Russian Journal of General Chemistry, Vol. 72, No. 5, 2002, pp. 820–821. Translated from Zhurnal Obshchei Khimii, Vol. 72, No. 5, 2002, pp. 877–878.
Original Russian Text Copyright © 2002 by Sheverdov, Ershov, Nasakin, Chernushkin, Efimov, Tafeenko.

LETTERS TO THE EDITOR

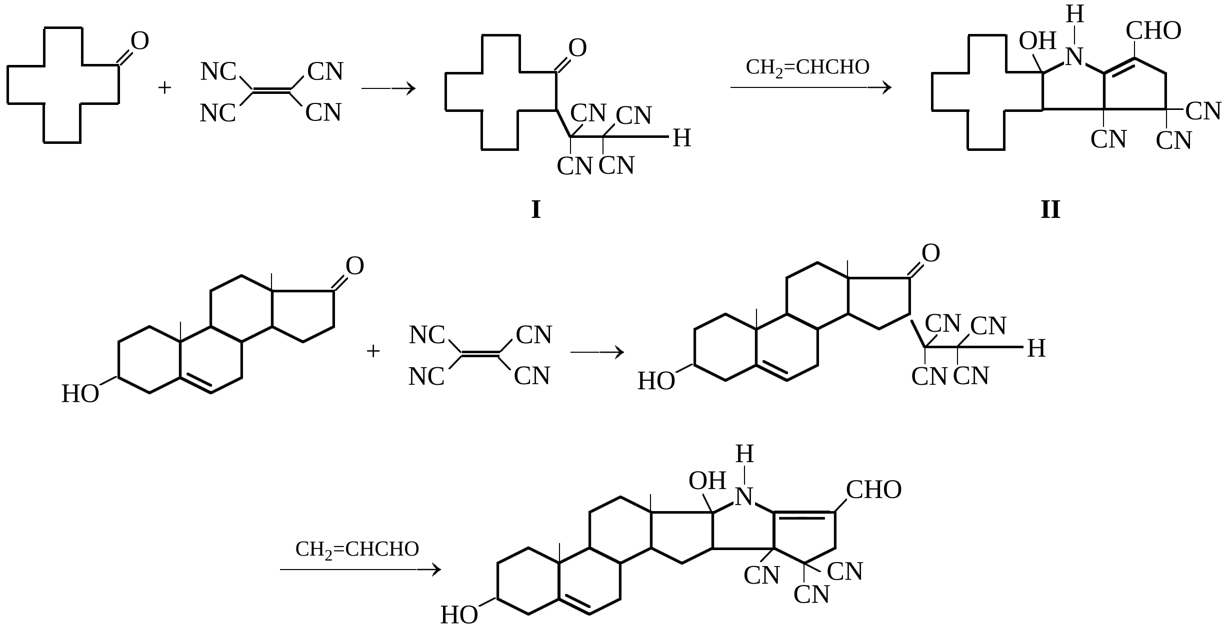
Tetracyanoethylation of Cyclodecanone and Dihydroepiandrosterone to β,β,γ,γ-Tetracyanoalkanones and Their Reaction with Acrolein

V. P. Sheverdov, O. V. Ershov, O. E. Nasakin,
A. N. Chernushkin, R. N. Efimov, and V. A. Tafeenko

Ul'yanov Chuvash State University, Cheboksary, Chuvashia, Russia

Received April 2, 2001

Tetracyanoethylation of ketones to β,β,γ,γ-tetracyanoalkanones and the properties of the latter are of considerable interest [1–3]. However, naturally occurring and biologically active ketones have never been brought in such reactions. We found that cyclodecanone and dihydroepiandrosterone can easily be converted into the corresponding β,β,γ,γ-tetracyanoalkanones **I** and **III** and nitrogen-containing heterocycles **II** and **IV**.



I

II

IV

These reactions provide a new synthetic approach to 1-azapentalenes and open the way to tetracyanoethylation and heterocyclization of more complex ketones than those studied in [1–3].

The structures of compounds **I**–**IV** were determined by ^{1}H and ^{13}C NMR and IR spectroscopy and mass spectrometry.

Tetracyanoalkanones I and III. Tetracyanoethylene, 0.01 mol, was dissolved under slight heating in 20 ml of 1,4-dioxane, 0.012 mol of ketone was

1070-3632/02/7205-0820 $27.00 © 2002 MAIK "Nauka/Interperiodica"

added and then, slowly, 3–4 drops of concentrated hydrochloric acid. When all tetracyanoethylene had been consumed, the reaction mixture was diluted with 100 ml of water. The precipitate that formed was filtered off and washed with water and 2-propanol. Yield of 1-(2-oxocyclododecyl)-1,1,2,2-ethanetetracarbonitrile (**I**) 78%, mp 175–176°C. IR spectrum, ν, cm^{-1}: 2270 (CN), 1710 (C=O). Found, %: C 70.02; H 7.29; N 11.86. $C_{18}H_{22}N_4O$. Calculated, %: C 69.65; H 7.14; N 18.05. Yield of 16-(1,1,2,2-tetracyanoethyl)-dihydroepiandrosterone (**III**) 85%, mp 196–197°C. IR spectrum, ν, cm^{-1}: 3420 (OH), 2270 (CN), 1695 (C=O). Found, %: C 71.98; H 6.79; N 13.6. $C_{25}H_{28}\cdot N_4O_2$. Calculated, %: C 72.09; H 6.78; N 13.45.

Reaction of tetracyanoalkanones I and III with acrolein. To a solution of 0.005 mol of tetracyanoalkanone **I** or **III** in 10 ml of 2-propanol we added 0.01 mol of acrolein, and the mixture was stirred until dissolution of the latter. After the reaction was complete, the mixture was diluted with 50 ml of water, the precipitate that formed was filtered off, washed with water, and recrystallized from acetic acid. Yield of 3-formyl-4*a*-hydroxy-1,2,4,4*a*,5,6,7,8,9,10,11,12,13,14,14*a*,14*b*-hexadecahydrocyclododeca[*b*]cyclopenta[*d*]pyrrole-1,1,14*b*-tricarbonitrile (**II**) 63%, mp 182–183°C. IR spectrum, ν, cm^{-1}: 3380 (OH), 3275 (NH), 2270 (CN), 1660 (C=O). Found, %: C 68.98; H 7.24; N 15.40. $C_{21}H_{26}N_4O_2$. Calculated, %: C 68.83; H 7.15; N 15.29. Yield of 8-formyl-2,6*b*-dihydroxy-4*a*,6*a*-dimethyl-2,3,4,4*a*,4*b*,5,6,6*a*,6*b*,7,9,10,10*a*,10*b*,11,11*a*,11*b*,12-octadecahydro-1*H*-cyclopenta[*b*]-naphtho[2',1';4,5]indeno[2,1-*d*]pyrrole-10,10,10*a*-tricarbonitrile (**IV**) 54%, mp 171–172°C. IR spectrum, ν, cm^{-1}: 3420 (OH), 3340 (OH), 3260 (NH), 2270 (CN), 1665 (C=O). Found, %: C 71.18; H 6.79; N 11.84. $C_{28}H_{32}N_4O_3$. Calculated, %: C 71.16; H 6.82; N 11.86.

The reaction progress and the purity of the products were controlled by TLC on Silufol UV-254 plates. The IR spectra were recorded on a UR-20 instrument in Vaseline oil.

REFERENCES

1. Middelton, W.I., Heckert, R.E., Little, E.L., and Krespan, C.G., *J. Am. Chem. Soc.*, 1958, vol. 80, no. 11, p. 2783.
2. Nasakin, O.E., Sheverdov, V.P., Moiseeva, I.V., Ershov, O.V., Chernushkin, A.N., and Tafeenko, V.A., *Zh. Obshch. Khim.*, 1999, vol. 69, no. 2, p. 302.
3. Nasakin, O.E., Sheverdov, V.P., Moiseeva, I.V., Lyshchikov, A.N., Ershov, O.E., and Nesterov, V.N., *Tetrahedon Lett.*, 1997, vol. 38, no. 25, p. 4455.