

Amplified Lab Summary

(1998-0369)

**“New” Compounds from Old Plastics;
Recycling PET Plastics via Depolymerization
-- an Activity for the Undergraduate Organic Lab**

Don Kaufman,* Geoff Wright, Ryan Kroemer, and Josh Engel

Department of Chemistry, University of Nebraska at Kearney, Kearney, NE 68849

Efforts continue to include more experiments in the undergraduate organic lab that illustrate the chemistry of the “real” world. Such experiments are particularly attractive if they are also truly related to topics discussed in the organic lecture. The depolymerization of the widely used plastic, polyethyleneterephthalate (PET), via an ester hydrolysis reaction in one lab period appears to be such an activity. One may also elect to use a second lab period to esterify the monomer, obtained during the first lab, to synthesize an easily characterized product. Pre-lab discussions accompanying these experiments can include not only the chemistry of the reactions involved, but also the recycling of plastics.

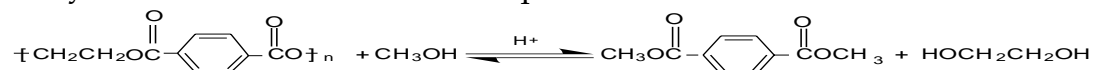
Many plastic products, particularly those used for packaging, have a short period of usefulness and are soon discarded. It is estimated that each year in the United States about 140 billion pounds of plastic products are discarded; that is more than 600 pounds per person (1). Currently, about 80% of discarded plastic ends up in landfills with the consequence that plastics account for nearly 25% of the volume of landfill refuse (2).

Since many areas are experiencing critical shortages of landfill space, considerable effort, including incentives for waste recycling, has been given to reduce the volume of landfill wastes. Whereas about 20% of paper products and 30% of aluminum cans are currently being recycled, only about 1% of discarded plastics are recycled (2). Several factors have contributed to the small amount of plastics currently being recycled. In some cases, the price of the recycled plastic is not competitive with that of “virgin” plastic made from petrochemicals. Another contributing factor involves the problem of sorting plastic waste products into various categories. If this sorting is not done, products made from mixtures of used plastics will often be of low grade, e.g., “plastic lumber”. To assist in the identification and hence in the sorting and recycling of plastic products, the Society of the Plastics Industry has developed a

plastics identification code (3). This code consists of a number from 1-7 placed within a triangle of three curved arrows. Although this coding is voluntary, one finds that many plastic products, particularly bottles, are stamped with this code which is usually found on the bottom of the product. For example, polyethyleneterephthalate (PET) is identified by 1, high density polyethylene (HDPE) by 2, polyvinylchloride (PVC) by 3, low density polyethylene (LDPE) by 4, polypropylene (PP) by 5, polystyrene (PS) by 6, and category 7 includes mixed plastics and all others that don't fit into any of the previous six.

Among the many products made from PET are the familiar two liter soft drink and other clear plastic bottles. The recycling of most PET bottles is done by a physical process in which they are washed, shredded, melted, and remolded to give various new products. However, if higher quality products are needed, the "old" PET product may be depolymerized to give monomers that are then purified and repolymerized.

DuPont Chemical depolymerizes post-consumer PET by an acid catalyzed transesterification reaction with methanol that is possible only under conditions of high temperature and pressure; there are sufficient traces of acid in the PET to catalyze the reaction as shown in equation 1.



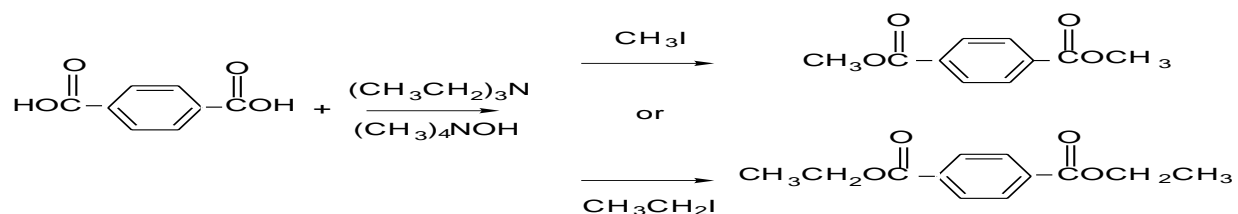
While PET can be industrially depolymerized via transesterification to give ethylene glycol and dimethylterephthalate, we have not been able to do this under conditions available in the undergraduate organic lab. Heating PET in methanol at reflux in the presence of a catalytic amount of sulfuric acid gave very little reaction, even over extended periods. The sparing solubility of PET in methanol is the likely reason for the lack of success of this reaction. (PET has only very limited solubility in common organic solvents.)

Although Williamson reports in his popular lab book (4) that PET "is remarkably resistant to hydrolysis" and states that "there will be no apparent reaction" when PET is refluxed with aqueous acid or base, we thought that under the correct conditions, PET might be depolymerized via hydrolysis as an alternative to transesterification. We found that PET can indeed be quite readily hydrolyzed by

refluxing with either potassium hydroxide or potassium tert-butoxide/water, i.e. "anhydrous hydroxide" (5), in pentanol (or the mixed isomers of commercially available amyl alcohol). This reaction can be completed in a typical organic lab period.

If one wishes to devote only a single lab period to this activity, it may be terminated at this point by characterizing the terephthalic acid obtained from the hydrolysis. However, this characterization is not achieved quite as readily as might be anticipated for terephthalic acid doesn't melt, but sublimes at temperatures above 300 °C. Still, it is very possible to obtain its IR spectrum using a Nujol mull (6) and its NMR spectrum using DMSO-d₆/CDCl₃ (7).

However, since both esterification and S_N2 reactions are included in many undergraduate organic labs, it may be advantageous to use a second lab period to convert the terephthalic acid obtained into a diester (e.g. the dimethyl or diethyl ester) via either a Fischer esterification reaction or by the S_N2 reaction of a diammonium terephthalate salt with an alkyl halide. These esters can be readily characterized by both melting point and NMR. We found that these diesters can both be readily obtained in high yield via the S_N2 reaction of a diammonium salt of terephthalic acid with ethyl or methyl iodide in a polar aprotic solvent such as acetonitrile (eqn. 2). The diammonium salt can be formed from the reaction of terephthalic acid with either triethylamine (8) or tetramethylammonium hydroxide (9). The latter gives somewhat better results, presumably because the tetramethylammonium cation coordinates less strongly with the terephthalate ion than does the triethylammonium cation thus permitting the terephthalate ion to function more freely as a nucleophile. The simpler Fischer esterification reaction can also be used to prepare these esters, but the yields are significantly lower. The sparing solubility of terephthalic acid in alcohols likely contributes to the less satisfactory yields with the Fischer reaction.



Summary:

The activities described here give students an opportunity to observe one way in which PET plastic may be recycled as they successfully conduct common organic lab reactions: base promoted ester hydrolysis and ester synthesis (either the Fischer esterification reaction or the S_N2 reaction of carboxylate salts). Our students have expressed satisfaction in converting discarded ketchup and soda bottles into “new” organic compounds and have indicated that the issue of recycling plastic products has become more meaningful to them.

Literature Cited:

1. Gebelin, C. G. *Chemistry and Our World*; Wm. C. Brown: Dubuque, IA, 1997; p 295
2. Snyder, C. H. *The Extraordinary Chemistry of Ordinary Things*, 2nd ed.; Wiley: New York, 1995; p 559, 586, and 587.
3. Gebelin, C. G. *Chemistry and Our World*; Wm. C. Brown: Dubuque, IA, 1997; p 296
4. Williamson, K.L. *Macroscale and Microscale Organic Experiments*, 2nd ed.; Heath: Lexington, MA, 1994; p 690.
5. Gassman, P. G.; Schenk, W.N. *J. Org. Chem.* 1977, 42, 918.
6. *The Aldrich Library of IR Spectra*, 2nd ed.; Aldrich Chemical Co.: Milwaukee, WI, 1975; p 843 H
7. *The Aldrich Library of NMR Spectra*, Vol 6; Aldrich Chemical Co.: Milwaukee, WI, 1974; p 153 D
8. Mills, R. H.; Farrar, M. W. ; Weinkauff O. *J. Chem. Ind.* 1962, 2144.
9. Wagenknecht, J. H.; Baizer, M. M.; Chruma, J. L. *Synth. Commun.*, 1972, 2(4), 215.

Experimental Procedure

(with comments / suggestions for the instructor)

(#1998-0369)

Experimental Procedure:

Obtaining and preparing the PET sample: To save lab time, students should be instructed to obtain their own PET sample prior to lab by using scissors to cut a clean PET bottle into 1/4" pieces or smaller. Though 2-liter soda bottles are satisfactory, others such as Heinz ketchup bottles are better because they are constructed of 3 shells each of which is thinner than the single shell of soda bottles.

Hydrolysis of the PET Samples:

The quantity of PET used will be largely dictated by the amount of diester one wishes to obtain during the second lab. The cost of the base used for the hydrolysis reaction might also be a determining factor. If potassium hydroxide is used as the base, one will possibly decide to use larger PET samples than if the more expensive potassium tert-butoxide is used. The following yields may be helpful in deciding how much PET one wishes to use. PET hydrolysis using either potassium hydroxide or potassium tert-butoxide has given us terephthalic acid in yields of 85-95%. If esterification is done by the S_N2 reaction of a diammonium terephthalate salt, diester yields of about 90% are seen; if Fischer esterification is used, diester yields are only 10-20%.

To a 100 mL RB flask add 35 mL of 1-pentanol^{1,2} (or mixed pentanol isomers), 5.0 g of PET (0.052 mol equiv of ester), and 4.4 g of KOH (0.079 mol). Use a heating mantle and magnetic stirrer to heat and stir the reaction mixture at reflux. (The PET does not dissolve in the solvent.) After a short time a thick white suspension results; if stirring becomes impossible more solvent may be added. Reflux is continued for a total of 1 1/2 hr. (If magnetic stirrers are not available, the apparatus must be swirled often during the reflux period; when swirling was done briefly every 10 minutes, yields were very substantially reduced.)

After the reaction mixture has cooled, add 25 mL of water to the reaction flask and stir to dissolve the white terephthalate salt that is present. Transfer the mixture to a separatory funnel; care should be taken to prevent any small pieces of unreacted plastic from entering the separatory funnel. (We usually use suction filtration to

remove the small amount of unreacted PET which may be present. The water/pentanol reaction mixture often filters quite slowly via gravity.) Remove the bottom aqueous layer; wash the alcohol layer with an additional 25 mL of water; and combine the aqueous extracts. **Slowly** and with stirring add dil HCl to acidify the aqueous extracts. (If HCl is added rapidly it has been our experience that the terephthalic acid often forms such fine crystals that filtration proceeds exceedingly slowly.) Use suction filtration to collect the white terephthalic acid that forms and allow it to dry until the next lab period. Since terephthalic acid is not very soluble in acetone, we have washed the collected crystals with acetone to hasten drying. To help characterize the terephthalic acid, its IR spectrum may be obtained as a Nujol mull and its ^1H and ^{13}C NMR spectra may be obtained using $\text{DMSO-d}_6/\text{CDCl}_3$. Though terephthalic acid doesn't melt, one may ask students to observe that it does sublime (in the melting point capillary) at temperatures above $300\text{ }^\circ\text{C}$ as reported in the literature. For purposes of comparison, one might also wish to have students determine the mp of their starting PET ($240\text{-}250\text{ }^\circ\text{C}$); a razor blade can be used to scrape shavings from a PET bottle, which are small enough to be introduced into a capillary tube.

We have completed the above hydrolysis portion of this activity in a 3 hour lab period, but students must be efficient in their use of time. If possible, one may wish to do the pre-lab discussion/instruction during the previous lab period to provide students with as much lab time as possible. Alternatively, we have conducted discussions during the reflux period so that students could start the experiment immediately upon entering the lab.

Recently we have obtained $> 90\%$ yields of terephthalic acid using potassium hydroxide for the PET hydrolysis. In the past we had achieved slightly higher yields with a little shorter reflux periods using anhydrous hydroxide (1) formed from potassium tert-butoxide/water in place of potassium hydroxide in the procedure just discussed. However, the extra expense may not justify this choice. Following is the procedure used for those who decide to use potassium tert-butoxide.

Add 5.0 g (0.044 mol) of potassium tert-butoxide and 0.80 g (0.044 mol) of water³ to 35 mL of 1-pentanol² (or mixed pentanol isomers) in a 100 mL RB flask. Use a magnetic stirrer and a heating mantle to briefly warm and stir until most of the tert-butoxide has dissolved; then add 3.5 g of PET (0.036 mol equiv of ester); stir and heat

at reflux. After a short time a thick white suspension results; if stirring becomes impossible more pentanol may be added. Reflux is continued for a total of 90 min. Work-up of this reaction mixture is conducted as described above.

Syntheses of diethyl and dimethyl terephthalate via S_N2 reactions of diammonium terephthalate salts:

ATTENTION: Instructors must decide for themselves whether they are comfortable in having their undergraduate students work with methyl iodide (highly toxic and a cancer suspect agent) and ethyl iodide (a toxic irritant) especially if hood space is unavailable. At the very least, these reagents should be dispensed by the instructor and students required to wear gloves. The original procedure, which is described under Method 1, can be modified to reduce the likelihood of exposure to unreacted alkyl iodides during workup by making them the limiting reagents. This modification is described under Method 1'. Of course, the use of alkyl iodides to make the diesters can be avoided by using the Fischer esterification, which is also discussed.

Method 1: Add 50 mL of acetonitrile, 2.10 g (0.0127 mol) of terephthalic acid, and 5.00 g (0.0276 mol) of tetramethylammonium hydroxide pentahydrate (2) to a 3-neck 250 mL RB flask or a 1-neck RB flask equipped with a Claisen adapter. (A small excess of the hydroxide is used since it is very hygroscopic and some will likely be lost in transferring to the reaction flask.) Fit the flask with a reflux condenser and an addition/sep. funnel. As the mixture is stirred and warmed with a heating mantle, a cloudy suspension of the diammonium terephthalate salt forms. Add 5.00 g (0.0321 mol, a small stoichiometric excess) of ethyl iodide or 4.55 g (0.0321 mol, a small stoichiometric excess) of methyl iodide to the warm reaction mixture in a slow dropwise manner. As the alkyl iodide is added, the solution soon clears and a white solid, tetramethylammonium iodide, collects on the walls of the flask. Heat the reaction mixture at gentle reflux for 90 min. **(Remind the students that the reaction mixture still contains unreacted alkyl iodide and that care should be taken during the reaction workup to avoid contact with the reaction mixture.)**

Allow the reaction flask to briefly cool; then add 50 mL of water and 50 mL of dichloromethane. The ammonium iodide salt dissolves in the water and the diester

dissolves in the dichloromethane. Transfer the mixture to a separatory funnel; remove and save the lower dichloromethane layer. Extract the aqueous layer two times with 15 mL of dichloromethane. Combine the dichloromethane layers and dry over a drying agent such as sodium sulfate. Decant or filter the solution from the drying agent and strip the solvent on a steam bath in the hood. Since acetonitrile has been extracted into the dichloromethane layer, the last portion of solvent will evaporate rather slowly on the steam bath. If a rotary evaporator is available, use it to remove the last portion of solvent. After the solvent is removed, both of the crude diesters are present as white solids in yields of 85-95%.

The dimethyl ester is readily recrystallized from methanol to give a mp 140-41 °C (lit. 141-142 °C) and ^1H NMR spectrum (360 MHz, CDCl_3) δ 4.39 (s, 6 H) and δ 8.02-8.16 (s, 4H).

The diethyl ester is too soluble in methanol to be recrystallized from it, but is satisfactorily recrystallized from 5:1 methanol:water to give mp of 42-44 °C (lit. 44 °) and ^1H NMR spectrum (360 MHz, CDCl_3) δ 1.39 (t, 6 H), δ 4.39 (q, 4 H) and δ 8.02-8.16 (s, 4H).

Method 1': This procedure is basically the same as the one just described, except that alkyl iodides are made the limiting reagents in order that there might be less likelihood of there being unreacted alkyl iodides. There will be some unreacted terephthalic acid (and perhaps monoester) present in the reaction mixture, but this presents little problem in the reaction workup. Somewhat lower yields are obtained from this modified procedure.

The amounts of reagents used here are the same as given in Method 1 above except that 3.50 g (0.0247 mol) of methyl iodide or 3.85 g (0.0247 mol) of ethyl iodide are used. The unreacted terephthalic acid is essentially insoluble in both dichloromethane and water. Thus, the reaction workup is modified in the following manner. 50 ml of dichloromethane (but no water) is added to the cooled reaction mixture. This mixture is gravity filtered to remove undissolved solid (tetramethylammonium iodide, terephthalic acid, and maybe monoester). At this point one can simply evaporate the solvent, as previously described, to obtain the crude diester. However, both the crude and recrystallized products are contaminated

with a very small amount of a high melting compound (perhaps the ammonium iodide). It can be eliminated by extracting the dichloromethane/reaction solution with 25 mL of water prior to evaporation of the solvent. Yields of about 65% are obtained by this modified method.

Method 2: If tetramethylammonium hydroxide is not available, cheaper triethylamine (3) can be used, but somewhat lower yields should be expected. The procedure outlined for method 1 above is followed except that 2.60 g (0.0257 mol) of triethylamine are used in place of tetramethylammonium hydroxide. As before, **students should be reminded that the reaction mixture still contains unreacted alkyl iodide and that care should be taken during the reaction workup to avoid contact with the reaction mixture.** Also, during the workup, if the dichloromethane layer is cloudy due to a small amount of solid (unreacted terephthalic acid), it can be washed with a small amount of dilute aqueous sodium hydroxide solution. Yields of both diesters using this method were in the 50-60% range. Thus, one may wish to start with more terephthalic acid here than when tetramethylammonium hydroxide is used.

Method 2': One might also wish to modify this procedure by making the alkyl iodides the limiting reagents as described under Method 1'.

Syntheses of diethyl and dimethyl terephthalate via Fischer esterification reactions:

To 2.70 g of terephthalic acid and 20 mL of methyl alcohol (or ethyl alcohol) in a 50 mL RB flask, 3 mL of concentrated sulfuric acid are slowly added with cooling. This mixture is heated at reflux with stirring for 90 min; solid (unreacted terephthalic acid) will be present throughout the entire reflux period. The solution is then cooled and the solid is removed by gravity filtration. (It is preferable to remove the solid terephthalic acid at this point by filtration rather than later by extraction into aqueous NaOH. Though terephthalic acid is soluble in aqueous base, it dissolves very slowly and so it is best not to introduce solid terephthalic acid into the separatory funnel with the expectation that it will readily be removed by base extraction.) This solid is washed with 20 mL of dichloromethane to remove any dimethylterephthalate which may possibly have crystallized from solution. The

combined filtrate and dichloromethane wash are transferred to a separatory funnel where it is successively washed with 25 mL of water, twice with 25 mL of 10% NaOH solution, and 25 mL of half-saturated brine. After drying, the organic layer is stripped of solvent on the steam bath in the hood to give the crude dimethyl ester as a white solid in yields of about 20%. The crude diester is quite pure but may be recrystallized as described earlier. The NaOH extracts may be acidified with dil HCl to give additional unreacted terephthalic acid which may be collected via suction filtration and combined with that filtered earlier from the reaction mixture.

A similar procedure using ethyl alcohol to prepare diethyl terephthalate resulted in only a 10% yield.

It is seen that although the Fischer reaction is simpler and uses cheaper reagents, it gives significantly lower yields of the terephthalate diesters than does the S_N2 reaction of the diammonium terephthalate salts.

CAUTION: Appropriate precautions should be used in working with the several hazardous reagents used in this experiment. Among these reagents are: potassium tert-butoxide which is corrosive and water sensitive; triethylamine which is a highly flammable irritant; tetramethyl ammonium hydroxide which is very hygroscopic and corrosive; methyl iodide which is highly toxic and a cancer suspect agent; and ethyl iodide which is a toxic irritant. Students should also be informed that care must be used in working with dichloromethane and methanol. Gloves are suggested and work should be done in the hood if possible. The instructor is encouraged to dispense the methyl and ethyl iodide. Also, be sure to follow established procedures for the handling and disposal of the various residues/wastes in this experiment.

Summary:

The activities described here give students an opportunity to observe one way in which PET plastic may be recycled as they successfully conduct common organic lab reactions: base catalyzed ester hydrolysis and ester synthesis (either the Fischer esterification reaction or the S_N2 reaction of carboxylate salts). Our students have expressed satisfaction in converting discarded ketchup and soda bottles into “new”

organic compounds and have indicated that the issue of recycling plastic products has become more meaningful to them.

Notes:

1. Refluxing PET with KOH in water gave only about 15% hydrolysis in 1 3/4 hr.
2. 1-pentanol was used rather than solvents such as tert-butyl alcohol or THF, in order to have a solvent which is immiscible with water so as to simplify the reaction workup. Using the cheaper mixed primary isomers of amyl alcohol in place of 1-pentanol resulted in nearly the same yield of terephthalic acid.
3. Gassman (ref. 1) used 1 equiv of ester and 2 equiv of water for each 8 equiv of potassium tert-butoxide in his anhydrous hydroxide work. While this may be the optimum ratio, in order to reduce costs, we used less butoxide with satisfactory results. Since water is added to the reaction mixture, users of this experiment should realize that "old" bottles of the butoxide may be suitable. It may be interesting to note that in our initial work, hydrolysis was readily achieved without adding any water when an "old" bottle of the butoxide was used.

Literature Cited:

1. Gassman, P. G.; Schenk, W.N. *J. Org. Chem.* 1977, 42, 918.
2. Wagenknecht, J. H.; Baizer, M. M.; Chruma, J. L. *Syn. Com.*, 1972, 2(4), 215.
3. Mills, R. H.; Farrar, M. W. ; Weinkauff, O. *J. Chem. and Indust.*, 1962, 2144.

Experimental Procedure

(for students)

(1998-0369)

The instructor may wish to modify these student procedures to adjust the amounts of reactants suggested here in order to obtain the amounts of products they desire for their students. The instructor should also consult the more extensive Experimental Procedures for Instructors if they wish to use one of the alternative procedures described there.

Experimental Procedure:

CAUTION: Appropriate precautions should be used in working with the several hazardous reagents used in this experiment. Among these reagents are: tetramethyl ammonium hydroxide which is very hygroscopic and corrosive; triethylamine which is a highly flammable irritant; methyl iodide which is highly toxic and a cancer suspect agent; and ethyl iodide which is a toxic irritant. Care must also be exercised when working with dichloromethane and methanol. Gloves are suggested and work should be done in the hood if possible. Your instructor may wish to dispense the methyl or ethyl iodide. In addition, be sure to follow all precautions and suggestions that your instructor gives for working with the reagents used in this experiment and for the handling and disposal of the various residues/wastes in this experiment.

Obtaining and preparing the PET sample:

To save lab time, you are instructed to bring your own pre-cut PET sample to lab. Use a scissors to cut a clean PET bottle into 1/4" pieces or smaller. Though 2-liter soda bottles are satisfactory, others such as Heinz ketchup bottles are better because they are constructed of 3 shells each of which is thinner than the single shell of soda bottles. You will need at least 5.0 g of cut PET for this activity.

Hydrolysis of the PET Samples:

To a 100 mL RB flask add 35 mL of 1-pentanol (or mixed pentanol isomers), 5.0 g of PET (0.052 mol equiv of ester), and 4.4 g of KOH (0.079 mol). Use a heating mantle to heat the mixture to reflux while stirring with a magnetic stirrer. (The PET does not dissolve in the solvent.) After a short time a thick white suspension results; if stirring becomes impossible, more solvent may be added; check with your instructor before doing so. Continue the reflux for a total of 1 1/2 hr. (If magnetic stirrers are not available, the apparatus must be swirled often during the reflux period.)

After the reaction mixture has cooled to room temperature, add 25 mL of water to the reaction flask and stir to dissolve the white terephthalate salt that is present. Transfer the mixture to a separatory funnel; care should be taken to prevent any small pieces of unreacted plastic from entering the separatory funnel. (Your

instructor will suggest either suction filtration or gravity filtration using a funnel with a small plug of cotton to remove the solids.) Drain the bottom aqueous layer from the separatory funnel into a 125 mL erlenmeyer flask; extract the alcohol layer with an additional 25 mL of water; and combine the aqueous extracts. **Slowly** and with stirring, add dil HCl to acidify the aqueous extracts. (If HCl is added rapidly, the terephthalic acid may form such fine crystals that filtration proceeds exceedingly slowly.) Cool the acidified mixture in an ice bath. Use suction filtration to collect the white terephthalic acid that has formed and allow it to dry until the next lab period. You may be instructed to obtain an IR, and a ^1H or ^{13}C NMR spectrum of your product when it is dry.

Synthesis of dimethyl (or diethyl) terephthalate via the $\text{S}_{\text{N}}2$ reaction of a diammonium terephthalate salt:

Method 1: Add 50 mL of acetonitrile, 2.10 g (0.0127 mol) of terephthalic acid, and 5.00 g (0.0276 mol) of tetramethylammonium hydroxide pentahydrate (very hygroscopic) to a 3-neck 250 mL RB flask (or a 1-neck RB flask equipped with a Claisen adapter). Fit the flask with a reflux condenser and an addition/sep. funnel. As the mixture is stirred and warmed with a heating mantle, a cloudy suspension of the diammonium terephthalate salt forms. Obtain 4.55 g (0.0321 mol) of methyl iodide in a small erlenmeyer flask. Special care should be exercised in handling methyl iodide; your instructor should dispense it for you. Pour the methyl iodide into the addition funnel; rinse the flask with small amounts of acetonitrile to ensure complete transfer of the methyl iodide to the funnel. Add the methyl iodide to the warm reaction mixture in a slow dropwise manner with stirring. As the methyl iodide is added, the solution soon clears and a white solid, tetramethylammonium iodide, collects on the walls of the flask. Heat the reaction mixture at gentle reflux for 90 min.

Realize that the reaction mixture will contain unreacted methyl iodide. As you begin workup of this mixture, take special care to avoid contact with it.

Allow the reaction flask to cool to room temperature; then add 50 mL of water and 50 mL of dichloromethane. The ammonium iodide salt dissolves in the water and the diester dissolves in the dichloromethane. Transfer the mixture to a separatory funnel; drain the lower dichloromethane layer into a 125 mL erlenmeyer flask.

Extract the aqueous layer two times with 15 mL of dichloromethane. Combine the dichloromethane layers and dry over a drying agent such as sodium sulfate. Decant or filter the solution from the drying agent into a 250 mL erlenmeyer flask and strip the solvent on a steam bath in the hood. Since acetonitrile has been extracted into the dichloromethane layer, the last portion of solvent will evaporate rather slowly on the steam bath. If a rotary evaporator is available, use it to remove the last portion of solvent. After the solvent has been removed, the crude diester is present as a white solid in yields of 80-90%. It is readily recrystallized from methanol to give a mp 140-41 °C (lit. 141-142 °C) and ^1H NMR spectrum (360 MHz, CDCl_3) δ 4.39 (s, 6 H) and δ 8.02-8.16 (s, 4H).

If your instructor asks you to prepare the diethyl ester, the above procedure for preparing the dimethyl ester is followed except 5.00 g (0.0321 mol) of ethyl iodide are used in place of methyl iodide. The diethyl ester is too soluble in methanol to be recrystallized from it, but is satisfactorily recrystallized from 5:1 methanol:water to give mp of 42-44 °C (lit. 44 °) and ^1H NMR spectrum (360 MHz, CDCl_3) δ 1.39 (t, 6 H), δ 4.39 (q, 4 H) and δ 8.02-8.16 (s, 4H).

Your instructor may wish to modify the above procedure by making the alkyl iodides the limiting reagents so that there will be less likelihood of there being unreacted alkyl iodides. Though the yields are somewhat reduced, quite pure diesters are still obtained. There will be some unreacted terephthalic acid (and perhaps monoester) present in the reaction mixture, but this presents little problem in the reaction workup.

Method 2: If tetramethylammonium hydroxide is not available, the procedure outlined for method 1 above is followed except that 2.60 g (0.0257 mol) of triethylamine are used in place of tetramethylammonium hydroxide. During the workup of the reaction mixture, if the dichloromethane layer is cloudy due to a small amount of solid (unreacted terephthalic acid), it can be removed by washing with a small amount of dilute aqueous sodium hydroxide solution.

Synthesis of dimethyl terephthalate via a Fischer esterification reaction:

Your instructor may ask you to use the following procedure for the synthesis of dimethyl terephthalate as an alternative to the above procedures.

To 2.70 g of terephthalic acid and 20 mL of methyl alcohol in a 50 mL RB flask, slowly add 3 mL of concentrated sulfuric acid with cooling. Use a heating mantle to heat this mixture at reflux with stirring for 90 min; solid (unreacted terephthalic acid) will be present throughout the entire reflux period. After cooling to room temperature, filter the solution to remove solid (unreacted terephthalic acid) which will be present. (It is better to remove the solid terephthalic acid at this point by filtration rather than later by extraction into aqueous NaOH. Though terephthalic acid is soluble in aqueous base, it dissolves very slowly and so it is best not to introduce solid terephthalic acid into the separatory funnel with the expectation that it will readily be removed by base extraction.) Wash the collected solid with 25 mL of dichloromethane to remove any dimethylterephthalate which may possibly have crystallized from solution. Transfer the combined filtrate and dichloromethane wash to a separatory funnel. First wash with 25 mL of water, then twice with 25 mL of 10% NaOH solution, and finally with 25 mL of half-saturated brine. Dry the organic layer over magnesium sulfate or sodium sulfate for several minutes and then decant or filter the solution into a 125 mL erlenmeyer flask. Strip the solvent on the steam bath in the hood to give the crude dimethyl ester as a white solid in yields of about 20%. The crude diester is quite pure but may be recrystallized as described earlier. At the discretion of your instructor the NaOH extracts may be acidified with dil HCl to give additional unreacted terephthalic acid which may be collected via suction filtration and combined with that filtered earlier from the reaction mixture.

A similar procedure using ethyl alcohol to prepare diethyl terephthalate results in only a 10% yield and is not suggested as an alternative.

It is seen that although the Fischer reaction is simpler and uses cheaper reagents, it gives significantly lower yields of the terephthalate diesters than does the S_N2 reaction of the diammonium terephthalate salts.