Table III. Infrared Spectra of Tetrasubstituted Ureas and Their Thermal Decomposition Products

Table I Compound No.	Material	Remarks
I	Tetra-*n*-hexylurea	C=O at 1,655 cm.$^{-1}$ (s); $(CH_2)_{>4}$ at 730 cm.$^{-1}$ (s)
	Volatile decomposition products	>CH=CH_2 masked; N-H or O-H at 3,350 cm.$^{-1}$ (s)
II	Tetrakis (2-ethylhexyl) urea	C=O at 1.655 cm.$^{-1}$ (s); $(CH_2)_{>4}$ at 730 cm.$^{-1}$ (s)
	Volatile decomposition products	>CH=CH_2 at 1,650 cm.$^{-1}$ (m); N-H or O-H = none
IV	Tetra-*n*-octylurea	C=O at 1,660 cm.$^{-1}$ (s); $(CH_2)_{>4}$ at 720 cm.$^{-1}$ (s)
	Volatile decomposition products[a]	>CH=CH_2 at 1,650 cm.$^{-1}$ (m); N-H or O-H = none
V	Tetra-*n*-decylurea	C=O at 1,660 cm.$^{-1}$ (s); $(CH_2)_{>4}$ at 725 cm.$^{-1}$ (s)
	Volatile decomposition products	>CH=CH_2 at 1,645 cm.$^{-1}$ (m); N-H or O-H = none
X	Benzyltriphenylurea	C=O at 1,680 cm.$^{-1}$ (s);
	Volatile decomposition products	>CH=CH_2 masked; N-H or O-H at 3,400 cm.$^{-1}$ (s)
	Nonvolatile decomposition products	N-H or O-H at 3,400 cm.$^{-1}$ (m); band at 1,680 cm.$^{-1}$ broadened and decreasing intensity

[a] Spectrum matches spectrum of 1-octene (does not match spectra of other octenes). (s) and (m) refer to strong and medium band intensity.

The final step in the degradation process is the rapid decomposition of the trisubstituted urea into an isocyanate and a secondary amine:

$$R_2N-\overset{\overset{O}{\|}}{C}-\overset{H}{N}-R' \rightleftharpoons R'NCO + R_2NH$$

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The Synthesis of 3-Nitro-o-terphenyl and Acyl Derivatives of 3- and 4-Amino-o-terphenyl

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The synthesis of 3-nitro-o-terphenyl is reported. Acyl derivatives of 3-amino-o-terphenyl and 4-amino-o-terphenyl have been prepared.

ALTHOUGH five isomeric mono-nitro-*o*-terphenyls are possible, to date only three have been reported (*1, 2, 4*). Direct nitration of *o*-terphenyl yields the 4-nitro isomer; however, preparation of 3-nitro-*o*-terphenyl by this method is not feasible. The synthetic route employed during the course of this work involved the nitration of 4-acetamido-*o*-terphenyl yielding 3-nitro-4-acetamido-*o*-terphenyl. Subsequent removal of the acetamido group gave the desired 3-nitro-*o*-terphenyl.

Most of the derivatives reported for 4-amino-*o*-terphenyl have been of an unusual nature or have been oils that crystallized slowly. (*1,3*). During the course of the work, 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