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> SHORT COMMUNICATIONS

Synthesis of a New Organic Anion by Reaction of 4-Aryl(hetaryl)-4-oxobutane-1,1,2,2-tetracarbonitriles with Ammonia

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4-Oxoalkane-1,1,2,2-tetracarbonitriles are known to react with concentrated aqueous ammonia to produce compounds of two types. Adducts of tetracyanoethylene and cyclic ketones (such as cyclopentanone and cyclohexanone) give rise to 2,7-diazabicyclic compounds [1], whereas from aliphatic tetracyanoethylated ketones isonicotinic acid derivatives are formed [2].

There are no published data on reactions of aqueous ammonia with tetracyanoalkanones derived from methyl aryl(hetaryl) ketones. When such reactions were carried out under the conditions reported in [1, 2], strong tarring occurred, and no individual products were isolated. By varying the conditions of this reaction we succeeded in obtaining ammonium 4-aryl-1,1,2,2-tetracyano-4-oxobutan-1-ides **IIa–IIc** by mixing ketones **Ia–Ic** with a freshly prepared solution of ammonia in ethyl acetate at reduced temperature.

Structures analogous to **IIa–IIc** but having singly charged metal cations were reported in [3, 4]. Compounds **IIa–IIc** turned out to be unstable in the solid state: on exposure to air they lost hydrogen cyanide with formation of ammonium 4-aryl-1,1,2-tricyano-4oxobut-2-en-1-ides **IIIa–IIIc** that are derivatives of



R = 4-MeOC₆H₄ (**a**), 2-thienyl (**b**), 3,4-(MeO)₂C₆H₃ (**c**).

a new organic anion. Intermediate formation of ammonium salts **IIa–IIc** is confirmed by their transformation into initial ketones **Ia–Ic** by the action of dilute hydrochloric acid immediately after isolation. Some structural similarity of salts **IIIa–IIIc** to betaines described in [5] may be noted. The latter were synthesized from tetracyanoethylene and pyridinium ylides.

The structure of compounds **IIIa–IIIc** was confirmed by their IR, ¹H NMR, and mass spectra and elemental analyses. The synthesis of salts **III** is an example of new reaction pathway of 4-oxoalkane-1,1,2,2-tetracarbonitriles with ammonia.

Ammonium 1,1,2-tricyano-4-(4-methoxyphenyl)-4-oxobut-2-en-1-ide (IIIa). 4-(4-Methoxyphenyl)-4oxobutane-1,1,2,2-tetracarbonitrile (Ia), 0.139 g (0.5 mmol), was added to 2 ml of a freshly prepared solution of ammonia in ethyl acetate, cooled to -10° C, and the mixture was vigorously stirred until it became homogeneous. After several minutes, a solid separated and was filtered off, washed with cold ethyl acetate, and kept for 5-7 days on exposure to air. Yield 0.115 g (86%), mp 84–85°C. IR spectrum, v, cm⁻¹: 2230, 2199 (C=N); 1667 (C=O). ¹H NMR spectrum, δ , ppm: 3.81 s (3H, OCH₃), 6.51 s (1H, CH), 7.01 d (2H, H_{arom}), 7.07 br.s (4H, NH₄), 7.79 d (2H, H_{arom}). Mass spectrum: m/z 251 (I_{rel} 49%) [$M - NH_3$]⁺. Found, %: C 62.51; H 4.77; N 20.95. C₁₄H₁₂N₄O₂. Calculated, %: C 62.68; H 4.51; N 20.88.

Compounds **IIIb** and **IIIc** were synthesized in a similar way.

Ammonium 1,1,2-tricyano-4-oxo-4-(2-thienyl)but-2-en-1-ide (IIIb). Yield 0.096 g (79%), mp 85– 87°C. IR spectrum, v, cm⁻¹: 2221, 2196 (C=N); 1672 (C=O). ¹H NMR spectrum, δ , ppm: 6.41 s (1H, CH), 7.16 d.d (1H, H_{arom}), 7.19 br.s (4H, NH₄), 7.65 d.d (1H, H_{arom}), 7.82 d.d (1H, H_{arom}), Mass spectrum: m/z 227 (I_{rel} 35%) [$M - NH_3$]⁺. Found, %: C 53.97; H 3.37; N 22.99. C₁₁H₈N₄OS. Calculated, %: C 54.09; H 3.30; N 22.94.

Ammonium 1,1,2-tricyano-4-(3,4-dimethoxyphenyl)-4-oxobut-2-en-1-ide (IIIc). Yield 0.121 g (81%), mp 108–109°C. IR spectrum, v, cm⁻¹: 2235, 2197 (C=N); 1664 (C=O). ¹H NMR spectrum, δ, ppm: 3.80 s (3H, OCH₃), 3.82 s (3H, OCH₃), 6.52 s (1H, CH), 7.03 d (1H, H_{arom}), 7.08 br.s (4H, NH₄), 7.40 d (1H, H_{arom}), 7.42 d.d (1H, H_{arom}). Mass spectrum: m/z281 (I_{rel} 41%) [M – NH₃]⁺. Found, %: C 60.32; H 4.79; N 18.85. C₁₅H₁₄N₄O₃. Calculated, %: C 60.40; H 4.73; N 18.78.

The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates; spots were visualized under UV light, by treatment with iodine vapor, or by heating. The IR spectra were recorded on an FSM-1202 spectrometer from samples dispersed in mineral oil. The ¹H NMR spectra were measured on a Bruker DRX-500 spectrometer at 500.13 MHz using DMSO- d_6 as solvent and tetramethylsilane as internal reference. The mass spectra (electron impact, 70 eV) were obtained on a Finnigan MAT Incos 50 instrument.

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