logarithm of the rate constants against the reciprocal of the absolute temperatures. Computation work was done both at Michigan State University and the University of Michigan (CDC 3600), the work at the latter University having been made possible through the good offices of Milton Tamres of the Department of Chemistry at the University of Michigan.

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Preparation and Properties of Tetrachloroterephthalate Esters

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The preparation and properties of 12 tetrachloroterephthalate esters are reported. Several different types are described. Properties of the di-*n*-alkyl esters are compared with those of the isomeric ortho esters. The tetrachloroterephthalates are higher melting and have less tendency to form molecular complexes with aromatic hydrocarbons. Alkyl tetrachloroterephthalates resist saponification and transesterification. Several synthetic methods are illustrated. Some infrared absorption characteristics are also given.

Interest in the potential application of tetrachloroterephthalate esters as liquid phases for chromatography (*5–7*) led us to investigate the synthesis and properties of a number of the diesters that have not been described previously. A gas chromatographic investigation of the thermodynamics of solution of some of the alkyl diesters, used as liquid phases, has been reported earlier (*5*). Preparations of these diesters and others, some containing aromatic and halogenated aromatic nuclei, are described here. A comparison of properties of many of these compounds with the tetrachlorophthalates (*8*) is of further interest since both classes of materials are potential plasticizers (*10, 12*).

For the preparation of dialkyl diesters, the procedure of Rabjohn and others (*3, 10, 11*) involving direct reaction of tetrachloroterephthaloyl chloride with an excess of primary alcohol was most useful and convenient. While alkyl chlorides were not isolated from reaction of the alcohols with the generated hydrochloric acid, they presumably were formed to some extent. Procedures involving reaction of sodium alkoxides with the tetrachloroterephthaloyl chloride (*8*) and direct reaction of the dichloride with hydroxy compounds in the presence of pyridine were also found to be viable, especially with phenolic compounds. However, in other experiments, to be described at a later date, we found attempted reaction of a tertiary

Table I. Properties of Tetrachloroterephthalate Esters

Compound	Procedure[a]	Formula	Mp, °C	Some characteristic ir absorption wavelengths (see text)				
Di-*n*-propyl[b]	A1, A2	$C_{14}H_{14}O_4Cl_4$	90.0–91.0[c,d]	5.73	6.23	8.08	9.03	12.65 μ
Di-*n* butyl[e]	A1, A2	$C_{16}H_{18}O_4Cl_4$	62.0–63.0	5.73	6.24	8.15	9.08	12.70 μ
Di-*n*-pentyl[e]	A1, A2, C	$C_{18}H_{22}O_4Cl_4$	37.0–38.5	5.75	6.27	8.04	9.04	12.70 μ
Di-*n*-octyl[b,f]	B	$C_{24}H_{34}O_4Cl_4$	51.8–52.8	5.77	6.24	8.08	9.08	12.70 μ
Di-*n*-dodecyl[f]	B	$C_{32}H_{50}O_4Cl_4$	68.7–69.5	5.76	6.27	8.02	8.94	12.70 μ
Bis-cyclohexylmethyl[f,g]	D	$C_{22}H_{26}O_4Cl_4$	174.5–175.2	5.78	6.28	8.06	8.97	12.68 μ
Diphenyl[g]	C	$C_{20}H_{10}O_4Cl_4$	225.0–226.0	5.71	6.25	8.21	9.20	12.83 μ
Bis-3-methylphenyl[g]	C	$C_{22}H_{14}O_4Cl_4$	209.5–210.5	5.69	6.27	8.12	9.18	12.98 μ
Bis-*m*-fluorophenyl[g,h]	C	$C_{20}H_8O_4Cl_4F_2$	222.5–223.0	5.68	6.25	8.22	8.96	12.98 μ
Bis-*p*-fluorophenyl[g,h]	C	$C_{20}H_8O_4Cl_4F_2$	251.0–252.5	5.69	6.28	8.23	9.22	13.00 μ
Bis-pentafluorophenyl[g,h]	C	$C_{20}O_4Cl_4F_{10}$	196.0–197.0	5.57	6.04	8.38	9.03	12.93 μ
Diheptafluoro-1-butyl[b]	C	$C_{16}H_4O_4Cl_4F_{14}$	156.8–157.5	5.68	6.31	8.13	9.03	12.78 μ

[a] Some of procedures used from Experimental indicated; list not exhaustive, procedure may have been slightly modified. Recrystallized from: [b] Ethanol. [c] Reported mp 88.5–89°C, ref. *6*. [d] Boiling point 186–8°C/1 mm. [e] Methanol. [f] Propanol. [g] Benzene. [h] Dioxane.

amine salt of tetrachloroterephthalic acid with alkyl halide resulted in significant decarboxylation when a recommended procedure for ester formation (*9*) was tested.

The diesters prepared in this study are listed in Table I together with other pertinent characterization data. The most useful recrystallization solvents were the lower aliphatic alcohols for the dialkyl esters and benzene or dioxane for the aromatic esters. While our experimental procedures were satisfactory, they have not been optimized. We report several suitable for possible modification for improved yields.

Although gas chromatographic studies indicated solution interactions of alkyl tetrachloroterephthalates with aromatics closely resembling those observed for the alkyl tetrachlorophthalates (*5*), we were not successful in isolating molecular complexes of the para esters with hexamethylbenzene, 2-methylnaphthalene, and 1,2,4,5-tetramethylbenzene. Procedures were similar to those used for isolating solid hexamethylbenzene tetrachlorophthalate complexes (*8*). Other procedures involving cooling of the reaction mixture and mixing with excess ester also failed. Indeed, even characteristic visible colors did not appear on mixing of alkyl tetrachloroterephthalates with hexamethylbenzene (*8*). However, dimethylaniline gave a pale yellow color with di-*n*-propyl, di-*n*-butyl, and di-*n*-octyl tetrachloroterephthalate. No color on mixing with dimethylaniline was observed with the bis-2-methylphenyl ester, while the bis-pentafluorophenyl ester gave a darker yellow color probably owing to the electronegative fluorine substituents. The failure of the hydrocarbons to give visible spectral indications of interaction is probably due to steric hindrance of the type previously observed (*8*).

The alkyl tetrachloroterephthalate esters are more resistant to saponification than are the corresponding tetrachlorophthalate esters as observed here and by Profft and Timm (*10*). While accurate neutralization equivalents could be obtained for di-*n*-propyl tetrachlorophthalate in aqueous ethanol after 2 hr using a standard procedure (*8*), the same procedure with dimethyl tetrachloroterephthalate gave neutralization equivalents about 20–40% high, indicating incomplete saponification. Attempts to transesterify dimethyl tetrachloroterephthalate with *n*-propanol using *p*-toluenesulfonic acid, titanium isopropoxide, and sodium propoxide resulted in substantial recovery of the starting material.

As expected for symmetrical compounds, the tetrachloroterephthalate esters tend to be higher melting than the alkyl tetrachlorophthalates. For example, the diethyl and di-*n*-propyl tetrachloroterephthalates have melting points of 129°C (*10*) and 91°C, respectively, while the corresponding ortho esters have melting points of 60° and 26°C. The dibutyl *o*-ester is a liquid at room temperature and has not been crystallized (*8, 12*).

The alkyl and aryl tetrachloroterephthalates show strong standard infrared ester absorption maxima at 5.69–5.78 μ except for fluorine containing aromatics where absorption is shifted to lower wavelengths (*1, 2, 4*). Other characteristic ester peaks occur around 8.08 μ and 8.93–9.0 μ. Aromatic absorption at about 6.24 μ and medium absorption at 6.8 μ is also evident. A characteristic aromatic chlorine absorption apparently occurs at about 12.7 μ (*1, 4*) for alkyl tetrachloroterephthalates. Some of the characteristic absorption wavelengths in these regions are given in Table I. Complications and additional absorption bands appear, of course, with esters of phenolic compounds.

EXPERIMENTAL

A. Di-*n*-butyl Tetrachloroterephthalate. *1. Direct Reaction with Alcohol* (*3, 10, 11*). A mixture of 250 ml (2.7 moles) of *n*-butanol, dried by azeotropic distillation with benzene, and 53.4 grams (0.16 mole) of tetrachloroterephthaloyl chloride, mp 146–8°C, was refluxed for 9 hr in a flask fitted with a Claisen adapter, Dean-Stark trap, and condenser with drying tube. It stood for 24 days, and excess butanol was removed by distillation. Periodically, distillation was interrupted, the reaction mixture was cooled to room temperature, and the precipitate recovered by filtration. A total of 64.4 grams (98% yield) of crude product, mp 52–55.5°C was recovered. Recrystallization from methanol produced pure (46 grams) di-*n*-butyl tetrachloroterephthalate, mp 61.5–62.5°C. In similar preparations of other aliphatic diesters, standing times were varied from two days to months without affecting yields greatly.

2. Reaction of Sodium Alkoxide with Tetrachloroterephthaloyl Chloride (*8*). In apparatus similar to the above, 250 ml (2.7 moles) of dried *n*-butanol and 9.2 grams (0.4 mole) of sodium metal were reacted with gentle heating for 2.5 hr. Addition of 68 grams (0.2 mole) of crude tetrachloroterephthaloyl chloride, mp 140–4, was followed by 9 hr of reflux. The mixture stood one day, and the sodium chloride formed was removed by filtration and washed with hot benzene. After removal of volatile material by distillation, the reaction mixture was diluted with ether and extracted with dilute potassium hydroxide, then dried over magnesium sulfate. Filtration, removal of ether on the steam bath, followed by dilution with 100 ml of methanol and treatment with activated charcoal gave an initial crop of 14 grams (20% yield) of fairly pure product, mp 61.5–2.0°C. A second 14-gram crop of crude product, mp 49–55°C, was recovered upon concentration of the filtrate and cooling in an ice bath. Additional material, 12 grams (56% total yield), was recovered upon concentration, base extraction, charcoal treatment, and cooling. Recrystallization from methanol gave a total of 35 grams of pure di-*n*-butyl tetrachloroterephthalate, mp 62–3°C.

B. Di-*n*-dodecyl Tetrachloroterephthalate. In an apparatus similar to A.1, *n*-dodecyl alcohol, 120 ml (0.53 mole), and 70 ml of xylene were refluxed in a flask equipped with a thermal well to remove water by azeotropic distillation. Addition of 23.8 grams (0.07 mole) of tetrachloroterephthaloyl chloride and intermittent refluxing (40 hr) over 16 days eventually gave a solidified mixture. Additional xylene, 70 ml, was added followed by refluxing for 7 hr. Then, solvent and excess alcohol were removed by low-pressure distillation to a flask temperature of 210°C at a pressure of 9 mm. The 43 grams (95% yield) of remaining crude product, mp 68–9°C, were recrystallized first from *n*-butanol and then from *n*-propanol to give pure di-*n*-dodecyl tetrachloroterephthalate, mp 68.7–69.5°.

C. Bis-*p*-fluorophenyl Tetrachloroterephthalate. A mixture of 175 ml of dry benzene, 17 grams (0.05 mole) tetrachloroterephthaloyl chloride, 12.3 grams (0.11 mole) *p*-fluorophenol, and 7.9 grams (0.1 mole) pyridine was stirred and heated (50°C) for 7 hr, then allowed to stand 20 days. Filtration of the reaction mixture and washing of the solid with a large volume of water followed by dilute (0.01*N*) H_2SO_4 and 0.01*N* KOH gave 21.7 grams (82% yield) of crude product, mp 250–2°C. After the mixture was dissolved and refluxed with benzene to remove residual water azeotropically, 18 grams of purified product were recovered. Recrystallization from dioxane gave pure bis-*p*-fluorophenyl tetrachloroterephthalate, mp 251–2.5.

D. Bis-cyclohexylmethyl Tetrachloroterephthalate. To 25 grams of dry cyclohexylmethanol in 100 ml dioxan, 34 grams (0.1 mole) of tetrachloroterephthaloyl chloride were added followed by 15.8 grams (0.2 mole) of pyridine. The mixture was stirred for 3.5 hr, then allowed to stand 20 months. The reaction mixture, mostly a yellow solid, was distilled at low pressure to remove dioxane. The residue was treated with benzene and filtered to remove pyridine hydrochloride.

The 700 ml of benzene solution was washed with several times its volume of water and 0.01*N* sulfuric acid and 0.01*N* KOH. The benzene layer was dried over magnesium sulfate and filtered. Concentration to about 50 ml of solution resulted in 25 grams crude product, mp 161–7.5°. Additional crude material, 7 grams, was recovered on further concentration to give a yield of 64%. Pure product, mp 174–5°C, was obtained by two successive recrystallizations from propanol, charcoal being used in the last recrystallization. About 50 ml of solvent per gram of product was necessary. Benzene was also a satisfactory recrystallization solvent.

E. Transesterification Attempt. Dimethyl tetrachloroterephthalate, 25 grams (0.075 mole), was dissolved in a solution of 135 ml *n*-propanol, 35 ml benzene, and 2 grams *p*-toluenesulfonic acid. Intermittent heating and reflux over 8 days were accompanied with the addition of 60 ml benzene, 20 ml propanol, and acid (3 × 0.5 gram). Crystals obtained upon cooling were starting material, mp 157–8.5°C. Two additional crops from the reaction mixture were substantially the dimethyl ester.

Comparable attempts at transesterification with sodium propoxide and titanium isopropoxide as catalysts also failed.

F. Attempted Saponification. A mixture of 1 gram (0.003 mole) dimethyl tetrachloroterephthalate, 75 ml absolute ethanol, and 25 ml of 0.44*N* KOH was refluxed 3 hr. After it cooled, 50 ml of water and 25 ml of 0.1*N* HCl were added. Titration, using 0.1*N* HCl, to the phenolphthalein end point gave a neutralization equivalent, after blank correction, of 242 (theory is 166). The same procedure was used, and a saponification equivalent for di-*n*-propyl tetrachlorophthalate of 197 was found (calcd 194). Longer time and variants of this procedure with aliphatic tetrachloroterephthalates still did not give a satisfactory saponification equivalent. Substantially more drastic treatment resulted in an attack on the aromatic nucleus. Profft and Timm (*10*) do not report such an attack in their saponification procedure.

G. Complexation Studies. Previously described procedures did not give complexes of hexamethylbenzene with aliphatic tetrachloroterephthalates as were obtained with tetrachlorophthalate and tetrabromophthalate esters (*8*). With dimethylaniline, colors were observed with dipropyl (pale yellow), dibutyl (pale yellow), dioctyl (greenish yellow), and bis-pentafluorophenyl (dark yellow) tetrachloroterephthalates. Other observations are reported in the discussion.

H. Infrared Spectra. All were taken at 0.66% concentration in KBr pellets.

I. Elemental Analyses. All were made by Spang Microanalytical Laboratories of Ann Arbor, Mich. Analyses were in satisfactory agreement with calculated values and were made available to reviewers.

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Derivatives of Hexaphenylisobenzofuran

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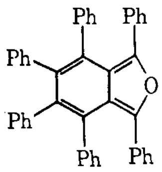
Diels-Alder adducts have been prepared from hexaphenylisobenzofuran and a variety of dienophiles, including benzyne. Benzyne adduct was the only one of those prepared that did not decompose by retrograde Diels-Alder reaction upon heating. Attempted aromatization reactions of adducts are described.

Hexaphenylisobenzofuran (**1**), a yellow-green fluorescent compound, was first reported in 1961 by Reid and Bonnighausen (*6*). It has not been investigated in any detail apart from some studies of its absorption and fluorescence spectra (*8*). Our interest in **1** stemmed from its potential as a precursor to some highly phenyl-substituted naphthalenes, compounds we desired for studying effects of steric crowding on thermal properties. While we were not successful in obtaining the latter by this route, we report here some aspects of the Diels-Alder chemistry of **1**.



1

In general, hexaphenylisobenzofuran undergoes the Diels-Alder reaction readily with olefinic or acetylenic dienophiles if the latter are not substituted with phenyl groups. For example, dienophiles which failed to react after several days in refluxing toluene or benzene or upon fusing with **1** include *trans*-stilbene, diphenylacetylene, cinnamaldehyde, cinnamonitrile, and α-phenylcinnamonitrile. Also, unexpectedly, fu-

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