Photochemical Solvolysis of Optically Active 3,5-Dimethoxy-α-d-Benzyl Acetate

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PHOTOCHEMICAL SOLVOLYSIS OF OPTICALLY ACTIVE
3,5-DIMETHOXY-α-β-BENZYL ACETATE

A thesis presented to the Committee on Graduate Studies and the Department of Chemistry of Union College, Schenectady, New York, in partial fulfillment of the requirements for the degree of Master of Science.

by Peter J. Frank, M.S. 1972

By

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Committee on Graduate Studies

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to the
Department of Chemistry of Union College
in partial fulfillment of the requirements of the degree of
Master of Science in Chemistry

is approved by

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Abstract

The purpose of this work was the stereochemical study of the photochemical solvolytic reaction of 3,5-dimethoxy-α-d-benzyl acetate.

From 3,5-dihydroxybenzoic acid, optically active 3,5-dimethoxy-α-d-benzyl alcohol was prepared. The specific rotation of the alcohol was compared to the alcohol produced from the photochemical solvolytic reaction of 3,5-dimethoxy-α-d-benzyl acetate.
Acknowledgement

I wish to thank Dr. Alan Maycock of Union College for his help. I would also like to thank the W. Howard Wright Research Center of Schenectady Chemicals Inc., the General Electric Company, and the State University of New York at Albany for use of their chemicals and facilities.
Zimmerman and Sandel have studied the solvolytic photochemical reaction of 3,5-dimethoxybenzyl acetate. They use the 3,5-dimethoxybenzyl carbonium ion to explain how the solvolysis products are produced. However, Zimmerman and Sandel do not prove that a carbonium ion is indeed present in their reaction.

This could be shown by making an optically active derivative of 3,5-dimethoxybenzyl acetate and after a solvolytic photochemical reaction the major product formed (3,5-dimethoxylbenzyl alcohol) could be tested for optical activity. If a free carbonium ion is involved the product will be racemic ($\text{SN}_1$). But if a pentavalent transition state is involved in solvolysis, inversion of configuration will be observed ($\text{SN}_2$).

A derivative that might be used is the 3,5-dimethoxy-\(\alpha\)-d-benzyl acetate. Besides containing the asymmetrical carbon atom to give optical activity, it preserves the electron configuration associated with 3,5-dimethoxybenzyl acetate.
Discussion

The route to the synthesis of the optically active 3,5-dimethoxy-α-d-benzyl acetate follows:

The 3,5-dihydroxybenzoic acid (I) was treated with excess dimethyl sulfate and 3,5-dimethoxybenzoic acid (II) was recovered in a 45% yield. Compound II was then reacted with an excess of thionyl chloride, and the liquid product formed solidified, after vacuum distillation.

Because of the expense of our deuterium source, in the synthesis of 3,5-dimethoxy-α-d-benzyl acetate (VI) we first used undeuterated materials to sharpen up on techniques. 3,5-dimethoxybenzyl alcohol was made by reducing both II and III with lithium aluminum hydride. It was found that the purity of the reducing agent was critical in obtaining a good yield of 3,5-dimethoxybenzyl alcohol and that III reduced much easier than II. This phenomenon is in agreement with March, where he shows in table 7 the ease of reduction of various functional groups with lithium aluminum hydride in ether. Having
the 3,5-dimethoxybenzyl alcohol, 3,5-dimethoxybenzyl acetate was made, using excess acetic anhydride and concentrated sulfuric acid as a catalyst. It is with this 3,5-dimethoxybenzyl acetate that solvolytic photochemical practice runs were made.

The next compound to be made was 3,5-dimethoxybenzaldehyde (IV). Some thought had to be given to the type of reducing conditions that would have to be used in preparing IV. If strong reducing conditions were used, II or III would be reduced to the 3,5-dimethoxybenzyl alcohol. The Rosenmund reduction was decided upon to reduce the acid chloride (III) to the corresponding aldehyde (IV), in a 58% yield.

A modified procedure developed by Streitwieser and Wolfe was used to make both 3,5-dimethoxybenzyl alcohol for practice and 3,5-dimethoxy-α-p-benzyl alcohol (V) at 50% yields. The stereospecific reducing agent isobornylcymagnesium bromide, prepared by the reduction of D-camphor with lithium aluminum hydride or deuteride followed by treatment of the alcohol with D-propyl magnesium bromide, was reacted with IV. Because of the geometry of the magnesium bromide salt of isoborneol, a single enantiomer of 3,5-dimethoxy-α-p-benzyl alcohol is obtained.
The infrared spectrum of V shows the C-D band at 4.77 \( \mu \) indicating that deuterium incorporation did, in fact, take place. Also, the NMR spectrum of 3,5-dimethoxybenzyl alcohol shows the proton absorption at 4.68 \( \delta \) indicative of protons attached to a carbon carrying an electronegative oxygen atom. The 3,5-dimethoxy-\( \alpha \)-dibenzyl alcohol, however, shows half as many hydrogens by integration. Also, optical rotations taken on compound V showed it to have a substantial rotation of \([\alpha]_{20}^{20^o} = -3.75 \pm 0.8\) at 450\( m\mu \) and \([\alpha]_{20}^{20^o} = -5.10 \pm 0.8\) at 400\( m\mu \). This substantiates the fact that an asymmetrical carbon atom is present due to a deuterium atom being present.
The solvolytic photochemical reaction of 3,5-dimethoxybenzyl acetate was achieved by the procedure of Zimmerman and Sandel. Before the solution of 3,5-dimethoxybenzyl acetate in dioxane-water was exposed to ultraviolet light (254 nm), aliquots were removed to obtain a 0 hr. reading and a "control" to measure any thermal solvolysis reaction that may take place. The 0 hr. reading ("blank") showed a substantial acidity and some problems were expected in obtaining complete conversion of the 3,5-dimethoxybenzyl acetate to the 3,5-dimethoxybenzyl alcohol. However, after 3 hr. of reaction, almost complete agreement was found with Zimmerman and Sandel's data. The "control" was an aliquot of the mixture in a test tube covered with aluminum foil placed along side the quartz reaction vessel. The Rayonet photochemical reactor, although equipped with a fan to expell the heat liberated by the U.V. lamps, developed a temperature of 40°. Using 0.002N sodium hydroxide titrations of the "control" after the solvolysis reaction was complete, showed no thermal solvolysis reaction had occurred. After 6 hr., the reaction slowed down considerably and an 88% conversion of the acetate VI to the alcohol was found by titration of the acetic acid liberated. Solvolytic photochemical reaction of the 3,5-dimethoxy-α-d-benzyl acetate was achieved in the same manner as the 3,5-dimethoxybenzyl acetate.

The "control" in this case also showed no thermal solvolysis reaction had taken place. A 98% conversion of the acetate to the alcohol was determined by the acetic acid liberated.
Chromatography on silica gel was used to separate products. A 45% yield was found for the preparative chromatography of 3,5-dimethoxybenzyl alcohol and a 50% yield of 3,5-dimethoxy-α-d-benzyl alcohol. Both products were shown to be pure by VPC analysis.

Optical rotations on the 3,5-dimethoxy-α-d-benzyl acetate and the 3,5-dimethoxy-α-d-benzyl alcohols were taken on both a Zeiss Wenkel and a Jasco polarimeter. However, the Zeiss Wenkel polarimeter was not accurate enough for our purposes, due to the low specific rotations of the optically active benzyl derivatives.

Using the Jasco, we attempted to obtain an optical rotatory dispersion curve showing a Cotton effect. However, a 10% solution of 3,5-dimethoxy-α-d-benzyl alcohol was found to have a high extinction coefficient and would not lend itself to this technique. Therefore, an "ORD curve" was obtained, showing the observed rotation versus wavelength.

Colorless solutions of the 3,5-dimethoxy-α-d-benzyl alcohol (V) and the 3,5-dimethoxy-α-d-benzyl acetate (VI) in ethanol were found to have a negative observed rotation compared to the "blank". A slightly opalescent solution of the 3,5-dimethoxy-α-d-benzyl alcohol, obtained from the photochemical solvolysis reaction, showed a very small positive observed rotation compared to the "blank".

Using the observed rotations at different wavelengths, several specific rotations were calculated using the formula:
\[
\begin{align*}
\left[ \alpha \right]_m^{20} &= \frac{\left[ \alpha \right]}{1 \times c} \\
\left[ \alpha \right]_m^{20} &= \text{specific rotation} \\
\left[ \alpha \right] &= \text{observed rotation} \\
l &= \text{cell length (dm)} \\
c &= \text{concentration (mg/ml)}
\end{align*}
\]

Also, using the "Drude" equation:

\[
\begin{align*}
\left[ \alpha \right]_m^{20} &= \frac{k}{\lambda_0^2 - \lambda^2} \\
\lambda &= \text{wavelength employed (\mu)}
\end{align*}
\]

observed versus calculated specific rotations were investigated.
Conclusion

Optically active 3,5-dimethoxy-α-β-d-benzyl alcohol and 3,5-dimethoxy-α-β-d-benzyl acetate were prepared. The 3,5-dimethoxy-α-β-d-benzyl alcohol obtained from the photochemical solvolysis of optically active 3,5-dimethoxy-α-β-d-benzyl acetate showed a very small positive specific rotation (+0.3 ± 0.2) compared to the "blank" (air). Realizing that a 67% error is associated with this specific rotation makes it an unreliable number. Also, no agreement was found in observed versus calculated (Drude equation) specific rotation.

Investigation of the ORD curve shows the alcohol absorption to be almost superimposable on the "blanks" absorption. This observation, along with the nonagreement with the Drude equation and the unreliability associated with the specific rotation of the alcohol, implies that the 3,5-dimethoxy-α-β-d-benzyl alcohol produced has no or very little optical activity. Therefore, 3,5-dimethoxy-α-β-d-benzyl alcohol is completely or nearly a racemic mixture. This conclusion would substantiate Zimmerman and Sandel's mechanism showing a benzyl carbonium ion as an intermediate in forming the solvolysis products.

A step further into this research could be a study of the make up of the real photochemical reactant, the excited state. As a start the solvolysis of 3,5-dimethoxybenzyl acetate could be studied using photochemical sensitizers. Different sensitizers at various triplet energies could be employed, resulting in intersystem crossing.
to the 3,5-dimethoxybenzyl acetate triplet and producing the solvolysis products. If solvolysis did take place some evidence for a triplet excited state could be proposed. Also, a State Diagram constructed from the absorption and emission spectrum of the 3,5-dimethoxybenzyl acetate would be of interest. Rate constant for internal conversion, intersystem crossing, fluorescence and phosphorescences may be determined.
Experimental

Melting points and boiling points are uncorrected. The infrared spectra were taken with a Perkin-Elmer Model 237-B. All NMR spectra were taken with a Varian A-60 instrument using chloroform-$d_4$ as a solvent and TMS as an internal standard. A Hewlett-Packard 5750 VPC with a thermal conductivity detector was employed, with a 6 ft. $1/8$ in. silicone gum rubber column at $180^\circ$. A carrier gas flow rate of 40 cc/min. was used. The photochemical reactions were preformed in a Rayonet Photochemical Reactor, using a bank of 15 lamps each emitting ultraviolet light of wavelength $254\text{ m}\mu$. Optical rotations of the deuterated compounds were taken with both a Zeiss Wenkel 178459 and a Jasco's Optical Rotatory Dispersion Model ORD/UV-5. With the Zeiss Wenkel polarimeter, readings could be made to the nearest 0.01 and with the Jasco, readings could be made to the nearest 0.002. The error is given as the standard deviation. Rotations obtained by the Zeiss Wenkel were taken in solutions using chloroform and acetone at concentrations of 200 to 100 mg/cc using a 0.5 dm cell. Rotations using the Jasco's were taken in ethanol using concentration ranging from 10 to 60 mg/cc. A 0.2 dm cell was used and an "ORD curve" was obtained scanning from 600 to 350 m\mu.

3,5-Dimethoxybenzoic acid

Fifty gm. (0.324 moles) 3,5-dihydroxybenzoic acid (Aldrich) was dissolved in 650 ml. (1.30 moles) 2M sodium hydroxide. To this solution at 40, 164.0 gm. (1.30 moles) dimethylsulfate was added
dropwise with agitation over a 15 min. period. The reaction was allowed to continue for 1 hr. and the pH checked. The pH was 2-3, and to assure complete reaction enough, 50% sodium hydroxide was added to make the solution basic. The reaction was continued for 30 min. and 18% hydrochloric acid was added to make the pH 1-2. The white solid 3,5-dimethoxybenzoic acid was then filtered and dried. The product was recrystallized from methanol to give 26.1 gm. (44%) of white solid m.p. 178-180 (lit. 184-186), I.R. 5.5µ.

3,5-Dimethoxybenzoyl chloride

3,5-dimethoxybenzoic acid 10.6 gm. (0.058 moles) was added to 20.3 gm. (0.175 moles) thionyl chloride. The mixture was then heated at 73° for 35 min. The dark solution was distilled to 90° and then vacuum distilled to obtain the product. The pure product distilled at 145-147° (8-9 mm), yield 8.3 gm. (72%) of a colorless liquid. I.R. 5.7µ and a lack of absorption between 2.6-3.2 µ.

3,5-Dimethoxybenzaldehyde

The Rosenmand reduction was used to prepare 3,5-dimethoxybenzaldehyde. Xylene 85.9 gm. was added to a flask along with 1 gm. 5% Pd/BaSO₄ catalyst and 10 mg. quinoline-sulfur regulator. The mixture was then refluxed with no water in the condenser and hydrogen was bubbled through for 1 hr. to remove any traces of water. 3,5-dimethoxybenzoyl chloride, 6.0 gm. (0.03 moles) was then added, the mixture was reacted for about 4.5 hrs. and the hydrochloric acid gas produced (90% of theoretical) was determined by titration.
The reaction mixture was centrifuged twice to remove the catalyst and vacuum distilled at 54-56 °C (8-9 mm) to obtain 3.5 gm. of the crude product. The crude product was recrystallized from n-hexane to obtain 2.9 gm. (58%) of 3,5-dimethoxybenzaldehyde as a white solid, m.p. 43-45 °C (lit. 48 °C) I.R. 5.89, 8.25 μ.

**Isoborneol**

d-Camphor 4.0 gm. (0.026 moles) was dissolved in 20 ml. ether and added dropwise to a slurry of 2.0 gm. (0.053 moles) LiAlH₄ and 30 ml. anhydrous ether. The mixture was allowed to react for 24 hr. Aliquots were taken periodically and checked for loss of the carbonyl absorption associated with the starting material d-Camphor, by I.R. Once the reaction seemed complete, the isoborneol was obtained by adding slowly 30 ml. water and 10 ml. 6N HCl and separating the aqueous layer from the ether layer. The aqueous layer was washed twice with 20 ml. ether and the layers were combined and dried with molecular sieves. Evaporation gave 3.2 g. (80%) isoborneol a white solid m.p. 176-178 °C. I.R. 3.0 μ, lack of absorption 5.5-6.0 μ; NMR 0.92-2.08 (16 H, multiplet), 2.96(1H, singlet, disappears upon addition of D₂O), 3.76(1H, multiplet).

**3,5-Dimethoxybenzyl alcohol**

Procedure I

3,5-Dimethoxybenzoyl-chloride 12.0 g. (0.06 moles) was dissolved in ether and added very slowly to an ether slurry of LiAlH₄ 3.4 gm. (0.09 moles). The mixture was allowed to react for one hour after
the 3,5-dimethoxybenzoyl chloride was added. Excess LiAlH$_4$ was removed by adding water and then 10 ml. 6N HCL was added. The ether layer was separated from the aqueous layer, and the aqueous layer was extracted twice more with ether.

The ether layers were combined and dried. The ether was evaporated and 3,5-dimethoxybenzyl alcohol, a white solid, 9.0 gm. (88%) was obtained; m.p. 43-45 $^\circ$ (lit. 47-48 $^\circ$), I.R. 3.0 $\mu$ lack of absorption 5.5-6.0 $\mu$; NMR (chloroform) 3.30 $\delta$ (6H singlet), 4. 25 $\delta$ (1H, singlet), 4.56 $\delta$ (2H, singlet), 6.3-6.7 $\delta$ (3H, multiplet).

Procedure II

One crystal of iodine and 0.252 gm. (0.0105 moles) magnesium were added to a flask. To this was added dropwise 1.26 gm. (0.0092 moles) $n$-propyl bromide in 10 ml. ether. The reaction was started using tepid water to warm the reaction vessel. After the $n$-propyl bromide was added, the reaction was continued for 1 hr. The Grignard reagent was then cooled to 0 $^\circ$, and 1.62 gm. (0.0105 moles) isoborneol dissolved in ether was added dropwise. The resulting white slurry was warmed to room temperature, and 40 ml. benzene was added. The reaction vessel was set for distillation, and the mixture was distilled to 75 $^\circ$. Again, the solution was set for reflux and cooled to room temperature, 3,5-dimethoxybenzaldehyde 1.0 gm. (0.00603 moles) was added and allowed to react for 1 hr. Water (50ml.) was then added and the organic layer was separated from the aqueous layer. The aqueous layer was extracted twice more with ether, and the organic layers were combined and added back into the flask, set for dis-
tillation. The organic mixture was distilled to 80°. After distillation 40 ml. water was added, and the flask was set for reflux using an air-cooled condenser. The solution was then refluxed until no more white camphor-isoborneol solids were noticed adhering to the condenser walls. The contents were added to a separatory funnel along with anhydrous potassium carbonate, and enough ether was added to obtain a good separation. The aqueous portion was extracted twice more with ether. The ether extracts were combined and distilled to 90°. The flask was then set for vacuum distillation and distilled up to 180° (8-9 mm). 3,5-dimethoxybenzyl alcohol, a white solid, 0.50 gm. (49%) was obtained, m.p. 43-45° (lit. 47-48°), I.R. 3.0 μ, lack of absorption 5.5-6.0 μ.

Deuterated isoborneol-borneol

d-Camphor 82.4 gm. (0.543 moles) was dissolved in ether and added dropwise to a slurry of 8.0 gm. (0.191 moles) lithium aluminum deuteride. Addition time was about 3 hr. The reaction mixture was then heated to reflux for 39 hr. to assure complete reaction. The mixture was then cooled to 0°, and 30 ml. of water was added slowly followed by 20 ml. of 6N HCL.

The ether layer was separated from the aqueous layer, and the aqueous layer was extracted twice more with ether. The ether layers were combined and dried with molecular seives. After evaporation of the ether, deuterated isoborneol, a white solid, was obtained 82.7 gm. (99.0%); m.p. 180-183°, I.R. 3.0μ, 4.7-4.8μ; NMR 0.92-2.0δ (16 H, multiplet), 2.97δ (1H, singlet, disappears upon addition of D2O),
lack of absorption at 3.7μ.

3,5-Dimethoxy-α-d-benzyl alcohol

Procedure II used in preparing the 3,5-dimethoxybenzyl alcohol was employed in making the 3,5-dimethoxy-α-d-benzyl alcohol. However, 10.0 gm. (0.0603 moles) 3,5-dimethoxybenzaldehyde was used, and the deuterated isoborneol was utilized to prepare optically active benzyl alcohol. The 3,5-dimethoxy-α-d-benzyl alcohol, a white solid, 5.3 gm. (52%) was obtained; m.p. 44-45° (lit. 47-48°); I.R. 3.0μ, 4.6-4.7μ, lack of absorption between 5.5-6.0μ; NMR 3.80δ (6H, singlet), 4.25δ (1H, singlet, disappears upon addition of D₂O), 4.56δ (1H, singlet), 6.4-6.7δ (3H, multiplet); [α]₀⁻²⁰ 20 -3.72 ± 0.80, [α]₀⁻₂⁰ 20 450μ 20 4.50, [α]₀⁻²⁰ 500μ calc., -2.8 ± 0.80

3,5-Dimethoxybenzyl acetate

3,5-Dimethoxybenzyl alcohol 8.0 gm. (0.0476 moles) was dissolved in 50 ml. anhydrous ether and 3 drops concentrated sulfuric acid. To this solution 18.6 gm. (0.106 moles) acetic anhydride was added slowly. Once the reaction was completed, the mixture was washed with a saturated solution of sodium bicarbonate until the aqueous layer remained basic. The ether layer was then distilled to 90° and vacuum distilled to obtain the clear oil, 3,5-dimethoxybenzyl acetate, b.p. 210-213° (8-9mm) (lit. 121.5° (0.4mm)) 9.0 gm. (90.0%). I.R. 5.75μ, lack of absorption at 3.0μ.

3,5-Dimethoxy-α-d-benzyl acetate

The above was used to make 3,5 dimethoxy-α-d-benzyl acetate. However,
3,5-dimethoxy-\(\alpha\)-d-benzyl alcohol 4.0 gm. (0.236 moles) was used and all other reagents were adjusted accordingly. 3,5-Dimethoxy-\(\alpha\)-d-benzyl acetate 4.3 gm. (87%) was obtained as a colorless liquid.

I.R., 4.5-4.6\(\mu\) and 5.75 \(\mu\), lack of absorption at 3.0 \(\mu\), \(\left[\alpha\right]_{250m\mu}^0 = -1.38 \pm 0.1\), \(\left[\alpha\right]_{400m\mu}^{20} = -1.75 \pm 0.1\), \(\left[\alpha\right]_{500m\mu}^{20} = -1.05 \pm 0.1\), \(\left[\alpha\right]_{500m\mu}^{250m\mu}\) calc. -1.1 \(\pm\) 0.1.

**Photochemical Reactions**

Photochemical solvolytic reaction of 3,5-dimethoxybenzyl acetate

3,5-Dimethoxybenzyl acetate 2.221 gm. (0.0105 moles) was added to a solution of 250 ml. 1,4-dioxane and 250 ml. water. The solution was contained in a quartz reaction vessel and 5 ml. aliquots were removed to use as a "control" to monitor any thermal reactions and as a "blank" to determine the acidity of the solution before photolizing.

The reaction was irradiated for 6 hrs. and aliquots were removed every hr. to determine the progress of the reaction. After 6 hr., titration of liberated acetic acid (0.002N NaOH) indicated an 88% conversion of 3,5 dimethoxybenzyl acetate. The "control" showed no thermal reaction had occurred.

Photochemical solvolytic reaction of 3,5-dimethoxy-\(\alpha\)-d-benzyl acetate

3,5-Dimethoxy-\(\alpha\)-d-benzyl acetate 1.9725 gm. (0.00936 moles) was photolized as above. The acetic acid generated in the reaction showed a 98% conversion of 3,5-dimethoxy-\(\alpha\)-d-benzyl acetate to 3,5-dimethoxy-\(\alpha\)-d-benzyl alcohol. The "control" showed no thermal reaction had taken place.
Preparative Chromatography of 3,5-Dimethoxybenzyl alcohol

The solution obtained from the photolysis of 3,5-dimethoxybenzyl acetate was reduced to a volume of 2-3 ml. by passing a nitrogen stream over the solution. The residue was chromatographed on a 3.2 x 21 cm. silicis acid column packed in 3% ether in hexane.

(All solutions were saturated with ethylene glycol and 250 ml. fractions were collected.) The first fraction collected, using 50% ether, was 0.1471 gm. of an oil. A second fraction, using 60% ether in hexane, contained 0.2141 gm. solid white residue m.p. 40-43 °C (lit. m.p. 44-48 °C). A third fraction of 70% ether in hexane gave 0.6543 gm. m.p. 42-44 °C (lit. m.p. 44-48 °C) white solid. A final fourth fraction of 70% ether in hexane was added, but gave no residue. Fractions two and three are 3,5-dimethoxybenzyl alcohol (45% recovery). I.R. 3.0 μ, lack of absorption between 5.5-6.0 μ.

Preparative Chromatography of 3,5-Dimethoxy-α-d-benzyl alcohol

The 3,5-dimethoxy-α-d benzyl alcohol was chromatographed in the above manner.

The first fraction gave 0.0852 gm. solid white residue, m.p. 41-43 °C.

The second fraction produced 0.3636 gm. white solid, m.p. 42-43.

The third fraction produced 0.4710 gm. white solid residue, m.p. 43-45 °C. The sum of the fractions accounted for a 59% recovery of 3,5-dimethoxy-α-d-benzyl alcohol. VPC analysis showed the 3,5-dimethoxy-α-d-benzyl alcohol to have a retention time of 4.9 min.

No 3,5-dimethoxy-α-d-benzyl acetate was found at retention time 7.1 min. I.R. 3.0 μ, 4.6-4.7 μ, lack of absorption between 5.5-6.0 μ,
Bibliography