ately substituted benzoyl chloride to react with dibenzoylmethane in the presence of sodium ethoxide. The *p*-nitro- and *p*-methoxytribenzoylmethane have been reported by Curtin and Russell[6] and their results were repeated. The *p*-chlorotribenzoylmethane seems to be new, and it apparently was obtained as a mixture of the enol and keto forms. Its melting point (uncorrected) remained at 189–204° after five recrystallizations from benzene–petroleum ether (b.p. 60–68°).

Anal. Calcd. for $C_{22}H_{15}ClO_3$: C, 72.83; H, 4.17. Found: C, 72.77; H, 4.35.

Hydrolysis of the tribenzoylmethanes. A mixture of 150 ml. of glacial acetic acid, to which a few milliliters of water had been added, and approximately 0.015 mole of the tribenzoylmethane was heated at reflux for 2 hr. The resulting solution was poured into 1 l. of water and the precipitate was removed by filtration. The solid was stirred with sodium bicarbonate solution to dissolve acidic materials, and the mixture of dibenzoylmethanes was removed by filtration. The combined filtrates, which were still acidic, were extracted ten times with ether and the crude acids were obtained by evaporation of the ethereal solutions under reduced pressure.

The mixtures of dibenzoylmethanes were separated by fractional crystallization from methanol. The mixed benzoic acids were dissolved in sodium carbonate solution and the solution was washed with petroleum ether (b.p. 60–68°). The acids were reprecipitated with hydrochloric acid and separated by fractional crystallization from water.

The melting points of the substituted dibenzoylmethanes and benzoic acids corresponded with those recorded in the literature. The percentage yields of the various cleavage products obtained are given in Table I.

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Synthesis of DL-Threoninol

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During the course of an investigation of the anticoagulant activity[1] of synthetic sphingosine[2] and its derivatives we became interested in studying the behavior of both diastereoisomers of threoninol which is the lowest homologue of dihydrosphingosine.

Carter and coworkers[3] obtained the pure oxalate of allothreoninol by hydrogenation of allothreonine methyl ester with Raney nickel under high pressure. However, an attempt to prepare threoninol similarly resulted in a mixture of the epimers. Recently threoninol has been prepared by reduction of threonine ethyl ester with lithium aluminum hydride,[4] and by hydrolysis of *N*-benzoylthreoninol obtained by treatment of *N*-benzoylthreonine ethyl ester with lithium borohydride.[5] In both cases, however, the raw products were converted directly into the dinitrophenyl derivatives without specification of yields. We wish now to report a convenient synthesis of threoninol.

When the benzamido esters of allothreonine and threonine were reduced with lithium aluminum hydride and the resulting benzylaminodiols were debenzylated with palladium-on-charcoal the pure oxalates of both allothreoninol and threoninol were obtained in excellent yields. The benzamido esters were prepared by selective reduction of ethyl α-benzamidoacetoacetate with sodium borohydride.[2]

EXPERIMENTAL

Reduction of ethyl α-benzamidoacetoacetate with sodium borohydride. Ten g. of 2-phenyl-4-(1-hydroxyethylidene)-oxazolone-5[6] were refluxed for 2 hr. with 100 cc. of absolute alcohol. The dark red solution was decolorized with charcoal and cooled to 20°. A solution of 0.8 g. sodium borohydride in 20 cc. of methanol (stabilized with a few drops of normal sodium hydroxide) was added dropwise and the mixture left for 30 min. Twenty ml. of water were then added and a few drops of acetic acid to bring the solution to *p*H 6. It was then evaporated *in vacuo* and the oil extracted with 60 cc. of hot chloroform. After evaporation of the solvent the residue was taken up with 15 cc. of ether and left overnight at 0°. A crystalline precipitate (3.5 g.) of m.p. 75–91° was collected which, after three crystallizations from ethyl acetate and petroleum ether (2:3) gave 2.5 g. of *N*-benzoylallothreonine ethyl ester, m.p. 101–102°. From the collected mother liquors the threonine ester was obtained following the procedure of Elliott.[7]

*N-benzyl-*DL*-allothreoninol.* To a stirred suspension of 2 g. of lithium aluminum hydride in 50 cc. of tetrahydrofuran (distilled over lithium aluminum hydride) was added slowly a solution of 4 g. of *N*-benzoylallothreonine ethyl ester in 50 cc. of tetrahydrofuran and the mixture was refluxed for 2 hr. After cooling in an ice bath 3 cc. of water was added followed by 3 cc. of 20% sodium hydroxide and 6 cc. of water. The precipitated inorganic salts were filtered off and washed with ether. The combined filtrates were washed with saturated sodium chloride solution and dried over sodium sulfate. Evaporation of the solvent left an oil which was dissolved in 20 cc. of hot benzene and precipitated with 40 cc. of petroleum ether. There was obtained 3.1 g. (99%) of crystals m.p. 56–60°. Crystallization from benzene–petroleum ether (2:3) yielded 2.3 g. of m.p. 62–63°.

Anal. Calcd. for $C_{11}H_{17}O_2N$: C, 67.6; H, 8.8; N, 7.1. Found: C, 67.0; H, 8.7; N, 6.6.

*N-benzyl-*DL*-threoninol*, prepared as above, was obtained in a 90% yield as an oil which could not be induced to crystallize and was used directly for debenzylation.

DL*-Allothreoninol.* 2.3 g. of *N*-benzylallothreoninol dissolved in 50 cc. of alcohol was hydrogenated with 1 g. palladium-on-charcoal (10%) at 50 p.s.i. and 40° for 15 hr. The oil obtained after evaporation of the filtrate was dissolved in 30 cc. absolute alcohol and converted into the

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neutral oxalate by adding a solution of 1 g. anhydrous oxalic acid in 10 cc. absolute alcohol. Yield 1.65 g. (93%). It was recrystallized from 80% alcohol and had a m.p. 201–202°.

Anal. Calcd. for $C_{10}H_{24}O_8N_2$: C, 40.0; H, 8.0; N, 9.3. Found: C, 39.9; H, 8.1; N, 9.3.

DL-*Threoninol.* Three and one half g. of raw *N*-benzylthreonine was debenzylated as above and converted into the neutral oxalate. Yield 2.55 g. (94%). After recrystallization from 80% alcohol, it had m.p. 211.5° (dec.).

Anal. Calcd. for $C_{10}H_{24}O_8N_2$: C, 40.0; H, 8.0; N, 9.3. Found: C, 40.0; H, 7.6; N, 9.3.

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C=N Stretching Frequency in Infrared Spectra of Aromatic Azomethines

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In conjunction with a study of the stereochemistry of aromatic Schiff-bases, 17 compounds of this type have been synthesized by standard techniques[1] and their infrared spectra determined. Each compound was found to exhibit an absorption band of medium intensity in the double-bond stretching region at 1613–1631 cm.$^{-1}$, as shown in Table I. This band, which occurs in the spectra just to the high frequency side of the normal aromatic band near 1600 cm.$^{-1}$, appears to be of considerable diagnostic value.

TABLE I

C=N STRETCHING FREQUENCIES IN AROMATIC SCHIFF BASES. (Measurements made on Beckman IR-3 spectrophotometer, NaCl optics.)

Compound	Frequency (cm^{-1})^a
N-benzylidineaniline*	1631
N-(2-hydroxy)benzylidineaniline*	1622
N-(4-hydroxy)benzylidineaniline	1629^b
N-(4-methoxy)benzylidineaniline*	1630
N-(2-nitro)benzylidineaniline	1621^b
N-(4-acetylamino)benzylidineaniline	1629^b
N-(4-dimethylamino)benzylidineaniline*	1626
N-benzylidine-2-aminophenol	1629
N-benzylidine-2-anisidine	1631^c
N-(4-methoxy)benzylidine-2-anisidine	1627^c
N-benzylidine-4-anisidine*	1629
N-(4-methoxy)benzylidine-4-anisidine	1626^b
N-benzylidine-4-toluidine	1628^c
N-benzylidine-*N'*-dimethyl-4-phenylenediamine*	1627
N-(2-hydroxy)benzylidine-2-aminophenol	1624^b
N-(4-dimethylamino)benzylidine-2-aminophenol	1613
N,*N'*-dibenzylidine-4-phenylenediamine	1628

^{a} in CCl_4 solution; ^{b} in $CHCl_3$ solution; ^{c} as KBr pellets; * indicates the compounds reduced using $NaBH_4$.

(1) Cf. G. Smets and A. Delvaux, *Bull. soc. chim. Belg.*, **56**, 106 (1947).

The absorption frequency characteristic of the stretching mode of the C=N group in compounds of this type has not been known with any degree of certainty.[2] Therefore, in order to ascertain whether the absorption band in this region was attributable to the C=N group, it was necessary to compare the infrared spectra of the Schiff-bases with those of similar compounds that do not contain this grouping. Consequently, six of the azomethines listed in Table I were reduced to the corresponding substituted *N*-benzylanilines by means of sodium borohydride, using a modification of the procedure of Chaikin and Brown.[3] Since this band is absent in the infrared spectra of these amines, this indicates that the absorption bands shown by *N*-benzylidine aniline and its ring-substituted derivatives are indeed due to the stretching mode of the C=N group.

It is also worth noting that the sodium borohydride reduction of aromatic azomethines usually proceeds very smoothly and results in fair yields (60–80% of theoretical). Consequently this reaction may find application in the synthesis of secondary amines of this type.

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Chloroalkyl and Chloroaryl Chloromethylphosphonates

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In 1950, Kabachnik and Medved reported the preparation of chloromethylphosphonic dichloride by the reaction of paraformaldehyde with phosphorus trichloride.[1] We have prepared and characterized several chlorinated esters from this acid chloride.

In order to prevent alkyl halide formation when an alcohol reacts with a phosphonic chloride, it is generally necessary to use a tertiary amine to absorb the liberated hydrogen chloride. We found, however, that 2-chloroethanol and 2,2,2-trichloroethanol could be successfully treated with chloromethylphosphonic dichloride at reflux tempera-

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