Benzyl esters of amino acids have been prepared by the coupling of amino acid chloride hydrochlorides with benzyl alcohol[4,5,6] and through the use of benzyl alcohol saturated with dry hydrogen chloride.[7] Bergmann, *et al.*,[8] have coupled N-carbonic acid anhydrides of amino acids with benzyl alcohol. These methods are laborious and tend to low yields. We have found that esterification takes place in good yield when the amino acid is rendered soluble in benzyl alcohol by the formation of a benzenesulfonic acid salt. The preparation of the benzyl esters of glycine, DL-phenylalanine and L-leucine is reported.

Experimental

Glycine Benzyl Ester.—A solution of 75 g. (1 mole) of glycine and 174 g. (1.1 moles) of benzenesulfonic acid dissolved in 500 g. of benzyl alcohol by gentle heating was distilled *in vacuo* with a bath temperature not exceeding 130°. After most of the benzyl alcohol was removed, the hot mass was poured into a mortar and a half-liter of ether was added as soon as it had cooled sufficiently to prevent the ether from boiling too vigorously. The mass was then rubbed until crystallization ensued, washed with ether and air-dried. The impure material (314 g.) was dissolved in 500 g. of benzyl alcohol, an additional 5 g. of benzenesulfonic acid was added and the benzyl alcohol was again removed *in vacuo* as described above. The crystallization (as above) yielded 323 g. (100%). This salt may have as impurity a small amount of unreacted glycine benzenesulfonate. For purification the salt may be converted to the hydrochloride.

To a suspension of 65 g. (0.2 mole) of the glycine benzyl ester benzenesulfonate in 300 ml. of chloroform at 0–5°, 20 g. (0.2 mole) of triethylamine was added over a period of ten minutes. After addition of one liter of absolute ether the mixture was allowed to stand for ten minutes after which time the precipitated triethylammonium benzenesulfonate was filtered off and the ethereal solution concentrated *in vacuo* with rigid exclusion of moisture. The remaining pale yellow oil weighed 23–26 g. (70–80%).

Glycine Benzyl Ester Hydrochloride.—An ethereal solution of glycine benzyl ester was treated with dry hydrogen chloride until no further precipitation of the hydrochloride occurred. The hydrochloride crystallized out in about 70% yield. It may be stored indefinitely and can be further purified by recrystallization from hot benzyl alcohol or ethylene glycol monomethyl ether acetate (methyl cellosolve acetate), m.p. 131–132°.[8]

Anal. Calcd. for $C_9H_{12}O_2NCl$ (201.7): Cl, 17.58. Found: Cl, 17.56.

The hydrochloride is readily converted to the free base by neutralization with triethylamine in the same manner as described for the glycine benzyl ester benzenesulfonate.

DL-Phenylalanine Benzyl Ester Hydrochloride.—To 8.7 g. (0.055 mole) of benzenesulfonic acid dissolved in 100 g. of warm benzyl alcohol 8.25 g. (0.05 mole) of DL-phenylalanine was added and esterification was carried out exactly as in the case of glycine ester. After the second removal of benzyl alcohol about 20 g. (97%) of the crude phenylalanine benzyl ester benzenesulfonate was obtained. This product was converted to the hydrochloride from the free base obtained by the action of triethylamine on the benzenesulfonate as in the method for glycine benzyl ester hydrochloride described above. The yield of phenylalanine benzyl ester hydrochloride was 10.9 g. (75%). It was recrystallized from hot benzyl alcohol, m.p. 196°.

Anal. Calcd. for $C_{16}H_{18}O_2NCl$ (291.8): Cl, 12.15. Found: Cl, 12.11.

L-Leucine Benzyl Ester Hydrochloride.—To 34.8 g. (0.22 mole) of benzenesulfonic acid dissolved in 100 ml. of warm benzyl alcohol 26.2 g. (0.2 mole) of L-leucine was added and esterification was carried out exactly as in the case of glycine ester. After the second removal of benzyl alcohol about 72 g. (95%) of the crude leucine benzyl ester benzenesulfonate was obtained. This product was suspended in 200 ml. of chloroform and 26.6 ml. (0.19 mole) of triethylamine was added over a period of 15 minutes while the suspension was continually stirred in an ice-bath. To the resulting solution 400 ml. of anhydrous ether was added and the precipitated triethylammonium benzenesulfonate was removed by filtration. The supernatant solution was saturated with dry HCl and taken to dryness *in vacuo*. The residue was dissolved in 25 ml. of hot chloroform and 350 ml. of hot cyclohexane was added. After 16 hours at 0–5°, the crystalline product was collected, washed with cyclohexane and dried *in vacuo* (yield 38 g). An additional yield of 7 g. was obtained from the mother liquor by the addition of another volume of cyclohexane (88% based on the amount of leucine used). It was recrystallized from chloroform–cyclohexane, m.p. 129°.

Anal. Calcd. for $C_{18}H_{20}O_2NCl$ (257.6): Cl, 13.76. Found: Cl, 13.80; $[\alpha]^{30}D$ −8° (2% in 0.1 *N* HCl).

The optical homogeneity of the ester was demonstrated by the optical rotation of the L-leucine derived from it by hydrogenation; $[\alpha]^{30}D$ +15.5° (2% in 6.09 *N* HCl) *cf.* Dunn, *et al.*[9] No racemization occurred, therefore, during the esterification.

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(9) Dunn, *et al.*, *J. Biol. Chem.*, **144**, 487 (1942).

DEPARTMENT OF BIOCHEMISTRY
COLLEGE OF PHYSICIANS AND SURGEONS
COLUMBIA UNIVERSITY, NEW YORK, AND THE
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Tris-(β-chloroallyl) Phosphate[1]

BY ROBERT M. REINHARDT

Tris-(β-chloroallyl) phosphate has been prepared by a method analogous to that of Whitehill and Barker[2] for the preparation of triallyl phosphate.

To a mixture of 240 g. (2.59 mole) of β-chloroallyl alcohol,[3] 240 g. of toluene and 400 g. of anhydrous pyridine in a 2-liter, 3-necked flask equipped with thermometer well, mechanical stirrer, and dropping funnel, was added 111 g. (0.72 mole) of phosphorus oxychloride in 111 g. of toluene, dropwise, and with stirring. The reaction temperature was maintained at −35 to −40° throughout the addition by immersion of the flask in an acetone–Dry Ice-bath. With rapid stirring the addition was complete in approximately 1 hour. The mixture was maintained at −40° for an additional hour; then allowed to warm to room temperature. One liter of distilled water was added to dissolve the pyridine hydrochloride formed in the reaction. The toluene layer was separated and washed successively, in a separatory funnel, with 600 ml. of water, 600 ml. of 15% sodium carbonate solution and 600 ml. of water. The toluene layer was dried over sodium carbonate and stripped of solvent and of unreacted β-chloroallyl alcohol under vacuum (18 mm.) at a temperature below 50° leaving 167 g. of crude product (71.8%).

Vacuum distillation of 21.4 g. of the crude product, with 0.3 g. of hydroquinone and 3 g. of sodium carbonate (to prevent explosion),[4,5] yielded 14.6 g. of tris-(β-chloroallyl)

(1) Contribution from the Southern Regional Research Laboratory, one of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

(2) L. N. Whitehill and R. S. Barker (to Shell Development Co.), U. S. Patent 2,394,829 (1946).

(3) Supplied through the courtesy of the Shell Development Company, Emeryville, California.

(4) Anon., *Chem. Eng. News*, **28**, 3452 (1950).

(5) E. P. Plueddemann (to Food Machinery and Chemical Corporation) U. S. Patent 2,494,310 (1950).

phosphate, b.p. 131–133° (1 mm.); was insoluble in water, soluble in toluene and ether; did not decolorize bromine in carbon tetrachloride at room temperature; η^{20} D 1.4866.

Anal. Calcd. for $C_9H_{12}O_4Cl_3P$: Cl, 33.08; P, 9.63. Found: Cl, 32.5; P, 9.43.

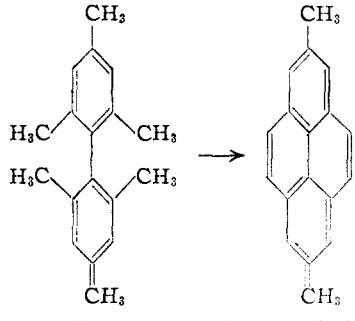
SOUTHERN REGIONAL RESEARCH LABORATORY
NEW ORLEANS, LOUISIANA RECEIVED NOVEMBER 2, 1951

Aromatic Cyclodehydrogenation. XI. Experiments with Dimesityl[1]

BY MILTON ORCHIN, LESLIE REGGEL AND R. A. FRIEDEL

In a continuation of cyclodehydrogenation experiments[2] designed to demonstrate conversion of simple aromatics to polynuclear compounds at temperatures comparable to those employed in the pyrolysis of coal, the behavior of dimesityl was studied. It has been shown previously that vapor-phase treatment of di-*o*-tolyl leads to 4-methylfluorene,[3] but with dimesityl it might be expected that the cyclization would be forced to give phenanthrenes and pyrenes. If demethylation occurred before cyclodehydrogenation, substituted fluorenes would be obtained.

A series of cyclodehydrogenation experiments under various conditions using sulfur, palladium-on-charcoal, selenium and chromia-on-alumina catalysts is described below. In only one case was a compound isolated to which a structure could unequivocally be assigned; treatment of 17.8 g. of dimesityl over chromia-on-alumina at 500° gave 3 mg. of 4,9-dimethylpyrene



In other experiments, evidence of less highly substituted pyrenes and mixtures of phenanthrenes and fluorenes was also obtained.

Experimental

The many ultraviolet spectra employed as a means of identifying the ring systems of various fractions were determined with a Beckman spectrophotometer and with a Cary Recording Spectrophotometer, using 95% ethanol as solvent. Because pure compounds were seldom isolated and the spectra of all the parent polynuclear ring systems are well-known and are collated elsewhere,[4] no spectra are given in this paper. We wish to thank Lois Pierce, Ruth Borgman, Lois Harnack, Marian Springer and Robert Zange for the spectra determinations. Microanalyses are by G. L. Stragand, University of Pittsburgh.

Sulfur Dehydrogenation (a).—Dimesityl was heated with sulfur for 0.5 hour at 270–280°. No fluorescent products were obtained.

(b).—A mixture of 14.09 g. of dimesityl and 15.20 g. of sulfur was heated at 320–360° for 15 minutes. Gas was evolved rapidly, and the material became black and tarry and foamed vigorously, but showed no tendency to distil. On cooling, a black, brittle, feathery mass formed. This was extracted with benzene (soxhlet, 24 hours). An attempt to remove the sulfur by chromatography failed. The solvents were distilled off, the product was dissolved in alcoholic potassium hydroxide, and the sulfur was oxidized to sulfate by means of hydrogen peroxide.[5] There was obtained 1.15 g. of red, tarry material, not further investigated.

In a preliminary experiment, a mixture of anthracene, pyrene and sulfur was treated with hydrogen peroxide in the presence of alcoholic alkali. Precipitation of the sulfur as barium sulfate resulted in a quantitative recovery; the organic fraction was colorless and gave no test for an anthraquinone, showing that no oxidation of the hydrocarbons had occurred.

(c).—A mixture of 5.00 g. of dimesityl and 2.69 g. of sulfur was heated at 245–255° (bath) for 15 minutes; there was no apparent reaction. The mixture was then distilled at the water-pump (bath temperature 275–290°); some gas was evolved. The residue was a tar. The distillate (2.50 g.) was chromatographed; no fluorescent band was found. Impure dimesityl (1.87 g.) was obtained; the absence of pyrenes and phenanthrenes was confirmed by the ultraviolet spectrum.

Selenium Dehydrogenation.—Dimesityl was heated with selenium in a sealed tube (a) for 27 hours at 344–420°; (b) for 8 days at 260–400°. In both experiments the products were chromatographed to give small amounts of fluorescent oils, but no crystalline material was obtained.

Palladium-on-charcoal Dehydrogenation (a).—Dimesityl heated up to 350° with palladium-on-charcoal[2,6] did not evolve gas.

(b).—During 3 hours, 1.89 g. of dimesityl was passed through a furnace[2] packed with palladium-on-charcoal[2,6] at 495–510°. The product (1.22 g.) was chromatographed on alumina–supercel. The fluorescent band gave 0.24 g. of an oil which was treated with *s*-trinitrobenzene. The complex (90 mg., m.p. 137–185°) was recrystallized twice from methanol, giving 3 mg. of material, m.p. 207–240°. The ultraviolet spectrum was that of pyrene, not of an alkyl pyrene.

Chromia-on-alumina Dehydrogenation (a).—During 3 hours, 17.80 g. of dimesityl was passed over 81 g. of chromia-on-alumina[7] catalyst at 475–525°. The product (16.94 g.) was recrystallized from 95% alcohol, giving 13.82 g. of unreacted dimesityl. The mother liquor was freed of alcohol, taken up in petroleum ether, chromatographed on alumina, and the blue fluorescent band eluted with benzene. The fluorescent material (1.18 g.) was then rechromatographed on alumina–supercel, and a purple-fluorescent band (0.79 g. of crystalline material) was separated. Fractional crystallization from ethanol and methanol gave, as the least soluble fraction, 3 mg. of material that began to soften at 216° and had a melting point of 228.0–232.0. This was identified as 4,9-dimethylpyrene by conversion to the 2,4,7-trinitrofluorenone complex, m.p. 227.3–228.0°, not depressed by an authentic sample.[8] The balance of the material was intensively investigated by means of chromatography and complexes with picric acid and *s*-trinitrobenzene, but no pure material could be isolated. Ultraviolet absorption spectra indicated the presence of pyrene derivatives other than 4,9-dimethylpyrene and of derivatives of phenanthrene, fluorene and 9,10-dihydrophenanthrene.

(b).—Sixteen grams of dimesityl was contacted with 2.09 g. of Cr-181 catalyst[7] at 414–450° and 127–150 p.s.i. (nitrogen atmosphere) for 5¾ hours in a small pressure-extraction apparatus. The black, tarry product was dissolved in benzene, chromatographed on alumina, and the column eluted. The fractions were taken to dryness and the ultraviolet spectra were determined. There was obtained 7.82 g. of dimesityl, 0.05 g. of a colorless oil consisting of dihydrophenanthrenes and dimesityl, 0.82 g. of a pale-yellow oil consisting of substituted dihydrophenanthrenes and fluorenes, 0.49 g. of a pale-yellow oil consisting of fluorenes and phenanthrenes, 0.13 g. of white low-melting solid consisting

(1) Not subject to copyright.

(2) M. Orchin, L. Reggel, R. A. Friedel and E. O. Woolfolk, Bureau of Mines Technical Paper 708 (1948).

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(7) Harshaw Chemical Co., Cleveland, Ohio; catalyst Cr-181.

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