Kurzmitteilung/Short Communication

Further Thienylchalcones, II[1,2]

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Four new thienylchalcones (1, 4, 5, and 6) were synthesized by condensing hydroxy-nitroacetophenones with 2-thiophene and 3-thiophenecarboxaldehydes in the presence of dilute NaOH.

Hydroxy-nitroacetophenones, all obtained by Fries rearrangements of the corresponding nitrophenyl ethanoates[3] were condensed with both 2-thiophene- and 3-thiophenecarboxaldehyde, resp., to give six thienylchalcones of which two (**2**, **3**) are known[2] and the rest are new compounds. The aldol condensation was carried out in a way similar to the experiments already published[2]. The yellow to light brown aqueous suspensions obtained in the condensation were acidified subsequently with dilute sulphuric acid to get the yellow thienylchalcones which were recrystallized from propanol ethanoic acid (1:1) to yield pure substances. Yields were over 70% for each of the chalcones. The structures were verified by IR and ^{1}H NMR spectroscopic investigation.

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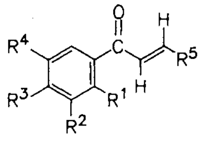
Experimental

A Perkin-Elmer 677 spectrophotometer and KBr pellets were used. – ^{1}H NMR spectra were prepared by using a Varian XL-100 FT 100 MHz apparatus, CDCl$_3$ as solvent, and Me$_4$Si as internal reference, Carbons in the benzene ring have been numbered C-1′ to C-6′ in NMR evaluation.

1-(2-Hydroxy-4-nitrophenyl)-3-(2-thienyl)-2-propen-1-one (**1**): IR (KBr): $\tilde{\nu}$ = 1641 cm^{-1} (C=O chelated), 1568 (C=C), 1524, 1350, 816 (NO$_2$). – ^{1}H-NMR (CDCl$_3$): δ = 8.14 (d, *J* = 15.0 Hz, β-H), 8.05 (d, *J* = 8.8 Hz, 6-H), 7.84 (d, *J* = 2.2 Hz, 3-H), 7.75 (dd, 5-H), 7.55 (d, *J* = 5.0 Hz, 3′-H), 7.48 (d, *J* = 3.6 Hz, 5′-H), 7.39 (d, α-H), 7.16 (dd, 4′-H), 12.95 (OH, chelated). On the basis of the 15.0 Hz value of *J*(α-H, β-H) the olefinic configuration is *E*. – ^{13}C NMR ([D$_6$]DMSO): δ = 113.5 (C-3), 115.1 (C-5), 124.3 (C-4′), 130.4 (C-6), 131.0 (C-1), 132.6, 133.0, 134.9 (C-α, -3′, -5′), 139.2 (C-β), 141.1 (C-1′), 152.0 (C-4), 160.4 (C-2), 192.9 (C=O).

1-(2-Hydroxy-4-nitrophenyl)-3-(3-thienyl)-2-propen-1-one (**4**): IR (KBr): $\tilde{\nu}$ = 1642 cm^{-1} (C=O chelated), 1566 (C=C), 1525, 1353 and 1338 (splitted band pair), 812 (NO$_2$). – ^{1}H NMR (CDCl$_3$): δ = 7.45 (broad multiplets, 3H, α-, 4′-, 5′-H), 7.8 (broad multiplets, 2H, 5-, 2′-H), 7.84 (d, *J* = 2.2 Hz, 3-H), 8.00 (d, *J* = 15.3 Hz, β-H), 8.06 (d, *J* = 8.8 Hz, 6-H), 12.93 (OH, chelated). The olefinic configuration is *E*: *J*(α-H,β-H) = 15.3 Hz. – ^{13}C NMR (CDCl$_3$): δ = 113.1 (C-3), 114.0 (C-5), 119.1 (C-4′), 123.9 (C-1), 125.3 (C-5′), 127.6 (C-2′), 130.5 and 131.3 (C-α, -6), 137.7 (C-3′), 140.9 (C-β), 152.0 (C-4), 163.8 (C-2), 193.2 (C=O).

1-(2-Hydroxy-5-nitrophenyl)-3-(3-thienyl)-2-propen-1-one (**5**): IR (KBr): $\tilde{\nu}$ = 1637 cm^{-1} (C=O chelated), 1585–1550 (broad band, C=C, ν_{as}NO$_2$), 1342, 842 (NO$_2$). – ^{1}H NMR ([D$_6$]DMSO): δ = 7.19 (d, *J* = 9.2 Hz, 3-H), 7.7 (broad multiplets, 4H, α-, β-, 4′-, 5′-H), 8.18 (d, *J* = 2.0 Hz, 2′-H), 8.34 (dd, 4-H), 8.73 (d, *J* =



Comp.	R^1	R^2	R^3	R^4	R^5	M.p.[a] [°C]	Ref.
1	OH	H	NO$_2$	H	2-thienyl	172–173	4)
2	OH	H	H	NO$_2$	2-thienyl	190–191	2)
3	H	NO$_2$	OH	H	2-thienyl	144–145	2)
4	OH	H	NO$_2$	H	3-thienyl	174–175	5)
5	OH	H	H	NO$_2$	3-thienyl	175–176	5)
6	H	NO$_2$	OH	H	3-thienyl	134–135	5)

[a] Melting points are uncorrected.

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2.8 Hz, 6-H), 12.85 (OH, chelated). The olefinic configuration is *E*: J(α-H,β-H) ≈ 15 Hz. – ^{13}C NMR ([D$_6$]DMSO): δ = 120.3 (C-3), 124.5 (C-4′), 124.8 (C-1), 128.1 and 128.2 (C-6, -5′), 129.7 (C-2′), 131.3 (C-4), 133.5 (C-α), 139.7 (C-3′), 141.1 (C-β), 141.4 (C-5), 166.7 (C-2), 193.8 (C=O).

1-(4-Hydroxy-3-nitrophenyl)-3-(3-thienyl)-2-propen-1-one (**6**): IR (KBr): $\tilde{\nu}$ = 3400 cm^{-1} (broad, OH), 1663 (C=O), 1587, 1288, 787 (NO$_2$). – ^{1}H NMR ([D$_6$]DMSO): δ = 7.26 (d, J = 8.8 Hz, 5-H), 7.67 (dd, 4′-H), 7.8 (broad multiplets, 3H, α-, β-, 5′-H), 8.13 (d, J = 2 Hz, 2′-H), 8.29 (dd, 6-H), 8.65 (d, J = 2.2 Hz, 2-H), 12.0 (broad, OH). Information about the olefinic configuration is not available due to singlet signal of α-H and β-H (nearly A$_2$ spin system). – ^{13}C NMR ([D$_6$]DMSO): δ = 121.0 (C-5), 122.7 (C-4′), 127.7 (C-2), 128.1 (C-5′), 129.4 (C-2′), 130.6 (C-1), 132.4 (C-α), 136.3 (C-6), 139.8 (C-β), 140.0 (C-3′), 157.4 (C-4), 188.2 (C=O).

CAS Registry Numbers

1: 118761-27-6 / **2**: 89720-62-7 / **3**: 118761-28-7 / **4**: 118761-29-8 / **5**: 118761-30-1 / **6**: 118761-31-2 / 2-thiophenecarboxaldehyde: 98-03-3 / 3-thiophenecarboxaldehyde: 498-62-4 / 2-hydroxy-4-nitroacetophenone: 1834-91-9 / 2-hydroxy-5-nitroacetophenone: 1450-76-6 / 4-hydroxy-3-nitroacetophenone: 6322-56-1

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1) Part I: See ref. 2) in this paper. The name "thiachalcone" used in Part I has been changed to "thienylchalcones" in line with up-to-date nomenclature.

2) T. Széll, A. Brand, Siriwan Ratanathanavongs, *Chem. Eng. Data* **26** (1981) 230.

3) T. Széll, *Chem. Ber.* **91** (1958) 2609; cf. ref. 8) in ref. 3) on p. 2611.

4) Chadha Surya, "Extended Essay", submitted to the International Baccalaureate Diploma requirement in 1987.

5) Megan Sweeney, "Extended Essay", submitted to the International Baccalaureate Diploma requirement in 1988.

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