October, 1973] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 3225—3227 (1973) 3225

Polycondensation of Malononitrile and Methylenedimalononitrile with Bis(chloromethyl)Aromatic Compounds Using Triethylamine as Acid Acceptor

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(Received November 16, 1972)

Malononitrile was found to undergo condensation reaction with benzyl chloride to give dibenzylmalononitrile in a quantitative yield under mild conditions when an organic base such as triethylamine was used as acid acceptor in dimethyl sulfoxide. The reaction was applied to the polycondensation of malononitrile and methylenedimalononitrile with *p*-xylylene dichloride and *p,p'*-bis(chloromethyl)diphenyl ether, polymers with intrinsic viscosity 0.14—0.22 dl/g being obtained in quantitative yields.

A number of research works have been carried out on the polycondensation of monomers which contain active hydrogen attached to oxygen, nitrogen or sulfur, *e.g.*, glycols, dibasic acids, diamines and dithiols. However, few works are found in the literature on the polycondensation of CH-acidic monomers.

It is well-known that active methylene compounds undergo condensation with alkyl halide to give mono- and/or dialkyl derivatives with the use of sodium hydride, sodium alkoxide, potassium alkoxide or other inorganic bases as acid acceptor. As example, the condensation of malononitrile with benzyl chloride using potassium hydroxide as base gives a mixture of mono- and dibenzylmalononitrile in 17.3 and 29.3% yields, respectively.[1] The same reaction with a combination of sodium hydride as base and dimethyl sulfoxide as solvent gives dibenzylmalononitrile in 75% yield.[2] The reaction was applied to polycondensation.[3] These reactions proceed *via* the formation of sodium or potassium salt of the active methylene compound as an intermediate, and eliminate alkali metal halides. They are thus condensations of salt of active methylene compound with organic halide. We have investigated the possibility of polycondensation of active methylene and methine compounds with bis(halomethyl)aromatic compounds without the use of an inorganic base as acid acceptor.

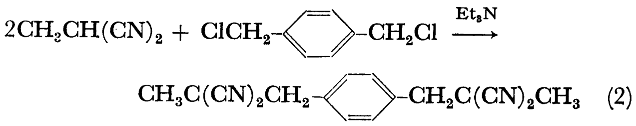
Results and Discussion

Model Reactions. Before carrying out the investigation, we first studied the condensation of malononitrile with benzyl chloride and related condensations as model reactions, and found that it proceeds smoothly at room temperature to give dibenzylmalononitrile (I) in a quantitative yield when an organic base such as triethylamine was used as acid acceptor in dimethyl sulfoxide under nitrogen atmosphere.

$$\mathrm{CH_2(CN)_2 + 2C_6H_5CH_2Cl \xrightarrow{Et_3N} \underset{\textbf{I}}{C_6H_5CH_2C(CN)_2CH_2C_6H_5}} \qquad (1)$$

The reaction needs equimolar amount of triethylamine and eliminates triethylamine hydrochloride, while classical condensation with the use of an inorganic base as acid acceptor eliminates alkali metal halide. The infrared spectrum of the product was identical to that of the authentic sample. Dimethyl sulfoxide seems to be necessary for the condensation reaction. The yield of I was much lower in other solvents, *e.g.*, tetrahydrofuran.

Under similar reaction conditions, *p*-xylylene dichloride was found to undergo condensation reaction with monomethylmalononitrile to give *p*-xylylenebis(methylmalononitrile) (II) in 92% yield.



II

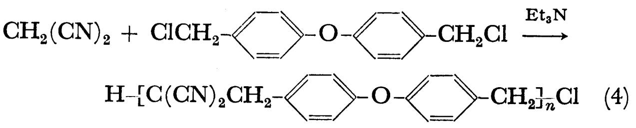
The structure of II was determined by elemental and spectral analyses.

Condensation of methylenedimalononitrile with benzyl chloride under similar conditions was found to afford methylenebis(benzylmalononitrile) (III) in 88% yield.

$$\mathrm{CH(CN)_2CH_2CH(CN)_2 + 2C_6H_5CH_2Cl \xrightarrow{Et_3N} \underset{\textbf{III}}{C_6H_5CH_2C(CN)_2CH_2C(CN)_2CH_2C_6H_5}} \qquad (3)$$

The structure of III was also determined by elemental and spectral analyses.

Polycondensation Reactions. Polycondensation of malononitrile with *p,p'*-bis(chloromethyl)diphenyl ether using triethylamine as an acid acceptor in dimethyl sulfoxide was carried out at room temperature in a similar manner to that for model reactions.



IV

Polymer IV was obtained as a white powder in a quantitative yield and soluble in dimethylformamide, dimethyl sulfoxide and chloroform. Its structure was determined by elemental and spectral analyses, intrinsic viscosity in dimethyl sulfoxide at 30 °C being 0.15 dl/g.

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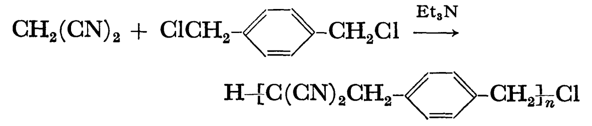
1) H. Normant and T. Cuvigny, *Bull. Soc. Chim. Fr.*, **1965**, 1881.

2) J. J. Bloomfield, *J. Org. Chem.*, **26**, 4112 (1961).

3) a) D. Brown, M. E. B. Jones, and W. R. Maltman, *J. Polym. Sci., Part B*, **6**, 635 (1968); b) Imperial Chemical Industries Ltd., Fr. 1 547 098 (1968); *Chem. Abstr.*, **71**, 40389f (1969).

The number average molecular weight of the polymer determined by vapor pressure osmometry in chloroform was 3200, *i.e.*, the number average degree of polymerization was about 12. Polycondensation of malononitrile with *p,p'*-bis(chloromethyl)diphenyl ether using sodium hydride as acid acceptor gave IV with a molecular weight of 5100.[3]

Polycondensation of malononitrile with *p*-xylylene dichloride under similar conditions gave polymer V in a quantitative yield.



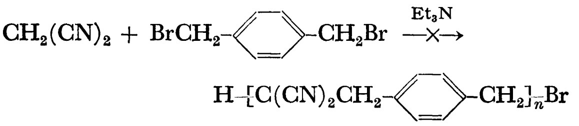
(5)

V

The polymer was soluble in sulfuric acid, but insoluble in most organic solvents. Its structure was determined by elemental and spectral analyses, intrinsic viscosity in sulfuric acid at 25 °C being 0.22 dl/g. Chemical analysis showed the presence of 0.96% of chlorine in the polymer. The result suggests that the number average degree of polymerization is about 22. Thermogravimetric analysis showed that the polymer was stable up to 330 °C under nitrogen atmosphere.

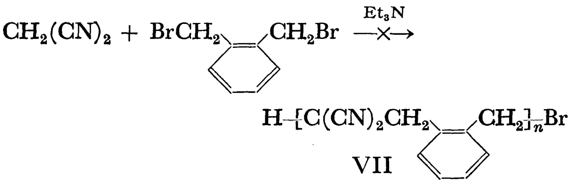
Efforts were made to increase the molecular weight of polymer V. Polycondensation (5) proceeded best in dimethyl sulfoxide. Polymer was obtained in neither diethyl ether nor chloroform. In tetrahydrofuran, low molecular weight oligomer was obtained only in 10% yield. In dimethylformamide, polymer was obtained in 60% yield, but its molecular weight was lower than that of the polymer obtained in dimethyl sulfoxide. The strong basicity of dimethyl sulfoxide seems to be essentially necessary for the polycondensation.

Polycondensation of malononitrile with *o*- and *p*-xylylene dibromides in a similar manner gave no polymeric material.



(6)

VI



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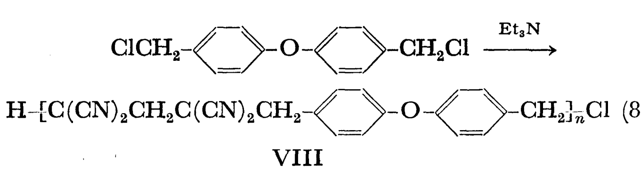
VII

Polycondensation of methylenedimalononitrile with *p,p'*-bis(chloromethyl)diphenyl ether under similar conditions was also found to proceed smoothly to give polymer VIII in a quantitative yield.

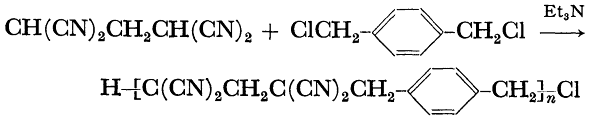


(8)

VIII

The polymer was soluble in dimethyl sulfoxide but not in most organic solvents, its intrinsic viscosity in dimethyl sulfoxide at 30 °C being 0.14 dl/g and number average degree of polymerization estimated from the chlorine content about 9.

A similar polycondensation of methylenedimalononitrile with *p*-xylylene dichloride gave polymer IX in a quantitative yield.



(9)

IX

The polymer was insoluble in most organic solvents, the number average degree of polymerization estimated from the chlorine content being about 8.

Reactions of bis(chloromethyl)aromatic compounds with diethyl malonate, methyl cyanoacetate, acetylacetone and fluorene under similar reaction conditions gave no polymeric products.

Experimental

Materials. Malononitrile was purified by distillation. Methylenedimalononitrile (1,1,3,3-tetracyanopropane) was prepared from malononitrile and formaldehyde in the presence of piperidine,[4] mp 134—135 °C (lit,[4] 136—137 °C). NMR (in a 2: 1 (volume ratio) mixture of CD_3CN and CCl_4, τ): 5.63 (2H, t, J=7.3 Hz), 7.23 (2H, t, J=7.3 Hz). Monomethylmalononitrile was prepared by the dehydration of monomethylmalonamide[5] with phosphorus pentoxide. Commercial *p*-xylylene dichloride and *o*- and *p*-xylylene dibromide were used without further purification. Benzyl chloride was purified by distillation. *p,p'*-Bis(chloromethyl)-diphenyl ether was prepared by the conventional method.[6] Triethylamine was purified by distillation in the presence of phenyl isocyanate. Dimethyl sulfoxide was refluxed over calcium hydride and distilled under reduced pressure. Tetrahydrofuran and diethyl ether were refluxed in the presence of benzophenone sodium ketyl and distilled. Chloroform was dried over calcium chloride and distilled. Dimethylformamide and dimethylacetamide were purified by distillation under reduced pressure. Nitrogen was purified by passing through a tube containing copper turnings in a furnace at 170 °C followed by drying with silica gel and molecular sieves.

General Procedure. Model reactions and polycondensations were carried out under a nitrogen atmosphere in Pyrex test tubes with magnetic stirring at room temperature. Organic halide and malononitrile or methylenedimalononitrile were dissolved in dimethyl sulfoxide. Triethylamine was added dropwise to the solution. Products were recovered by pouring into a large excess of water or methanol. Products of model reactions were purified by recrystallization from ethanol. Polymers IV and VIII were purified by reprecipitation from dimethyl sulfoxide with methanol followed by drying *in vacuo* over phosphorus pentoxide for prolonged periods at 120 and 90 °C, respectively. Polymers

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[4] O. Diels, H. Gärtner, and R. Kaack, *Chem. Ber.*, **55**, 3439 (1922).

[5] a) R. Meyer and P. Bock, *Ann. Chem.*, **347**, 98 (1906); b) N. Weiner, "Organic Syntheses," Coll. Vol. II, p. 279 (1943).

[6] H. Plieninger, L. Horn, and A. Lutz, *Arch. Pharm.* (Weinheim), **286**, 285 (1953).

V and IX were purified by drying *in vacuo* over phosphorus pentoxide at 190 and 150 °C, respectively, for prolonged periods of time.

Elemental analyses were performed at the Elemental Analyses Center of Kyoto University. Infrared spectra were recorded on a Japan Spectroscopic Co. Model 402G spectrometer. Proton magnetic resonance spectra were obtained with a Japan Electron Optics Lab. Model 4H-100 spectrometer using tetramethylsilane as an external standard. Viscosity measurements of polymer solutions were carried out in dimethyl sulfoxide at 30 °C or in sulfuric acid at 25 °C with an Ubbelohde-type dilution viscometer. The number average molecular weight of polymer was determined by vapor pressure osmometry in chloroform using a Hitachi-Perkin-Elmer Model 115 Molecular Weight Apparatus. Thermogravimetric analysis was performed with a thermobalance (wire-torsion balance) under nitrogen atmosphere.

Dibenzylmalononitrile (I). Condensation of malononitrile (20 mmol, 1.3 ml) with benzyl chloride (40 mmol, 4.6 ml) using triethylamine (42 mmol, 5.9 ml) as an acid acceptor in 5.0 ml of dimethyl sulfoxide for 18 hr gave I in a quantitative yield, mp 131.5 °C (lit,[2] 131.8—132.5 °C). The IR and NMR spectra were identical to those of an authentic sample.[2]

p-Xylylenebis(methylmalononitrile) (II). Reaction of monomethylmalononitrile (20 mmol, 1.60 g), *p*-xylylene dichloride (10 mmol, 1.75 g) and triethylamine (20 mmol, 2.8 ml) in dimethyl sulfoxide (10.0 ml) for 24 hr afforded II in 92% yield, mp 206 °C. Found: C, 73.53; H, 5.27; N, 21.51%. Calcd for $C_{16}H_{14}N_4$: C, 73.26; H, 5.38; N, 21.36%. NMR (CD_3COCD_3, τ): 3.18 (4H, s), 7.30 (4H, s), 8.80 (6H, s). IR (KBr disk): $\nu_{C\equiv N}$, 2250 cm^{-1}.

Methylenebis(benzylmalononitrile) (III). Reaction of methylenedimalononitrile (10 mmol, 1.44 g), benzyl chloride (20 mmol, 2.3 ml) and triethylamine (20 mmol, 2.8 ml) in 4.9 ml of dimethyl sulfoxide for 18 hr afforded III in 88% yield, mp 207 °C. Found: C, 77.85; H, 4.94; N, 17.23%. Calcd for $C_{21}H_{16}N_4$: C, 77.76; H, 4.97; N, 17.27%. NMR (CD_3COCD_3, τ): 3.10 (10H, s), 7.03 (4H, s), 7.59 (2H, s). IR (KBr disk): $\nu_{C\equiv N}$, 2250 cm^{-1}.

Polymer IV. Reaction of malononitrile (10 mmol, 0.66 g), *p,p'*-bis(chloromethyl)diphenyl ether (10 mmol, 2.67 g) and triethylamine (20 mmol, 2.8 ml) in 5.0 ml of dimethyl sulfoxide for 18 hr afforded polymer IV as a white powder in a quantitative yield. Found: C, 77.42, 77.43; H, 4.70, 4.75; N, 10.40; Cl, 0.73%. Calcd for $H(C_{17}H_{12}N_2O)_{12}Cl$: C, 77.54; H, 4.63; N, 10.64; Cl, 1.12%. NMR ($CDCl_3$, τ): 2.78 (8H, A_2B_2), 6.78 (4H, s). IR (KBr disk): $\nu_{C\equiv N}$, 2250 cm^{-1}.

Polymer V. Reaction of malononitrile (20 mmol, 1.32 g), *p*-xylylene dichloride (20 mmol, 3.50 g) and triethylamine (40 mmol, 5.6 ml) in 20.0 ml of dimethyl sulfoxide for 18 hr afforded polymer V in a quantitative yield. Found: C, 77.69; H, 4.49; N, 16.16; Cl, 0.96%. Calcd for $H(C_{11}H_8N_2)_{22}Cl$: C, 77.78; H, 4.77; N, 16.49; Cl, 0.95%. IR (KBr disk): $\nu_{C\equiv N}$, 2250 cm^{-1}. The IR spectrum showed a characteristic absorption of *p*-disubstituted benzene in the region 5—6 μ.

Polymer VIII. Reaction of methylenedimalononitrile (5 mmol, 0.72 g), *p,p'*-bis(chloromethyl)diphenyl ether (5 mmol, 1.34 g) and triethylamine (10 mmol, 1.4 ml) in 10.0 ml of dimethyl sulfoxide for 18 hr afforded polymer VIII in a quantitative yield. Found: C, 73.86; H, 4.22; N, 16.54; Cl, 1.21%. Calcd for $H(C_{21}H_{14}N_4O)_9Cl$: C, 73.66; H, 4.15; N, 16.36; Cl, 1.15%. NMR (CD_3SOCD_3, τ): 2.86 (8H, A_2B_2), 6.55 (4H, s), 7.06 (2H, s). IR (KBr disk): $\nu_{C\equiv N}$, 2250 cm^{-1}.

Polymer IX. Reaction of methylenedimalononitrile (10 mmol, 1.44 g) *p*-xylylene dichloride (10 mmol, 1.75 g) and triethylamine (20 mmol, 2.8 ml) in 20.0 ml of dimethyl sulfoxide for 24 hr afforded polymer IX in a quantitative yield. Found: C, 71.68, 71.73; H, 4.17, 4.33; N, 20.70, 21.09; Cl, 1.77, 1.80%. Calcd for $H(C_{15}H_{10}N_4)_8Cl$: C, 71.83; H, 4.07; N, 22.34; Cl, 1.77%. IR (KBr disk): $\nu_{C\equiv N}$, 2250 cm^{-1}. The IR spectrum showed a characteristic absorption of *p*-disubstituted benzene in the region 5—6 μ.