two readily prepared solid derivatives were obtained.

EXPERIMENTAL

4-Nitro-o-terphenyl. Commercial *o*-terphenyl was nitrated by the method of Allen and Burness (*1*).

4-Acetamido-o-terphenyl. 4-Nitro-*o*-terphenyl was reduced in benzene solution with hydrogen and platinum oxide. The resulting amine was acylated by refluxing with acetic anhydride to yield 4-acetamido-*o*-terphenyl, m.p. 158.5–159.5° C., in 85% yield. Anal. Calcd. for $C_{20}H_{17}ON$: C, 83.59; H, 5.96. Found: C, 83.33; H, 6.08.

4-Benzamido-o-terphenyl. A suspension of 4-amino-*o*-terphenyl and benzoyl chloride was shaken with aqueous sodium hydroxide. The white crystals of the amide melted at 184–186° C. Anal. Calcd. for $C_{24}H_{20}ON$: C, 85.68; H, 5.46. Found: C, 85.68; H, 5.72.

3-Nitro-4-acetamido-o-terphenyl. A solution of 4-acetamido-*o*-terphenyl in acetic acid was nitrated with fuming nitric acid (*d*.1.5). A total yield of 84% for the nitro amide was obtained. The orange-red crystals of 3-nitro-4-acetamido-*o*-terphenyl melted at 152.2–153.2° C. Anal. Calcd. for $C_{20}H_{16}O_3N_2$: C, 72.27; H, 4.85. Found: C, 72.84; H, 4.93.

3-Nitro-4-amino-o-terphenyl. A refluxing solution of 3-nitro-4-acetamido-*o*-terphenyl in dioxane was hydrolyzed by adding an aqueous solution of potassium hydroxide. The 3-nitro-4-amino-*o*-terphenyl was obtained in 77% yield as golden-orange flakes, m.p. 160–161° C. Anal. Calcd. for $C_{18}H_{14}O_2N_2$: C, 74.45; H, 4.86. Found: C, 74.60; H, 5.09.

3-Nitro-o-terphenyl. An acetic acid solution of 3-nitro-4-amino-*o*-terphenyl was diazotized by treatment with a solution of sodium nitrite in cold concentrated sulfuric acid. Deamination was effected by slowly adding the deep red diazonium solution to a refluxing mixture of water, ethanol, and copper sulfate. The light orange crystals of 3-nitro-*o*-terphenyl, m.p. 88–89.5° C., were obtained in 87% yield. Anal Calcd. for $C_{18}H_{13}O_2N$: C, 78.52; H, 4.75. Found: C, 78.66; H, 4.65.

3-Amino-o-terphenyl. 3-Nitro-*o*-terphenyl was reduced in ethanolic solution with hydrogen and platinum oxide. The white crystals of 3-amino-*o*-terphenyl which formed on cooling in a freezer melted to a clear viscous oil at room temperature.

3-Acetamido-o-terphenyl. A solution of 3-amino-*o*-terphenyl in acetic anhydride was refluxed with a few drops of pyridine. After crystallization the 3-acetamido-*o*-terphenyl yielded a white solid melting at 160–161° C. Anal. Calcd. for $C_{20}H_{17}ON$: C, 83.59; H, 5.96. Found: C, 83.51; H, 6.24.

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Syntheses of Optically Active and Racemic Menthyl Terephthaloyl Chlorides and Their Intermediates

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IN CONNECTION with a program to react cellulose with bulky acid chlorides (*4*), the authors became interested in obtaining the acid chlorides of the monomenthyl terephthalates. The immediate goal was to synthesize one of the optically active forms and the racemic modification.

A literature search showed that the desired acid chlorides had not been prepared previously. The only reference which could be found concerning the preparation of any of the desired menthyl terephthalate derivatives was that of Cohen and de Pennington (*1*). With this reference as a starting point, work on the syntheses of the desired acid chlorides and the necessary intermediates was begun.

EXPERIMENTAL

Microanalyses were performed by Galbraith Laboratories, Inc.

Reagents. The terephthaloyl chloride and the *dl*-menthol were Eastman Practical Grade. The *l*-menthol was Eastman White Label. The *d*-menthol was obtained by the resolution of *dl*-menthol as described by Ingersoll (*3*).

Preparation of the Mixture of Bis(*l*-menthyl) Terephthalate, Bis(*d*-menthyl) Terephthalate, and *l*-Menthyl *d*-Menthyl Terephthalate. A sample of *dl*-menthol weighing 78 grams (0.5 mole) was melted on a boiling water bath. To this was added 51 grams (0.25 mole) of terephthaloyl chloride. The mixture was heated for 2 hours in a boiling water bath. Water was then added to convert the unreacted terephthaloyl chloride to terephthalic acid. Excess menthol was removed by steam distillation. The remaining water was decanted. Hot benzene was added to dissolve the esters and to separate them from the nearly insoluble terephthalic acid. Part of the benzene was then distilled to remove water.

Fractionation of the Mixture of Bis(*l*-menthyl) Terephthalate, Bis(*d*-menthyl) Terephthalate, and *l*-Menthyl *d*-Menthyl Terephthalate. As the benzene solution of the mixture of diesters cooled, crystals formed. These crystals (52 grams) were caught on a filter and identified as *A*. Evaporation of the mother liquor yielded a sticky solid (52 grams) identified as *B*.

The crystals *A* were washed with boiling ethanol and dried in a vacuum oven. The crystals melted over a range 168–176° C. with previous softening. After two recrystallizations from benzene, they melted at 179–180.5° C. Anal. Calcd. for $C_{28}H_{42}O_4$: C, 76.02; H, 9.50. Found: C, 75.80; H, 9.40.

The sticky solid *B* obtained from the mother liquor was heated with absolute ethanol. The alcohol was filtered to remove some undissolved solid. Upon cooling, crystals formed in the alcohol. These were caught on a filter. After drying, the crystals melted over a range 112–126° C. After standing overnight, the mother liquor yielded a second crop of crystals which melted at 109–112° C. A third crop melted at 109–114° C. Because the second crop had the sharpest melting point, it was selected for elemental analysis. Anal. Calcd. for $C_{28}H_{42}O_4$: C, 76.02; H, 9.50. Found: C, 75.78; H, 9.68.

The elemental analyses indicated that one sample was a racemic modification, bis(*l*-menthyl) terephthalate plus bis(*d*-menthyl) terephthalate, and the other, the meso ester, *l*-menthyl *d*-menthyl terephthalate.

Direct Indentification of B as the Racemic Modification, Bis(*l*-menthyl) Terephthalate plus Bis(*d*-menthyl) Terephthalate, and

Indirect Identification of *A* as the Meso Ester, *l*-Menthyl *d*-Menthyl Terephthalate. Terephthaloyl chloride and *l*-menthol were converted to bis(*l*-menthyl) terephthalate by the method of Cohen and de Pennington (*1*). The crude product was recrystallized from ethanol to give the pure ester, m.p. 76–78° C. [lit. (*1*) m.p. 77–78° C.]. Terephthaloyl chloride and *d*-menthol treated in the same manner yielded bis(*d*-menthyl) terephthalate, m.p. 76–79° C. An equal quantity of each ester was dissolved in ethanol, and then this solution was evaporated to dryness. The resulting racemic modification melted at 111–112° C. Fraction *B*, then, was the racemic diester, while the higher melting fraction *A* was the meso diester.

Partial Saponification of Diesters Made from Menthol and Terephthaloyl Chloride. In testing Cohen and de Pennington's method for partial saponification of bis(*l*-menthyl) terephthalate, some monoethyl terephthalate was isolated along with the *l*-monomenthyl terephthalate. This result was similar to that reported by Hearst and Noller (*2*) who obtained some monomethyl ester during the partial saponification of bis(*l*-menthyl) nitroterephthalate using methanolic potassium hydroxide. They presumed the methyl half ester was formed by ester exchange from the methanolic potassium hydroxide solution.

Because monomethyl terephthalate is soluble in hot water and can be readily separated from the monomenthyl terephthalates with this solvent, methanol was used in later partial saponifications. To reduce the amount of ester exchange and to increase the solubility of the diesters, especially the meso isomer, dioxane was added as a diluent. Under these conditions, the half esters were obtained as crystalline rather than resin-like materials.

A 100-gram sample of the diester was dissolved in 200 ml. of hot dioxane. To this was added 200 ml. of a methanolic solution containing 18 grams of potassium hydroxide and 18 ml. of water. A magnetic stirrer was added, and the cloudy solution was refluxed for 2 hours. A precipitate formed during this time. Most of the solvent was then evaporated and 850 ml. of water was added. The mixture was extracted twice with 200-ml. portions of benzene to remove menthol and unreacted diester. The water layer was acidified with 6*N* hydrochloric acid to precipitate crude monomenthyl terephthalate. The half ester was extracted with hot water to remove monomethyl terephthalate and dissolved in hot benzene to remove relatively insoluble terephthalic acid. Crystals were obtained from the benzene by the addition of petroleum ether and cooling.

***l*-Monomenthyl Terephthalate.** When bis(*l*-menthyl) terephthalate was used as starting material in the partial saponification procedure the product was *l*-monomenthyl terephthalate, m.p. 126–128° C., $[\alpha]^{24}_{D}$ −86.3° (c 2, benzene) [lit. (*1*) $[\alpha]^{18}_{D}$ −85.1° (c 2, benzene)]. Anal. Calcd. for $C_{18}H_{24}O_4$: C, 71.06; H, 7.89. Found: C, 70.90; H, 8.00.

***dl*-Monomenthyl Terephthalate.** When a mixture of racemic and meso diesters was used as starting material in the partial saponification procedure, the product was *dl*-monomenthyl terephthalate, m.p. 135.5–137° C. Anal. Calcd. for $C_{18}H_{24}O_4$: C, 71.06; H, 7.89. Found: C, 70.87; H, 7.78.

***l*-Menthyl Terephthaloyl Chloride.** A 5-gram sample of *l*-monomenthyl terephthalate was refluxed with 10 ml. of thionyl chloride for 1.5 hours. Most of the thionyl chloride was then removed under reduced pressure. Final traces of chloride were removed by adding benzene and evaporating and then by adding petroleum ether and evaporating. The resulting sirup had $[\alpha]^{21}_{D}$ − 85.4° (c 2, benzene). Anal. Calcd. for $C_{18}H_{23}O_3Cl$: C, 66.97; H, 7.18; Cl, 10.98. Found: C, 67.04; H, 7.28; Cl. 10.73.

***dl*-Menthyl Terephthaloyl Chloride.** The same procedure was used for the preparation of the racemic acid chloride as was used for the optically active acid chloride. In this case, however, the sirup soon crystallized, m.p. 55–58° C. Anal. Calcd. for $C_{18}H_{23}O_3Cl$: C, 66.97; H, 7.18; Cl, 10.98. Found: C, 66.72; H, 6.98; Cl, 10.91.

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Association of Diphenylketene

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The association of solutions of diphenylketene in cyclohexane and benzene has been determined. It is found to be that expected from the dipole moment and it remains constant with time, within the limitations of the experimental method used.

STUDY of the degree of association of diphenylketene was undertaken to explain several unusual properties of diphenylketene. First, diphenylketene and ketenes in general undergo several types of addition (*7*) and cycloaddition (*8*) reactions in which two molecules of the ketene add to one molecule of the other reactant, even though the other reactant is present in excess. Second, diphenylketene and ketenes, in general, dimerize readily (*3*). Third, samples of diphenylketene which have been kept under nitrogen, either as a liquid at room temperature or as a solid at −78° C., have been observed to become less soluble in petroleum hexane and to require hours or days to react under conditions where freshly distilled material reacted in minutes. (The yields of products in the reactions were the same.) The possibility