Russian Journal of General Chemistry, Vol. 72, No. 6, 2002, pp. 909–911. Translated from Zhurnal Obshchei Khimii, Vol. 72, No. 6, 2002, pp. 972–974.
Original Russian Text Copyright © 2002 by Sheverdov, Bulkin, Ershov, Nasakin, Tafeenko.

Reactivity of 1,1,2,2-tetracyano-3-(2,2-dimethylhydrazino)cyclopentanes Toward Amines

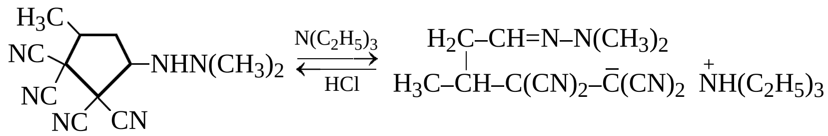
V. P. Sheverdov, V. V. Bulkin, O. V. Ershov, O. E. Nasakin, and V. A. Tafeenko

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

Received August 28, 2000

Abstract — Substituted 1,1,2,2-tetracyano-3-(2,2-dimethylhydrazino)cyclopentanes were reacted with amines to synthesize substituted 1,5,5-tricyano-4-(2,2-dimethylhydrazino)-1-cyclopentenes and 5-cyano-2-(dicyanomethylene)-1-(dimethylamino)pyrrolidines.

1,1,2,2-tetracyano-3-(2,2-dimethylhydrazino)cyclopentanes have been prepared by reactions of 1,1,2,2-tetracyanoethane with dimethylhydrazones of α,β-unsaturated aldehydes [1]. They exhibit a very high reactivity, undergoing an exceptionally facile C^2–C^3 bond cleavage [2]. This bond is cleaved even when substituted tetracyanocyclopentanes are dissolved in organic solvents [3]. Therewith, the C^3 signal in the ^{13}C NMR spectra is broadened [1]. The decyclization of tetracyanocyclopentane **Ia** by the C^2–C^3 bond have been proved by the formation of salt **II** on mixing of **Ia** with equimolar amount of triethylamine in dioxane [1].



Ia **II**

Since the **Ia** → **II** conversion occurs at room temperature within 1–2 min, we considered it interesting to study the decyclization and to perform reactions of the CN, C=N, and $C(CN)_2$ functional groups with amines at higher temperatures.

Heating of cyclopentanes **Ia**–**Ic** in dioxane with triethylamine at a 1 : (0.0005–0.0007) molar ratio gave cyclopentenes **Va**–**Vc** (Table 1).

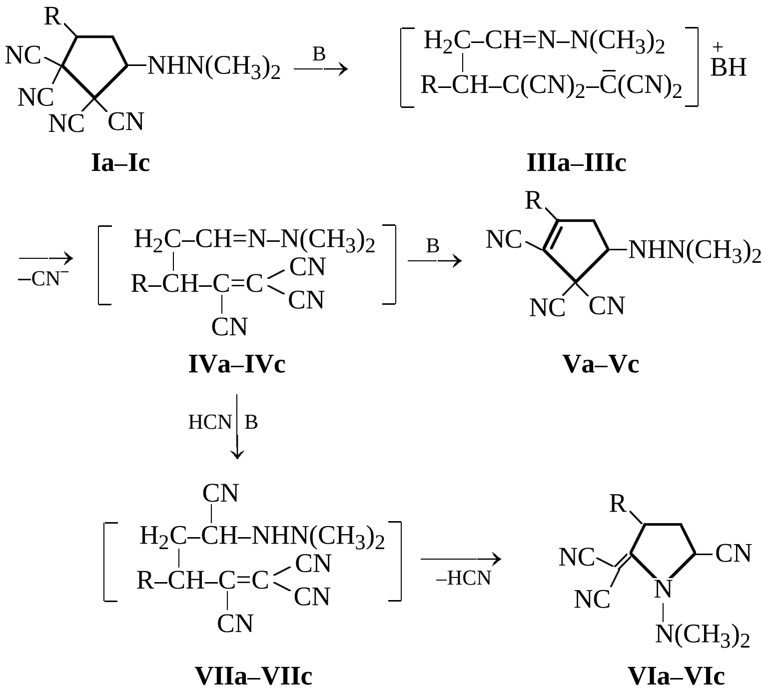
Table 1. IR and ^{13}C NMR spectra and elemental analyses of compounds **Va–Vc** and **VIa–VIc**

Comp. no.	IR spectrum, ν, cm^{-1}	Chemical shift, δ_C, ppm						
		C^1	C^2	C^3	C^4	C^5	C^6	CN
Va	3230, 2239, 1650	102.05	170.63	40.5	66.20	47.54	–	112.46
Vb	3210, 2228, 1612	100.68	165.36	39.38	66.36	50.0	–	115.25, 114.79, 113.14
Vc	3250, 2227, 1628	94.01	150.16	35.65	65.45	48.08	–	113.69
VIa	2228, 2220, 1584	–	175.0	45.13	33.64	38.2	51.2	116.02, 120.8, 119.06
VIb	2230, 2220, 1585	–	171.09	47.82	35.53	45.29	52.06	116.41, 114.07, 118.30
VIc	2229, 2221, 1600	–	174.5	42.8	34.5	45.13	50.36	117.11, 119.16

1070-3632/02/7206-0909 $27.00 ©2002 MAIK "Nauka/Interperiodica"

Table 1. (Contd.)

Compound no.	Found, %			Formula	Calculated, %		
	C	H	N		C	H	N
Va	61.35	6.11	32.54	$C_{11}H_{13}N_5$	61.38	6.09	32.53
Vb	69.33	5.43	25.23	$C_{16}H_{15}N_5$	69.29	5.45	25.25
Vc	62.89	4.89	26.23	$C_{14}H_{13}N_5O$	62.91	4.90	26.20
VIa	61.34	6.11	32.55	$C_{11}H_{13}N_5$	61.38	6.09	32.53
VIb	69.27	5.46	25.27	$C_{16}H_{15}N_5$	69.30	5.45	25.25
VIc	64.19	7.05	28.76	$C_{13}H_{17}N_5$	64.18	7.04	28.78



R = CH_3 (**Va, VIa**), C_6H_5 (**Vb, VIb**), 2-furyl (**Vc**), C_3H_7 (**VIc**).

This reaction, as the reactions of cyclopentanes **I** with $N(C_2H_5)_3$, yielding compounds like **II**, involves intermediates **IIIa**–**IIIc**.

It is known that the tetracyanoethanide anion forms a tricyanovinyl fragment [4–8]. Therefore, we suppose that the second stage involves decyanation to give intermediates **IVa**–**IVc** and final products **Va**–**Vc**.

A different reaction pathway was observed on treatment of cyclopentanes **I** with a 2–3-fold excess of $N(C_2H_5)_3$ in 2-propanol–water, followed by heating of the reaction mixture to boiling. The reaction products were pyrrolidines **VIa**–**VIc**. Probably, the first two stages of this reaction are similar to the formation of cyclopentenes **Va**–**Vc**. The HCN liberated in the course of the reaction adds to the C=N bond of intermediates **IVa**–**IVc**, thus yielding labile compounds **VIIa**–**VIIc** and then pyrrolidines **VIa**–**VIc**. The structures of compounds **Va**–**Vc** and **VIa**–**VIc** were proved by X-ray diffraction and ^{13}C NMR and IR spectroscopy (Table 1).

Probably, the action of triethylamine and other bases on cyclopentanes **Ia**–**Ic** consists in that it ensures formation of salts **IIIa**–**IIIc** in the beginning of the reaction. Salts **IIIa**–**IIIc** are unstable and convert into **Va**–**Vc** or **VIa**–**VIc**, depending on the reaction conditions.

Compared with $N(C_2H_5)_3$, ammonia and other amines [$C_2H_5NH_2$, $(C_2H_5)_2NH$] react with compounds **Ia**–**Ic**, yielding cyclopentenes **Va**–**Vc** and pyrrolidines **VIa**–**VIc**, for a longer time. The highest yields of

Table 2. Reaction times, yields, and melting points of compounds **Va**–**Vc** and **VIa**–**VIc**

Comp. no.	Reaction time, min				Yield, %				mp, °C
	NH_3[a]	NH_2Et[a]	$NH(Et)_2$	$N(Et)_3$	NH_3[a]	NH_2Et[a]	$NH(Et)_2$	$N(Et)_3$	
Va	5–7	5–7	5–7	5–6	32	15	35	42	102–103
Vb					33	24	38	47	126–127
Vc					21	9	25	33	148–149
VIa	25–30	25–30	20–25	10–15	51	15	43	42	169–170
VIb					33	14	27	30	165
VIc					41	18	33	38	118–119

[a] Aqueous solution.

pyrrolidines **VIa**–**VIc** are from cyclopentanes **Ia**–**Ic** and ammonia. Comparable yields of cyclopentenes **Va**–**Vc** and pyrrolidines **VIa**–**VIc** were obtained with $N(C_2H_5)_3$ and $NH(S_2N_5)_2$. In the other cases, the yields are lower than with $N(C_2H_5)_3$ (Table 2).

Cyclopentenes **Va**–**Vc** and pyrrolidines **VIa**–**Vc** present interest in terms of antiviral activity [9].

EXPERIMENTAL

The IR spectra were obtained on a UR-20 instrument in Vaseline oil. The ^{13}C NMR spectra were measured in CD_3CN on a WH-90 instrument (22.63 MHz) with broad-band proton decoupling and off-resonance decoupling; the reference was HMDS.

X-ray diffraction study of compound **Va** was performed on a DAR-UM diffractometer, CuK_α radiation, direct method, Rentgen-75 program. The X-ray diffraction study of compound **VIa** was performed a CAD-4 four-circle diffractometer. The structures were solved by direct methods using the MULTAN program of the SDP package.

Principal crystallographic data for compound **Va**: a 10.577(2), b 6.980(2), c 15.884(3) Å; β 100.38(2)°, V 1150.9 Å^3, Z 4, space group $P21/b$, R 0.078. Principal crystallographic data for compound **VIa**: a 10.553(4), b 23.906(16), c 9,750(2) Å; γ 95.12°, V 2455.2 Å^3, Z 8, space group $P21S$, R 0.043.

The reaction progress and the purity of the products were controlled by TLC on Silufol UV-254 plates.

Substituted 1,5,5-tricyano-4-(2,2-dimethylhydrazino)-1-cyclopentenes Va–Vc. A mixture of 0.02 mol of cyclopentane **Ia**–**Ic**, 40 ml of dioxane, and 5 drops of a base was heated under reflux for 5–7 min. After the reaction was complete, the reaction mixture was cooled with cold water and diluted with 100 ml of water. The precipitate was filtered off, washed with 15–20 ml of a 1:1 2-propanol–water mixture, and recrystallized from 2-propanol.

Substituted 5-cyano-2-(dicyanomethylene)-1-(dimethylamino)pyrrolidines VIa–VIc. A mixture of 0.01 mol of cyclopentane **Ia**–**Ic**, 35 ml of 2-propanol, 10 ml of water, and 0.02–0.03 mol of base was heated under reflux for 10–30 min. After the reaction was complete, the reaction mixture was cooled to 0–5°C, diluted with 60 ml of water, the precipitate was filtered off, washed with 25–30 ml of 2-propanol, and recrystallized from 2-propanol.

REFERENCES

1. Nasakin, O.E., Sheverdov, V.P., Lukin, P.M., Tafeenko, V.A., and Bulai, A.F., *Zh. Org. Khim.*, 1992, vol. 28, no. 9, pp. 1841–1849.
2. Nasakin, O.E., Lukin, P.M., Sheverdov, V.P., and Tafeenko, V.A., *Dokl. Ross. Akad. Nauk*, 1994, vol. 334, no. 2, pp. 187–189.
3. Avtomyan, L.O., Zolotoi, A.B., Sergeev, N.M., Buevich, A.V., Lukin, P.M., Nasakin, O.E., Konovalikhin, S.V., and Sheverdov, V.P., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, no. 5, pp. 1075–1079.
4. Hamer, N.K. and Stubbs, M.E., *J. Chem. Soc., Perkin Trans. 1*, 1972, no. 23, pp. 2971–2976.
5. Rappoport, Z., *J. Chem. Soc.*, 1963, no. 9, pp. 4498–4512.
6. Medici, A., Pedrini, P., Venturoli, C., and Dondoni, A., *J. Org. Chem.*, 1981, vol. 46, no. 13, pp. 2790–2793.
7. Fries, S. and Gollnic, K., *Angew. Chem.*, 1980, vol. 92, no. 10, pp. 848–849.
8. Foster, R. and Hanson, P., *Tetrahedron*, 1965, vol. 21, no. 21, pp. 255–260.
9. Nasakin, O.E., Lukin, P.M., Sheverdov, V.P., and Lyshchikov, A.N., *Khim.-Farm. Zh.*, 1998, vol. 32, no. 5, pp. 21–23.