

Behaviour of Nitrile Oxides towards Nucleophiles. Part IV.¹ Heteromacrocycles from Acetonitrile Oxide

By **Alberto Brandi**, **Francesco De Sarlo**,* and **Antonio Guarna**, Centro di studio sulla chimica e la struttura dei composti eterociclici e loro applicazioni, C.N.R., Istituto di Chimica organica, Università di Firenze, Italy

Several polymers of acetonitrile oxide have been obtained by treatment of the pure monomer with pyridine or trimethylamine. Spectroscopic properties of dimer, hexamer, heptamer, and octamer support stereoregular unsaturated monocyclic structures; this has been confirmed, for one of them, by crystallographic analysis. Another polymer, which is the main product from very concentrated solutions of acetonitrile oxide and trimethylamine, is believed to have a linear structure. A polymerization mechanism is suggested.

THE isolation of acetonitrile oxide has been reported briefly,² but the experimental procedure was not described. The preparation and purification of acetonitrile oxide reported here allowed us to examine its reactivity with trimethylamine and with pyridine, in

ethanol as solvent. Acetonitrile oxide exhibits a strong $\nu_{C\equiv N}$ band at $2\ 315\ \text{cm}^{-1}$ (in ethanol) and a singlet at

¹ Part III, F. De Sarlo and A. Guarna, preceding paper.

² G. Zinner and H. Günther, *Angew. Chem. Internat. Edn.*, 1964, **3**, 383.

8 2.25 in the ^1H n.m.r. spectrum (in ethanol). Dimerisation to dimethylfurazan *N*-oxide requires several hours for completion: this is shown by i.r. spectroscopy (disappearance of the $\nu_{\text{C=N}}$ band) or by the replacement of the n.m.r. signal at δ 2.25 by two singlets at δ 2.19 and 2.38. Earlier reports on the low stability of this nitrile oxide² are considered to refer to the pure substance above its m.p.

The high solubility of acetonitrile oxide in ethanol allows reactions with nucleophiles to be performed in much more concentrated solutions than those attainable with aromatic nitrile oxides.^{4,3} In this way, higher polymers are easily obtained, as well as some dimers analogous to those from aromatic nitrile oxides. Mention has been made, among others,⁴ of polymers of acetonitrile oxide⁵ and of benzonitrile oxide, the last having been obtained from benzonitrile oxide with trimethylamine as catalyst.⁶

With pyridine in ethanol, acetonitrile oxide gives mainly a dimer in dilute solution. At higher acetonitrile oxide concentration a precipitate of molecular formula $(\text{C}_2\text{H}_3\text{NO})_6$ is also obtained, soluble in chloroform, which does not melt below 320 °C, but decomposes slowly above 250 °C. In very concentrated solution, the same polymers prepared with trimethylamine can be identified, in addition to the dimer.

With alcoholic trimethylamine, the same hexamer as produced with pyridine is obtained in moderately dilute solution; another polymer, insoluble in common organic solvents, precipitates from a concentrated solution. The mother liquor from the latter reaction gives, on concentration *in vacuo*, more precipitate, soluble in chloroform and in ethanol, containing two main constituents (t.l.c.), a heptamer and an octamer, which have been isolated by column chromatography. From all the above reactions some 3,4-dimethylfurazan *N*-oxide was detected in solution by g.l.c.

Yields of polymers generally increase with the concentrations of both acetonitrile oxide and trimethylamine. At high reagent concentration (*ca.* 3M in nitrile oxide and 2.5 or 1M in nucleophile) the insoluble polymer is prevalent among the products, whereas the hexamer, the heptamer, and the octamer predominate at lower concentrations (*ca.* 1M in each reagent); in more dilute solution (*ca.* 0.1M in nitrile oxide and 0.2M in nucleophile) only 3,4-dimethylfurazan *N*-oxide is detected, together with unidentified by-products.

Spectral properties of the polymers are collected in Tables 1 and 2.

On the basis of spectroscopic evidence, the dimer obtained with pyridine can be identified as 3,6-dimethyl-1,4,2,5-dioxadiazine (1; R = Me) analogous to the dimers obtained from aromatic nitrile oxides and pyridine.³ Only one signal, at δ 1.97, appears in its ^1H n.m.r. spectrum (Table 1), indicating that the two methyl groups are equivalent; no u.v. absorption maximum

³ F. De Sarlo, *J.C.S. Perkin I*, 1974, 1951.

⁴ References in Ch. Grundmann and P. Grünanger, 'The Nitrile Oxides,' Springer-Verlag, New York, 1971, p. 83.

⁵ H. Wieland, *Ber.*, 1909, 42, 816.

occurs above 200 nm (in ethanol) (thus conjugated double bonds can be excluded); and finally the mass spectral fragmentation (Table 3) closely resembles that for aryl-substituted dioxadiazines (1; R = Ar).

TABLE 1

U.v. and n.m.r. spectra of polymers of acetonitrile oxide

Polymer	U.v. ^a	N.m.r. ^b		
		^1H	^{13}C	$^{13}\text{C}=\text{N}$
Dimer (1; R = Me)	<200	1.97(s)	15.1	161.3
Hexamer	208 °	2.14(s)	15.4	160.3
Heptamer	217 (4.708)	2.10(s)	15.6	161.3
Octamer	217 (4.716)	2.06(s)	15.5	162.4

^a $\lambda_{\text{max.}}/\text{nm}$ (log ϵ); solvent methanol. ^b δ Values; solvent deuteriochloroform. ^{13}C Spectra are decoupled. ° Qualitative spectrum, owing to low solubility.

We will discuss the structures of the hexamer, the heptamer, and the octamer together. In the mass spectra, the molecular ion peaks, though not very intense, confirm the molecular weights found in solution; among other fragments, the dimer and the monomer were prominent, in addition to those produced by further breakdown of the dimer (1; R = Me). U.v. spectra (Table 1) indicate the absence of conjugated double bonds; therefore the monomer units must be linked, as in the dimer (1; R = Me), *via* O-C bonds. Each polymer gives, in the n.m.r. spectra, only a singlet ^1H signal and two ^{13}C signals (decoupled spectra) (Table 1); this means that all monomeric units are in equivalent positions, and cyclic structures must therefore be considered. Raman and i.r. spectra (Table 2), indicating C=N and N-O-C linkages, confirm the postulated mode of linkage; moreover, the great similarity of the spectra of the hexamer, the heptamer, and the octamer suggests that their structures are strictly analogous. In view of the equivalence of the monomeric units, each structure must contain all double bond systems in the same geometrical configuration, *i.e.* either all *syn*- or all *anti*-methyl. In conclusion, the hexamer has to be formulated as 3,6,9,12,15,18-hexamethyl-1,4,7,10,13,16-hexaoxa-2,5,8,11,14,17-hexa-azacyclo-octadeca-2,5,8,11,14,17-hexaene, either *syn* (2) or *anti* (3); the analogous possible structures for the heptamer and the octamer are not illustrated.

The geometrical configuration of these heteromacrocycles was established by X-ray crystallographic analysis of the octamer; the results confirm the proposed cyclic structure, in the *anti*-methyl configuration.⁷ This conclusion can be extended with confidence to the hexamer [structure (2) is rejected in favour of (3)] and to the heptamer, in view of the similarity of ^{13}C n.m.r. data (Table 1) and of the mode of formation (see later).

The so-called 'insoluble polymer' exhibits the same kind of vibrational spectra as the other polymers (Table 2). However, its behaviour is otherwise unusual: it undergoes deflagration on heating; it exploded under laser irradiation during an attempt to obtain a Raman

⁶ G. Speroni and M. Bartoli, 'Sopra gli ossidi di benzonitrile,' nota VIII, Stabilimento tipografico Marzocco, Firenze, 1952; quoted in ref. 4, p. 82.

⁷ S. Menchetti and C. Sabelli, *J.C.S. Perkin II*, in the press.

spectrum; in the high vacuum of the mass spectrometer, at 50 °C, it produces repeatedly sudden pressure rises. In the mass spectrum the most intense peak corresponds to the monomer; no appreciable fragments corresponding to a dimer or at higher m/e values were observed.

These facts lead to the assignment of a linear structure of the type: $-C(Me)=N-O-C(Me)=N-O-C(Me)=N-O-$,

tions are dilute, both nucleophile release and isomerization to the *syn*-methyl configuration are slower than further nucleophilic attack on more acetonitrile oxide. This process leads to stereoregular intermediates (6; Nu = NMe₃); at very high nitrile oxide concentration, the chain in the intermediates (6; Nu = NMe₃) is rapidly lengthened so that the insoluble polymer is the

TABLE 2
Raman and i.r. spectra of polymers of acetonitrile oxide ^a

Raman ^b				I.r. ^c				Insoluble polymer	Approx. description
Dimer	Hexamer	Heptamer	Octamer	Dimer	Hexamer	Heptamer	Octamer		
2 983w	3 012m	3 005sh	3 000m	3 004w	3 010w	3 000w	3 008w	3 000w	} ν_{C-H}
	2 988m	2 990m	2 984w		2 988w	2 990w	2 982w	2 990w	
2 931s	2 936vs	2 937vs	2 932vs	2 935w	2 937w	2 938w	2 936w	2 933w	} $\nu_{C=N}$
1 663w	1 662vs	1 659vs	1 676m	1 658s	1 675m	1 670vs	1 662vs	1 656vs	
	1 644s		1 655vs	1 639m	1 655vs	1 650vs	1 645vs		} δ_{OH_2}
1 428w	1 430s	1 430s	1 430s	1 445w	1 423m	1 424s	1 418s	1 422w	
1 386w	1 394w	1 387m	1 380m	1 415m	1 427m				
				1 382vs	1 378vs	1 380s	1 374s	1 380vs	} ν_{N-O-O}
				1 293vs	1 282vs	1 340w	1 324w	1 310vs	
				1 240w		1 318m	1 294s	1 248w	
	1 225w	1 230w	1 227w			1 270vs	1 254vs		
	1 044m	1 038m	1 040m	1 071w		1 045sh	1 035s		
	1 017w	1 020w	1 025w	1 063w	1 033vs	1 038sh	1 022s	1 041s	
	971w	963w	957m	1 039w		1 028vs			
				988vs	969vs	970vs	965vs	980s	
908w							945sh		
	872m								
		847w	837w				852w	861w	
		820s	814m		850s	842s	832s	830w	
805vs				811s					
				731s					
		621m	620w		614m	647w	640w		
						630m	625w	611w	
						618sh	610sh		
595w	593s	574m	584m		591w	585w	581w	592w	
					585w				
						565w			
			512w	543w					
480vs				480w					
	414w	415w							

^a In cm⁻¹. ^b Powdered samples. ^c KBr pellets, except for the dimer (solid film at liquid N₂ temperature).

TABLE 3
Mass spectra of substituted 1,4,2,5-dioxadiazines (1) ^a

R	Fragments:	<i>M</i>	<i>M</i> + 1	<i>M</i> - 16	RCNO	RCO	RCN
Me		15.6	1	1	2.2	21	100
Ph ^b		12	2	1	9	40	100
4-MeC ₆ H ₄		32	6	1	25	100	86
4-MeO·C ₆ H ₄		11	2.5	4	24	47	100
4-ClC ₆ H ₄		10	1.7	0.8	9	60	100
4-NO ₂ ·C ₆ H ₄		26	5	1	5.5	100	45
2,4,6-Me ₃ C ₆ H ₂ ^b		1.5	0.3	0.5	30	40	70

^a Relative abundances of the main fragments (%); spectra were taken at 70 eV by direct insertion, except for compound (1; R=Me), injected by g.l.c. ^b S. Morrocchi, A. Ricca, A. Selva, and A. Zanarotti, *Gazzetta*, 1969, **99**, 165.

analogous to the structure postulated for an explosive polymer obtained from benzonitrile oxide.⁶

In the light of our previous results on aromatic nitrile oxides,^{1,8} we tentatively rationalize the polymerization of acetonitrile oxide in terms of the illustrated reaction scheme. With trimethylamine as nucleophile, two successive nucleophilic additions afford the intermediate (5; Nu = NMe₃). Then, unless the nitrile oxide solu-

main product. At low reagent concentrations, other processes are prevalent, but these have not yet been examined. At intermediate concentrations, chain growth leading to the intermediates (6; Nu = NMe₃) occurs at such a rate that ring closure, when $n = 4, 5$, or 6 , is prevalent over further linear polymerization. Ring closure of the intermediates (6) can occur *via* C-O bonds

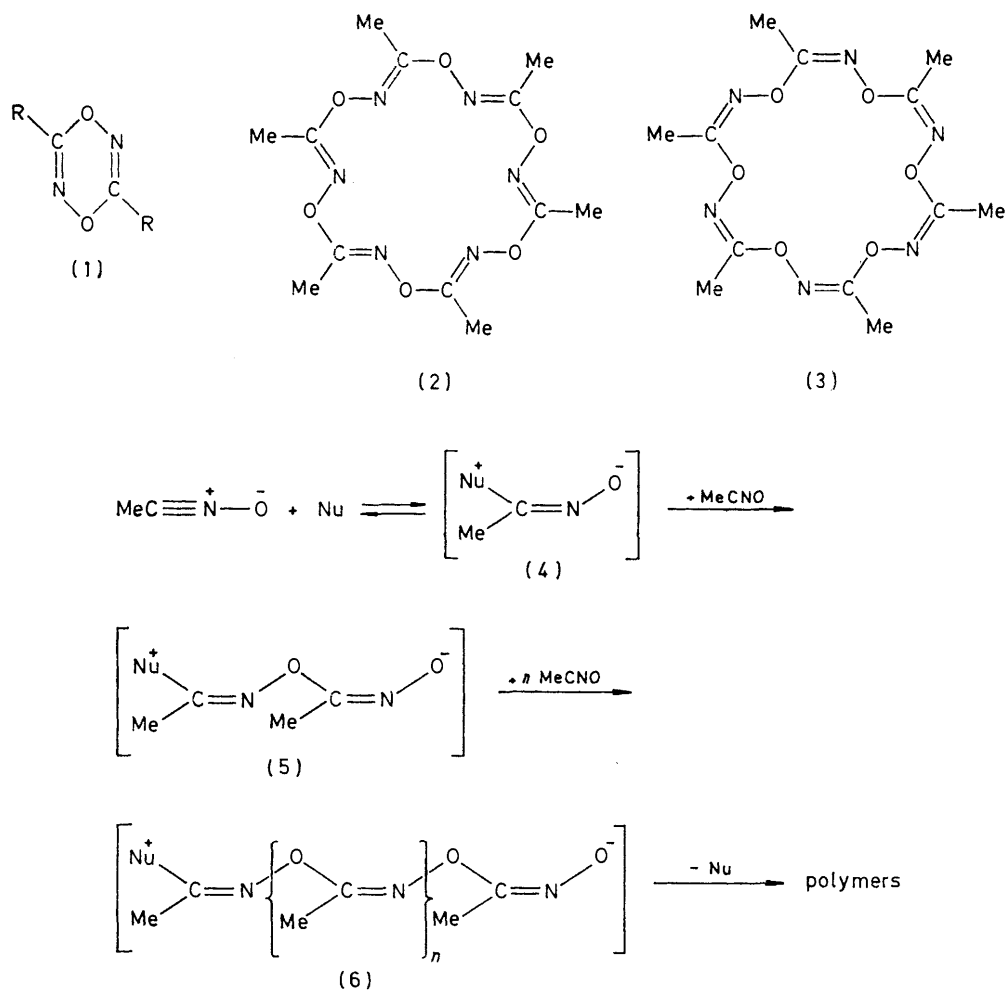
⁸ F. De Sarlo and A. Guarna, *J.C.S. Perkin II*, 1976, 626.

with either nucleophile, without steric hindrance; suitable conformations can be attained with chains of this length. The formation of small amounts of polymers of molecular weight intermediate between the dimer and the hexamer cannot be excluded. Likewise, we cannot exclude the production of some 3,5-dimethyl-1,2,4-oxadiazole 4-oxide from the intermediate (5; Nu = NMe₃) by loss of nucleophile followed by ring closure. On the other hand, higher polymers are formed from benzonitrile oxide under similar reaction conditions,⁶ as already mentioned.

bonds: the nucleophilic centre binds to the carbon atom of the nitrile oxide triple bond, and the lone pair settles on the nitrogen atom in the *trans* orientation. This feature has already been observed in the addition of hydrochloric acid to nitrile oxides.^{9,10}

EXPERIMENTAL

Instruments used were: Perkin-Elmer F 21 preparative gas chromatograph; Hitachi-Perkin-Elmer 115 osmometer (for molecular weights); Perkin-Elmer 270 spectrometer (for mass spectra); Perkin-Elmer 421 spectrophotometer



SCHEME

With pyridine as nucleophile, the main reaction path in dilute solution is dimerization to (1; R = Me) through the intermediate (5; Nu = pyridine), as for aromatic nitrile oxides.⁸ However, at high acetonitrile oxide concentration, chain growth to give the intermediates (6; Nu = pyridine) is also possible, and all the described polymers have been found amongst the reaction products.

The stereochemical course of acetonitrile oxide polymerizations, leading to *anti*-methyl cyclic polymers, is in agreement with the usual *trans*-addition to unsaturated

(for i.r. spectra); Cary 81 spectrometer equipped with an Ar⁺ laser source selecting the 4 880 Å line as exciting light (for Raman spectra); Cary 14 spectrophotometer (for u.v. spectra); Perkin-Elmer R 32 spectrometer (for ¹H n.m.r. spectra); Bruker W H-90 PFT spectrometer (for ¹³C n.m.r. spectra).

Acetohydroxamoyl Chloride.—The crude material, prepared as reported,¹¹ was recrystallized from petroleum at -60 °C, filtered off quickly in a dry-box at -5 °C, and stored in solid carbon dioxide.

¹⁰ J. P. Guetté, J. Armand, and L. Lacombe, *Compt. rend.*, 1967, **264C**, 1509.

¹¹ H. Wieland, *Ber.*, 1907, **40**, 1677.

⁹ H. E. Ungnade, G. Fritz, and L. W. Kissinger, *Tetrahedron*, 1963, **19**, Suppl. 1, 235.

Acetonitrile Oxide.—Acetohydroxamoyl chloride (2 g) was dissolved in petroleum (250 ml), and triethylamine (3 ml; slight excess) was added to the cold solution. After removal of the precipitated hydrochloride, the solution was shaken with solid potassium hydrogen sulphate, decanted, and cooled at -60°C . The precipitated product was collected in a cooled dry-box and immediately dissolved for use; yield 43% (from integrated n.m.r. spectrum; reference ethanol).

Acetonitrile Oxide and Trimethylamine; the Hexamer (3), the Heptamer, the Octamer, and the Insoluble Polymer.—The acetonitrile oxide prepared from 4 g of acetohydroxamoyl chloride was dissolved in ethanol at *ca.* 0°C , then added to concentrated ethanolic trimethylamine to give 6 ml of solution (*ca.* 3M in nitrile oxide* and *ca.* 2.5M in nucleophile). The precipitate was collected and washed with ethanol, then with chloroform to give insoluble polymer (0.52 g, 50%), which darkens near 150°C and deflagrates at $180\text{--}183^{\circ}\text{C}$ [Found: C, 42.0; H, 5.35; N, 24.8. Calc. for $(\text{C}_2\text{H}_3\text{NO})_n$: C, 42.1; H, 5.3; N, 24.55%]. The chloroform solution afforded, on dilution with ethanol, the *hexamer* (26 mg); this product becomes dark above 250°C , but does not melt below 320°C [Found: C, 42.0; H, 5.3; N, 24.8%; *M*, 363, 334, 342. $(\text{C}_2\text{H}_3\text{NO})_6$ requires C, 42.1; H, 5.3; N, 24.55%; *M*, 342.3].

From the mother liquor, combined with ethanol washings, a mixture of heptamer and octamer precipitated on partial concentration (60 mg): more of these polymers were contained in the residue obtained by complete evaporation, together with unidentified by-products. On t.l.c. [silica gel (Merck F₂₅₄, 0.25 mm thickness); eluant 1:1 chloroform–diethyl ether] the heptamer and the octamer gave R_F values of 0.81 and 0.66, respectively; they were isolated by column chromatography with silica gel (Merck 70–325 mesh ASTM; same eluant). The *heptamer* was recrystallized from methanol; m.p. $174\text{--}176^{\circ}\text{C}$ (decomp.) [Found: C, 42.2; H, 5.3; N, 25.4%; *M*, 378, 408, 396. $(\text{C}_2\text{H}_3\text{NO})_7$

* Concentrations and yields are calculated on the assumption that 1.05 g of acetonitrile oxide are produced from 4 g of acetohydroxamoyl chloride.

requires C, 42.1; H, 5.3; N, 24.55%; *M*, 399.35]. The *octamer* was also recrystallized from methanol; m.p. 171°C (decomp.) [Found: C, 42.2; H, 5.4; N, 24.9%; *M*, 444, 451, 466. $(\text{C}_2\text{H}_3\text{NO})_8$ requires C, 42.1; H, 5.3; N, 24.55%; *M*, 456.4].

With 1M-trimethylamine and the same nitrile oxide concentration, a decrease in the yields of the above products was observed. At lower trimethylamine concentration (0.2M) the yield of insoluble polymer was more severely reduced (*ca.* 5%) and those of the other polymers were scarcely affected.

Reactions of 0.6M-acetonitrile oxide gave, with concentrated trimethylamine (*ca.* 3M), *ca.* 10% yield of insoluble polymer and smaller amounts of the other polymers; with 1M-trimethylamine only 15 mg of insoluble polymer but increased yields of the other polymers (10% of isolated *hexamer*) were obtained; with 0.2M trimethylamine, 5% of the *hexamer* and smaller amounts of *heptamer* and *octamer* were isolated, but no insoluble polymer.

At lower acetonitrile oxide concentration (0.06M) no such polymers were obtained, whatever the trimethylamine concentration.

Acetonitrile Oxide and Pyridine; the Dimer (1; R = Me).—The nitrile oxide obtained from 4 g of acetohydroxamoyl chloride was dissolved in ethanol (70 ml) and added to pyridine (12 ml). The *hexamer (3)* (50 mg) precipitated from the yellow mixture: the clear solution was concentrated with a fractionating column at atmospheric pressure. The *dimer, 3,6-dimethyl-1,4,2,5-dioxadiazine (1; R = Me)* could then be isolated by preparative g.l.c. [2 m column packed with OV 17 (10%) on Chromosorb A; constant temp. 100°C] or by concentrating a solution in chloroform washed with dilute sulphuric acid; m.p. 61° (sublimed) (Found: C, 42.6; H, 5.3; N, 24.8. $\text{C}_2\text{H}_3\text{NO}$ requires C, 42.1; H, 5.3; N, 24.55%). The molecular weight could not be measured by the isopiestic method owing to the high vapour pressure of the compound.

In very concentrated solution, acetonitrile oxide and pyridine produced all the polymers described above.

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