

## LETTERS TO THE EDITOR

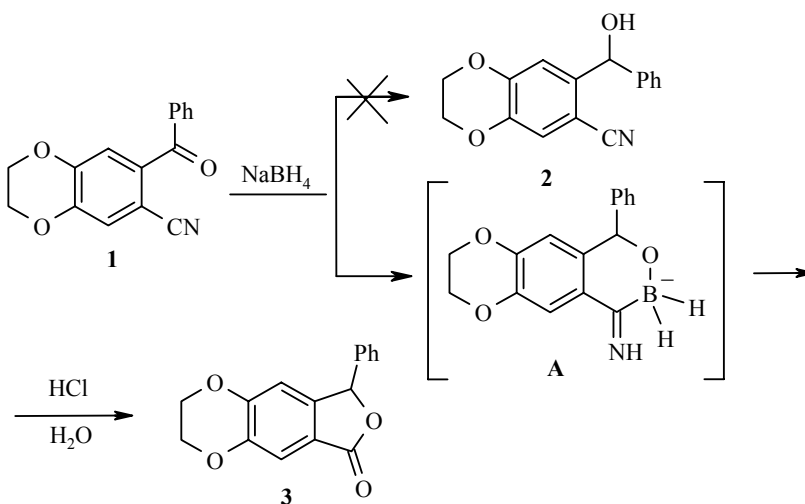
### MEDIATED HYDROLYSIS OF BENZO-NITRILE INITIATED BY NaBH<sub>4</sub>

M. I. Khasanov and S. S. Mochalov

**Keywords:** 5,6-ethylenedioxy-3-phenylphthalide, 2-cyano-4,5-ethylenedioxybenzophenones, mediated hydrolysis.

Benzonitriles do not react with NaBH<sub>4</sub>, though they can be reduced by the action of diborane to give benzylamines. The discrepancy in the reductive activity of these boron hydrides has been attributed to the capacity of diborane, in contrast to NaBH<sub>4</sub>, to coordinate at the cyano group nitrogen atom, thereby enhancing the activity of the cyano group carbon atom toward nucleophilic attack of the hydrogen atom in the B-H bond [1].

In our search for a synthesis of *ortho*-cyanobenzhydrols such as **2** required for a study of intramolecular acid-catalyzed cyclization and considering the inertness of the cyano group under NaBH<sub>4</sub> reduction conditions, we attempted to reduce the carbonyl group in 2-cyano-4,5-ethylenedioxybenzophenone to a alcoholic group by the action of this reducing agent. However, we found that in conditions, under which, for example, ethylenedioxybenzophenones containing amide fragments in the *ortho* position readily form the corresponding benzhydrols [2], cyanobenzophenone **1** is converted to 3-phenylphthalide **3** in high yield rather than alcohol **2**.



M. V. Lomonosov Moscow State University, 119992 Moscow, Russia; e-mail: ssmoch@org.chemmsu.ru.  
Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 2, pp. 293-294, February, 2008. Original article submitted January 16, 2008.

This result may be interpreted as a sequence of reduction reactions of the carbonyl group, mediated hydrolysis of the cyano group, and intramolecular cyclization. We propose that intermediate **A**, probably already formed under reducing conditions, is responsible for the mediated hydrolysis of the cyano group.

The  $^1\text{H}$  NMR spectrum was taken on a Varian VXR-400 spectrometer at 400 MHz in  $\text{CDCl}_3$  with residual  $\text{CDCl}_3$  as the internal standard. The electron impact mass spectrum was taken on a Finnigan MAT INCOS 50 mass spectrometer at 70 eV.

**5,6-Ethylenedioxy-3-phenylphthalide (3).** 2-Cyano-4,5-ethylenedioxybenzophenone (**1**) (2.61 g, 0.01 mol) was added with stirring to a suspension of  $\text{NaBH}_4$  (0.38 g, 0.01 mol) in ethanol (32 ml) over 30 min. The reaction mixture was heated at 40-50°C and then left for 24 h and then 10% hydrochloric acid was added dropwise until the mixture was slightly acidic. The reaction mixture was poured into water (150 ml) and heated at reflux for 1 h. The precipitate formed was filtered off and recrystallized from ethanol to give 2.35 g (88%) **3**, mp 167-168°C.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm (*J*, Hz): 4.26-4.31 (4H, m,  $\text{OCH}_2\text{CH}_2\text{O}$ ); 6.26 (1H, s,  $\text{CHC}_6\text{H}_5$ ); 6.75 (1H, s, H-4); 7.24-7.28 (2H, m) and 7.35-7.38 (3H, m, ArH); 7.40 (1H, s, H-7). Electron impact mass spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 268 [ $\text{M}]^+$  (78), 239 (23), 191 (26), 168 (32), 163 (100), 152 (10), 139 (90), 134 (31), 127 (12), 105 (32), 89 (12), 77 (84), 74 (24), 69 (18), 63 (36), 50 (90), 39 (19). Found, %: C 71.41; H 4.32.  $\text{C}_{16}\text{H}_{12}\text{O}_4$ . Calculated, %: C 71.63; H 4.51.

## REFERENCES

1. G. Tennant, in: *Comprehensive Organic Chemistry* [Russian translation], vol. 3, Khimiya, Moscow (1982), p. 675.
2. R. A. Gazzaeva, M. I. Khasanov, S. S. Mochalov, and N. S. Zefirov, *Khim. Geterotsikl. Soedin.*, 941 (2007). [*Chem. Heterocycl. Comp.*, **43**, 799 (2007)].