ISSN 1070-4280, Russian Journal of Organic Chemistry, 2012, Vol. 48, No. 7, pp. 1005–1006. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © L.V. Baichurina, R.I. Baichurin, N.I. Aboskalova, M.M. Zobacheva, V.M. Berestovitskaya, 2012, published in Zhurnal Organicheskoi Khimii, 2012, Vol. 48, No. 7, pp. 1007–1008.

SHORT
COMMUNICATIONS

Reaction of α-Nitroacrylates with Acetylacetone

L. V. Baichurina, R. I. Baichurin, N. I. Aboskalova,
M. M. Zobacheva, and V. M. Berestovitskaya

Herzen State Pedagogical University of Russia, nab. r. Moiki 48, St. Petersburg, 191186 Russia
e-mail: kohrgpu@yandex.ru

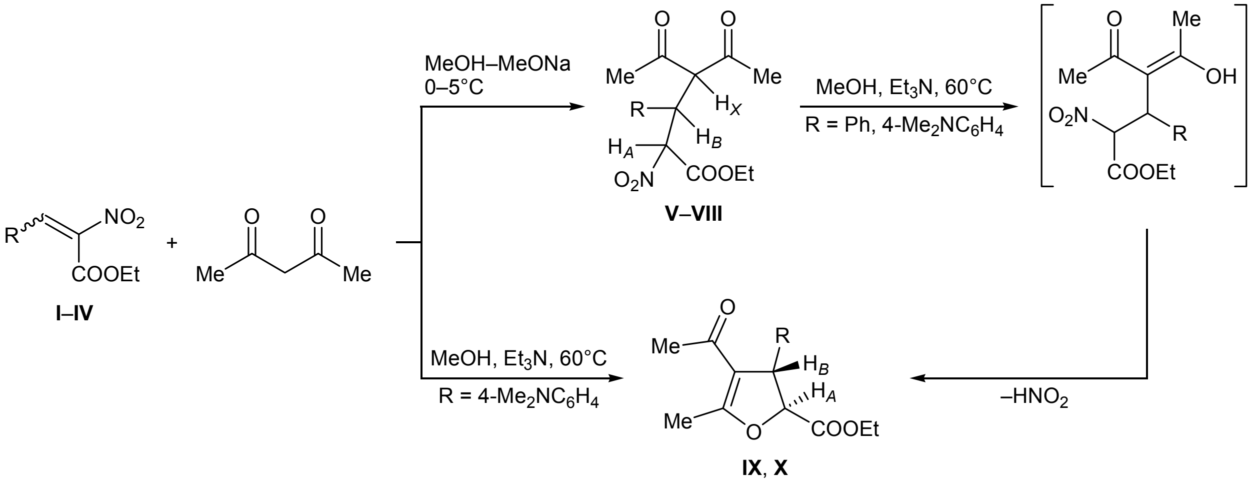
Received March 16, 2012

DOI: 10.1134/S1070428012070196

Aryl- and hetaryl-substituted α-nitroacrylates are preparatively accessible compounds and promising building blocks for the design of novel linear and heterocyclic structures [1].

α-Nitrocinnamic acid esters **I**–**III** and their thiophene-containing analog **IV** successfully react with an equimolar amount of acetylacetone in anhydrous methanol in the presence of sodium methoxide at 0–5°C to give addition products **V**–**VIII**. On heating in methanol in the presence of triethylamine (60°C, 2 h), adducts **V** and **VII** are converted into the corresponding tetrasubstituted dihydrofurans **IX** and **X**. Presumably, the latter are formed via intramolecular O-alkylation of the enol form of **V**–**VIII** with elimination of nitrous acid. Compound **X** was also synthesized in one-pot mode by heating α-nitroacrylate **III** with acetylacetone in acetonitrile in the presence of triethylamine (60°C, 2 h). The structure of adducts **V**–**VIII** was confirmed by their elemental compositions and IR and ^{1}H NMR spectra. The IR spectra of **V**–**VIII** contained strong absorption bands due to stretching vibrations of the acetyl and ester carbonyl groups (1700–1710, 1740–1755 cm^{-1}) and unconjugated nitro group (1560–1565, 1360 cm^{-1}). According to the ^{1}H NMR data, compounds **V**–**VIII** were isolated as single diastereoisomers. In the ^{1}H NMR spectrum of **V** in $CDCl_3$, the H_A, H_B, and H_X protons gave rise to an *ABX* spin system, and their signals were located at δ 5.47, 4.57, and 4.59 ppm, respectively. Signals at δ 1.24 (t) and 4.17 ppm (q) were assigned to the ester ethoxy group, and methyl protons in the acetyl fragments resonated at δ 1.86 and 2.25 ppm. Aromatic proton signals were observed at δ 7.25–7.30 ppm (m).

The assumed structure of dihydrofuran derivatives **IX** and **X** is confirmed by the similarity of their spectral parameters to those reported for the same compounds synthesized by different methods [2–4]. The coupling constant for H_A and H_B (^3J 4.88–4.98 Hz)



I, **V**, **IX**, R = Ph; **II**, **VI**, R = 4-$MeOC_6H_4$; **III**, **VII**, **X**, R = 4-$Me_2NC_6H_4$; **IV**, **VIII**, R = thiophen-2-yl.

indicate their *trans* orientation with respect to each other [2, 3].

Compound **IV** was synthesized according to the procedure described in [5], and compounds **I**–**III** were prepared in a similar way; their properties were consistent with published data [6].

Ethyl 4-acetyl-2-nitro-5-oxo-3-phenylhexanoate (V). Yield 37%, colorless crystals, mp 90–92°C (from EtOH). IR spectrum, ν, cm^{-1}: 1755, 1700 (C=O); 1560, 1360 (NO_2). ^{1}H NMR spectrum, δ, ppm: 1.24 t (3H, CH_3), 1.86 s and 2.25 s (3H each, $COCH_3$), 4.17 q (2H, OCH_2), 4.57 d.d (1H, H_B, $^3J_{BX}$ = 8.40, $^3J_{AB}$ = 4.20 Hz), 4.59 d.d (1H, H_X, $^4J_{AX}$ = 2.53, $^3J_{BX}$ = 8.40 Hz), 5.47 d.d (1H, H_A, $^3J_{AB}$ = 4.20, $^4J_{AX}$ = 2.53 Hz), 7.25–7.29 m (5H, H_{arom}). Found, %: N 4.14. $C_{16}H_{19}NO_6$. Calculated, %: N 4.36.

Ethyl 4-acetyl-3-(4-methoxyphenyl)-2-nitro-5-oxohexanoate (VI). Yield 33%, colorless crystals, mp 116–118°C (from EtOH). IR spectrum, ν, cm^{-1}: 1740, 1700 (C=O); 1565, 1360 (NO_2). ^{1}H NMR spectrum, δ, ppm: 1.23 t (3H, CH_3), 1.89 s and 2.24 s (3H each, $COCH_3$), 3.75 s (OCH_3), 4.16 q (2H, OCH_2), 4.51 d.d (1H, H_B, $^3J_{AB}$ = 5.88, $^3J_{BX}$ = 10.08 Hz), 4.54 d (1H, H_X, $^3J_{BX}$ = 10.08 Hz), 5.43 d (1H, H_A, $^3J_{AB}$ = 5.88 Hz), 6.80 d, 7.18 d (4H, H_{arom}). Found, %: C 58.20; H 5.68; N 3.53. $C_{17}H_{21}NO_7$. Calculated, %: C 58.11; H 6.02; N 3.99.

Ethyl 4-acetyl-3-(4-dimethylaminophenyl)-2-nitro-5-oxohexanoate (VII). Yield 48%, yellow crystals, mp 114–116°C (from EtOH). IR spectrum, ν cm^{-1}: 1740, 1700 (C=O); 1565, 1360 (NO_2). ^{1}H NMR spectrum, δ, ppm: 1.26 t (3H, CH_3), 1.86 s and 2.23 s (3H each, $COCH_3$), 2.90 s (6H, NCH_3), 4.46 d.d (1H, H_B, $^3J_{AB}$ = 6.90, $^3J_{BX}$ = 11.27 Hz), 4.47 q (2H, OCH_2), 4.52 d (1H, H_X, $^3J_{BX}$ = 11.27 Hz), 5.40 d (1H, H_A, $^3J_{AB}$ = 6.90 Hz), 6.57 d and 7.06 d (2H each, H_{arom}). Found, %: N 7.32. $C_{18}H_{24}N_2O_6$. Calculated, %: N 7.69.

Ethyl 4-acetyl-2-nitro-5-oxo-3-(thiophen-2-yl)-hexanoate (VIII). Yield 40%, colorless crystals, mp 94–96°C (from EtOH). IR spectrum, ν, cm^{-1}: 1740, 1700 (C=O); 1565, 1360 (NO_2). ^{1}H NMR spectrum, δ, ppm: 1.24 t (3H, CH_3), 2.01 s and 2.25 s (3H each, $COCH_3$), 4.19 q (2H, OCH_2), 4.59 d (1H, H_B, $^3J_{AB}$ = 6.10, $^3J_{BX}$ = 10.68 Hz), 4.79 d.d (1H, H_X, $^3J_{BX}$ = 10.68 Hz), 5.59 d (1H, H_A, $^3J_{AB}$ = 6.10 Hz), 6.90–7.25 m (3H, H_{arom}). Found, %: N 4.20. $C_{14}H_{17}NO_6S$. Calculated, %: N 4.28.

Ethyl 4-acetyl-5-methyl-3-phenyl-*trans*-2,3-dihydrofuran-2-carboxylate (IX). Yield 48%, colorless crystals, mp 55–56°C (from EtOH); published data [2]: mp 57–59°C. IR spectrum, ν, cm^{-1}: 1755, 1710 (C=O). ^{1}H NMR spectrum, δ, ppm: 1.32 t (3H, C**H**$_3$$CH_2$), 1.94 s and 2.42 s (3H each, CH_3), 4.28 q (2H, OCH_2), 4.46 d (1H, H_B, $^3J_{AB}$ = 4.88 Hz), 4.77 d (1H, H_A, $^3J_{AB}$ = 4.88 Hz), 7.21–7.34 m (5H, H_{arom}). Found, %: C 69.16; H 6.93. $C_{16}H_{17}O_4$. Calculated, %: C 69.57; H 6.52.

Ethyl 4-acetyl-3-(4-dimethylaminophenyl)-5-methyl-*trans*-2,3-dihydrofuran-2-carboxylate (X). Purification by column chromatography using diethyl ether as eluent gave compound **X** as a yellow oily substance. Yield 38%, R_f 0.73 (Silufol UV 254; hexane–acetone, 3:1). IR spectrum, ν, cm^{-1}: 1750, 1710 (C=O). ^{1}H NMR spectrum, δ, ppm: 1.32 t (3H, C**H**$_3$$CH_2$), 1.92 s and 2.40 s (3H each, CH_3), 2.93 s (6H, NCH_3), 4.27 q (2H, OCH_2), 4.38 d (1H, H_B, $^3J_{AB}$ = 4.98 Hz), 4.73 d (1H, H_A, $^3J_{AB}$ = 4.98 Hz), 6.67d and 7.07 d (4H, H_{arom}).

The ^{1}H NMR spectra were recorded from solutions in $CDCl_3$ on a Jeol JNM-ECX400A spectrometer at 399.78 MHz using the residual proton signal of the solvent as reference. The IR spectra were measured on a Shimadzu IR-Prestige-21 spectrometer with Fourier transform from solutions in chloroform (*c* = 0.1–0.001 M). The elemental compositions were determined on a EuroVector EA 3000 analyzer (CHN Dual configuration). The products were isolated and purified by recrystallization or column chromatography on Macherey-Nagel Silica 60 (240–400 mesh) using eluotropic solvent series [7].

This study was performed under financial support by the Government of St. Petersburg (diploma no. 11036).

REFERENCES

1. Perekalin, V.V., Lipina, E.S., Berestovitskaya, V.M., and Efremov, D.A., *Nitroalkenes. Conjugated Nitro Compounds*, Chichester: Wiley, 1994.
2. Zheng, J.-C., Zhu, C.-Y., Sun, X.-L., Tang, Y., and Dai, L.-X., *J. Org. Chem.*, 2008, vol. 73, p. 6909.
3. Yang, Z., Fan, M., Mu, R., Liu, W., and Liang, Y., *Tetrahedron*, 2005, vol. 61, p. 9140.
4. Feng, C., Lu, C., Chen, Z., Dong, N., Shi, J., and Yang, G., *J. Heterocycl. Chem.*, 2010, vol. 47, p. 671.
5. Baichurina, L.V., Baichurin, R.I., Aboskalova, N.I., and Berestovitskaya, V.M., *Russ. J. Gen. Chem.*, 2010, vol. 80, p. 2022.
6. Lehnert, W., *Tetrahedron*, 1972, vol. 28, p. 663.
7. Becker, H.G.O., *Organikum. Organisch-chemisches Grundpraktikum*, Berlin: Wissenschaften, 1964, 3rd ed. Translated under the title *Obshchii praktikum po organicheskoi khimii*, Moscow: Mir, 1965, p. 81.