oxygen-free water and decomposed with a solution of I_2 in pyridine. The amount of evolved CO corresponded to a Ni/CO ratio of 3.00/7.95. The amount of nickel present in the aqueous solution, presumably as $[Ni_3(CO)_8]^{-2}$, corresponded to 57% of the nickel in the $Ni(CO)_4$ used as a starting material.

Formation of Tetraphenylbutadiene and α-Phenylcinnamic acid, by Treating Diphenylacetylene with a Solution Containing $[Ni_3(CO)_8]^{-2}$.—Five ml. (0.04 mole) of $Ni(CO)_4$ was added to 75 ml. of a saturated solution of NaOH in methanol and the mixture shaken under helium for a total of 80 hours. The dark red mixture was diluted with 100 ml. of methanol and the solution extracted with petroleum ether to remove any unreacted $Ni(CO)_4$. Five grams (0.028 mole) of diphenylacetylene was added to the solution and the mixture shaken for a total of 80 hours. The absence of $[Ni_3(CO)_8]^{-2}$ in the reaction mixture was demonstrated by adding oxygen-free water to a sample of the reaction mixture. The addition of water caused separation into a dark brown precipitate, probably tetraphenylbutadiene and polymeric nickel carbonyls, and a colorless aqueous solution. No precipitate formed on addition of $Ni(o\text{-}phen_3)_3Cl_2$ to this solution. The reaction mixture was acidified and the precipitate separated into a neutral and acidic fraction by treatment with aqueous $NaHCO_3$.

The neutral fraction, 1,2,3,4-tetraphenylbutadiene, weighed 2.9 g., corresponding to a yield of 57.8%; the acidic fraction, α-phenyl-*trans*-cinnamic acid, weighed 1.9 g., corresponding to a yield of 30.3%.

Acknowledgment.—This work was carried out in coöperation with International Nickel Company.

[COMMUNICATION NO. 2063 FROM THE KODAK RESEARCH LABORATORIES, EASTMAN KODAK CO.]

Polyesteramides

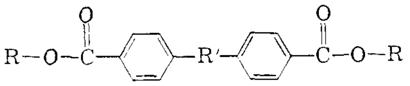
BY T. M. LAAKSO AND D. D. REYNOLDS

RECEIVED OCTOBER 31, 1959

Polyesteramides have been prepared by the condensation of glycols with bis-esters having the general structure, ROOCR'NHCOR'COOR and ROOCR'NHCOR''CONHR'COOR, where R is alkyl, R' is phenylene and R'' is alkylenes The amide links are stable under condensation conditions when R' is aromatic and when R' is aromatic with R'' aliphatic. Physical properties are tabulated.

Introduction

After Whinfield and Dickson[1] demonstrated that aryl-*p*-dicarboxylic acids react with glycols to give crystalline polymers having high melting points, many *p*-substituted dicarboxylic acids were prepared and converted to polyesters. Polyesters have been prepared from compounds having the general formula shown, where R' has been varied widely.[2]



Since the amide group is a contributing factor to the desirable properties of polyamides, it was of interest to study polyesters composed of aromatic nuclei linked through the *p*-positions by chains possessing amide linkages. Numerous polyesteramides have been described in the literature,[3] but, for the most part, they are aliphatic. They have been prepared by the reaction of a dibasic acid or its ester with amino alcohols, or with a mixture of a diamine and a glycol. In some cases amino acids were used. When free amines are used in such condensations, it is difficult to avoid color formation. We have prevented this by using esters of the general structure ROOCR'NHCOR'COOR and ROOCR'NHCOR''CONHR'COOR, which contain a preformed amide link.

The stability of the amide linkage, and as a direct result the color of the final polymer, is dependent upon the nature of R' and R''. When R' is aromatic, as in the case of 4,4'-dicarbethoxybenzanilide, the linkage is very stable and light-colored polymers are obtained. When R' is aromatic with R'' aliphatic, *e.g.*, bis-[N-*p*-carbethoxyphenyl]-sebacamide, the amide linkage is likewise stable. In all cases where R' was aliphatic with R'' aromatic, there was decomposition accompanied by the liberation of free amine which produced colored products.

This paper is concerned with polyesteramides prepared by the condensation of glycols with: (i) 4,4'-dicarbethoxybenzanilide, (ii) 4,4'-dicarbethoxybenzanilide plus 4,4'-dicarbutoxydiphenyl sulfone, (iii) bis-[N-*p*-carbethoxyphenyl]-sebacamide, (iv) bis-[N-*p*-carbethoxyphenyl]-azelamide, and (v) bis-N-*p*-carbethoxyphenyl]-suberamide.

Experimental

Diethyl terephthalate (m.p. 42–44°, lit. 43–44°) was prepared by the esterification of terephthalic acid according to the procedure of Koelsch.[4]

Ethyl hydrogen terephthalate (m.p. 170–171°, lit. 168–170°) was prepared according to the procedure of Cohen and de Pennington.[5]

Anal. Calcd. for $C_{10}H_{10}O_4$: C, 62.0; H, 5.1. Found: C, 62.1; H, 5.1.

***p*-Carbethoxybenzoyl Chloride.**—Ethyl hydrogen terephthalate (5820 g., 30 moles) and 6720 g. (56.46 moles) of thionyl chloride were mixed together in a 12-liter flask equipped with a reflux condenser. The reaction mixture was heated gently on a steam-bath until a homogeneous solution was obtained. The excess thionyl chloride was distilled and the residue fractionated through an 18-inch column filled with glass helices; yield 95%, b.p. 134° (6 mm.).

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(1) J. R. Whinfield and J. T. Dickson, British Patent 578,079 (1946).

(2) (a) J. T. Dickson, British Patent 579,462 (1946); (b) R. H. Griffith and J. H. G. Plant, British Patent 643,388 (1950); (c) A. R. Lowe, British Patent 604,075 (1948); (d) J. G. Cook, J. T. Dickson, H. P. W. Huggill and A. R. Lowe, British Patent 604,074 (1948); (e) E. R. Wallsgrove and F. Ruder, British Patent 636,429 (1950); (f) J. R. Whinfield and J. T. Dickson, U. S. Patent 2,465,319 (1949); (g) L. J. Tyler, U. S. Patent 2,601,646 (1952).

(3) W. H. Carothers, U. S. Patent 2,071,250 (1937); E. L. Martin, U. S. Patent 2,359,867 (1944); E. L. Kropa, U. S. Patents 2,440,516 (1948), 2,463,977 (1949); E. A. Lasher, U. S. Patent 2,475,034 (1949). British Patents: R. E. Christ, 561,108 (1944); Wingfoot Corporation, 571,017 (1945); J. Drewitt and G. Harding, 621,977 (1949); Am. Viscose Corporation, 671,141 (1952).

(4) C. F. Koelsch, "Organic Syntheses," H. Adkins, editor, Vol. 26, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 95.

(5) J. B. Cohen and H. S. de Pennington, *J. Chem. Soc.*, **113**, 57 (1918).

TABLE I

BIS-(-*p*-CARBETHOXYPHENYL)-AMIDES

Bis-[N-(*p*-carbethoxyphenyl)]-	Yield, %	M.p., °C.		Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
Adipamide	81.5	215–217	$C_{24}H_{28}N_2O_6$	65.4	65.6	6.3	6.5	6.3	6.5
Suberamide	79.5	189–191	$C_{26}H_{32}N_2O_6$	66.7	66.7	6.8	6.8	5.9	5.8
Azelamide	81.5	175–176	$C_{29}H_{34}O_6N_2$	68.7	68.4	6.8	6.9	5.5	5.6
Sebacamide	82.9	181–183	$C_{28}H_{36}N_2O_6$	67.7	67.7	7.2	7.3	5.6	5.8

Anal. Calcd. for $C_{10}H_9ClO_3$: C, 56.4; H, 4.2; Cl, 16.6. Found: C, 56.4; H, 4.2; Cl, 16.4.

4,4'-Dicarbethoxybenzanilide.—Ethyl *p*-aminobenzoate (343 g., 2.08 moles) was dissolved in 4 liters of benzene. Two liters of water was added and then, with cooling (5°) and vigorous stirring, one-half of 442 g. (2.08 moles) of *p*-carbethoxybenzoyl chloride was added. After stirring for 5 min., 200 ml. of a solution containing 83.2 g. (2.08 moles) of sodium hydroxide in 390 ml. of water was added, followed in 5 min. by one-half of the remaining alkali solution; and so on until all of these reagents had been added. The reaction mixture was stirred for an additional 10 min. and filtered by suction. The product was washed thoroughly with water and then twice crystallized from ethyl alcohol; yield 620 g. or 90.1%, m.p. 166–168°.

Anal. Calcd. for $C_{19}H_{19}O_5N$: C, 66.9; H, 5.5; N, 4.1. Found: C, 66.9; H, 5.5; N, 4.2.

Bis-(N-*p*-carbethoxyphenyl)-amides shown in Table I were prepared by an analogous procedure.

Sodium hydrogen titanium butoxide[6] was prepared by dissolving 1 g. of sodium in 99 g. of 1-butanol, adding 14.78 g. of freshly distilled titanium butoxide and diluting to 200 ml. with 1-butanol.

General Procedure for the Preparation of the Polymers.—The reactants were mixed together with the catalyst in a reaction flask equipped with a nitrogen inlet tube and a side-arm. Nitrogen was passed through the flask heated in an oil-bath maintained at the temperature indicated for the first stage. After having continued the reaction for the first-stage reaction time, the nitrogen inlet tube was replaced by a stainless-steel stirrer equipped with a ball-and-socket-type stirrer seal. A water pump was attached to the side-arm, the reaction mixture was stirred and the excess glycol thus removed. This step constituted part of the second stage. The water pump then was replaced by a mechanical vacuum pump and the stirring was continued at a pressure of 0.1–1.0 mm. for the time necessary to complete the second stage. During this period the temperature of the bath was maintained as indicated. At the end of the reaction, nitrogen was let into the flask and it was removed from the bath. After cooling to room temperature, the polymer was removed by breaking the flask. The inherent viscosities were calculated from the relative viscosity of a 0.25% solution of the polymer in a 60:40 (by weight) mixture of phenol and tetrachloroethane.

Discussion

The polymers formed by the condensation of 4,4'-dicarbethoxybenzanilide with ethylene glycol, 1,3-propanediol and 1,4-butanediol melted above 300° and therefore solidified in the early stages of polymerization to yield low molecular weight products.

1,5-Pentanediol gave a polymer which melted in the range of 235-240°. It was quenchable and could be stretched and heat set. The modulus was low. When 300 g. of 4,4'-dicarbethoxybenzanilide was treated with 1,5-pentanediol (150 g.) for 60 minutes at 240° followed by 180 minutes in vacuum at 260°, the resulting polymer had an intrinsic viscosity of 0.73; 1 ml. of catalyst was used.

TABLE II

POLYESTERS PREPARED FROM 4,4'-DICARBETHOXYBENZANILIDE, 4,4'-DICARBUTOXYDIPHENYL SULFONE AND 1,5-PENTANEDIOL

(a) g.[a]	Mole %	(b) g.	Mole %	(c) g.	Catalyst, ml.	1st stage °C./min.	2nd stage °C./min.	Intrinsic visc., cs.
42.5	25	157.5	75	150	1	240/60	270/70	0.70[b]
25.5	15	177.5	85	150	1	230/60	260/85	[c]
8.5	5	199	95	150	1	240/60	240–300/60	0.57[d]

[a] (a) 4,4'-Dicarbethoxybenzanilide, (b) 4,4'-dicarbutoxydiphenyl sulfone, (c) 1,5-pentanediol. [b] Good color; crystallized slowly and completely; cold-drawn; m.p. 215-219°. [c] M.p. 225–260°. [d] Melting point is so high that some thermal degradation occurs.

TABLE III

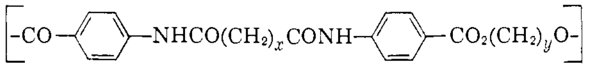
POLYESTERS PREPARED FROM 4,4'-DICARBETHOXYBENZANILIDE, 4,4'-DICARBUTOXYDIPHENYL SULFONE AND 1,6-HEXANEDIOL

(a) g.[a]	Mole %	(b) g.	Mole %	(c) g.	Catalyst, ml.	1st stage °C./min.	2nd stage °C./min.	Intrinsic visc., cs.
205	90	28	10	140	1	230/45	275/110	0.72[b]
700	80	217	20	440	3	250/60	260/265	0.76[c]

[a] (a) 4,4'-Dicarbethoxybenzanilide, (b) 4,4'-dicarbutoxydiphenyl sulfone, (c) 1,6-hexanediol. [b] Excellent color; cold-drawn; rapid crystallization; m.p. 230-235°. [c] M.p. 237-241°.

TABLE IV

POLYESTERAMIDES



x	*y*	M.p., °C.	I.V.	Modulus × 10⁴ kg./cm.²	Yield stress, kg./cm.²	Tensile strength, kg./cm.²	Elongation, %
6	4	250	0.68	9.6	3150	3450	17
6	6	247	.73	8.0	2500	3400	27
7	4	233	.63	5.8	2000	2700	43
7	6	233	.72	5.9	2500	3400	47
8	4	233	.69	5.9	2200	3100	19
8	6	232	.74	5.8	2500	3300	34

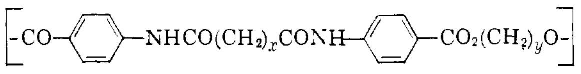
The 1,6-hexanediol polymer melted between 250-260° and crystallized so readily that quenching was difficult. The product which resulted from treating 200 g. of 4,4'-dicarbethoxybenzanilide with 140 g. of 1,6-hexanediol at 260° for 60 minutes and then at 285° in vacuum for 85 minutes had an intrinsic viscosity of 0.63; 2 ml. of catalyst was used. The polymer was extruded without excessive degradation.

In order to improve quenchability, a series of copolymers was prepared in which 4,4'-dicarbutoxydiphenyl sulfone was incorporated as a second monomer. Data concerning some of the resulting polymers are shown in Tables II and III. The best physical properties were obtained from the copolymer prepared from 1,4-butanediol and a 75:25 mole ratio of 4,4'-dicarbethoxybenzanilide and 4,4'-dicarbutoxydiphenyl sulfone. An inherent viscosity of 0.6 to 0.7 was found to be sufficient for good fiber-forming properties. The products melted in the range of 270-280°. The physical

(6) J. Caldwell, U. S. Patent 2,720,502 (1955).

properties as measured on drawn monofils are: Young's modulus 7.47 × 10^4kg./cm.^{2}, yield stress 1100 kg./cm.^{2}, tensile strength 2700 kg./cm.^{2}, elongation 32%.

Polymers prepared by condensing bis-(*p*-carbethoxyphenyl)-amides with glycols and having the basic structure



are relatively high melting. The best products were obtained from the C_5–C_{10}-aliphatic dibasic acids. The lower molecular weight acids gave products with melting points so high that crystallization occurred before high molecular weights could be obtained. The physical properties are shown in Table IV. It would appear feasible on the basis of the melting points to extend the series to adipic acid, but preparative difficulties were encountered in all such efforts. The best fiber properties are found in the suberic acid derivatives.

ROCHESTER 4, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY]

Photochemical Transformations of Simple Troponoid Systems. I. Photo-γ-tropolone Methyl Ether[1]

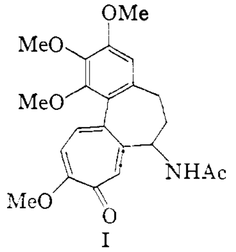
BY O. L. CHAPMAN AND D. J. PASTO

RECEIVED NOVEMBER 11, 1959

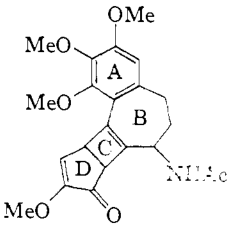
Irradiation of γ-tropolone methyl ether (IV) gives photo-γ-tropolone methyl ether (V). Acid treatment of V and the corresponding dihydro (VII) and tetrahydro derivative (VIII) gives γ-tropolone, 2-cycloheptene-1,4-dione and cycloheptane-1,4-dione. The acid-catalyzed ring opening of tetrahydrophoto-γ-tropolone methyl ether is complete in one minute under conditions in which V and VII do not react. Photo-γ-tropolone methyl ether has been found to undergo a facile pyrolysis to γ-tropolone methyl ether. An attempt to convert γ-tropolone methyl ether to tropone *via* V has met with only minor success.

Photochemical isomerization of unsaturated molecules has become a topic of rapidly increasing interest and significance. Recent examples of photoisomerization include conjugated dienones,[2,3] cross conjugated dienones,[4–7] conjugated dienes[8–11] and trienes,[12,13] α,β-unsaturated ketones,[14] unconjugated dienes[15,16] and even simple cyclic ketones[17] and ethers.[18]

Prior to the completion of our investigation of the photoisomerization of γ-tropolone methyl ether[1] only one troponoid compound, the naturally occurring alkaloid colchicine, had been reported to undergo photochemical change.[19] Colchicine (I) on prolonged exposure to sunlight gave three photoisomers, the α, β- and γ-lumicolchicines.[20,21] Forbes has designated the β- and γ-photoisomers as stereoisomers of II.[22] Gardner has assigned steric structures to the β- and γ-lumicolchicines.[23,24] The structure of α-lumicolchicine is not known.



I



II

Contemplation of the variety of valence tautomerization type photoisomerization reactions potentially available to simple troponoid systems leads to consideration of several quite novel chemical transformations. A simple tropolone or substituted tropone might, in principle, undergo three types of light-induced valence tautomerization. These reaction types are illustrated below for a 2-substi-

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[1] This report was presented in part before the Division of Organic Chemistry, April 8, 1959. A preliminary communication of a portion of the results now reported has been published (O. L. Chapman and D. J. Pasto, THIS JOURNAL, **80**, 6685 (1958)).

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(16) R. C. Cookson, E. Crundwell and J. Hudec, *Chemistry & Industry*, 1003 (1958); R. C. Cookson and E. Crundwell, *ibid.*, 1004 (1958).

(17) R. Srinivasan, THIS JOURNAL, **81**, 1546 2601, 2604 (1959).

(18) J. D. Margerum, J. N. Pitts, Jr., J. G. Rutgers and S. Searles, *ibid.*, **81**, 1549 (1959).

(19) We have since been informed by Professor W. G. Dauben that irradiation of α-tropolone in aqueous solution gives 4-oxo-2-cyclopentene-1-acetic acid (W. G. Dauben, K. Koch and W. E. Thiessen, *ibid.*, **81**, 6087 (1959).

(20) R. Grewe and W. Wolf, *Ber.*, **84**, 621 (1951).

(21) F. Šantavý, *Biol. Listy*, **31**, 246 (1950).

(22) E. J. Forbes, *J. Chem. Soc.*, 3864 (1955).

(23) P. D. Gardner, R. L. Brandon and G. R. Haynes, THIS JOURNAL, **79**, 6334 (1957).

(24) The unprecedented epimerization of β- to γ-lumicolchicine in base[23] has posed a major objection to acceptance of the structure II. This objection is now obviated by mechanistic considerations based on observations pertinent to photo-γ-tropolone methyl ether (*vide infra*).