Chemistry of Heterocyclic Compounds, Vol. 47, No. 7, October 2011 (Russian original Vol. 47, No. 7, July, 2011)

LETTERS TO THE EDITOR

SYNTHESIS OF NEW CYCLOPENTENONES FROM PHENACYLFURANS

O. V. Serdyuk[1]*, V. T. Abaev[2], and A. V. Butin[3]*

Keywords: phenacylfurans, furans, cyclopentenones, recyclization.

Substituted cyclopentenones are known as precursors of modified prostaglandins [1, 2] and compounds displaying various kinds of biological activity [3]. Despite the many methods for the preparation of cyclopentenones, there have been only a few methods described for the synthesis of such systems containing an acyl group [4–6]. 1,4-Dicarbonyl compounds (in one-step procedures) or furan derivatives (in two-step procedures) have often been used as starting compounds [7]. There have been only very few examples of the preparation of cyclopentenones from furans in one step [6, 8, 9]. We propose the use of phenacylfurans **1** recently obtained in our laboratory [10] for this purpose.

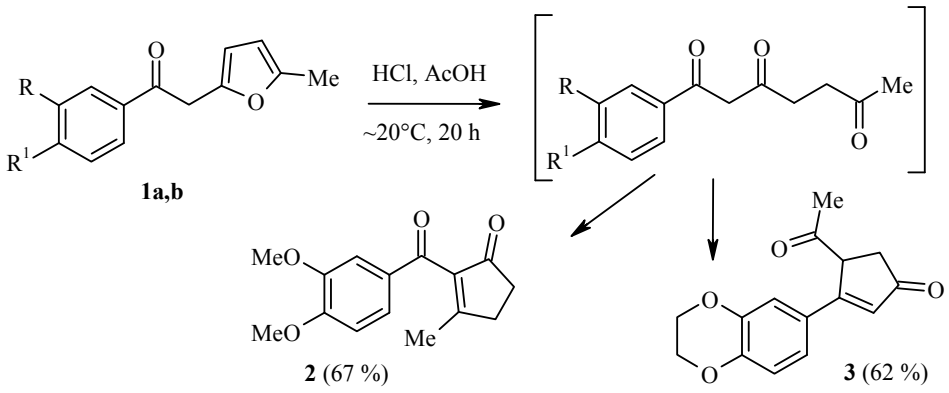
Indeed, we have found that the treatment of phenacylfurans **1a,b** with a mixture of acetic and hydrochloric acids leads to cyclopentenones **2** and **3**. The reaction proceeds at room temperature in good yield. ^{1}H NMR spectra of the crude product mixtures indicated the formation of isomeric cyclopentenones **2** and **3** in each case. However, the predominance of one of these compounds and their different solubility permitted the isolation of only one isomer as a pure compound. Further studies of the factors affecting the reaction course and modification of the procedure would provide a convenient method for the synthesis of cyclopentenones which are of antibacterial and other useful properties.

The IR spectra were measured on an FSM-1202 spectrometer for samples in vaseline mull. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 250 spectrometer at 250 and 62.6 MHz, respectively, in $CDCl_3$ solution with TMS as internal standard. The electron impact mass spectra were measured on a Kratos MS-30 spectrometer. The ionizing voltage was 70 eV. The temperature of the ionization chamber was 200°C.

*To whom correspondence should be addressed, e-mail: oserduke@mail.ru, alexander_butin@mail.ru.

[1]Southern Federal University, Department of Chemistry, 194/2 Stachka Ave., Rostov-on-Don 344090, Russia.
[2]North Ossetian State University, 46 Vatutina St., Vladikavkaz 362025, Russia.
[3]Research Institute of Heterocyclic Compounds Chemistry, Kuban State Technological University, 2 Moskovskaya St., 350072 Krasnodar, Russia.

Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 1102–1104, July, 2011. Original article submitted June 27, 2011.



1 a R = R^1 = OMe; **b** R + R^1 = OCH_2CH_2O

The starting compounds **1** were prepared according to the described procedure [10].

Synthesis of Cyclopentenones 2 and 3 (General Method). A solution of phenacylfurans **1a** or **1b** (0.01 mol) in a mixture of glacial acetic acid (12.5 ml) and concentrated hydrochloric acid (7.5 ml) was stirred at room temperature for 20 h. The mixture was poured into water (100 ml), brought to pH ~7 by adding sodium bicarbonate, and extracted with chloroform (3x30 ml). The organic layer was separated, dried over anhydrous calcium chloride, and evaporated on a water bath. The residue was recrystallized from ethanol.

2-(3,4-Dimethoxybenzoyl)-3-methylcyclopent-2-en-1-one (2) was obtained in 67% yield (167 mg) as beige crystals; mp 143–145°C (ethanol). IR spectrum, ν, cm^{-1}: 1694, 1646, 1625, 1581, 1539, 1463, 1394, 1357, 1276, 1163, 1053, 900. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.17 (3H, s, CH_3); 2.59–2.63 (2H, m, CH_2); 2.74-2.78 (2H, m, CH_2); 3.96 (6H, s, $2OCH_3$); 6.88 (1H, d, *J* = 8.5, H-5); 7.32 (1H, dd, *J* = 1.8, *J* = 8.4, H-6); 7.54 (1H, d, H-2). ^{13}C NMR spectrum, δ, ppm: 19.0; 33.0; 35.7, 56.4 (2C); 110.4; 110.8; 126.0; 130.4; 142.1; 149.7; 154.5; 178.8; 192.3; 205.5. Mass spectrum, *m/z* (I_{rel}, %): 260 $[M]^+$ (100), 259 (33), 245 (24), 230 (17), 229 (85), 217 (27), 201 (27), 187 (41), 165 (98), 138 (85), 123 (74), 77 (26), 67 (26), 59 (24), 43 (26). Found, %: C 69.07; H 6.23. $C_{15}H_{16}O_4$. Calculated, %: C 69.22; H 6.20.

4-Acetyl-3-(2,3-dihydro-1,4-benzodioxin-6-yl)cyclopent-2-en-1-one (3) was obtained in 62% yield (160 mg) as beige crystals; mp 155–158°C (ethanol). IR spectrum, ν, cm^{-1}: 1706, 1677, 1572, 1510, 1458, 1317, 1287, 1192, 1068, 898. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.02 (3H, s, CH_3); 2.47 (1H, dd, *J* = 2.2, *J* = 18.6) and 2.82 (1H, dd, *J* = 7.6, *J* = 18.6, CH_2); 4.21–4.32 (5H, m, OCH_2CH_2O and CH); 6.56 (1H, d, *J* = 2.0, H-5); 6.89 (1H, d, *J* = 8.8, H-8); 7.08 (1H, dd, *J* = 2.0, *J* = 8.8, H-7); 7.10 (1H, s, CH). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 26.2; 39.4; 55.3; 64.6; 65.0; 116.7; 118.5; 121.5; 126.7; 128.4; 144.3; 147.3; 171.4; 206.0; 207.0. Mass spectrum, *m/z* (I_{rel}, %): 258 $[M]^+$ (100), 217 (22), 216 (98), 215 (50), 160 (13), 149 (11), 136 (74), 115 (30), 103 (16), 102 (16), 77 (24), 59 (15), 44 (33). Found, %: C 69.89; H 5.51. $C_{15}H_{14}O_4$. Calculated, %: C 69.76; H 5.46.

Financial support was provided by Russian Foundation of Basic Research (grant 10-03-00254-a) and Council of President of Russian Federation for Grants (grant MK-2367.2011.3).

REFERENCES

1. C. Fionda, F. Nappi, M. Piccoli, L. Frati, A. Santoni, and M. Cippitelli, *Mol. Pharmacol.*, **72**, 1246 (2007).

2. E. Cernuda-Morollón, E. Pineda-Molina, F. J. Cañada, and D. Pérez-Sala, *J. Biol. Chem.*, **276**, 35530 (2001).
3. K. Tonari, K. Machiya, I. Ichimoto, and H. Ueda, *Agric. Biol. Chem.*, **45**, 295 (1981).
4. R. D'Ascoli, M. D'Auria, C. Iavarone, G. Piancatelli, and A. Scettri, *J. Org. Chem.*, **45**, 4502 (1980).
5. Y. Liu, R.-J. Song, and J.-H. Li, *Synthesis*, 3663 (2010).
6. E. Holtz, V. Köhler, B. Appel, and P. Langer, *Eur. J. Org. Chem.*, 532 (2005).
7. G. Piancatelli, M. D'Auria, and F. D'Onofrio, *Synthesis*, 867 (1994).
8. F. D'Onofrio, G. Piancatelli, and M. Nicolai, *Tetrahedron*, **51**, 4083 (1995).
9. G. Csákÿ, M. Mba, and J. Plumet, *Tetrahedron Asymm.*, **15**, 647 (2004).
10. V. T. Abaev, K. V. Bosikova, O. V. Serdyuk, and A. V. Butin, *Khim. Geterotsikl. Soedin.*, 772 (2009). [*Chem. Heterocycl. Comp.,* **45,** 611 (2009)].