[CONTRIBUTION FROM PIONEERING RESEARCH SECTION, TECHNICAL DIVISION, RAYON DEPARTMENT, E. I. DU PONT DE NEMOURS AND COMPANY]

Condensation of Substituted Malonic Esters with Diamines

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The phenyl esters of some disubstituted malonic acids were prepared and condensed with aliphatic diamines to produce high molecular weight, heat stable polyamides. The polyamides could be melt spun into strong, resilient, orientable fibers. Some of the properties of the intermediates and the polymers are given.

Discussion

The general method for the preparation of polyamides as disclosed by Carothers[1] involves heating equivalent amounts of a dibasic acid with a diamine. Equivalent amounts of acid and diamine are more readily obtained by the initial preparation of the intermediate salt. This method is generally applicable to dibasic acids having six or more carbon atoms in the main chain and diamines having four or more carbon atoms.

The general method for the preparation of polyamides cannot be used for polycondensation of malonic acids with diamines. It is known that malonic acids decarboxylate rapidly at temperatures from 115–185° with little dependence upon the degree or type of substitution.[2] In attempts to condense malonic acid with diamines or diamine salts of malonic acid to polyamides, complete decarboxylation of the acid occurred in preference to condensation with the diamine.

Since malonic esters are known to be more stable thermally than malonic acid itself, it was thought that malonic esters might condense with diamines to form polyamides without decarboxylation. This was found to be the case. Diethyl malonate condensed readily with decamethylenediamine to form a high molecular weight polyamide. Unfortunately, this polymer became very colored and soon gelled under polymerization conditions. Since decarboxylation did not appear to have occurred, it was thought that this instability was due to the very active hydrogens on the methylene groups of the malonic acid portion of the polymer. Subsequent work revealed that the instability could be overcome by replacing one or both of the active hydrogens of malonic acid with either alkyl or aryl groups. Both ethyl ethylmalonate and ethyl diethylmalonate were condensed with decamethylene diamine. In both cases light-colored polymers having no tendency to gell or decompose under polymerization conditions were obtained. The polymers obtained, however, were of rather low molecular weight as evidenced by low melt and intrinsic viscosities, due apparently to sluggishness of the reaction and probable loss of unreacted ester during polymerization.

In order to obtain a more rapid and complete reaction, the phenyl esters of several disubstituted malonic acids were investigated.[1] These phenyl esters were found to condense completely and rapidly with various diamines to form high molecular weight polyamides. The polyamides obtained possessed a heat stability comparable to that of polyhexamethyleneadipamide. In general the hexamethylenediamine polymers of the substituted malonic acids had sticking temperatures in the range of 120°. These polymers were quite soluble in such solvents as a chloroform–methanol mixture (88:12 by wt.), and ethyl alcohol in addition to the standard nylon solvents. Polymer solutions in chloroform–methanol could be cast readily into films which were clear and tough. The polyamides were readily melt spun into orientable fibers possessing attractive tensile properties. The polyamides prepared together with some of their properties are listed on Table I.

It was rather surprising to find that phenyl esters of the disubstituted malonic acids apparently will not condense to an appreciable extent with disecondary diamines. Thus, equivalent quantities of phenyl 1,1-cyclohexanedicarboxylate and N,N′-diethylhexamethylenediamine reacted only slightly when subjected to the standard polyamidation conditions. Likewise, when equivalent quantities of anhydrous piperazine and phenyl *n*-butylethylmalonate were given the regular polymerization cycle, little or no phenol was formed and no polymeric product was obtained. It was also found that the ethyl esters of the more highly substituted malonic acids such as *n*-butylethylmalonic acid condensed very incompletely with diamines and no polymeric products could be obtained from them.

Experimental

Preparation of Diphenyl Malonates. Hydrolysis of Diethyl Malonates.—In general, the diphenyl malonates were prepared by hydrolysis of the corresponding ethyl esters, followed by conversion to the acid chlorides and subsequent condensation with phenol.

Table II lists the disubstituted malonic acids prepared along with their acid chlorides and phenyl esters and some of their properties. The alkyl esters of disubstituted malonic acids are quite difficult to hydrolyze in aqueous solutions.[3] However, hydrolysis can be brought about by boiling 50% potassium hydroxide solution. A better method is hydrolysis in alcoholic potassium hydroxide. An example of the latter method will be described.

Di-*n*-butylmalonic Acid.—A solution of 123 g. of potassium hydroxide in 500 cc. of absolute ethanol was heated to the reflux and 100 g. of ethyl di-*n*-butylmalonate (Eastman Kodak Co. White Label) gradually added. Hydrolysis took place almost immediately and some salt precipitated out toward the end of the reaction. After complete addition of the ester, the mixture was refluxed for 1–2 hours. It was then cooled and acidified with concentrated hydrochloric acid. The resulting mixture was filtered to remove the potassium chloride which was washed with ether. The filtrate was extracted with ether and the ether extractions and washings combined. The ether solution was extracted with an excess of three portions of sodium carbonate solution in water. The sodium carbonate solution was treated with Norite, cooled and acidified with concentrated hydrochloric acid. After cooling, the crystallized di-*n*-butylmalonic acid was collected on a filter, washed with cold

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(1) W. H. Carothers, U. S. Patent 2,130,523, Sept. 20, 1938.

(2) F. C. B. Marshall, *Rec. trav. chim.*, **51**, 233 (1932).

(3) F. C. B. Marshall, *J. Chem. Soc.*, 2336 (1931); G. Vavon and J. Ducasse, *Bull. soc. chim.*, **10**, 325 (1943).

TABLE I

PREPARATION AND PROPERTIES OF POLYAMIDES FROM PHENYL DISUBSTITUTED MALONATES

Reactants (equiv. amts.)	Polymerization Time, hr.	Polymerization Temp., °C.	Polymerization Press., mm.	Polymer Stick temp.,[a] °C.	$\eta_{inh.}$[b]	Remarks
Decamethylenediamine, ethyl malonate	4	200	Sld.[c]	185–190	0.93	Orange-red, brittle, partially gelled
	1/2	283	atm.			
	1 1/4	283	3			
Decamethylenediamine, ethyl ethylmalonate	20	200	Sld.	95–100	.26	Clear, light yellow, brittle, not spinnable
	1	283	atm.			
	2 1/4	283	3			
Decamethylenediamine, ethyl diethylmalonate	20	200	Sld.	120–125	.72	Pale yellow
	1	283	atm.			
	7	283	3			
Decamethylenediamine, phenyl dimethylmalonate	6	200	Sld.	120–125	.93	Clear, colorless, tough. Mechanically spun into tough drawable fibers
	1	259	atm.			
	2	273	14			
Hexamethylenediamine, phenyl dimethylmalonate	6	200	Sld.	115–120	.93	Clear, colorless, tough, spinnable
	1	260	atm.			
	2	273	14			
	6	273	3			
Bis-(*p*-aminomethyl)-benzene, phenyl dimethylmalonate	5	210	Sld.	110–115	.51	Manually spinnable
	1	273	atm.			
	1/2	273	14			
	5	273	3			
p-Xylylenediamine, phenyl dimethylmalonate	5	210	Sld.	260	.35	White, opaque, brittle
	1	283	atm.			
	3	283	3			
Tetramethylenediamine, phenyl diethylmalonate	4	210	Sld.	100–105	.30	Clear, colorless, brittle
	2	260	atm.			
	6	273	3			
Hexamethylenediamine, phenyl diethylmalonate	5	210	Sld.	95–100	.69	Clear, tough, spinnable. Sol. in ethanol, $CHCl_3$-methanol (88/12)
	1	273	atm.			
p-Xylylenediamine, phenyl diethylmalonate	5	210	Sld.	165–170	.38	Clear, brittle
	1	273	atm.			
	3	273	3			
Hexamethylenediamine, *n*-butylethylmalonic acid	20	200	Sld.	.....	..	Complete decarboxylation at 283°
		283	atm.			
Hexamethylenediamine, phenyl *n*-butylethylmalonate	2	210	Sld.	115–120	.41	Clear, little color. Manually spinnable and drawable
	1	260	atm.			
	9	260	3			
p-Xylylenediamine, phenyl *n*-butylethylmalonate	5	210	Sld.	170–175	.48	Clear, colorless, brittle
	1	273	atm.			
	2 1/2	273	3			
Hexamethylenediamine, phenyl *n*-dibutylmalonate	14	210	Sld.	140–145	.66	Tough and strong
	1	265	atm.			
	5	265	3			
Hexamethylenediamine, phenyl 1,1-cyclohexanedecarboxylate	14	210	Sld.	193–197	.63	Semi-opaque. Hard and tough. Mechanically spun into strong, drawable resilient fibers
	1	273	atm.			
	5	273	3			
Bis-(*p*-aminomethyl)-benzene, phenyl 1,1-cyclohexanedecarboxylate	1 1/4	260	Atm.	185–190	.52	Clear, pale yellow. Spinnable
	3 3/4	273	3			
Hexamethylenediamine, phenyl phenylethylmalonate	14	210	Sld.	.....	.17	Soft and sticky at room temp.
	1	273	atm.			
	5	273	1			

[a] Temp. at which polymer begins to stick when a fresh surface of polymer is touched to a polished copper block. [b] $\eta_{inh.}$ = inherent viscosity = $(2.3 \log \eta_{rel})/C$. Determined in *m*-cresol at 0.5% concn. [c] Sld.—reagents heated in an evacuated sealed tube.

water, and dried; yield 78 g. (98%); m.p., 160°. *Anal.* Calcd. for $C_{11}H_{20}O_4$: neut. equiv., 108.0. Found: neut. equiv., 109.9.

Preparation of Acid Chlorides.—The preferred reagent for conversion of the malonic acids to acid chlorides was phosphorus pentachloride. The use of thionyl chloride was attempted but found to be unsatisfactory from the standpoint of both yield and quality of the product.

***n*-Butylethylmalonyl Chloride.**—This preparation will serve to illustrate the method of preparation of the acid chlorides. One hundred grams (0.53 mole) of *n*-butylethylmalonic acid was placed in a flask and 200 g. (1 mole) of phosphorus pentachloride added portionwise. After the initial reaction had subsided (some cooling was necessary), the mixture was heated at reflux for 1–2 hours and then distilled. A yield of 108 g. (91%) of the desired acid chloride, b.p. 145–155° (30–50 mm.), was obtained.

Phenyl Esters.—The phenyl esters were prepared in a manner similar to that described by Doebner[4] and Weselsky.[5]

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(4) O. Doebner, *Ann.*, **210**, 249 (1882).

(5) P. Weselsky, *Ber.*, **2**, 519 (1869).

TABLE II

PREPARATION OF SOME PHENYL DISUBSTITUTED MALONATES

Disubst. malonic acid[a]	M.p. of acid, °C.	Acid chloride[b] Yield, %	B.p., °C.	Mm.	Diphenyl ester[c] Yield, %	B.p., °C.	Mm.	M.p., °C.	Anal. of phenyl ester Calcd. C	H	Found C	H
Dimethyl[e]	182	90	96–104	150	75	215–225	18	99	71.81	5.67	71.56	5.71
Diethyl[d,f]	125	72	130–135	120	73	159	1–2	...				
n-Butylethyl[d,g]	110	90	145–155	40	80	176–178	1–2	57	74.09	7.11	73.90	7.15
Di-*n*-butyl[d,h]	160	75	160–178	85	66	191–192	1–2	49	74.74	7.84	75.00	7.61
1,1-Dicarboxycyclohexane[i]	182	95	158–170	115	54	.....	..	87	74.07	6.22	73.65	6.40
Phenylethyl[d,j]	...	...	176–185	60	60	190–215	1	78–80	76.50	5.60	76.67	5.56

[a] Obtained by alkaline hydrolysis of ethyl ester. [b] Prepared by action of PCl_5 on the acid. [c] Prepared by treating acid chloride with dry phenol. [d] Obtained as ethyl ester from Eastman Kodak Co. [e] W. Konigs and J. Hoerlin, *Ber.*, **26,** 2049 (1893), m.p. of acid 192–193°. Acid chloride: Franchimont, *Rec. trav. chim.*, **4,** 207 (1885), b.p. 165°. [f] C. Daimler, *Ann.*, **249,** 173 (1888), m.p. of acid, 125°; acid chloride, b.p. 196–197°, E. Fischer and A. Dilthey, *Ber.*, **35,** 844 (1902); phenyl ester, b.p. 215–225° (15 mm.), "Beilstein," Vol. VI (suplmt.), p. 88. [g] Raper, *J. Chem. Soc.*, **91,** 1837 (1907), m.p. of acid, 116°. [h] P. A. Lenene and L. H. Cretcher, *J. Biol. Chem.*, **33,** 505 (1918), m.p. of acid, 163°. [i] A. I. Vogel, *J. Chem. Soc.*, 1487 (1929), m.p. of acid, 179.5°. [j] Tassilly, Belot and Descombs, *Compt. rend.*, **186,** 149 (1928), m.p. of acid, 182.5°.

Equivalent amounts of phenol and the desired acid chloride were heated at about 200° until evolution of hydrogen chloride was virtually complete. The product was purified generally by distillation at reduced pressure followed by recrystallization from a suitable solvent, such as alcohol. Table II lists the phenyl esters prepared and some of their properties along with analytical data.

Since the preparation of phenyl malonates through the route of the acid chlorides involves several steps and is rather tedious, some attempts were made to prepare them by a shorter route. Therefore, the action of phenol on ethyl malonate was studied. In one experiment ethyl malonate was heated at 185° with a large excess of phenol for about 30 hours in the presence of a small amount of litharge. Some low boiling material was removed but this was found to be mostly ethyl acetate along with a little ethanol. Distillation of the reaction mixture yielded no phenyl malonate. This reaction was repeated using concentrated sulfuric acid as catalyst but with the same results. It was therefore concluded that phenyl esters of malonic acids could not be obtained conveniently by this method.

Preparation of Polymers.—The polymers listed on Table I were prepared by the fusion of equivalent quantities of phenyl ester with diamine. Equivalent quantities of diamine and phenyl ester were accurately weighed into glass tubes which were evacuated and then sealed. The sealed tube with the reactants was then heated for a specified length of time at 200–210°. After cooling, the tube was opened and attached to an apparatus so designed that the reactants could be heated in an atmosphere of nitrogen or under reduced pressure. The reactants were then heated in an atmosphere of nitrogen at atmospheric pressure at a temperature of 260–280° for a given length of time, after which the pressure was gradually reduced to 2–3 mm. Agitation was effected by bubbling nitrogen through a capillary tube into the polymer during the reduced pressure cycle. The polymerization conditions for each polymer prepared are given on Table I.

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Studies on Thioaldehydes. I. The Monohalothiobenzaldehydes

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Conversion of all of the monochloro-, monobromo- and monoiodobenzaldehydes to the thiobenzaldehyde analogs has been effected using hydrogen sulfide. Each thiobenzaldehyde has been isolated in two geometrical forms. Formation of symmetrically substituted stilbenes by heating the thioaldehyde with freshly precipitated copper powder has been achieved in satisfactory yields.

The simple thioaldehydes have, for the most part, been investigated rather thoroughly. In particular, Wörner[1] has studied these compounds. However, little success has been realized in the study of the conversion of halobenzaldehydes to the corresponding halothiobenzaldehydes.[2] As a result only two halothioaldehydes have been prepared, these being obtained from the corresponding benzaldehyde derivative as white crystalline masses along with some oily products.[1] Conversion of aryl thioaldehydes into stilbene analogs and homologs by heating with copper powder has been reported previously.[3] By use, therefore, of these reactions, it was considered possible to prepare from the halobenzaldehydes the corresponding symmetrical halostilbene derivatives in satisfactory yields. Several of these stilbenes have not been reported. The reactions are shown in the formula chart.

Although several methods are available, the one most widely used for preparing thiocarbonyl compounds involves the action of dry hydrogen sulfide on the corresponding oxo-carbonyl compound.[4] Usually the oxo-compound is dissolved in a suitable solvent such as alcohol or ethyl acetate, the solution saturated with dry hydrogen chloride, and a stream of hydrogen sulfide passed into the solution. The thio-compound usually precipitates. It should be mentioned that the monomeric thioaldehyde is not isolated, but only the trimer or a linear polymer is obtained. No pure monomeric aryl thial has been described. The resulting halothiobenzaldehyde should be obtainable, therefore, in two iso-

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[1] E. Wörner, *Ber.*, **29**, 139 (1896).

[2] C. L. Jackson and J. H. White, *ibid.*, **11**, 1042 (1878).

[3] (a) J. Klinger, *ibid.*, **9**, 1893 (1876); **10**, 1877 (1877); (b) J. H. Wood, J. A. Bacon, A. W. Meibohm, W. H. Throckmorton and G. P. Turner, THIS JOURNAL, **63**, 1334 (1941).

[4] For an excellent review on thiones and thials, see E. Campaigne, *Chem. Revs.*, **39**, 1 (1946).