(PPh_3)_2]Cl_2$ in 180 ml of triethylamine, propiolic acid ethyl ester (10 mmoles) was added under nitrogen atmosphere with light protection and the reaction mixture was heated at reflux for 4-6 hours. The precipitate was collected by filtration and washed with methanol. It was purified by column chromatography on silica gel using chloroform/methanol (97:3) as the eluent and further recrystallization from methanol.

Ethyl *E*-3-(9*H*-Carbazol-9-yl)acrylate (**2a**).

This general procedure gave **2a** as colorless needles, mp 95° (methanol); ir (potassium bromide): ν 3030, 2990, 1710, 1600, 1580, 1480, 1455, 1360, 1190, 980 cm^{-1}; uv (methanol): λ max (log ϵ) 227 nm (4.61), 234 (4.56), 242 (4.48), 278 (4.21), 304 (4.25), 318 (4.30), 330 (4.41); ^{1}H-nmr (deuteriochloroform): δ 1.36 (t, J = 7.11 Hz, 3H, $-CH_2CH_3$), 4.31 (q, J = 7.14 Hz, 2H, $-CH_2CH_3$), 6.27 (d, J = 14.29 Hz, 1H, 2'-H), 7.32 (ddd, J = 7.64 Hz and 1.03 Hz, 2H, 3-H 6-H), 7.46 (ddd, J = 7.74 Hz and 1.33 Hz, 2H, 2-H 7-H), 7.69 (dd, J = 7.82 Hz and 0.98 Hz, 2H, 1-H 8-H), 7.97 (dd, J = 7.64 Hz and 1.35 Hz, 2H, 4-H 5-H), 8.44 (d, J = 14.32 Hz, 1H, 1-H); ^{13}C-nmr (deuteriochloroform): δ 14.47 ($-CH_2CH_3$), 60.35 ($-CH_2CH_3$), 101.75 (C-2'), 111.74 (C-1 C-8), 120.32 (C-4 C-5), 122.61 (C-3 C-6), 125.47 (C-4a C-4b), 126.92 (C-2 C-7), 137.05 (C-1'), 139.09 (C-8a C-8b), 167.99 (C-3'); ms: (70 eV) m/z (%) 265 (92, M^+), 237 (22, $M^+ - C_2H_4$), 220 (100, $M^+ - OC_2H_5$), 192 (71, 220-CO), 167 (21), 140 (15, 192-C_4H_4), 110 (22), 95 (12), 63 (14).

Anal. Calcd. for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.53; H, 5.91; N, 5.09.

Ethyl *Z*-3-(9*H*-Carbazol-9-yl)acrylate (**2b**).

The same general procedure gave **2b** as colorless needles, mp 43° (methanol); ir (potassium bromide): ν 3030, 2990, 1710, 1600, 1580, 1480, 1455, 1360, 1190, 980; ^{1}H-nmr (deuteriochloroform): δ 0.94 (t = 7.08 Hz, 3H, $-CH_2CH_3$), 4.03 (q, J = 7.10 Hz, 2H, $-CH_2CH_3$), 5.96 (d, J = 9.01 Hz, 1H, 1'-H), 7.36 (d, J = 9.06 Hz, 1H, 1'-H), 7.24-7.50 (m, 5H, 1-H 2-H 3-H 6-H 7-H 8-H), 8.10 (dd, J = 7.65 Hz and 1.35 Hz, 2H, 4-H 5-H); ^{13}C-nmr (deuteriochloroform): δ 14.03 ($-CH_2CH_3$), 60.74 ($-CH_2CH_3$), 111.42 (C-1 C-8), 112.16 (C-2'), 120.44 (C-4 C-5), 121.61 (C-3 C-6), 124.75 (C-4a C-4b), 125.32 (C-2 C-7), 133.47 (C-1'), 139.80 (C-8a C-8b), 165.23 (C-3'); ms: (70 eV) m/z (%) 265 (100, M^+), 237 (21, $M^+ - OC_2H_4$), 220 (94, $M^+ - OC_2H_5$), 192 (50, M^+ -COOEt), 167 (25), 140 (23, 192-C_4H_4), 110 (22), 95 (11), 63 (14).

Anal. Calcd. for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 77.02; H, 5.69; N, 5.29.

Ethyl *E*-3-(1*H*-Indol-1-yl)acrylate (**4a**).

The same general procedure gave **4a** as rose-colored needles, mp 86-87° (methanol); ir (potassium bromide): ν 3040, 2990, 1700, 1610, 1500, 1470, 1170, 1010 cm^{-1}; uv (methanol): λ max (log ϵ) 266 nm (4.53), 318 (4.61); ^{1}H-nmr (deuteriochlorroform): δ 1.32 (t, J = 7.16 Hz, 3H, $-CH_2CH_3$), 4.27 (q, J = 7.13 Hz, 2H, $-CH_2CH_3$), 5.94 (d, J = 14.05 Hz, 1H, 2'-H), 6.71 (d, J = 3.59 Hz, 1H, 3-H), 7.22 (dd, J = 7.66 Hz and 1.28 Hz, 1H, 6-H), 7.32 (dd, J = 8.14 Hz and 1.37 Hz, 1H, 5-H), 7.36 (d, J = 3.56 Hz, 1H, 2-H), 7.58 (dd, J = 8.25 Hz and 1.10 Hz, 1H, 7-H), 7.60 (dd, J = 7.56 Hz and 1.30 Hz, 1H, 4-H), 8.27 (d, J = 14.04 Hz, 1H, 1'-H); ^{13}C-nmr (deuteriochloroform): δ 14.41 ($-CH_2CH_3$), 60.33 ($-CH_2CH_3$), 100.72 (C-2'), 108.71 (C-3), 110.07 (C-7), 121.50 (C-4), 122.44 (C-5), 123.59 (C-6 [4]), 123.92 (C-2 [4]), 129.84 (C-3a), 136.18 (C-7a), 137.16 (C-1'), 167.39 (C-3'); ms: (70 eV) m/z (%) 216, $M^+ + H$), 233 (30, $M^+ + NH_4$).

Anal. Calcd. for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.51; H, 6.00; N, 6.33.

Ethyl *Z*-3-(1*H*-Indol-1-yl)acrylate (**4b**).

The same general procedure gave **4b** as rose-colored needles, mp 52-54° (methanol); ir (potassium bromide): ν 3030, 2980, 1700, 1600, 1490, 1460, 1160, 1000 cm^{-1}; uv (methanol): λ max (log ϵ) 266 nm (4.34), 316 (4.32); ^{1}H-nmr (deuteriochloroform): δ 1.27 (t, J = 7.14 Hz, 3H, $-CH_2CH_3$), 4.21 (q, J = 7.15 Hz, 2H, $-CH_2CH_3$), 5.36 (d, J = 10.66 Hz, 1H, 2'-H), 6.65 (d, J = 3.68 Hz, 1H, 3-H), 7.20 (dd, J = 7.70 Hz and 1.48 Hz, 1H, 6-H), 7.24 (d, J = 10.55 Hz, 1H, 1'-H), 7.25 (dd, J = 7.39 Hz and 1.62 Hz, 1H, 5-H), 7.40 (dd, J = 7.20 Hz and 1.85 Hz, 1H, 7H), 7.58 (dd, J = 7.42 Hz and 1.58 Hz, 1H, H-4), 8.53 (d, J = 3.68 Hz, 1H, 2-H); ^{13}C-nmr (deuteriochloroform): δ 14.28 ($-CH_2CH_3$), 60.24 ($-CH_2CH_3$), 100.39 (C-2'), 106.83 (C-3), 109.57 (C-7), 121.21 (C-4), 122.34 (C-5), 123.17 (C-6), 129.28 (C-2), 133.06 (C-1'), 133.91 (C-3a), 137.15 (C-7a), 165.49 (C-3'); ms: (70 eV) m/z (%) 216 (100, $M^+ + H$), 233 (36, $M^+ + NH_4$).

Anal. Calcd. for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.51. Found: C, 73.03; H, 6.09; N, 6.52.

Ethyl *E*-3-(1*H*-Pyrrolo[2,3-*b*]pyridin-1-yl)acrylate (**5**).

The same general procedure gave **5** as yellow needles, mp 65-66° (methanol); ir (potassium bromide): ν 3010, 2980, 1710, 1600, 1480, 1460, 1350, 1190, 995, 735 cm^{-1}; uv (methanol): λ max (log ϵ) 272 nm (4.52), 300 (4.35); ^{1}H-nmr (deuteriochloroform): δ 1.24 (t, J = 7.12 Hz, 3H, $-CH_2CH_3$), 4.28 (q, J = 7.14 Hz, 2H, $-CH_2CH_3$), 6.33 (d, J = 14.32 Hz, 1H, 2'-H), 6.64 (d, J = 3.87 Hz, 1H, 1-H), 7.17 (dd, J = 7.81 Hz and 4.77 Hz, 1H, 5-H), 7.43 (d, J = 3.86 Hz, 1H, 2-H), 7.89 (dd, J = 7.82 Hz and 1.62 Hz, 1H, 6-H), 8.38 (dd, J = 4.75 Hz and 1.60 Hz, 1H, 4-H), 8.62 (d, J = 14.37 Hz, 1H, 1'-H); ^{13}C-nmr (deuteriochloroform): δ 14.44 ($-CH_2CH_3$), 60.32 ($-CH_2CH_3$), 102.85 (C-1), 105.77 (C-2'), 118.36 (C-5), 122.17 (C-6a), 124.38 (C-2), 129.33 (C-6), 136.13 (C-1'), 144.30 (C-4), 147.80 (C-2a), 167.23 (C-3); ms: (70 eV) m/z (%) 216 (14, M^+), 171 (18, $M^+ - C_2H_5O$), 143 (100, M^+ -COOEt), 118 (12), 89 (7), 63 (15).

Anal. Calcd. for $C_{12}H_{12}N_2O_2$: C, 66.75; H, 5.59; N, 12.95. Found: C, 66.56; H, 5.68; N, 12.62.

REFERENCES AND NOTES

[1] Part **23**: see [3].

[2] Part of the Diplomarbeit Stefan Dittmann, Universität Münster, 1991.

[3] J. Reisch and Stefan Dittmann, *J. Heterocyclic Chem.*, **29**, 1857 (1992).

[4] Signals cannot be absolutely identified, may be exchanged.