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Polymerizations by 1,3-Dipolar Cycloaddition Reactions. V. The 1,3-Dipolar Polycycloadditions of Dinitrile *N*-Oxides with Diolefins

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Terephthalonitrile di-*N*-oxide and isophthalonitrile di-*N*-oxide were synthesized from the corresponding hydroxamic chlorides by dehydrochlorination with triethylamine. Their chemical properties and the polycycloadditions with diolefins were examined. The polymers obtained were amorphous and their molecular weights were not so high. The thermal gravimetric analyses of them showed that the polymers were stable up to 300—350°C in air.

Since Werner and Buss¹⁾ reported the formation of benzonitrile *N*-oxide in 1894, the reaction of nitrile *N*-oxides, particularly those involving benzonitrile *N*-oxide, have been thoroughly investigated and it is well known that almost all types of olefins react with nitrile *N*-oxides to form 2-isoxazolines.[2,3] It is also known that, in cycloadditions of nitrile *N*-oxides to mono- or 1,1-disubstituted olefins, the substituents exclusively appear in the 5-position of the 2-isoxazolines.[4]

We have already reported the isolation of terephthalonitrile di-*N*-oxide by the action of triethylamine on terephthalohydroxamic dichloride in the earlier communication[5] and it was the first example of the isolation of dinitrile di-*N*-oxide. By the same procedure, isophthalonitrile di-*N*-oxide was also isolated and its diagnostic investigation in the polycycloaddition has also been reported.[6] In this paper, we wish to present further investigation in the reaction of those nitrile *N*-oxides and their polycycloadditions with diolefins.

Terephthalonitrile di-*N*-oxide (Ia) is rather stable and it can be stored almost unchanged for a few days, while isophthalonitrile di-*N*-oxide (Ib) is less stable and spontaneously changes into yellowish mass which is considered to be polyphenylenefuroxan on the basis of its infrared spectrum.[7,8]

These nitrile *N*-oxides gave the corresponding hydroxamic chlorides reversely by the reactions with hydrogen chloride. The treatment of them with triethyl phosphite afforded terephthalonitrile and isophthalonitrile respectively by deoxygenation in almost quantitative yields.

The 1,3-dipolar cycloadditions of Ia and Ib were carried out with various dipolarophiles to give the corresponding addition products as shown in Tables 1 and 2. When α,β-unsaturated carbonyl compounds were used as dipolarophiles, the reaction proceeded almost quantitatively. In the case of the reactions with olefins, the reaction products, 3,3′-phenylene bis(2-isoxazoline)s, have one asymmetric carbon at 5-position of each isoxazoline ring, where the substituents appear. Therefore, two isomeric products, *dl* and *meso*, should be formed in the each reaction. In fact, we have obtained the two isomers in the case of the reactions with methyl methacrylate, methyl acrylate and vinyl acetate. The NMR spectrum (60 Mc, in CH_3CN) of one of the two isomers obtained from Ib and methyl acrylate, having a lower melting point, has a methine triplet centered at 4.72 τ and a methylene doublet, overlapped with OCH_3 singlet (6.21 τ) centered at 6.30 τ ($J_{CH-CH_2}=9.3$ cps). That of the other, having a higher melting point, has a methine triplet centered at 4.77 τ and a methylene doublet, also overlapped with OCH_3 signal (6.24 τ), centered at 6.32 τ ($J_{CH-CH_2}=9.6$ cps). Methyl 3-phenyl-2-isoxazoline-5-carboxylate of known and unequivocal structure,[9] prepared

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1) A. Werner and H. Buss, *Ber.*, **27**, 2193 (1894).

2) A. Quilico, G. S. D'Alcontres and P. Grünanger, *Nature*, **166**, 226 (1950); *Gazz. chim. ital.*, **80**, 479 (1950).

3) G. S. D'Alcontres and P. Grünanger, *ibid.*, **80**, 831 (1950); P. Grünanger, *ibid.*, **84**, 359 (1954); A. Quilico, P. Grünanger and R. Mazzini, *ibid.*, **82**, 349 (1952); G. S. D'Alcontres and G. L. Vecchio, *ibid.*, **90**, 1239 (1960).

4) R. Huisgen, *Angew. Chem.*, **75**, 742 (1963).

5) Y. Iwakura, M. Akiyama and K. Nagakubo, This Bulletin, **37**, 767 (1964).

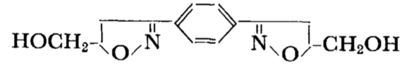
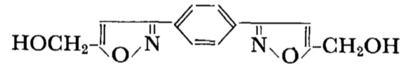
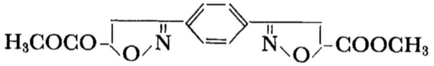
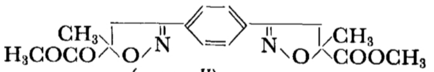
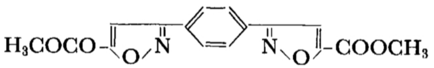
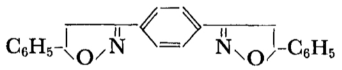
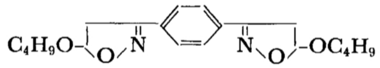
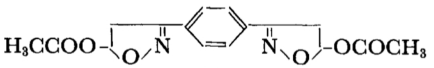
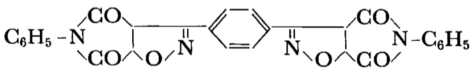
6) Y. Iwakura, M. Akiyama and S. Shiraishi, *ibid.*, **38**, 335 (1965).

7) N. E. Boyer, G. M. Czerniak, H. S. Gutowsky and H. R. Synder, *J. Am. Chem. Soc.*, **77**, 4238 (1955).

8) Y. Imai, M. Akiyama, K. Uno and Y. Iwakura, *Makromol. Chem.*, **95**, 275 (1966).

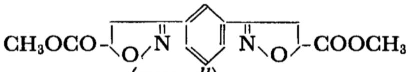
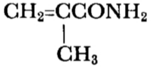
9) G. Bianchi and P. Grünanger, *Tetrahedron*, **21**, 817 (1965).

TABLE 1. 1,3-DIPOLAR CYCLOADDITION COMPOUNDS OF TEREPHTHALONITRILE DI-*N*-OXIDE

Product	Dipolarophile	Mp, °C	Recryst. solvent	Anal., % Found (Calcd) C	H	N
	CH_2=$CHCH_2OH$	227—228	Aq. MeOH	60.44 (60.86	5.87 5.84	10.16 10.14)
	CH≡CCH_2OH	225—226	Aq. MeOH	61.52 (61.76	4.43 4.44	10.30 10.29
 (*meso, dl*)	CH_2=$COOCH_3$	133—136 182—184	MeOH AcOEt	57.75 58.15 (57.83	4.97 5.16 4.85	8.42 8.47 8.43)
 (*meso, dl*)	CH_2=$C(CH_3)COOCH_3$	172—173* 176—178*	MeOH AcOEt	60.16 60.03 (59.99	5.48 5.92 5.59	8.03 7.67 7.77)
	CH≡$CCOOCH_3$	250—251	Dioxane	58.68 (58.54	3.76 3.68	8.76 8.53)
	CH_2=CHC_6H_5	248—250	Benzene	78.29 (78.24	5.49 5.47)	
	CH_2=$CHOC_4H_9$(*n*-)	83.5—84.5	*n*-Hexane	66.64 (66.75	7.83 7.77	7.77 7.98)
 (*meso, dl*)	CH_2=$CHOCOCH_3$	185—187 145—150	MeOH Aq. MeOH	58.05 (57.83	4.68 4.85	8.68 8.43)
	*N*-Phenylmaleimide	>300				

* Admixture of the two melted at 144—163°C.

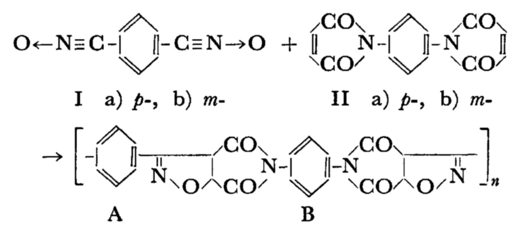
Table 2. 1,3-Dipolar cycloaddition compounds of isophthalonitrile di-*N*-oxide

Product	Dipolarophile	Mp, °C	Recryst. solvent	Anal., % Found (Calcd) C	H	N
	$CH_2{=}CHCH_2OH$	127—135	Aq. MeOH	60.51 (60.86	5.91 5.84	10.12 10.14)
	$CH{\equiv}CCH_2OH$	154—155	Aq. MeOH	61.60 (61.76	4.53 4.44	10.36 10.29)
 (*meso*, *dl*)	$CH_2{=}CHCOOCH_3$	Viscous liq. 130—132	AcOEt	58.46 (57.83	5.24 4.85	8.56 8.43)
	$CH{\equiv}CCOOCH_3$	190—193	MeOH	58.52 (58.54	3.86 3.68	8.64 8.53)
	$CH_2{=}CHCONH_2$	195—210 (Decomp.)	Water	54.51 (55.62	5.18 4.67	18.54 18.54)
	 $CH_2{=}\underset{\displaystyle CH_3}{C}CONH_2$	228—232 (Decomp.)	Water	58.15 (58.17	5.21 5.49	16.83 16.96)
	*N*-Phenylmaleimide	Gradual decomp. >220	*1	65.55 (66.40	4.74 3.58	10.72 11.06)

*1 Reprecipitated from a methanolic solution with water.

from benzohydroxamic chloride and methyl acrylate with use of triethylamine as a hydrogen chloride acceptor, has a methine triplet centered at 4.66 τ and a methylene doublet centered at 6.27 τ ($J_{CH-CH_2}=9.6$ cps), one peak of which is overlapped with OCH_3 peak at 6.17 τ. These NMR data indicate the two products are diastereomeric isomers of 3,3'-*m*-phenylene bis-(5-carbomethoxy-2-isoxazoline). The orientation of the cycloaddition may be considered to be the same for the other examples of the reaction summarized in Tables 1 and 2. Similar aspects were reported in the reaction of cyanogen di-*N*-oxide with olefins by Grundmann and his coworkers[10] and also in the reaction of Ia with styrene and with cyclopentadiene by Overberger and Fujimoto.[11] The adducts obtained by the both reactions of Ib with vinyl acetate and with methyl methacrylate have a low crystallinity and therefore the separation of the two isomers was unsuccessful. The reaction products, however, were confirmed to be the corresponding isoxazoline derivatives from their infrared absorption spectra.

The 1,3-dipolar polycycloadditions were conducted with *p*- and *m*-phenylenedimaleimide (IIa and IIb) and with ethylenedimethacrylate (III) as difunctional dipolarophiles. Polymerization proceeded by the repetition of the 1,3-dipolar cycloaddition, in which cyclic shift of electrons accompanied, forming 2-isoxazoline rings along the growing polymer main chains as shown below.

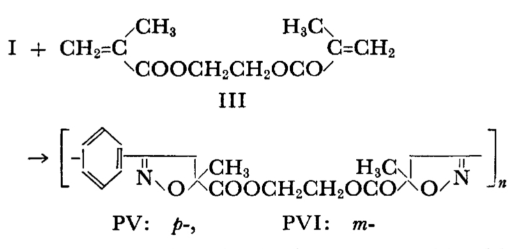


I a) *p*-, b) *m*-

II a) *p*-, b) *m*-

A B

	A	B
PI	*p*-	*p*-
PII	*p*-	*m*-
PIII	*m*-	*p*-
PIV	*m*-	*m*-



III

PV: *p*-, PVI: *m*-

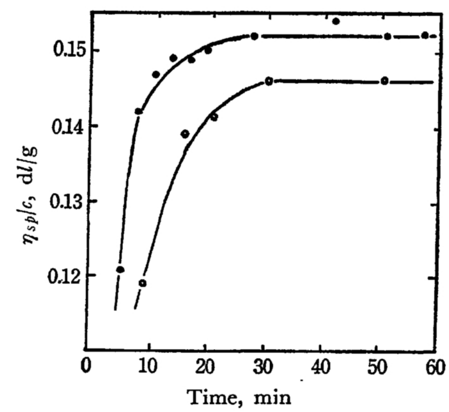


Fig. 1. Viscosity increase *versus* reaction time.
—●— 60°C —○— 30°C
0.5 mmol of each Ib and IIb in 25 m*l* of dimethylformamide.

The rate of polycycloaddition was considerably fast. Polycycloaddition of Ib with IIb was carried out in an Ubbelohde's viscometer at the concentration of 0.5 mmol of each Ib and IIb in 25 m*l* of dimethylformamide at 30°C and 60°C. After 30 min, no more increase of viscosity of the reaction mixture was observed in either case as seen in Fig. 1.

The polymerization conditions and the results are summarized in Tables 3 and 4. The degree of polymerization was rather low, even in the case of homogeneous polymerization using a polar solvent as a reaction medium. The polymers derived from II are insoluble in benzene, tetrahydrofuran and anisole, and therefore, when such a solvent was used as the reaction medium, precipitation of polymer occurred before a high degree of polymerization was attained. In the case of polymerization of Ia with IIa, the polymer formed precipitated as the reaction proceeded even when a polar solvent was used as the reaction medium. The polymer (PI) was only soluble in concentrated sulfuric acid among the solvents tested.

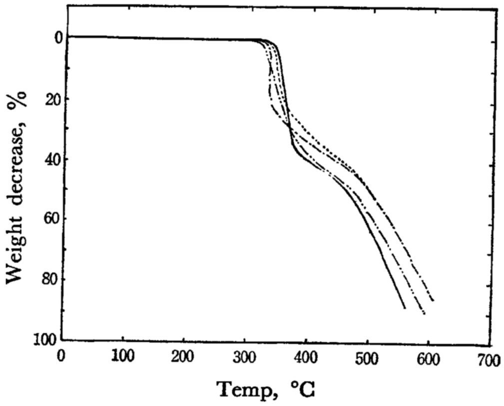


Fig. 2. Thermogravimetric analysis curves for polyphenylene-Δ^2-isoxazolinopyrrolidinediones.
—— PI ······ PII —·— PIII —··— PIV
(2.5°C/min, in air)

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[10] C. Grundmann, V. Mini, J. M. Dean and H-D. Frommeld, *Ann.*, **687**, 191 (1965).
[11] C. G. Overberger and S. Fujimoto, *Polymer Letters*, **B3**, 735 (1965).

TABLE 3. 1,3-DIPOLAR POLYCYCLOADDITION OF TEREPHTHALONITRILE DI-*N*-OXIDE

Exp. No.	Diolefin	Solvent mmol/*ml*	React. temp. °C	React. time hr	η_{sp}/c[*1]	PMT[*2] °C	N anal., %	
							Found	Calcd
PI-1	IIa	DMF (1.25/5)a)	R. t.c)	20	0.19d)	Gradual decomp. >310		
2		DMF (1.25/5)	R. t.	20	0.29d)		11.96	13.08
3		DMAc (2.5/10)	55	1	—			
PII-1	IIb	DMF (2.5/10)	R. t.	20	0.11	Gradual decomp. >320	12.40	13.08
2		DMF (2.5/10)a)	R. t.	20	0.09		12.34	13.08
3		DMAc (2/10)	R. t.	12	0.11			
4		DMAc (2/10)b)	R. t.	24	0.11			
5		Anisole (2.5/10)	50	1	0.10			
PV-1	III	Benzene (2.85/5)	R. t.	1	0.30	147—152	8.43	7.82

[*1] 0.2 g/100 *ml* DMF, 30°C.

[*2] Measured by using a capillary tube.

a) 3% of LiCl was added.

b) IIIb was 5 mol% less than equivalent amount.

c) R. t. means that the reaction mixture was not heated. As the polymerization reaction was exothermal, the temperature of the reaction mixture rose up to 50°C or higher at the beginning.

d) 0.2 g/100 *ml* 95%-H_2SO_4, 30°C.

TABLE 4. 1,3-DIPOLAR POLYCYCLOADDITION OF ISOPHTHALONITRILE DI-*N*-OXIDE

Exp. No.	Diolefin	Solvent mmol/*ml*	React. temp. °C	React. time hr	η_{sp}/c[*1]	PMT[*2] °C	N anal., %	
							Found	Calcd
PIII-1	IIa	DMF (2/5)	R. t.	1	0.21	Gradual decomp. <310	12.42	13.08
2		DMF (2/5)a)	R. t.	1	0.21			
PIV-1	IIb	DMF (2/4)	R. t.	2.5	(0.19)	Gradual decomp. >310	12.09	13.08
2		DMF (2/4)	75	2.5	(0.26)			
3		DMF (3.2/5)	R. t.	1	0.13			
4		DMAc (2/5)	R. t.	20	0.08		12.53	13.08
PVI-1	III	Dioxane (2/2.6)	R. t.	24	(0.21)		8.09	7.82
2		Benzene (4/5)	R. t.	1	0.20	121—130		

[*1] 0.2 g/100 *ml* DMF, at 30°C except the parenthesized which were measured at the concentration of 0.5 g/100 ml DMF.

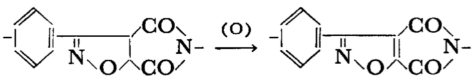
[*2] Measured by using a capillary tube.

a) Ten mol% less than equivalent amount of isophthalonitrile di-*N*-oxide was allowed to react with IIIa for 15 min, and then the shortage of the nitrile oxide was supplied to attain the equivalency.

The structures of the polymers obtained were verified by means of the comparison of their infrared spectra with those of the model compounds described above. Absorption bands at around 905 and 1180 cm^{-1} of medium intensity were characteristic of the isoxazoline polymers. Besides them, characteristic absorptions of imide carbonyl were observed at 1725 (strong) and at 1790 cm^{-1} (weak) in PI, PII, PIII and PIV. Whereas strong absorption of ester carbonyl was at 1740 cm^{-1} in the case of PV and PVI.

The X-ray diffraction diagrams of the polyphenyleneisoxazolinopyrrolidinediones measured by powder method with use of nickel-filtered Cu$K\alpha$ radiation indicated that PII, PIII and PIV were amorphous and that PI, in which all of phenylene groups were linked at *p*-position, was only slightly crystalline. Such poor crystallinity of them, in spite of their rigid structure, resulted presumably from the random distribution of asymmetric carbons, *i. e.* random ordination of *dl* and *meso* configuration units of the isoxazoline linkages along the polymer chains.

The thermal analyses of PI, PII, PIII and PIV showed that the oxidative degradation occurred at the temperatures above 300°C. The thermal stability of them decreased in the order of PI>PII>PIII>PIV, but even PI showed an abrupt weight loss at 350°C. Figure 2 shows the thermal gravimetric analysis curves of them. The curves may indicate that partial aromatization, besides the oxidative degradation, occurred as shown by the equation below and consequently the thermal stability was retained temporarily in each case.



Experimental

Terephthalonitrile Di-*N*-oxide (Ia) and Isophthalonitrile Di-*N*-oxide (Ib). To a stirred solution of the corresponding hydroxamic chloride in methanol, a methanolic solution containing an equivalent amount of triethylamine was added dropwise at a temperature below −10°C. The nitrile oxide soon precipitated out of the mixture as colorless powder, which was filtered and washed thoroughly with methanol. The yield was higher than 70% of the theoretical. Ia decomposed explosively when it was put into a bath heated at a temperature above 150°C, and Ib also decomposed abruptly at a temperature above 90°C. When they were heated slowly, only gradual discoloration was observed without melting up to 300°C.

The Reaction of Ia and Ib with Hydrogen Chloride. Hydrogen chloride gas was introduced into a suspension of the corresponding nitrile oxide in methanol with occasional shaking until the suspension turned into a clear solution by exothermal reaction. Then, the reaction mixture was let stand for ten minutes. After that, the mixture was poured into water to give a white precipitate which was identified with the corresponding hydroxamic chloride by melting point and IR spectrum.

The Reaction of Ia and Ib with Triethylphosphite. To a stirred suspension of the corresponding nitrile oxide in methanol, a methanolic solution of triethylphosphite was added gradually with ice-cooling. The reaction was exothermal and almost instantaneous. After the mixture was let stand for an additional hour, methanol and excess triethylphosphite were distilled off under reduced pressure and the residue was recrystallized from aqueous methanol. The products from Ia and Ib were identified with terephthalonitrile and isophthalonitrile respectively.

1,3-Dipolar Cycloadditions of Ia and Ib. A typical example is described below. Ia was added portionwise into a tetrahydrofuran solution of 50 mol% excess of methyl acrylate with stirring. As the reaction proceeded exothermally, Ia dissolved into the solution. A few minutes later than the solution became clear, colorless crystals began to precipitate. The reaction mixture was let stand for an hour and then the precipitate was gathered by filtration and recrystallized twice from ethyl acetate, giving crystals; mp 182—184°C. The mother liquor of the tetrahydrofuran solution was evaporated under reduced pressure. The residual mass was recrystallized twice from methanol, giving colorless crystals; mp 133—136°C. The yield of the sum of those two substances was higher than 70% of the theoretical.

The analytical data and the other reaction products are summarized in Tables 1 and 2.

1,3-Dipolar Polycycloadditions: Materials and Solvent. *p*- (IIa) and *m*-Phenylenedimaleimide (IIb) were prepared in the usual way by the conversion of the phenylenediamines into the maleamic acids, followed by dehydration cyclization with acetic anhydride. IIa melted at 300—303°C when it was inserted into a bath preheated at the temperature, but it did not melt at the temperatures above 380°C, when heated gradually (lit.[12] mp 346—350°C). The melting point of IIb was 198—199°C (lit.[12] 202°C).

Ethylenedimethacrylate was obtained commercially and purified by distillation.

The solvents used were purified by usual way.

Polymerization Procedures. A typical example is as follows: Into a solution of 0.402 g (0.002 mol) of IIb in 4.0 m*l* of dimethylformamide, 0.320 g (0.002 mol) of Ib was added portionwise with stirring at room temperature. Then the mixture was let stand for an additional hour with stirring and poured into methanol. The polymer precipitated was gathered by filtration and washed thoroughly with hot methanol and dried under vacuum at 110°C to give an almost colorless powder.

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[12] P. Kovacic and R. W. Hein, *J. Am. Chem. Soc.*, **81**, 1187 (1959).