CHEMISTRY OF 1,1,2,2-TETRACYANOETHANE. REACTION OF 1,1,2,2-TETRACYANOETHANE WITH α-DICARBONYL COMPOUNDS

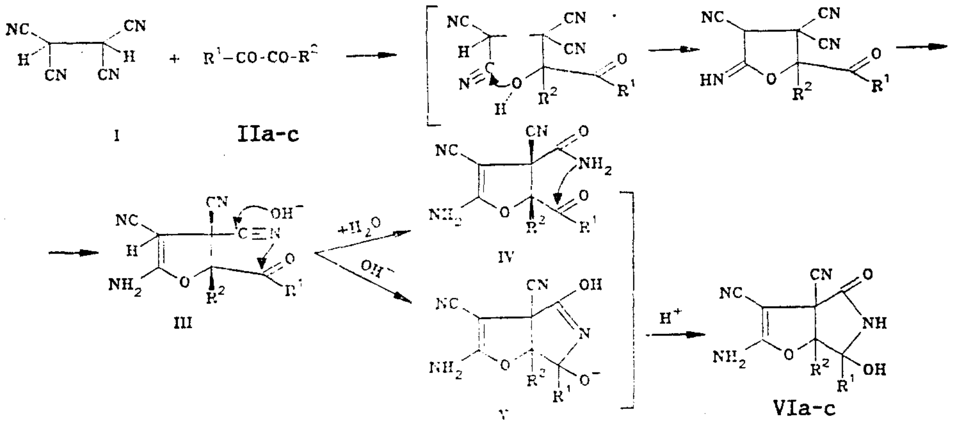
O. E. Nasakin, P. M. Lukin, V. P. Sheverdov,
A. N. Lyshchikov, A. Kh. Bulai, P. B. Terent'ev,
and A. B. Zolotoi

UDC 547.722.6.04'422'239.
07:543.51

1,1,2,2-Tetracyanoethane reacts with α-dicarbonyl compounds in water to form 7-amino-4-hydroxy-1,8-dicyano-3-aza-6-oxabicyclo-[3.3.0]oct-7-en-2-ones. Their structures were confirmed by IR, ¹³C NMR and mass spectra.

We have previously shown that 1,1,2,2-tetracyanoethane (I) reacts with aliphatic and aromatic aldehydes to give 5-amino-3,3,4-tricyano-2,3-dihydrofurans [1-3]. In the case of a β-dicarbonyl compound (acetylacetone), the reaction also gave the corresponding dihydrofuran, hence only involving one of the carbonyl groups.

We now consider further the reaction of α-dicarbonyl compounds. Freshly prepared aldehydoketones and diketones IIa-c react with nitrile I but their reactivities are different. Aldehydoketones IIa, b react exothermically, but IIc does not. The unexpected products obtained in high yield are the 7-amino-4-hydroxy-1,8-dicyano-3-aza-6-oxabicyclo[3.3.0]oct-7-en-2-ones (VIa-c).



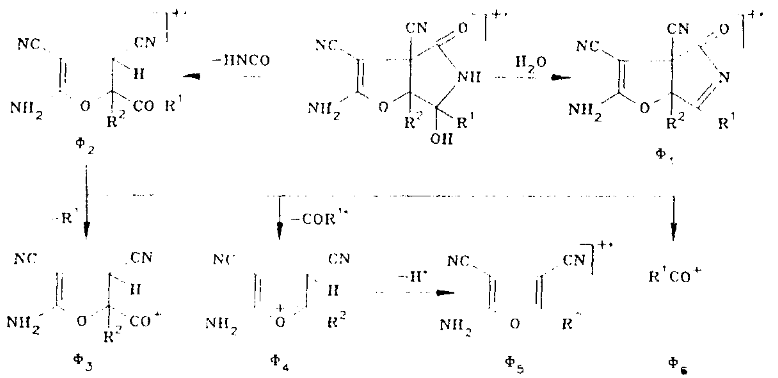
II—VIa $R^1=CH_3$, $R^2=H$; b $R^1=C_2H_5$, $R^2=H$; c $R^1=R^2=CH_3$

The reaction probably begins with formation of the dihydrofuran ring (intermediate III [1-3]) but there then occurs an unusually facile nucleophilic addition of water to one of the geminal nitrile groups. The latter process undoubtedly involves the α-keto group since a significant range of substituents at position 2 of the dihydrofuran ring gives no effect. The subsequent course of the reaction can occur via two pathways, either as an induced intramolecular attack at the carbonyl group or via sequential formation of amide IV by intramolecular closing of the γ-lactam ring.

In the infrared spectra of VIa-c the absorption bands of the enaminonitrile fragment of the dihydropyran ring are observed in the region 3405-3195 cm^{-1}, in agreement with literature data [4, 5]. The ν_{NH} pyrrolidine ring vibrations are also found in this region [5]. The presence of both conjugated and nonconjugated nitriles is evidenced by the corresponding bands of high and low intensity at 2265-2252 and 2220-2200 cm^{-1} (Table 1). Strong bands for the absorptions of the C=O (amide I) and the

---

I. N. Ul'yanov State University. Cheboksar 428015. M. V. Lomonosov Moscow State University, Moscow 117234. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 821-824, June, 1990. Original article submitted April 26, 1988.



Scheme 1

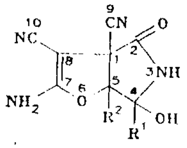
TABLE 1. Data for Compounds VIa-c

Compound	Empirical formula	mp, °C	IR spectrum, cm^{-1}					Mass spectrum,* m/z (relative intensity, %)	Yield, %
			ν_{OH}, ν_{NH}	δ NH_2	δ C≡N	δ C=O	δ C=C		
VIa	$C_9H_8N_4O_3$	210...211	3590, 3420, 3328, 3299, 3235, 3190, 3100	1665	2250, 2205	1730	1595	220 (18), 202 (58), 177 (32), 174 (11), 162 (20), 160 (36), 149 (34), 134 (100), 133 (60), 107 (28)	33
VIb	$C_{10}H_{10}N_4O_3$	183...184	3570, 3480, 3370, 3280, 3180	1665	2252, 2200	1730	1595	234 (7), 216 (14), 201 (7), 191 (20), 174 (14), 162 (62), 134 (100), 133 (25), 107 (12), 91 (91)	8
VIc	$C_{10}H_{10}N_4O_3$	216...217	3590, 3420, 3328, 3299, 3235, 3190, 3100	1665	2260, 2205	1730	1600	234 (6), 216 (13), 191 (16), 174 (18), 118 (63), 147 (30), 146 (16), 44 (20), 43 (100), 42 (15)	20

---

*Values given for the molecular ion and ten most abundant ion peaks.

TABLE 2. ^{13}C NMR and Mass Spectra of VIa-c



Compound	Chemical shift, ppm								W_M	Intensity of characteristic ion peaks					
	$C_{(1)}$	$C_{(2)}$	$C_{(4)}$	$C_{(5)}$	$C_{(7)}$	$C_{(8)}$	$C_{(9)}$	$C_{(10)}$		Φ_1	Φ_2	Φ_3	Φ_4	Φ_5	Φ_6
VIa	54,97	167,25	88,15	95,48	168,14	51,17	116,82	115,74	2,0	6,0	3,6	1,8	10,0	5,6	8,5
VIb	50,91	168,61	89,34	101,3	168,61	51,23	117,15	116,58	1,0	1,6	2,3	7,2	11,6	2,9	4,3
VIc	51,12	167,98	87,28	90,66	168,52	51,36	117,11	116,47	1,0	2,7	2,6	0,5	10,5	17,0	5,0

δ_{NH_2} vibrations were seen at 1730-1710 and 1680-1665 cm^{-1}. The carbon chemical shifts for the heterocyclic fragments agreed with [6] (Table 2). The mass spectra of VIa-c were characterized by low intensity peaks for the molecular ion (Table 2), initially losing water (ion Φ_1) or HNCO (ion Φ_2). The latter further eliminates either the R^1 radical (ion Φ_3) or, with greater probability, the whole acyl R^2CO residue with the formation of the oxonium ion Φ_4 (further stabilized by loss of hydrogen, apparently from the β-position) (ion Φ_5). The mass spectra also showed quite intense peaks for the R^1CO^+ ions (Φ_6). For ion structures see Scheme 1. All of these fragmentations are in good agreement with the structures VIa-c.

EXPERIMENTAL

IR spectra were recorded on a UR-20 instrument in Vaseline mull. ^{13}C NMR spectra were taken on a Bruker WH-90 instrument and mass spectra on a Varian MAT-212 with ionization energy 70 eV and direct introduction of the sample into the ionization source.

Monitoring of the purity of the synthesized compounds and the reaction course was carried out using TLC on Silufol UV-254 plates.

Nitrile I (50 mmoles) was added portionwise to a soluton of the dicarbonyl compound (50-70 mmoles) in water (50 ml) and the temperature of the mixture held at 40-45°C. (For the reaction with diacetyl the solution was held for 1 week at room temperature.) The product was heated at 50°C until disappearance of nitrile I (3.5-6 h), the precipitate was separated, washed with water, and recrystallized from aqueous dioxane (1:1). Spectral and other data are given in Table 1.

LITERATURE CITED

1. O. E. Nasakin, V. V. Alekseev, V. K. Promonenkov, A. Kh. Bulai, and S. Yu. Sil'vestrova, *Khim. Geterotsikl. Soedin.*, No. 1, 121 (1981).
2. O. E. Nasakin, V. V. Alekseev, V. K. Promonenkov, A. Kh. Bulai, and S. Yu. Sil'vestrova, *Khim. Geterotsikl. Soedin.*, No. 6, 744 (1981).
3. O. E. Nasakin, V. V. Alekseev, P. B. Terent'ev, A. Kh. Bulai, and V. A. Shmorgunov, *Khim. Geterotsikl. Soedin.*, No. 12, 1605 (1982).
4. N. K. Kochetkov (ed.), *General Organic Chemistry*, Vol. 4 [in Russian], Khimiya, Moscow (1983), p. 431.
5. A. I. Malyshev, Yu. I. Kotov, A. Ya. Chernikhov, M. N. Yakovlev, V. I. Isaeva, O. V. Kachevskaya, T. N. Zhukova, O. E. Nasakin, and I. A. Anisimova, *Atlas of Spectra of Chemical Products*, No. 2 [in Russian], Novosibirsk Institute of Organic Chemistry (1984), p. 377.
6. A. Kh. Bulai, O. E. Nasakin, P. M. Lukin, E. G. Nikolaev, V. I. Mamatyuk, V. A. Furina, and O. V. Toropov, *Atlas of Carbon Magnetic Resonance Spectra*, No. 5 [in Russian], Novosibirsk Institute of Organic Chemistry (1986), p. 158.