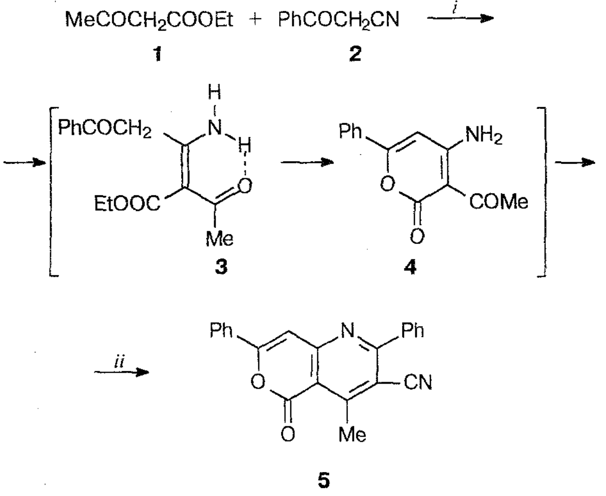
Condensation of ethyl acetoacetate with benzoylacetonitrile catalyzed by nickel acetylacetonate

V. A. Dorokhov, S. V. Baranin, A. Yu. Yagodkin, V. S. Bogdanov, and Z. K. Dem'yanets*

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 117913 Moscow, Russian Federation.
Fax: +7 (095) 135 5328

Ethyl acetoacetate (**1**) and benzoylacetonitrile (**2**) do not react upon boiling in xylene. Addition of basic or acidic catalysts (EtONa, AcONa, Et_3N, or TsOH) results in unidentified resinification products. However, we found that in the presence of catalytic amounts of nickel acetylacetonate ($Ni(acac)_2$), compounds **1** and **2** react in boiling xylene in a ratio of 1 : 2 (Scheme).



Conditions and reagents: *i.* Xylene, 5—10 mol.% $Ni(acac)_2$, 130 °C, 5 h; *ii.* $PhCOCH_2CN$.

The condensation product (according to the data of IR, NMR, and mass spectrometry and elemental analysis) has the structure of 3-cyano-4-methyl-2,7-diphenylpyrido[3,2-*c*]pyran-5-one (**5**). Formation of the latter compound may be represented by the scheme, in which adduct (**3**) is a key intermediate obtained as a result of addition of methylene-active ester **1** at the C≡N bond of reagent **2** (*cf.* the conversion of acacH and malononitrile to 3-acetyl-4-hydroxy-1,3-pentadienecarbonitrile in the presence of $Ni(acac)_2$).[1]

Actually, we succeeded in isolating ester **3** by the reaction of compound **2** and the nickel complex of ethyl acetoacetate (equimolar amounts of reagents, boiling in xylene for 4 h) followed by acidification of the mixture with glacial AcOH in $CHCl_3$. Because of the preferential involvement of the acetyl group in formation of an intramolecular N—H...O hydrogen bond, adduct **3** has, apparently, an *E* configuration. The subsequent conversion of **3** to bicyclic compound **5** proceeds, apparently, through formation of pyranone **4** and its condensation with nitrile **2**.

3-Cyano-4-methyl-2,7-diphenylpyrido[3,2-*c*]pyran-5-one (5) was isolated from the reaction mixture by chromatography on SiO_2 with $CHCl_3$; the yield was 51 %, m.p. 237—238 °C (benzene). Mass spectrum (*m/z*): 338 $[M^+]$. ^1H NMR ($CDCl_3$, δ): 7.95, 7.60, 7.52 (3 m, 10 H, 2 Ph); 7.23 (s, 1 H, CH=); 3.18 (s, 3 H, Me). ^{13}C NMR ($CDCl_3$, δ, *J*/Hz): 136.94, 131.70, 131.22, 130.68, 129.53, 129.28, 129.23, 128.86, 126.03 (2 Ph); 165.96 (C-5); 159.90 (s, C-2); 159.70 (d, C-7, $^2J = 5.9$); 159.20 (q, C-4, $^2J = 5.8$); 157.57 (d, C-8a, $^2J = 2.0$); 108.67 (s, C-4a); 113.53 (C-3); 116.32 (s, CN); 103.84 (d, C-8, $^1J = 171$); 20.82 (q, Me). IR (CH_2Cl_2, ν/cm^{-1}): 2225 (C≡N); 1740 (C=O); 1640, 1590, 1560 (C=N, C=C).

Ethyl 2-acetyl-3-amino-5-oxo-5-phenylpent-2-enoate (3) was obtained from the organic layer of the reaction mixture after evaporation of the solvent; the yield was 21 %, m.p. 106—107 °C (1 : 3 benzene : hexane). Mass spectrum (*m/z*): 275 $[M^+]$. ^1H NMR ($CDCl_3$, δ): 11.43 (br.s, 1 H, NH); 8.00, 7.60, 7.50 (3 m, 5 H, Ph); 6.49 (br.s, 1 H, NH); 4.29 (s, 2 H, CH_2); 4.13 (q, 2 H, OCH_2); 2.34 (s, 3 H, Me); 1.22 (t, 3 H, Me). IR (KBr, ν/cm^{-1}): 3320, 3230 (NH); 1675 (C=O); 1605 (C=C).

The results of elemental analysis are in agreement with the calculated data.

The work was supported by the International Science Foundation and the Government of the Russian Federation (Grant No. M5Q300) and by the Russian Foundation for Basic Research (Project No. 94-03-08964).

References.

1. V. A. Dorokhov, O. G. Azarevich, V. S. Bogdanov, B. I. Ugrak, and L. S. Vasil'ev, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 1432 [*Russ. Chem. Bull.*, 1994, 1356 (Engl. Transl.)].

Received July 17, 1995

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 2295—2296, November, 1995.