

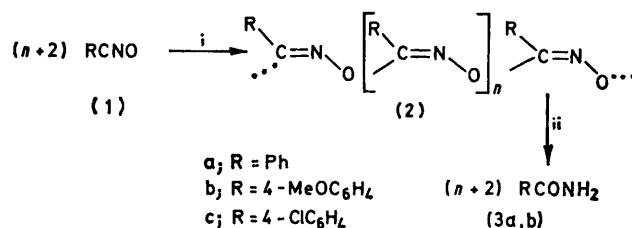
Behaviour of Nitrile Oxides towards Nucleophiles. Part 5.¹ Polymerization of Aromatic Nitrile Oxides

By 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

Aromatic nitrile oxides undergo polymerization by treatment with trimethylamine in dimethyl sulphoxide. Chain lengthening occurs *via* the C–O bonds, as shown by the catalytic hydrogenation of such polymers to aroylamides. The apparent degree of polymerization ranges from 15 up to *ca.* 100 monomer units. These polymers are quite stable in the solid state, but slowly decompose in solution; they do not give the typical reactions of nitrile oxides.

ACETONITRILE OXIDE and benzonitrile oxide have been previously reported to polymerize when treated with nucleophilic catalysts (*e.g.* trimethylamine).^{1,2} Polymers of other nitrile oxides (other than dimers) have been observed in alkaline medium, but the monomers were considered to be possible intermediates, rather than being isolated.³

parations have similar properties and decomposition temperatures, but can exhibit large differences in molecular weight. The apparent degree of polymerization, determined only for those products which are soluble in chloroform [(2a and b)], ranges from 15 to *ca.* 100. The mass spectra of polymers (2) show no appreciable peaks above those corresponding to the trimers; the base peak



Reagents: i, NMe₃; ii, H₂, Pd–C

Aromatic nitrile oxides have been reported to dimerize upon treatment with pyridine⁴ or trimethylamine⁵ in ethanol. Since their solubility is higher in dimethyl sulphoxide (DMSO) than in ethanol, trimethylamine (either pure or in ethanol) was added to concentrated solutions of aromatic nitrile oxides (1) in DMSO: the

is always due to the monomer fragment (RCNO⁺). The most significant fragment ions are reported in the Table. The i.r. absorptions ascribed to $\nu_{\text{C}=\text{N}}$ (Table) accord with the structures previously reported for polymers (2; R = Me or Ph).^{1,2} This mode of chain formation is supported by the results of catalytic hydrogen-

I.r. and mass spectra of polymers (2)

Relative abundance of main fragments ^a

Polymer	(RCNO) ₃ ⁺	R ₂ C ₂ N ₂ O ⁺	RCNO ⁺	RCO ⁺	RCN ⁺	$\nu_{\text{C}=\text{N}}/\text{cm}^{-1}$ ^b
(2a)	1	6	100	46	26	1 620vs
(2b)	6	57	100	85	57	1 600vs
(2c)		2	100	62	48	1 620s

^a Direct insertion of the sample at *ca.* 90 °C and 70 eV. ^b KBr pellets.

polymers (2) were produced in low yield. Some nitrile oxides gave no polymer (R = 4-NO₂C₆H₄) or low yields of impure product (R = 4-MeC₆H₄). All these polymers deflagrate on heating, as reported for the polymer of benzonitrile oxide.² Among the side-products, 3,4-diarylfuroxans, 3,5-diaryl-1,2,4-oxadiazoles, and the corresponding oxides were mainly found.

Systematic variation of the reaction conditions (*i.e.* ratio between DMSO and ethanol, reagent concentrations, and reaction time) indicates that the procedures reported in the Experimental section are the most convenient, although other solvents might also be efficient.²

The polymer samples obtained from different pre-

paration, which converted the polymers (2a and b) into the corresponding aroylamides (3a and b). The configuration at the double bonds is assumed to be as illustrated (Z), by analogy with previous results.^{1,6}

The solvent has an influential role in these reactions: it has been pointed out that removal of trimethylamine is slow in the catalysed dimerization of aromatic nitrile oxides in ethanol.⁵ According to the reported polymerization mechanism for acetonitrile oxide,¹ the enhancement of polymerization *versus* dimerization observed for aromatic nitrile oxides in DMSO is due to the lower ability of this solvent to remove the nucleophile, † rather than to the higher nitrile oxide concentrations

† The solubility of trimethylamine at 20 °C is >4.5 mol l⁻¹ in ethanol and 1.4 mol l⁻¹ in DMSO.

employed. Furthermore, the addition of ethanol, which is required in some cases to produce a precipitate, is not for the purposes of reducing the solubility since the polymers are insoluble in DMSO.

Polymers (2) are apparently stable in the solid state, but are slowly converted in solution (chloroform, ethanol) into several products, among them, 3,5-diaryl-1,2,4-oxadiazoles and the corresponding 4-oxides. Attempts to carry out typical reactions of nitrile oxides (with aniline or phenylacetylene) using these polymers failed.

EXPERIMENTAL

Instruments used were a Perkin-Elmer 457 spectrophotometer for i.r. spectra, a Perkin-Elmer 270 spectrometer for mass spectra, and a Hitachi-Perkin-Elmer 115 osmometer for molecular weights. M.p.s were determined on a Kofler apparatus. Nitrile oxides were prepared as previously described.⁷

Polymer (2a) of Benzonitrile Oxide.—The pure monomer (1a) (1.7 g) was treated at ca. 5 °C with a mixture of DMSO (5 ml) and trimethylamine in ethanol (4.5M, 1.25 ml), and set aside in a refrigerator for several hours. A sticky mass separated and was converted into a powder (4–6%), m.p. 105–106 °C (decomp.), by washing with ethanol [removal of by-products was monitored by t.l.c. on Merck F₂₅₄ silica gel plates, 0.25 mm thickness, eluant benzene-n-hexane-methanol 4 : 4 : 1; only polymer (2a) has R_F 0] (Found: C, 70.4; H, 4.5; N, 11.65%; M , 1 800 g mol⁻¹. C₇H₅NO requires C, 70.6; H, 4.2; N, 11.8%; M , 119.1 g mol⁻¹). More polymer precipitates, mixed with other products, on addition of ethanol to the mother liquor.

A similar polymer was obtained by bubbling trimethylamine in a 10% solution (w/v) of benzonitrile oxide (1a) in DMSO and working up the sticky precipitate as above, m.p. 112–113 °C (decomp.) (Found: C, 70.5; H, 4.3; N, 12.5%; M , 7 000 g mol⁻¹). Lower yields have been obtained with other solvents (dimethylformamide-ethanol, acetone-ethanol). All samples were identified by i.r. comparison.

Polymer (2b) of 4-Methoxybenzonitrile Oxide.—Treatment of 4-methoxybenzonitrile oxide (1b) (0.5 g) with trimethylamine in DMSO (1.4M, 5 ml) gave a precipitate only upon addition of ethanol (3 ml) after 3 h. The precipitate was washed thoroughly with ethanol, until no more by-product was detected by t.l.c. (conditions as above), m.p. 99–101 °C (decomp.) (Found: C, 64.1; H, 4.8; N, 9.2%; M , 6 000 g mol⁻¹. C₈H₇NO₂ requires C, 64.4; H, 4.7; N, 9.4%; M , 150.1 g mol⁻¹).

Alternatively, a solution of 4-methoxybenzonitrile oxide (1b) (1 g) in DMSO (5 ml) was treated with trimethylamine in ethanol (4.7M, 2.5 ml). Ethanol (7.5 ml) was added after 0.5 h and the precipitate (1%) collected ca. 0.5 h later, before extensive precipitation of the main products occurred. Samples with M 14 000 or 20 000 g mol⁻¹ were obtained: all samples had similar m.p.s and gave identical i.r. spectra.

Polymer of 4-Chlorobenzonitrile Oxide.—Trimethylamine in ethanol (ca. 3M, 0.8 ml) was added to a solution of 4-chlorobenzonitrile oxide (1c) (776 mg) in DMSO (3.2 ml). The mixture was set aside for 1 h at room temperature and the precipitate was collected (225 mg), washed thoroughly with ethanol, and then with chloroform (100 ml). The residue (67 mg, 8.6%) had m.p. 140–141 °C (decomp.) (Found: C, 54.1; H, 2.7; N, 9.5. C₇H₄ClNO requires C, 54.8; H, 2.6; N, 9.1%). This polymer is insoluble in common organic solvents, therefore neither molecular weight measurements nor catalytic hydrogenation could be carried out.

Catalytic Hydrogenation.—A solution of the polymer (2a) (172 mg) of benzonitrile oxide in tetrahydrofuran (40 ml) containing 10% palladium on activated carbon was treated with hydrogen at room temperature and atmospheric pressure for 1 h. Addition of ethanol (40 ml), stirring, filtration, and removal of the solvent give crude benzamide (3a) (146 mg, 85%), identified by i.r. and t.l.c. comparison of the recrystallized product with an authentic sample; t.l.c. was carried out on Merck F₂₅₄ silica gel plates, 0.25 mm thickness, using 2 : 1 ether-THF as eluant. The polymer has R_F 0, benzamide has R_F 0.26.

Similarly, from polymer (2b) (89 mg) in THF (10 ml), anisamide (3b) was obtained (i.r. and t.l.c. comparison with an authentic sample, 1 : 1 benzene-THF as eluant, R_F 0.4–0.6 for the polymer, 0.2 for the amide).

[8/1501 Received, 15th August, 1978]

REFERENCES

- Part 4, A. Brandi, F. De Sarlo, and A. Guarna, *J.C.S. Perkin I*, 1976, 1827.
- G. Speroni and M. Bartoli, 'Sopra gli ossidi di benzonitrile, nota VIII,' Stabilimento tipografico Marzocco, Firenze, 1952, quoted in ref. 3, p. 82.
- Ch. Grundmann and P. Grünanger, 'The Nitrile Oxides,' Springer-Verlag, New York, 1971, p. 83.
- F. De Sarlo, *J.C.S. Perkin I*, 1974, 1951.
- F. De Sarlo and A. Guarna, *J.C.S. Perkin I*, 1976, 1825.
- K. J. Dignam, A. F. Hegarty, and P. L. Quain, *J. Org. Chem.*, 1978, **43**, 388.
- F. De Sarlo and A. Guarna, *J.C.S. Perkin II*, 1976, 626.