Anal. Calcd. for poly-3-(*p*-nitrophenylazo)-L-tyrosine (*n* average 30): C, 57.6; H, 3.9; N, 17.9. Found: C, 57.5; H, 4.2; N, 17.7.

Poly-3-(*p*-nitrophenylazo)-L-tyrosine is soluble in aqueous and ethanolic alkali (red-violet color), ethanol (orange-red), butylamine and ethanolamine (deep blue), and is insoluble in water, benzene and carbon tetrachloride.

Paper chromatography and paper electrophoresis of the product of reduction and hydrolysis of the polymeric azo derivative (10% stannous chloride–6 *N* hydrochloric acid, 12 hours) yielded results identical with those obtained in the case of 3,3′-di-(*p*-nitrophenylazo)-DL-tyrosine anhydride.

Poly-3,5-di-(*p*-bromophenylazo)-L-tyrosine was prepared by coupling poly-L-tyrosine (*n* average 28) with *p*-bromobenzenediazonium chloride (2 moles for each mole of tyrosine residue). After precipitation with dilute hydrochloric acid, the polymer was purified by dissolving in dilute ethanolic sodium hydroxide and reprecipitating with dilute sulfuric acid.

Anal. Calcd. for poly-3,5-di-(*p*-bromophenylazo)-L-tyrosine (*n* average 28): N, 13.2; Br, 30.1. Found: N, 13.0; Br, 29.9.

The azopolypeptide is soluble in dioxane and chloroform (yellow-greenish color), ethanolic alkali, aniline, pyridine and butylamine (dark red). It is sparingly soluble in acetone and carbon tetrachloride, and insoluble in water, ethanol, ether, aqueous acids and alkali.

Poly-*p*-(1-hydroxynaphthyl-4-azo)-DL-phenylalanine.—Poly-*p*-amino-DL-phenylalanine[5] (*n* average 20) was diazotized in the usual way, and the polymeric diazonium chloride coupled with α-naphthol. The product was precipitated with hydrochloric acid, dissolved in ethanolic sodium hydroxide, and reprecipitated with dilute hydrochloric acid.

Anal. Calcd. for poly-*p*-(1-hydroxynaphthyl-4-azo)-DL-phenylalanine (*n* average 20): C, 71.7; H, 4.8; N, 13.2. Found: C, 69.0; H, 4.9; N, 13.0.

Poly-*p*-(1-hydroxynaphthyl-4-azo)-DL-phenylalanine is soluble in ethanolic alkali (dark red color), dimethylformamide, pyridine, ethanolamine and dioxane–water (9:1 v./v.). It is sparingly soluble in aqueous alkali and in 90% ethanol, and it is insoluble in water, aqueous acids, absolute ethanol, anhydrous dioxane, benzene, acetone and chloroform.

Coupling of L-tyrosine with the diazonium salt derived from poly-*p*-aminophenylalanine (*n* average 20) yielded a **polymer of tyrosineazophenylalanine** which separated out. It was dissolved in hot dimethylformamide and precipitated with water.

Anal. Calcd. for $(C_{18}H_{18}N_4O_4)_{20}\cdot H_2O$: C, 61.0; H, 5.1; N, 15.8; equiv. wt., 354. Found: C, 60.9; H, 5.0; N, 15.9; neut. equiv., 370, determined in hot dimethylformamide by titration with 0.1 *N* sodium methoxide in benzene–methanol (1:1), using thymol blue as indicator.

The polymer is soluble in ethanolamine (red color) and dimethylformamide (yellow).

An insoluble product was obtained upon coupling poly-L-tyrosine (*n* average 30) with the diazonium salt derived from poly-*p*-aminophenylalanine (*n* average 20). On suspending the insoluble material in alkali it turned dark red.

Hydrobromide of a L-Lysine-L-tyrosine Copolymer.—ε,N-Carbobenzoxy-α,N-carboxy-L-lysine anhydride was mixed with O-carbobenzoxy-N-carboxy-L-tyrosine anhydride[4] in a molar ratio of 10:1. The mixture was polymerized in bulk[10] and the copolymer obtained was dissolved in dimethylformamide and precipitated with water.

Anal. Calcd. for a copolymer of ε,N-carbobenzoxy-L-lysine and O-carbobenzoxy-L-tyrosine in a molar ratio of 10:1 (*n* average 20): N, 10.2; amino N, 0.26. Found: N, 10.1; amino N, 0.26 (Van Slyke).

The N- and O-carbobenzoxy groups of the copolymer described above were removed with a 33% solution of anhydrous hydrogen bromide in glacial acetic acid[4,11] and the decarbobenzoxylated copolymer was precipitated with dry ether and purified by dissolving it in the minimum of water and precipitating with anhydrous ethanol and dry ether.

Anal. Calcd. for the hydrobromide of a copolymer of L-lysine and L-tyrosine in a molar ratio of 10:1 (*n* average 20): N, 13.0; amino N, 6.3; Br, 35.6; tyrosine residue, 7.2. Found: N, 13.1; amino N, 6.5 (Van Slyke); Br, 35.7; tyrosine residue, 7.3 (ultraviolet absorption).

Hydrochloride of a Copolymer of L-Lysine and 3-(*p*-Nitrophenylazo)-L-tyrosine (in a molar ratio of 10:1) (*n* average 20).—The hydrobromide of the lysine–tyrosine copolymer was coupled with *p*-nitrobenzenediazonium chloride (one mole for each mole of tyrosine residue). The colored copolymer was precipitated with picric acid, and the polymeric picrate was transformed into the hydrochloride.

Anal. Calcd. for the hydrochloride of a copolymer of L-lysine and 3-(*p*-nitrophenylazo)-L-tyrosine (in a molar ratio of 10:1) (*n* average 20): *p*-nitrophenylazotyrosine residue, 13.0. Found: 13.2, as estimated colorimetrically at 5300 Å. and *p*H 13 (residue molar extinction coefficient ε 6350).

Hydrobromide of a Copolymer of L-Aspartic Acid and *p*-Amino-DL-phenylalanine.—β-Benzyl-N-carboxy-L-aspartate anhydride was mixed with *p*,N-carbobenzoxyamino-α,N-carboxy-DL-phenylalanine anhydride[5] in a molar ratio of 9:1. The mixture was polymerized in bulk[12] and the copolymer obtained was dissolved in dimethylformamide and precipitated with water.

Anal. Calcd. for a copolymer of β-benzyl L-aspartate and *p*,N-carbobenzoxyamino-DL-phenylalanine in a molar ratio of 9:1 (*n* average 50): N, 7.2; amino N, 0.13. Found: N, 7.0; amino N, 0.13 (Van Slyke).

The benzyl and carbobenzoxy groups of the copolymer described above were removed with a 33% solution of anhydrous hydrogen bromide in glacial acetic acid[5,11] and the debenzylated copolymer was precipitated with ether.

Anal. Calcd. for a hydrobromide of a copolymer of L-aspartic acid and *p*-aminophenylalanine in a molar ratio of 9:1 (*n* average 50) N, 12.1; α-amino N, 0.22; Br, 6.2; neut. equiv., 127.7. Found: N, 12.1; amino N, 0.23 (Van Slyke); Br, 5.9; neut. equiv., 126, as determined by dissolving the copolymer in an excess of sodium hydroxide and back titration with hydrochloric acid, using phenolphthalein as indicator.

Copolymer of L-Aspartic Acid and *p*-(1-Hydroxynaphthyl-4-azo)-DL-phenylalanine.—The above described copolymer was diazotized and coupled with α-naphthol.

Anal. Calcd. for a copolymer of L-aspartic acid and *p*-(1-hydroxynaphthyl-4-azo)-DL-phenylalanine in a molar ratio of 9:1 (*n* average 50): *p*-(1-hydroxynaphthyl-4-azo)-phenylalanine residue, 23.4. Found: *p*-(1-hydroxynaphthyl-4-azo)-phenylalanine residue, 19.7, as estimated colorimetrically at 5180 Å. in ethanolamine solution (residue molar extinction coefficient ε 10000).

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Imidocarboxylate Homologs of Phenylcarbamates

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RECEIVED DECEMBER 8, 1954

Work published at the close of World War II by Templeman and Sexton[1] which mentioned the herbicidal potentiality of phenylcarbamate esters led to the investigation of a homologous series for toxicity. The resulting discovery of the plant growth regulating properties of isopropyl phenylcarbamate by this group[2] and corroborating work by Allard, *et al.*,[3] opened up a new field to botanical research.[4-6] Templeman[2] tested ethyl phenylimido-

(1) W. Templeman and W. Sexton, *Nature*, **156**, 630 (1945).

(2) W. Templeman and W. Sexton, *Proc. Roy. Soc.* (*London*), **B133** 480 (1946).

(3) R. Allard, *et al.*, *Botan. Gazette*, **107**, 589 (1946).

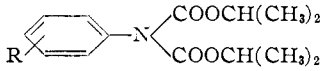
(4) R. Weaver, *ibid.*, **109**, 72 (1947).

(5) R. Weaver, *ibid.*, **109**, 276 (1948).

(6) W. Ennis, *ibid.*, **109**, 473 (1948).

TABLE I

ISOPROPYL PHENYLIMIDODICARBOXYLATES



R	Carbamate M.p. or b.p. (mm.), °C.	Imidodicarboxylate M.p. or b.p. (mm.), °C.	Nitrogen, %[b] Found	Calcd.	Carbon, % Found	Calcd.	Hydrogen, % Found	Calcd.
H	Not taken	82–83	5.2	5.3	63.68	63.37	7.16	7.23
3-Cl	Not taken	46–47[a]	4.7	4.7	55.92	56.09	5.94	6.06
3-CH_3	142–145 (4)	138–140(4)	4.9	5.0	65.92	64.48	7.73	7.59
3-F	60–62 (5)	69–71	5.0	4.9	59.53	59.34	6.40	6.42
4-F	85–86	59–60	4.7	4.9	59.56	59.34	6.33	6.42
4-Cl	55–57	68–69	4.3	4.7	56.10	56.09	6.10	6.06
3-Br	145–148	59.60	4.1	4.1	49.06	48.84	5.26	5.28
4-Br	Not taken	93–94	4.2	4.1	48.86	48.84	5.23	5.28
3-I	50–52	42–43	3.3	3.6	43.75	42.98	4.89	4.65
4-I	114–115	126–127	3.4	3.6	43.05	42.98	4.80	4.65

[a] Melts at 38°, resolidifies and remelts at 46–47°. [b] Kjeldahl N.

dicarboxylate as well and found it toxic, but published no further work on this series. As these compounds are relatively unknown, the synthesis and properties of some ring substituted phenylimidodicarboxylates are reported herewith.

Diels and Nawiasky[7] and Tompkins and Degering[8] obtained phenylimidodicarboxylic esters by treating alkyl phenylcarbamates with sodium and then adding alkyl chloroformates to the salt thus formed. This procedure was adapted successfully to the synthesis of ring-halogenated phenylimidodicarboxylates by treating the corresponding carbamates with finely divided sodium in ether at room temperature. Compounds containing each of the four common halogens were prepared and under these conditions no extensive reaction occurred at the halogen atom with sodium since yields of the halophenylimidodicarboxylates were better than 50%.

The method failed with β-chloroethyl phenylcarbamate, and 3-phenyl-2-oxazolidone was the only product isolated.

Although the hitherto unreported carbamates were not analyzed, their structure is established by the well-known method of their preparation and the analyses of their corresponding imidodicarboxylate derivatives. Where the phenylimidodicarboxylate was a solid, mixed melting points were taken with the corresponding carbamates. In all cases depression was observed.

Experimental

General Method for the Preparation of Isopropyl Phenylimidodicarboxylates.—The appropriate halosubstituted phenylcarbamate was prepared from the aniline and isopropyl chloroformate by the Schotten–Baumann reaction and purified either by recrystallization or distillation under reduced pressure. Sodium powder (0.1 mole) and the carbamate (0.1 mole) were stirred together at room temperature in 200 ml. of sodium-dried ether for 24 to 36 hours until all of the sodium had reacted to form the sodium salt of the carbamate by replacement of the amide hydrogen.

Isopropyl chloroformate (0.1 mole) in 50 ml. of absolute ether then was added in portions over a period of 2 hours (causing refluxing) and stirring continued for an additional 24 hours. The resulting mixture was washed with water to remove the sodium chloride that had formed, and the ether solution dried over sodium sulfate. The solvent was removed by evaporation in an air stream on the steam-bath, leaving a sirup which usually crystallized upon cooling. This was recrystallized from petroleum ether (d. 0.67–0.69), or ether ligroin, or redistilled to give the pure phenylimidodicarboxylate.

Allyl Phenylimidodicarboxylate.—The allyl phenylcarbamate was added to an equivalent amount of sodium powder as described above, and stirred for 48 hours. Half the requisite amount of allyl chloroformate was added at once, whereupon the ether commenced to boil rapidly. After 30 minutes the remainder of the chloroformate was added and the resulting mixture refluxed 24 hours and worked up. A clear colorless oil was obtained, b.p. 148–150° (5 mm.).

Anal. Calcd. for $C_{14}H_{15}NO_4$: N, 5.4; C, 64.35; H, 5.80. Found: N, 5.4; C, 64.64; H, 6.01.

2,3-Dibromopropyl Phenylimidodicarboxylate.—Allyl phenylimidodicarboxylate (0.1 mole) was dissolved in 50 ml. of glacial acetic acid and 0.2 mole of bromine was added dropwise with stirring. After the addition was complete, the mixture was stirred an additional 30 minutes and then diluted with water. An oil separated which solidified upon standing for two days. This solid was recrystallized from ether–ligroin to give colorless crystals of 2,3-dibromopropyl phenylimidodicarboxylate, m.p. 105–107°.

Anal. Calcd. for $C_{14}H_{15}Br_4NO_4$: N, 2.4; C, 28.94; H, 2.81. Found: N, 2.3; C, 26.20; H, 2.57.

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Triton B in Synthesis of 3-Phenylcyclohexenones

BY GORDON N. WALKER

RECEIVED FEBRUARY 21, 1955

Among the known methods of synthesis of unsaturated 3-(or 5)-phenylcyclohexanones are Knoevenagel condensation of benzaldehydes with two molecules of β-ketoester, a process which gives rise initially to dicarbalkoxy-3-hydroxy-5-phenylcyclohexanones, such as Ia,[1] and later, after treatment with a sodium alkoxide, the unsaturated ketone[2,3]; and addition of β-ketoesters to phenyl vinyl ketones or Mannich bases equivalent to such ketones,[4] which reaction also involves cyclization and furnishes 3-phenyl-6-carbethoxycyclohex-2-ene-1-ones, such as II, from which 3-phenylcyclohex-2-ene-1-ones (V) are obtained by hydrolysis and decarboxylation.

A new method for preparing V now has been found. Reaction of ethyl benzoylacetate and methyl vinyl ketone in the presence of benzyltrimethylammonium hydroxide (Triton B) in *t*-butyl alco-

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