

mg. (87.5% yield) of white leaves, m.p. 83.5–86.0° (lit.⁵ 86–87°). Treatment with acetic anhydride and pyridine gave 3-acetamidophenanthrene, m.p. 202.5–203.5° (lit.¹⁰ 200–201°).

9-Phenanthrylamine was obtained from 9-bromo-10-nitrophenanthrene (in 91% yield) in a manner analogous to the preparation of the 3-isomer. It crystallized in white felted needles, m.p. 136.8–137.8° (lit.¹¹ 136–137.5°). The acetyl derivative formed white needles, m.p. 214.5–215.0° (lit.⁶ 213–215°).

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Preparation and Molecular Complexes of Tetrahalophthalate Esters

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The molecular complexing properties of tetrahalophthalic anhydrides have been the subject of several studies,^{1–5} but the molecular complexing properties of the tetrahalophthalate esters have not been investigated, although the yellowish green color of a dimethyl tetrachlorophthalate-dimethylaniline mixture has been reported.² This report on some of the complexing properties and synthesis of several tetrahalophthalates, two of which have not previously been characterized, resulted from finding that these materials were useful gas chromatographic liquid phases for aromatic materials.⁶ Separation and retention on gas chromatographic columns containing the tetrahalophthalates is a function of the electron donor characteristics of the aromatic hydrocarbons. Details will be reported elsewhere.

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The molecular complexing behavior of the tetrahalophthalates reported here and their low melting points suggest that they may be useful reagents for separation and/or purification of the polyalkylaromatic fractions from coal tar and petroleum. Conversely, interaction with an aromatic hydrocarbon could be used for purifying and separating the tetrahalophthalate esters themselves.

Data on the tetrahalophthalate esters that were prepared are listed in Table I. Where possible, we prefer a modification of the azeotropic distillation procedure of Nordlander and Cass⁷ for preparation of the symmetrical diesters. The reaction of the potassium salt of the monoalkyl ester and the alkyl halide⁸ was used for preparation of the mixed ester.

Solid hexamethylbenzene 1:1 complexes of di-*n*-propyl tetrachlorophthalate, di-*n*-butyl tetrachlorophthalate, and di-*n*-propyl tetrabromophthalate were isolated from solution. All were white crystalline solids. The intensity of yellow color on initial mixing of the chlorophthalates with hexamethylbenzene was in the order di-*n*-butyl > di-*n*-propyl. Methyl propyl tetrachlorophthalate did not give a solid complex with hexamethylbenzene by our procedure; mixtures of these two materials gave only a faint yellow color even in concentrated solution.

The light yellow colors observed on mixing the tetrachlorophthalates with durene, isodurene, and hemimellitene probably indicate complex formation. Evidently interaction with mesitylene (no color) is weaker; this may be due to a steric factor.⁹

The interactions of the tetrahalophthalates with dimethylaniline are also of interest. The colors of the solutions obtained undoubtedly indicate complex formation and suggest the possible use of tetrahalophthalates as liquid substrates for aromatic amines in gas chromatography.

EXPERIMENTAL

*A. Di-*n*-propyl tetrachlorophthalate.* A mixture of 288 grams (1.01 mole) of tetrachlorophthalic anhydride, 360 grams (6 moles) of propyl alcohol, 4 grams (0.021 mole) of *p*-toluenesulfonic acid monohydrate, and 35 ml. of benzene was refluxed continuously for 16 days in a flask, fitted with a 6-in. Vigreux column connected to a Dean-Stark trap and condenser. With slow reflux, a total of 25.5 ml. of aqueous phase separated in the trap. At intervals, additional *p*-toluenesulfonic acid (3 × 1 g.) and small aliquots of benzene were added.

Volatile material was distilled from the flask up to a pot temperature of 168°. The cooled residue was extracted with 6% aqueous sodium bicarbonate which was then extracted with benzene.

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TABLE I
 DIALKYL TETRAHALOPHTHALATES

	B.P., °C./ (mm.)	n_D^{25}	Sapon. Equiv.		Literature
			Calcd.	Found	
Methyl propyl tetrachloro- phthalate	176/1.3 M.p. 37.6–39.2	1.5491	180	180	
Di- <i>n</i> -propyl tetrachloro- phthalate	191/2, 174/1 M.p. 26°	1.5365 d_4^{20} 1.37	194	193	B.p. 170–175°/1, n_D^{25} 1.5348 ^a B.p. 159–184°/1, m.p. 26° ^b
Di- <i>n</i> -butyl tetrachloro- phthalate	194–195/1 178/0.5	1.5288 d_4^{20} 1.31	208	209	B.p. 180–185°/1, n_D^{25} 1.5292 ^a B.p. 207–214°/3 ^b
Di- <i>n</i> -propyl tetrabromo- phthalate	206/0.7 M.p. 64–65.2		283	283	

^a Reference 7. ^b Reference 10.

The sodium salt of the monoalkyl ester or diacid (formed during extraction of unreacted acid) tends to solvate or emulsify the diester (as well as solvents such as chloroform and carbon tetrachloride) in water; to minimize formation of these salts, reaction should be carried as near to completion as practical. During product recovery, aqueous solutions are easier to handle if all unreacted acid is not extracted initially. That is, sufficient sodium bicarbonate need be used to assure only removal of the *p*-toluenesulfonic acid catalyst in the first extraction with sodium bicarbonate.

The organic layers were combined, diluted with additional benzene, and extracted again with an excess of sodium bicarbonate solution. The benzene solution was washed, dried with magnesium sulfate, and filtered.

After removal of solvent and two distillations at reduced pressure, 235 g. (60.5% yield) of product, n_D^{25} 1.5367–69, was recovered. Recrystallization at room temperature (<26°) gave pure propyl tetrachlorophthalate n_D^{25} 1.5365. Additional pure product was recovered after bicarbonate extraction of mother liquor and redistillation.

Anal. Calcd. for $C_{12}H_{10}O_4Cl_4$: C, 43.32; H, 3.64; Cl, 36.55. Found: C, 43.49; H, 3.71; Cl, 36.86.

*B. Di-*n*-butyl tetrachlorophthalate.* Procedure was similar to A. Initial *p*-toluenesulfonic acid concentration was doubled. Toluene was added to help remove water azeotropically. Yield was 62.8% after 2 successive vacuum distillations.

*C. Di-*n*-propyl tetrabromophthalate.* A mixture of 347.8 g. (0.75 mole) of tetrabromophthalic anhydride (Michigan Chemical Co., St. Louis, Mich.), 270 g. (4.5 moles) propyl alcohol, 6 g. (0.032 mole) of *p*-toluenesulfonic acid monohydrate and 40 ml. of benzene was reacted as in A continuously for 21 days. An additional 5 g. of *p*-toluenesulfonic acid monohydrate and benzene were added at intervals during reaction. Aqueous phase removed totaled 25.4 ml. The product was extracted and recovered as in A. During the second extraction with sodium bicarbonate, a copious precipitate, apparently a sodium salt of tetrabromophthalic acid or the monopropyl ester, formed, and was removed by filtration with suction through a Buchner funnel.

After solvent removal, product was distilled twice at reduced pressure to give a total of 119.8 g. (28.3% yield) of crude product, b.p. 206–213°/0.7 mm., which solidified on cooling. Several recrystallizations of heart-cut material from ethyl alcohol gave pure product with m.p. 64–65.2°.

Anal. Calcd. for $C_{14}H_{14}O_4Br_4$: C, 29.71; H, 2.49; O, 11.31. Found: C, 29.76; H, 2.67; O, 11.20.

D. Reaction of potassium monoalkyl tetrachlorophthalate with propyl bromide. Methyl propyl tetrachlorophthalate. After 1 mole of tetrachlorophthalic anhydride had been refluxed with 6 moles of methyl alcohol for 6 hr. and cooled, 76 g. (0.55 mole) of pulverized potassium carbonate was added, with stirring and gentle heating. After 1.5 hr., 148 g. (1.2 moles) of propyl bromide was added, followed by

addition of 1.5 ml. of triethylamine. The mixture was refluxed 10.5 hr. and volatile material removed by distillation. One l. of water and 300 ml. of benzene were added. The organic layer was washed and dried with magnesium sulfate before removal of solvent. Two distillations at reduced pressure gave 17.6% yield of liquid product, n_D^{25} 1.5491, which solidified on standing.

Anal. Calcd. for $C_{12}H_{10}O_4Cl_4$: C, 40.03; H, 2.80; Cl, 39.39. Found: C, 40.07; H, 2.90; Cl, 39.10.

*Molecular complexes. E. Hexamethylbenzene/di-*n*-propyl tetrachlorophthalate complex.* This procedure was typical of those used for isolating the hexamethylbenzene complexes. To 1.030 g. (2.65×10^{-3} mole) di-*n*-propyl tetrachlorophthalate in 1 ml. absolute ethanol was added 0.426 g. (2.63×10^{-3} mole) hexamethylbenzene (recrystallized, m.p. 165.4–166°); a yellow color appeared on mixing. After addition of 5 ml. of ethanol and warming to complete solution, the yellow color disappeared. The mixture was allowed to stand overnight, filtered, and the precipitate washed with 1/2 ml. of methanol and dried *in vacuo* at 10 mm. for 15 min. Product, 1.21 g. of white needles, had decomposition temperature 80.6°.

Anal. Calcd. for $C_{12}H_{18}.C_{14}H_{14}O_4Cl_4$: C, 56.74; H, 5.86; Cl, 25.77; sapon. equiv., 275. Found: C, 56.45; H, 5.94; Cl, 25.88; sapon. equiv., 273.

*F. Hexamethylbenzene/di-*n*-butyl tetrachlorophthalate complex.* Procedure as in E; bright yellow color on mixing. Twenty % excess of the ester was used. White crystals, dec. 49.6°.

Anal. Calcd. for $C_{12}H_{18}.C_{18}H_{18}O_4Cl_4$: C, 58.14; H, 6.27; Cl, 24.52. Found: C, 58.64; H, 6.49; Cl, 24.14.

*G. Hexamethylbenzene/di-*n*-propyl tetrabromophthalate.* As in E, m.p. 94.6–95.5°.

Anal. Calcd. for $C_{12}H_{18}.C_{14}H_{14}O_4Br_4$: C, 42.88; H, 4.43; O, 8.79. Found: C, 42.29; H, 4.36; O, 8.79.

H. Hexamethylbenzene/methyl propyl tetrachlorophthalate complex. Procedure as in E resulted in recovery of hexamethylbenzene. No color was observed on mixing methyl propyl tetrachlorophthalate with hexamethylbenzene. In carbon tetrachloride where the other tetrachlorophthalates gave clear yellow solutions with hexamethylbenzene, methyl propyl tetrachlorophthalate gave only the faintest yellow color.

I. Qualitative tests. Color tests were made by mixing approximately equal parts of tetrahalophthalate and hydrocarbon and warming to solution where necessary.

1. The tetrahalophthalates of Table I were tested by examining solutions of these materials with 1,2,4,5-tetramethylbenzene (durene), 1,2,3,5-tetramethylbenzene (isodurene), 1,2,3-trimethylbenzene (hemimellitene), and mesitylene. Methyl propyl tetrachlorophthalate gave no color with these hydrocarbons, and mesitylene gave no color with any of the tetrahalophthalates. The two symmetrical dialkyl tetrachlorophthalates gave light yellow solutions in the approximate order of intensity (shortly after mixing) durene > isodurene > hemimellitene. The only polymethyl-

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benzene which gave a yellow color (faint) with propyl tetrabromophthalate was hemimellitene.

2. Dimethylaniline. On mixing with dimethylaniline, dibutyl and dipropyl tetrachlorophthalates were orange-red and brown-red respectively, while the bromophthalate and methyl propyl tetrachlorophthalate were yellow-green and yellow, respectively.

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Preparation of 1-Alkylated 2-Haloethers by the Grignard Method. 2-Bromo-1,1-dimethylethyl Ethyl Ether¹

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In the course of an investigation of the properties of 2-haloethers the authors have had occasion to prepare 2-bromo-1,1-dimethylethyl ethyl ether, which has not previously been reported. This compound is of special interest because it cannot lose hydrogen bromide in a simple way or rearrange to a 1-haloether, two possibilities in the thermal decomposition³ of 2-bromoethers, without the breaking of a carbon-carbon bond.

The desired 2-bromoether was synthesized following the general procedure of Sherrill and Walter^{3c} for a similar 2-bromo-1,1-dialkylated ether, modified to employ ethyl vinyl ether as a starting material,⁴ from which 1,2-dibromoethyl ethyl ether was made. The over-all yield (25%, based on starting vinyl ether) was considerably better than those previously given^{5,3c} for such compounds.

During the work reported here it was found that 2-chloro-1-methylethyl ethyl ether could not be made from 1,2-dichloroethyl ethyl ether and the Grignard reagent prepared from methyl iodide. Reaction was violent and by either mode of addition, Grignard reagent to halogenated ether or halogenated ether to Grignard reagent only tars

and small quantities of impure products resulted.⁶ This compound could, however, be synthesized in good yield (48%, based on the dichloro ether)⁷ when methyl chloride was used instead of methyl iodide.

EXPERIMENTAL⁸

2-Bromo-1-methylethyl ethyl ether (I). To 144 g. (2.00 moles) of redistilled (fraction boiling at 34.4°) ethyl vinyl ether (General Aniline and Film Corp.) and 700 ml. of sodium-dried diethyl ether in a 3-necked, 2-liter flask fitted with a dropping funnel, mercury-sealed stirrer, and reflux condenser, immersed in a Dry Ice-acetone bath at -70°, bromine was added at the rate of one drop per second. All openings to the system were fitted with drying tubes. The bromine color was lost rapidly after the addition of each drop. Addition was stopped when the bromine color persisted (320 g., 2.00 moles, of bromine), and a few drops of the vinyl ether were added to decolorize the solution. This solution of 1,2-dibromoethyl ethyl ether was then removed from the bath and added at 0°, in an assembly like that just described, to a Grignard solution, in excess, made from methyl bromide (65.2 g., 2.68 g.-atoms, magnesium and 840 ml. ether, with about 10% excess methyl bromide). Addition required about 5 hr. whereupon the mixture was refluxed with stirring for 8 hr. Then the product was poured onto ice and dilute hydrochloric acid, the ether layer separated, washed with 10% sodium bicarbonate and then with water until the washings were neutral. After drying over calcium chloride, the bulk of the solvent ether was removed by fractionation at atmospheric pressure. The remaining 2-bromoether was distilled (Vigreux column) at reduced pressure over a few sodium hydroxide pellets. The main fraction boiled at 39°/18 mm. and weighed 275 g. (82%). Redistillation gave 252 g. (75%) of a product of constant boiling point and refractive index, b.p. 36.5°/16.5 mm., n_D^{25} 1.4396, d_4^{25} 1.2689.

Ethyl isopropenyl ether (II). Dehydrohalogenation was effected with solid potassium hydroxide in a copper flask, according to the procedure of Sherrill and Walter.^{3c} Careful control of the temperature was necessary to moderate the vigorous reaction that ensued. From 208 g. (1.24 moles) of I, 81.2 g. (76%) of II was obtained upon redistillation, b.p. 59.2-61.2/733 mm., n_D^{27} 1.3882.

2-Bromo-1,1-dimethylethyl ethyl ether (III). Bromine was added to 74.5 g. (0.865 mole) of II in 435 ml. of diethyl ether as in the preparation of I except that the temperature of the bath was kept at -30°, since the bromination was slower and at lower temperatures an increasing amount of frozen bromine collected at the bottom of the flask. An almost theoretical amount of bromine (138.5 g., 0.867 mole) was used, with the solution pale yellow at the end of the addition. This solution was then added dropwise with stirring to the Grignard reagent (made from 30.2 g., 1.24 g.-atoms, magnesium, 390 ml. ether and a slight excess of

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(7) The authors are indebted to Mr. W. A. Dickens of this laboratory for help in this preparation. The physical constants of the product obtained, which was distilled to constant boiling point and refractive index, differ from those previously recorded and give a better value for the molar refraction; b.p. 30.3°/25 mm., n_D^{25} 1.4103, d_4^{25} 0.9582, M_R Calcd. 31.80 (Ref. 10), M_R found 31.72. See L. C. Swallen and C. E. Boord, *J. Am. Chem. Soc.*, **52**, 651 (1930); A. Dewael, *Bull. soc. chim. Belg.*, **39**, 395 (1930); V. A. Sklyarov, *J. Gen. Chem. U.S.S.R.*, **9**, 2121 (1939); A. K. Seleznev and A. Balakirev, *Zhur. Priklad Khim.*, **27**, 650 (1954).

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