TETRACYANOALKANONES IN THE SYNTHESIS OF HETEROCYCLES. SYNTHESIS OF 3,4-DICYANO-2(1H)-PYRIDONES BY THE INTERACTION OF TETRACYANOALKANONES WITH PYRUVIC ACID

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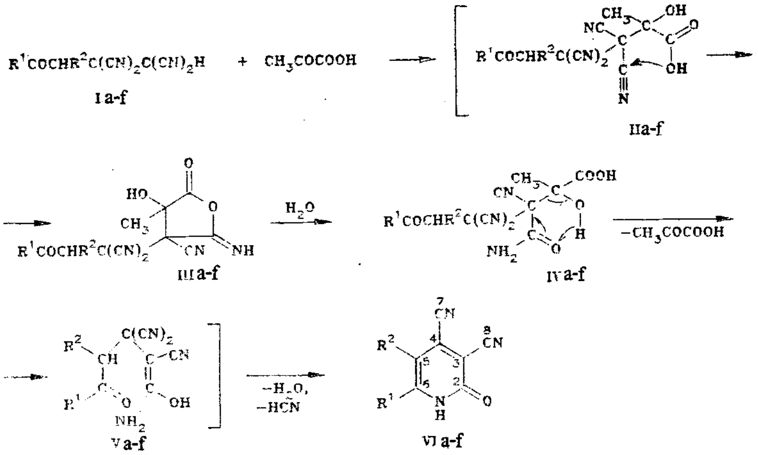
Tetracyanoalkanones react with pyruvic acid with the formation of 3,4-dicyano-5,6-dialkyl-2(1H)-pyridones, the structure of which was confirmed by IR, ^{13}C NMR, and mass spectra.

We recently reported in [1] a convenient means of obtaining tetracyanoalkanones (Ia-f) and some of their properties in [2]. While studying their reaction with carbonyl compounds we established that the interaction of tetracyanoethylated ketones (Ia-f) with pyruvic acid in aqueous acetone occurred at room temperature in an unusual manner and led in high yield (Table 1) to substituted pyridones (VIa-f). On using other acids (acetic, monochloroacetic, trichloroacetic, trifluoroacetic) in this reaction pyridones were not formed and pyruvic acid ethyl ester did not generally react with ketones (Ia-f).



We assume that the initial cyanides (I) interact with pyruvic acid as with other carbonyl compounds [3] by an aldol addition scheme with the formation of carbinol (II) in which an intramolecular iminoacylation occurs due to the steric proximity of the carbonyl oxygen atom to the electrophilic carbon atom of the cyano group. The iminoanhydride (III) formed in this way readily hydrolyzes to the amino acid (IV) which then splits off a molecule of pyruvic acid and amide (V) formed in this way cyclizes and is then dehydrocyanated to pyridones (VIa-f).

In the IR spectra of all the isolated compounds (VIa-f) (Table 2) an intense band was observed for the stretching vibrations of a carbonyl group at 1660-1670 cm^{-1} and also stretching (3330, 3160 cm^{-1}) and deformation (1600-1618 cm^{-1}) vibrations for an NH group which is characteristic of 2-pyridone derivatives according to [4, 5]. The stretching vibrations of the cyano group were displayed as a weak band at 2238-2240 cm^{-1}.

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TABLE 1. Properties of Compounds (VIa-f)

Compound	R^1	R^2	Mp*, deg C	Found, %			Empirical formula	Calculated, %			Yield, %
				C	H	N		C	H	N	
VIa	CH_3	H	241—242 (241—242 [11])	60,5	3,2	26,2	$C_8H_5N_3O$	60,4	3,1	26,4	77
VIb	CH_3	CH_3	265—267	62,6	4,2	24,1	$C_8H_7N_3O$	62,4	4,1	24,3	76
VIc	CH_3	n-C_3H_7	238—239	65,8	5,6	20,7	$C_{11}H_{11}N_3O$	65,7	5,5	20,9	71
VId	CH_3	n-C_5H_{11}	192—194	68,3	6,7	18,3	$C_{13}H_{15}N_3O$	68,1	6,6	18,3	86
VIe	$(CH_2)_4$		266—267	66,4	4,7	21,0	$C_{11}H_9N_3O$	66,3	4,5	21,1	57
VIf	C_6H_5	H	315—316†	70,7	3,3	18,7	$C_{13}H_7N_3O$	70,6	3,2	19,0	60

*Compounds (VIb, e) were crystallized from DMF, (VIc) from a mixture of acetone—propan-2-ol 1:1, (VId, f) from propan-2-ol.
†According to data of [11], decomposition point 300°C.

TABLE 2. Spectral Characteristics of Compounds (VIa-f)

Compound	IR spectrum, cm^{-1}				Mass spectrum*: m/z (relative intensity, %)
	ν_{N-H}	δ_{N-H}	$\nu_{C=O}$	$\nu_{C\equiv N}$	
VIa	3330	1618	1663	2238	159 (76), 131 (44), 130 (100), 105 (4), 104 (7), 103 (6), 89 (25), 77 (12), 63 (15), 62 (12), 52 (12)
VIb	3325 3150	1610	1664	2239	173 (94), 145 (37), 144 (100), 130 (41), 104 (14), 103 (13), 77 (29), 76 (39), 52 (22), 51 (22), 50 (17)
VIc	3327 3153	1603	1664	2238	201 (18), 173 (17), 172 (100), 144 (4), 104 (4), 103 (3), 102 (6), 77 (7), 76 (10), 52 (5), 51 (5)
VId	3328 3160	1600	1660	2239	229 (23), 201 (8), 173 (82), 172 (100), 145 (12), 144 (18), 129 (8), 118 (7), 102 (9), 76 (14), 57 (56)
VIe	3325 3168	1596	1662	2240	199 (89), 198 (40), 172 (12), 171 (100), 143 (24), 129 (11), 116 (11), 77 (13), 76 (14), 52 (14), 51 (12)
VIf	3332 3165	1600	1672	2240	221 (100), 193 (51), 165 (15), 139 (16), 121 (6), 104 (12), 89 (21), 77 (34), 63 (18), 62 (11), 51 (44)

*The peaks of the molecular ion and the 10 most intense ion peaks are given.

TABLE 3. Chemical Shifts of Carbon Atoms of the Heterocycle in ^{13}C NMR Spectra of Pyridones (VIb-f) (ppm)

Compound	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$	$C_{(7)}$	$C_{(8)}$
VIb	158,62	102,15	130,82	114,15	155,57	114,53	113,72
VIc	159,01	*	131,77	118,50	154,78	114,24	113,78
VId	159,31	108,23	132,04	119,17	154,88	114,48	113,99
VIe	158,16	*	130,79	114,28	154,87	114,50	113,04
VIf	161,06	108,40	131,98	114,42	156,01	114,15	*

*Signal lost in noise.

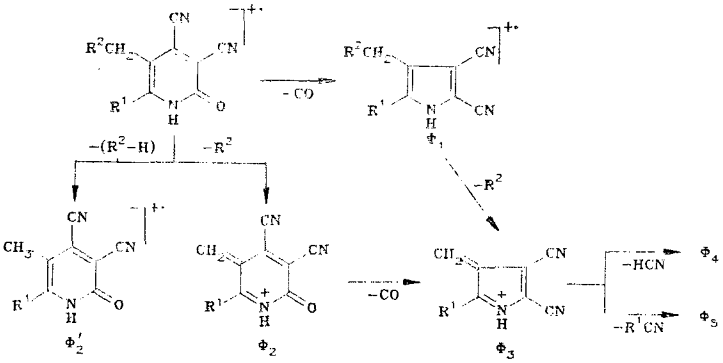
TABLE 4. Intensities of Peaks of Characteristic Ions in the Mass Spectra of Compounds (VIa-f) (J, %, Σ_{50})

Compound	W_M	Φ_1	$\Phi_2(\Phi'_2)$	Φ_3	Φ_4	Φ_5
VIa	17,6	10,0	—	23,0	1,7	—
VIb	13,8	5,4	2,5	14,2	1,8	1,9
VIc	6,9	6,8	38,3	1,7	—	3,0
VId	3,8	1,4	17,5 (13,8)	3,0	1,3	1,5
VIe	15,0	16,7	[(M—H) 6,7]	[(Φ_1—C_2H_4) 4,0]	1,8	—
VIf	15,2	7,7	—	—	2,5	3,2*

*In addition there was an ion of m/z 77, the peak intensity of which was 5.2%.

Signals for the heterocyclic carbon atoms were observed in the ^{13}C NMR spectra of all the pyridones, the chemical shifts of which were in good agreement with the data for cyano and other derivatives of pyridone from [6].

Intense peaks for molecular ions were observed in the mass spectra of the compounds isolated by us (Table 2), the stability of which fell rapidly with lengthening of radical R^2 (Table 4). Decomposition of the molecular ions of pyridones (VIa-f) was on the one hand linked with loss of a molecule of CO (ion Φ_1) which is characteristic of the fragmentation of 2-pyridones according to [7, 8]. On the other hand a "benzylic" fission of the α,β C—C bond of the R^2 radical occurred both in the molecular ion and in ion Φ_1 leading to ions Φ_2 and Φ_3 respectively which is a characteristic of dissociative ionization processes of β-alkylpyridones [9] and of alkylpyridols [10].



Further fission of ion Φ_3 proceeds with loss of HCN or R^1CN (ions Φ_4 and Φ_5). In the case of tetramethylenepyridone (VIe) the ion Φ_1 either sheds a hydrogen ion or undergoes a retrodiene fission which is characteristic of tetramethylenehetarenes [10]. The total intensity of ion peaks M, Φ_1—Φ_5 was from 33 to 56% which indicates the high selectivity of fission of these compounds under electron impact.

The reaction of tetracyanoethylated aliphatic, alicyclic, and aliphatic—aromatic ketones with pyruvic acid is a new preparative method for the synthesis of cyano substituted 2-pyridones.

EXPERIMENTAL

The ^{13}C NMR spectra were taken on a Bruker WH-90 instrument and mass spectra on a Varian MAT-212 at an ionization energy of 70 eV with direct insertion into the ion source. IR spectra were drawn on a UR-20 instrument in Nujol mulls.

General Procedure for the Synthesis of Pyridones (VIa-f). A solution of tetracyanoalkanone (Ia-f) (50 mmole) in acetone or dioxane (50 ml) was added to a solution of pyruvic acid (4.4 g: 50 mmole) in water (30 ml). The mixture was stirred for 2-3 h at room temperature, the precipitated solid filtered off, the filtrate evaporated, the obtained solid substances were combined, and recrystallized from the appropriate solvent. Yields and properties of compounds are seen in Table 1.

LITERATURE CITED

1. O. E. Nasakin, V. A. Kukhtin, G. N. Petrov, E. G. Nikolaev, V. V. Alekseev, and Yu. S. Sil'vestrova, Authors' Certificate No. 759,507 (USSR): Byull. Izobr. No. 38 (1980).
2. O. E. Nasakin, E. G. Nikolaev, P. M. Lukin, and B. A. Khaskin, Summaries of Reports of the 1st All-Union Conference on Chemical Means of Plant Protection, Ufa (1982), Section 1, p. 124.
3. O. E. Nasakin, E. G. Nikolaev, P. B. Terent'ev, A. Kh. Bulai, B. A. Khaskin, and K. Dager, Zh. Geterotsikl. Soedin., No. 11, 1462 (1984).
4. Yu. N. Sheinker and Yu. I. Pomerantsev, Zh. Fiz. Khim., 30, 79 (1956).
5. P. Sensi and G. G. Gallo, Ann. Chim., 44, 232 (1954).
6. G. Levy and G. Nelson, Carbon-13 Nuclear Magnetic Resonance for Organic Chemists, Wiley (1972).
7. G. Spiteller and E. Spiteller-Friedmann, Monatsh. Chem., 93, 1395 (1962).
8. W. A. Auer, T. E. Habgood, V. Donloffen, and H. R. Juliani, Tetrahedron, 21, 2169 (1965).

9. R. A. Khmel'nitskii, P. B. Terent'ev, A. A. Polyakova, and A. N. Kost, Dokl. Akad. Nauk SSSR, 167, 1066 (1966).
10. P. B. Terent'ev, Mass Spectrometry in Organic Chemistry [in Russian], Vyssh. Shkola, Moscow (1979), p. 124.
11. W. J. Middleton, R. E. Heckert, E. Z. Little, and C. G. Krespan, J. Am. Chem. Soc., 80, 2783 (1958).