

SHORT
COMMUNICATIONS

Carbanion Cleavage in 3-Benzoylcyclopropane-1,1,2,2-tetracarbonitrile Effected by Alcoholates

I. N. Bardasov, O. V. Kayukova, Ya. S. Kayukov, O. V. Ershov, O. E. Nasakin, and M. Yu. Belikov

Ulyanov Chuvash State University, Cheboksary, 428015 Russia
e-mail: barkas12@mail.ru

Received April 25, 2007

DOI: 10.1134/S1070428007100296

Tetracyanocyclopropanes containing five or six electron-withdrawing groups are known to be prone to chemical reactions with nucleophilic reagents, therewith reactions with hard nucleophiles, alcohols or oximes, occur prevalingly at cyano or acyl groups with retention of the cyclopropane ring, and with soft nucleophiles, with the opening of the cycle. However in contrast to this general trend in some reactions with alcoholates and oximates the cycle opening was observed leading to the formation of furan [1–3] or pyrroline [4] derivatives. A similar transformation we found studying reactions of 3-benzoylcyclopropane-1,1,2,2-tetracarbonitrile (**I**) [5] with alcoholates.

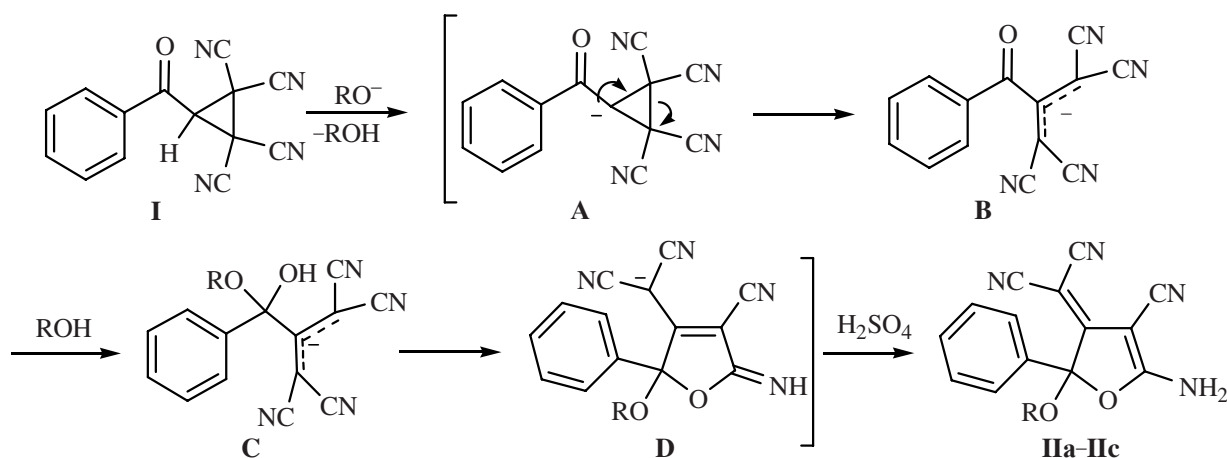
In reaction of compound **I** with sodium alcoholate in the corresponding alcohol [2-alkoxy-5-amino-4-cyano-

2-phenylfuran-3(2*H*)-ylidene]malononitriles **IIa–IIc** were obtained in 90–95% yield (see Scheme).

The structure of dehydrofurans **IIa–IIc** obtained was confirmed by IR, ¹H NMR, and mass spectra.

In the first stage of the mechanism we presume the alcoholate acting as a base abstracts a sufficiently acidic hydrogen from the cyclopropane ring providing a cyclopropyl carbanion **A**. Further the cycle opening follows which may be regarded either as a three-centered four-electron electrocyclic reaction or as electrophilic carbanion cleavage resulting in propenoid **B** stabilized by resonance. The process completes by the formation of furan derivative **D** via intermediate hemiketal **C**. The final reaction products, dehydrofurans **IIa–IIc**, arise at neutralizing the reaction mixture with sulfuric acid.

Scheme.



R = CH₃ (**a**), CH₂CH₂OH (**b**), CH₂CH₃ (**c**).

[5-Amino-4-cyano-2-methoxy-2-phenylfuran-3(2H)-ylidene]malononitrile (IIa). To a solution of 1.08 g (0.02 mol) of sodium methylate in 10 ml of methanol was added at stirring a dispersion of 2.46 g (0.01 mol) of compound **I** in 10 ml of methanol. The stirring was continued till the completion of the reaction (TLC monitoring). Then the reaction mixture was neutralized with 5% sulfuric acid solution and extracted with ethyl acetate. The organic layer was dried with calcined sodium sulfate, the solvent was distilled off, the residue was ground with 10 ml of water. The precipitate was filtered off and washed with water. Yield 2.36 g (90%), mp 138–139°C (decomp.) (ethyl acetate–hexane). IR spectrum, ν , cm^{-1} : 1683 (C=C), 2225 (C≡N), 3140, 3280 (NH₂). ¹H NMR spectrum, δ , ppm: 10.35 s (2H, NH₂), 7.5 m (5H, C₆H₅), 3.5 m (3H, OCH₃). Mass spectrum, m/z (I_{rel} , %): 278 (30). Found, %: C 64.55; H 3.66; N 20.10. C₁₅H₁₀N₄O₂. Calculated, %: C 64.74; H 3.62; N 20.13.

Compounds **IIb** and **IIc** were similarly prepared.

[5-Amino-4-cyano-2-(2-hydroxyethoxy)-2-phenylfuran-3(2H)-ylidene]malononitrile (IIb). Yield (95%), mp 132–133°C (decomp.). IR spectrum, ν , cm^{-1} : 1685 (C=C), 2223 (C≡N), 3150, 3270 (NH₂). ¹H NMR spectrum, δ , ppm: 10.35 s (2H, NH₂), 7.45–7.55 m (5H, C₆H₅), 4.9 t (1H, OCH₂CH₂OH), 3.6–3.7 m (4H, OCH₂CH₂OH). Mass spectrum, m/z (I_{rel} , %): 308 (10). Found, %: C 62.37 H 3.94; N 18.20. C₁₆H₁₂N₄O₃. Calculated, %: C 62.33; H 3.92; N 18.17.

[5-Amino-4-cyano-2-ethoxy-2-phenylfuran-3(2H)-ylidene]malononitrile (IIc). Yield (90%), mp 155–156°C (decomp.). IR spectrum, ν , cm^{-1} : 1681 (C=C), 2226 (C≡N), 3160, 3280 (NH₂). ¹H NMR spectrum, δ ,

ppm: 10.35 s (2H, NH₂), 7.5 m (5H, C₆H₅), 3.75 q (2H, OCH₂CH₃), 1.3 t (3H, OCH₂CH₃). Mass spectrum, m/z (I_{rel} , %): 292 (30). Found, %: C 65.78; H 4.10; N 19.10. C₁₆H₁₂N₄O₂. Calculated, %: C 65.75; H 4.14; N 19.17.

The purity of compounds synthesized was checked by TLC on Silufol UV-254 plates, development under UV irradiation, in iodine vapor, and by thermal treatment. IR spectra were recorded on an IR Fourier spectrometer FSM-1202 from thin films (or mulls in mineral oil). ¹H NMR spectra were registered on a spectrometer Bruker DRX-500, operating frequency 500.13 MHz, solvent DMSO-*d*₆, internal reference TMS. Mass spectra were measured on a Finnigan MAT INCOS-50 instrument (electron impact, 70 eV).

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