SYNTHESES BASED ON NITRILE OXIDES.
1. REACTION OF AROMATIC NITRILE OXIDES WITH N-CYANIMIDES

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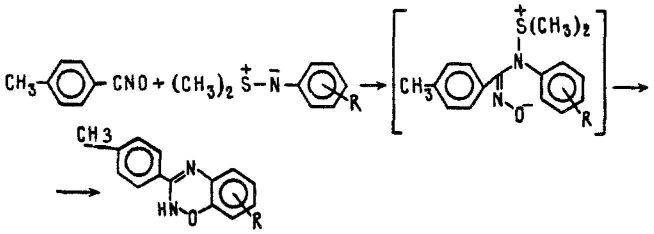
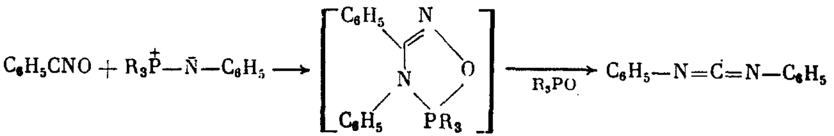
The reaction of trialkylaminocyanimides with aromatic nitrile oxides leads to trialkylamino-(3-aryl-1,2,4-oxadiazol-5-yl)imides, while the corresponding reactions with sulfylcyanimines and phosphincyanimides do not take place. Using x-ray structural analysis the principal structural features of the 1,2,4-oxadiazole products have been elucidated.

The reaction of aromatic nitrile oxides with sulfylimines [1] and phosphinimides [2] is known to occur via addition of the carbon atom in the nitrile oxide group to the imide nitrogen atom, leading to either cyclic or linear addition products, depending on the nature of the starting materials.



R = H, NO_2, Cl.



R = C_6H_5, C_2H_5O.

We have examined the reaction of aromatic nitrile oxides ArCNO (Ia-d) (Ar = C_6H_5 (a), o-$NO_2C_6H_4$ (b), m-$NO_2C_6H_4$ (c), p-$NO_2C_6H_4$ (d)) with sulfur, phosphorus, and nitrogen cyanimides of general formula $R_n\overset{+}{E}\overset{-}{N}{-}CN$, where E = S, n = 2, R = CH_3 (II); E = P, n = 3, R = C_6H_5 (III); E = N, n = 3, R = CH_3 (IVa) and C_2H_5 (IVb).

We have found that neither sulfylimine (II) nor phosphinimide (III) reacts with (Ia-d). After 24 h reaction time both (II) and (III) were recovered in quantitative yields from the reaction mixtures, while the nitrile oxides dimerized to give the corresponding furoxanes.

In contrast, amino imide (IVa) reacts with (Ia-d) immediately after the reagents have been mixed. However, instead of the expected reaction at the imide nitrogen atom, 1,3-dipolar addition of the nitrile group to the nitrile oxide was observed, leading to the formation of 1,2,4-oxadiazoles (Va-d); increasing the length of the hydrocarbon chain in the substituent attached to the ammonium nitrogen atom did not affect the reaction course, since reaction of amino imide (IVb) with (Id) also gave a 1,2,4-oxadiazole (Ve).

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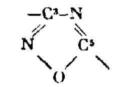
TABLE 1. Yields and Physical Chemical Properties of Trialkylamino(3-aryl-1,2,4-oxadiazol-5-yl)imides (Va-e)

Compound	R	R'	Yield, %	mp, °C	Molecular formula (M^+, m/e)	Found/Calculated, %			IR spectrum ν, cm^{-1}	NMR spectrum δ, ppm*				
						C	H	N		R'	RC_6H_4		NO_2	$-NR_3'$
(Va)	H	CH_3	81	161–162	$C_{11}H_{14}N_4O$ (218)	60,23 60,55	6,39 6,42	25,33 25,69	1580 (Ph) 1570 (C=N)	54,98	128,42 128,52 129,15 129,91	165,89 (C^3) 175,50 (C^5)	–	–297,99
(Vb)	o-NO_2	CH_3	60	199–201	$C_{11}H_{13}N_5O_3$ (263)	49,75 50,19	4,83 4,92	26,18 26,62	1575 1530 } NO_2, C=N, Ph 1390 (NO_2)	54,69	121,79 123,44 129,58 131,21 132,13 149,24	163,20 (C^3) 175,29 (C^5)	–2,90	–303,12
(Vc)	m-NO_2	CH_3	75	246–248	$C_{11}H_{13}N_5O_3$ (263)	49,91 50,19	4,92 4,92	26,00 26,62	1570 (NO_2, C=N, Ph) 1480 1390 (NO_2) 1320	55,06	120,69 124,61 130,45 130,65 132,51 148,01	164,42 (C^3) 175,45 (C^5)	–7,48	–298,59
(Vd)	p-NO_2	CH_3	77	251–253	$C_{11}H_{13}N_5O_3$ (263)	50,26 50,19	4,98 4,92	26,40 26,62	1560 1550 } NO_2, C=N, Ph 1510 1500 1320 (NO_2)	55,01	123,90 127,55 135,31 148,22	164,61 (C^3) 175,62 (C^5)	–	–300,71
(Ve)	p-NO_2	CH_3CH_2	73	145–176	$C_{14}H_{19}N_5O_3$ (305)	55,06 55,08	6,21 6,23	22,91 22,95	1575 1560 } NO_2, C=N, Ph 1520 1520 1320 (NO_2)	8,40 54,67	124,57 128,51 137,08 149,51	165,93 (C^3) 176,03 (C^5)	–11,18	–286,52

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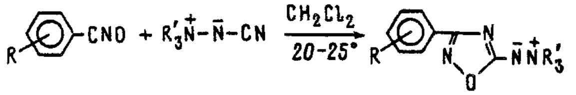
*^{13}C and ^{14}N NMR spectra of (Va-d) were taken in DMSO-d_6 solutions, (Ve) in acetone-d_6 solution.

TABLE 2. Atomic Coordinates in the Molecular Structure of (Ve)

Atom	Molecule A			Molecule B		
	X	Y	Z	X	Y	Z
O^1	0,1289(1)	0,1583(2)	0,6183(1)	0,2842(1)	−0,1534(2)	−0,0409(1)
O^2	0,5918(1)	−0,0673(2)	0,9230(2)	0,6959(2)	−0,5364(2)	0,1464(2)
O^3	0,6293(1)	0,0456(2)	0,8427(2)	0,7337(2)	−0,4124(2)	0,0811(3)
N^1	0,1973(1)	0,1032(2)	0,6868(2)	0,3654(1)	−0,1700(2)	−0,0318(2)
N^2	0,2390(1)	0,2334(2)	0,6157(2)	0,3255(1)	−0,3022(2)	0,0387(2)
N^3	0,1032(1)	0,2934(2)	0,5150(2)	0,1920(1)	−0,2303(2)	0,0041(2)
N^4	0,1350(1)	0,3738(2)	0,4705(2)	0,1710(1)	−0,3207(2)	0,0492(2)
N^5	0,5787(2)	0,0062(2)	0,8672(2)	0,6849(2)	−0,4531(2)	0,1067(2)
C^1	0,2579(2)	0,1525(2)	0,6802(2)	0,3831(2)	−0,2585(2)	0,0142(2)
C^2	0,1595(2)	0,2359(2)	0,5789(2)	0,2647(2)	−0,2360(2)	0,0042(2)
C^3	0,3413(2)	0,1191(2)	0,7352(2)	0,4625(2)	−0,3066(2)	0,0396(2)
C^4	0,4030(2)	0,1662(2)	0,7170(2)	0,5203(2)	−0,2633(3)	0,0122(3)
C^5	0,4810(2)	0,1316(3)	0,7616(2)	0,5937(2)	−0,3101(3)	0,0354(3)
C^6	0,4962(2)	0,0490(2)	0,8249(2)	0,6080(2)	−0,4008(3)	0,0855(2)
C^7	0,4376(2)	0,0041(3)	0,8485(2)	0,5525(2)	−0,4460(3)	0,1149(2)
C^8	0,3596(2)	0,0389(3)	0,8030(2)	0,4794(2)	−0,3982(3)	0,0920(2)
C^9	0,1765(2)	0,3286(3)	0,4072(3)	0,1647(2)	−0,4162(3)	−0,0115(3)
C^{10}	0,1267(3)	0,2545(4)	0,3306(3)	0,1070(3)	−0,4086(3)	−0,1172(3)
C^{11}	0,0592(2)	0,4302(3)	0,4065(2)	0,0894(2)	−0,2910(3)	0,0482(3)
C^{12}	0,0705(2)	0,5185(3)	0,3465(3)	0,0527(2)	−0,3697(3)	0,0929(3)
C^{13}	0,1922(2)	0,4459(3)	0,5464(3)	0,2300(2)	−0,3422(2)	0,1545(2)
C^{14}	0,1612(3)	0,4860(3)	0,6185(3)	0,2501(3)	−0,2508(3)	0,2207(3)

TABLE 3. Bond Lengths in Molecules A and B (α, Å)

Bond	α		Bond	α	
	A	B		A	B
O^1-N^1	1,441(2)	1,437(3)	N^5-C^6	1,481(3)	1,469(4)
O^1-C^2	1,383(3)	1,381(3)	C^1-C^3	1,468(3)	1,474(3)
O^2-N^5	1,221(3)	1,211(3)	C^3-C^4	1,388(3)	1,379(4)
O^3-N^5	1,220(3)	1,208(3)	C^3-C^8	1,390(3)	1,388(4)
N^1-C^1	1,307(3)	1,310(3)	C^4-C^5	1,376(3)	1,376(4)
N^2-C^1	1,367(3)	1,353(3)	C^5-C^6	1,377(4)	1,363(4)
N^2-C^2	1,322(3)	1,331(3)	C^6-C^7	1,367(3)	1,371(4)
N^3-N^4	1,466(3)	1,473(3)	C^7-C^8	1,378(3)	1,378(4)
N^3-C^2	1,313(3)	1,314(3)	C^9-C^{10}	1,488(5)	1,492(4)
N^4-C^9	1,521(4)	1,509(3)	$C^{11}-C^{12}$	1,510(4)	1,505(4)
N^4-C^{11}	1,513(3)	1,518(3)	$C^{13}-C^{14}$	1,472(5)	1,489(4)
N^4-C^{12}	1,513(4)	1,518(3)			



(Ia-d) (IVa, b) (Va-e)

As the reactions proceed over time, however, the nitrile oxides undergo partial dimerization to the corresponding diarylfuroxanes (VIa-d).

The factor apparently responsible for this unusual behavior of cyanimides is the strong electron-withdrawing effect of the nitrile group, which renders attack of the nitrile oxide carbon atom at the imide nitrogen atom impossible.

The structures of compounds (Va-e) were established based on the results of elemental analysis, as well as their IR, mass, and NMR spectroscopic data (Table 1).

For an objective determination of the structures of these newly prepared compounds, as well as to elucidate the structural features or characteristics of amino imides in the oxadiazole series, we have carried out an x-ray structural analysis of triethylamino[3-(4-nitrophenyl)-1,2,4-oxadiazol-5-yl]imide (Ve).

It was found that compound (Ve) is in fact an amino imide with a coplanar arrangement or orientation of its amino imide, oxadiazole, and nitrophenyl fragments.

TABLE 4. Bond Angles in Molecules A and B (ω, deg)

Angle	ω		Angle	ω	
	A	B		A	B
$N^1O^1C^2$	106,4(2)	106,3(2)	$O^1C^2N^2$	111.1(2)	111.1(2)
$O^1N^1C^1$	102,6(2)	102.4(2)	$O^1C^2N^3$	112.9(2)	113.4(2)
$C^1N^2C^2$	103,8(2)	103.4(2)	$N^2C^2N^3$	136.0(2)	135,5(3)
$N^4N^3C^2$	113.3(2)	112,8(2)	$C^1C^3C^4$	119,5(2)	121,7(2)
$N^3N^4C^9$	111,5(2)	111,7(2)	$C^1C^3C^8$	121,4(2)	119,2(2)
$N^3N^4C^{11}$	101,9(2)	102.2(2)	$C^4C^3C^8$	119,0(2)	119,1(3)
$N^3N^4C^{13}$	113,0(2)	113,7(2)	$C^3C^4C^5$	121,0(2)	120,9(3)
$C^9N^4C^{11}$	110,8(2)	110,9(2)	$C^4C^5C^6$	118.2(2)	118,6(3)
$C^9N^4C^{13}$	109,3(2)	107,9(2)	$N^5C^6C^5$	118.6(3)	118,7(3)
$C^{11}N^4C^{13}$	110.2(2)	110,5(2)	$N^5C^6C^7$	119,0(3)	118,8(3)
$O^2N^5O^3$	123.8(3)	122.8(3)	$C^5C^6C^7$	122,4(2)	122,4(3)
$O^2N^5C^6$	118,4(3)	118.7(3)	$C^6C^7C^8$	118,9(2)	118,5(3)
$O^3N^5C^6$	117,8(3)	118.4(3)	$C^3C^8C^7$	120,4(2)	120,5(3)
$N^1C^1N^2$	116,1(2)	116,8(2)	$N^4C^9C^{10}$	114,4(3)	114,6(2)
$N^1C^1C^3$	121,6(2)	121.4(3)	$N^4C^{11}C^{12}$	115,8(2)	114.5(2)
$N^2C^1C^3$	122.2(2)	121,8(2)	$N^4C^{13}C^{14}$	113,9(3)	114,1(2)

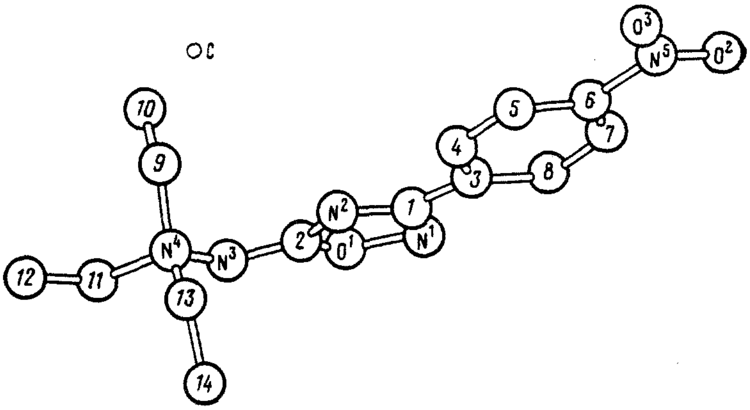


Fig. 1. Structure of compound (Ve). Molecule A.

The unit cell of crystal (Ve) contains two crsytallographically independent molecules A and B, which have identical structures; in Fig. 1, therefore, we have shown the structure only of molecule A.

The atomic coordinates, as well as bond length and bond angle data, are presented in Tables 2, 3, and 4, respectively, which reveal that the quaternized ammonium nitrogen atom N^4 exists in a slightly distorted tetrahedral configuration, with bond angles ranging between 101.9 and 113.7°.

The N^3—N^4 bond length, equal to 1.466(3) Å in molecule A and 1.473(3) Å in molecule B, is similar in value to known data for amino imides, namely 1.471(5) Å, [3]. The bond order or multiplicity of this bond may be regarded as closer to unity the more its bond length overlaps that of a N—N single bond, for example in hydrazines, where the bond length is 1.454 Å [4]. The imide fragment N^3—N^4 exists in a cis orientation relative to the endocyclic C^2—N^2 bond in the oxadiazole ring, which is probably the result of electrostatic interaction of the quaternized nitrogen atom N^4 with the N^2 atom in the heterocycle. Indeed, the N^4...N^2 distance, which is equal to 2.866 Å in molecule A, and 2.877 Å in molecule B, is less than the sum of the van der Waals radii for these atoms (3.00 Å).

The planarity of the oxadiazole, nitrophenyl, and amino imide fragments leads to delocalization of electron density over the entire molecule, as evidenced by the shortened distances between the imide nitrogen atom N^3 and the ipso-carbon atom C^2 in the heterocycle (1.322(3) Å in A and 1.331(3) Å in molecule B), as well as between the ipso-carbon atoms in the benzene and oxadiazole rings (1.468(3) Å in A, and 1.474(3) Å in B); this bond shortening or contraction is characteristic of course of conjugated systems.

EXPERIMENTAL

IR spectra were recorded on a Specord spectrophotometer using KBr pellets; mass spectra were obtained on a Varian CH-6 spectrometer. ^{13}C and ^{14}N NMR spectra were measured on a Bruker AM-300 spectrometer at operating frequencies of 75.5 and 21.6 MHz, respectively, relative to TMS as internal standard and nitric acid as external standard in each case.

Nitrile oxides (Ia-d) were prepared according to [5]; trialkylaminocyanimides, triphenylphosphinecyanimine, and dimethylsulfylcyanimide were prepared according to [6].

Reaction of Aromatic Nitrile Oxides with Trialkylaminocyanimides. To a solution of 2 mmoles aryl nitrile oxide (Ia-d) in 10 ml methylene chloride was added while stirring 2 mmoles of amino imide (IVa) or (IVb). The mixture was stirred for 6 h at 20-25°C, the solvent was evaporated, and the residue was treated with 2 ml acetone and 10 ml hexane. The resulting precipitate of 1,2,4-oxadiazoles (Va-e) was removed by filtration and dried in air. The yields, spectral characteristics, elemental analysis data, and melting points of compounds (Va-e) are summarized in Table 1.

The mother liquor was also evaporated, and the residue was recrystallized from CCl_4 to give the corresponding diarylfuroxanes: (VIa, Ar = C_6H_5), 15% yield, mp 112-114°C, cf. [7]; (VIb, Ar = o-$NO_2C_6H_4$), 32% yield, mp 198-199°C, cf. [7]; (VIc, Ar = m-$NO_2C_6H_4$), 21% yield, mp 182°C, cf. [7]; (VId, Ar = p-$NO_2C_6H_4$), yield from reaction with (IVa), 13%, from reaction with (IVb), 19%, mp 203-204°C, cf. [7].

X-Ray Structural Analysis of Triethylamino-(3-(4-nitrophenyl)-1,2,4-oxadiazol-5-yl)-imide (Ve). Crystals of (Ve), $C_{14}H_{19}N_5O_3$ are monoclinic at 23°C, a = 18.072(3), b = 13.045(2), c = 14.646(6) Å, β = 113.09(3)°, V = 3176.0 A°^{3}, d_{calc} = 1.277 g/cm^3, Z = 8, space group P2(1)/C, two independent molecules.

The unit cell parameters and intensities of 2349 reflections with $F^2 \geq 3\sigma$ were measured on an Enraf-Nonius CAD-4 automated diffractometer (λ Mo K_α, graphite monochromator, $\omega/2\theta$-scanning, $2\theta \leq 60°$).

The structure was solved by direct methods using the MULTAN program and was refined by full matrix least squares using anisotropic (thermal) approximations. Hydrogen atoms were localized in calculated positions and were included in the final refinement cycles. The final dispersion factors were K = 0.039 and R_w = 0.047. All calculations were carried out on a PDP-11/23 computer using the SDP system of programs. The atomic coordinates, and bond length and bond angle data, are presented in Tables 2, 3, and 4, respectively.

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