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THE CHEMISTRY OF sym-TETRACYANOETHANE.

1. CONDENSATION OF sym-TETRACYANOETHANE WITH ALDEHYDES AND KETONES

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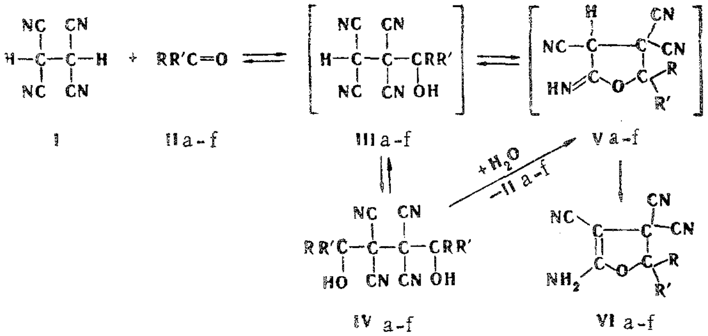
In an aqueous dioxane solution sym-tetracyanoethane adds to aldehydes and ketones with subsequent cyclization to 3,3,4-tricyano-5-amino-2,3-dihydrofurans.

Very little study has been devoted to sym-tetracyanoethane (I) and its derivatives, probably in connection with the complexity involved in the preparation of I [1]. We have developed a number of relatively accessible methods for the preparation of I [2], which makes it possible to begin a systematic study of its chemistry in order to search for potentially physiologically active preparations and amino nitrile monomers.

The reactions of I with aliphatic and aromatic aldehydes and ketones were investigated. Compound I reacts exothermally with acetaldehyde in the presence of water to give 3,3,4-tricyano-5-amino-2,3-dihydrofuran (VIa) as the final product. Chloral hydrate reacts similarly. Aliphatic ketones and aromatic and heterocyclic aldehydes react with I in the form of the bisulfite compounds or under basic catalysis conditions. The characteristics of VIa-f are presented in Table 1. The probable reaction scheme is given below:



II—VI a R=H, R′=CH_3; b R=H, R′=CCl_3; c R=H, R′= 3-nitrophenyl; d R=H, R′=2-furyl ; e R=R′=CH_3; f R=CH_3, R′=$CH_2C(O)CH_3$

The intermediately formed tetracyanoglycol IVa was obtained by the reaction of I with 2 moles of IIa in absolute alcohol. Its IR spectrum contains a band of medium intensity at 3290

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TABLE 1. Characteristics of VI

Compound	mp, °C	IR spectrum, cm^{-1}	PMR spectrum, δ, ppm	Found, %			Empirical formula	Calculated, %			Yield, %
				C	H	N		C	H	N	
VIa	156—157	3410—3180, 1665 (NH_2), 2205 ($C\equiv N$), 1590 ($C=C$)	1,5 (3H, d, CH_3), 5,4 (1H, q, CH), 8,34 (2H, s, NH_2)	55,1	3,3	32,2	$C_8H_6N_4O$	55,1	3,5	32,1	65
VIb	181 (dec.)	3430—3180, 1660 (NH_2), 2200 ($C\equiv N$), 1585 ($C=C$)	6,65 (1H, s, CH), 8,87 (2H, s, NH_2)	34,4	1,2	20,2	$C_8H_3Cl_3N_4O$	34,6	1,0	20,2	65
VIc	238 (dec.)	3450—3166, 1665, (NH_2), 2210 ($C\equiv N$), 1580 ($C=C$), 1520 ($C=C$ arom.)	7,2—7,5 (4H, m, 4H ring) , 7,9 (1H, s CH), 8,5 (2H, s, NH_2)	55,5	2,6	24,6	$C_{13}H_7N_5O_3$	55,6	2,5	24,9	46
VId	165	3420—3190, 1660, (NH_2), 2205 ($C\equiv N$), 1580 ($C=C$), 1600, 1500 ($C=C$ ring)	6,6—6,9 (3H, m, 3H ring), 7,88 (1H, s, CH), 8,58 (2H, s, NH_2)	58,3	2,8	24,8	$C_{11}H_6N_4O_2$	58,4	2,7	24,8	65
VIe	209 (dec.)	3460—3170, 1655 (NH_2), 2205 ($C\equiv N$), 1580 ($C=C$)	1,71 (6H, s, $2CH_3$), 8,28 (2H, s, NH_2)	57,4	4,2	29,7	$C_9H_8N_4O$	57,4	4,3	29,8	45
VIf	179 (dec.)	3440—3190, 1665, (NH_2), 2200 ($C\equiv N$), 1710 ($C=O$), 1590 ($C=C$)	1,63 (3H, s, CH_3), 2,22 [3H, s, $CH_3C(O)$], 3,41, 3,58 (2H, d, CH_2), 8,29 (2H, s NH_2)	57,4	4,3	24,3	$C_{11}H_{10}N_4O_2$	57,4	4,4	24,3	65

cm^{-1} (ν_{OH}) and a band of weak intensity at 2260 cm^{-1} ($\nu_{C\equiv N}$), which is characteristic for unconjugated nitriles. The reaction product was also characterized by the results of elementary analysis and by the mass spectrum. In the presence of water IVa undergoes partial conversion to VIa. The low yield of the desired product makes it possible to propose that the reaction also proceeds through other intermediates, the most likely of which is IIIa, but we were not able to isolate it. When IVa is dissolved in organic solvents that do not contain water, one observes its decomposition to I and IIa.

It is known that reactions of the Thorpe—Ziegler type [3, 4] are catalyzed by acids and bases. The investigated reactions also take place without a catalyst (the use of bisulfite compounds of IIa-f or basic catalysts somewhat increases the yields of the desired products). Hypothetical imines Va-f, the formation of which is proposed by the scheme of the Thorpe reaction, were not detected in the PMR spectra within the limits of the sensitivity of the method.

EXPERIMENTAL

The course of the reactions and the purity of the compounds were monitored on Silufol UV-254 plates in an acetone—petroleum ether system (1:1). The IR spectra of suspensions of the compounds in mineral oil were recorded with a UR-20 spectrometer. The PMR spectra of 15-20% solutions in DMSO and d_6-DMSO were obtained with a Bruker WH-90 spectrometer with hexamethyldisiloxane as the internal standard.

2-Methyl-3,3,4-tricyano-5-amino-2,3-dihydrofuran (VIa). A 6-ml (0.1 mole) sample of IIa was added dropwise at 5-10°C to a suspension of 6.5 g (0.05 mole) of I in 25 ml of water, and the resulting solution was maintained at 20°C for 10 min, after which it was diluted with 100 ml of water. The precipitated crystals were removed by filtration, washed with water, dried, and recrystallized from dioxane—water to give 5.7 g of VIa.

2-Trichloromethyl-3,3,4-tricyano-5-amino-2,3-dihydrofuran (VIb). A reaction mixture consisting of 6.5 g (0.05 mole) of I, 25 g (0.15 mole) of IIb, and 10 ml of water was refluxed for 10 min, after which it was diluted with 100 ml of water and cooled to 10°C. The precipitated crystals were removed by filtration, washed with water, dried, and reprecipitated from solution in ethyl acetate by the addition of heptane to give 9 g of VIb.

2-(3-Nitrophenyl)-3,3,4-tricyano-5-amino-2,3-dihydrofuran (VIc). A mixture of 2.6 g (0.02 mole) of I, 10.2 g (0.04 mole) of the bisulfite compound of IIc, 30 ml of acetonitrile, and 50 ml of water was heated at 70°C for 10 min, after which it was diluted with 50 ml of water. The precipitated crystals were removed by filtration, washed with water, dried, and recrystallized from dioxane—water to give 2.5 g of VIc.

2-(2-Furyl)-3,3,4-tricyano-5-amino-2,3-dihydrofuran (VId). This compound was similarly obtained from 6.5 g (0.05 mole) of I and 20 g (0.1 mole) of the bisulfite compound of IId after heating at 40°C for 5 h. The yield was 7.3 g.

2,2-Dimethyl-3,3,4-tricyano-5-amino-2,3-dihydrofuran (VIe). A) A mixture of 6.5 g (0.05 mole) of I, 16.5 g (0.1 mole) of the bisulfite compound of IIe, 50 ml of IIe, and 50 ml of water was allowed to stand at 20°C for 14-15 h, after which it was diluted with 150 ml of water. The precipitated crystals were removed by filtration, washed with water, dried, and recrystallized from ethyl acetate to give 3.8 g (40%) of VIe.

B) A mixture of 6.5 g (0.05 mole) of I, 50 ml of IIe, 30 ml of water, and 1 g of sodium acetate was stirred at 20°C, after which it was diluted with 200 ml of water. The precipitated crystals were removed by filtration, washed with water, dried, and recrystallized from dioxane to give 4.2 g (45%) of product.

2-Methyl-2-acetonyl-3,3,4-tricyano-5-amino-2,3-dihydrofuran (VIf). A mixture of 13 g (0.1 mole) of I, 40 ml of acetylacetone, 40 ml of water, and 1 g of sodium formate was stirred at 40-50°C for 40 min, after which it was diluted with 100 ml of water. The precipitated crystals were removed by filtration, washed with water, dried, and recrystallized from dioxane to give 15 g of VIf.

3,3,4,4-Tetracyano-2,5-hexanediol (IVa). A mixture of 6.5 g (0.05 mole) of I, 7.5 ml (0.15 mole) of freshly distilled IIa, and 8 ml of absolute ethanol was maintained at 22°C for 45 h, after which the precipitated crystals were removed by filtration, washed with absolute ethanol, and air dried to give 6.3 g (58%) of a product with mp 82°C (dec.). Found: C 55.3; H 4.7; N 25.8%. M (mass-spectrometrically) 218. $C_{10}H_{10}N_4O_2$. Calculated: C 55.0; H 4.6; N 25.7%. M 218.

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