

crystallized from acetone in colorless crystals; mixed m.p. determination with the photoproduct gave no depression; yield 70% and more.

**Thermal Decomposition.**—Ia was heated in a boiling ethyl phthalate-bath under reduced pressure (oil pump vacuum) for fifteen minutes. The reaction vessel was left to cool in vacuum. The crystals collected on the upper parts were recrystallized from methyl alcohol and proved to be stilbene (m. p. and mixed m. p.).

***o*-Phenylenediamine and Ia.**—Equimolecular amounts in acetic acid (90%) were refluxed for two hours and the mixture left to cool. The crystals separated were washed with methyl alcohol and proved to be Ia (mixed m. p.).

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### Esters of Tetraphenylphthalic Acid

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Only the methyl and ethyl esters of tetraphenylphthalic acid have been described. The methyl ester has been obtained by the action of diazomethane on the free acid,<sup>2</sup> by heating methyl acetylenedicarboxylate with tetracyclone (tetraphenylcyclopentadienone) at 160°,<sup>2</sup> and by heating methyl maleate with tetracyclone over a free flame.<sup>3</sup> The ethyl ester has not been prepared directly, but has been synthesized from ethyl acetylenedicarboxylate and tetracyclone.<sup>2,3</sup> Attempts to saponify these esters have failed.<sup>2,3</sup> In an effort to prepare a series of these esters in order to study their unique unreactivity, a new synthesis was applied.

Synerholm has recently reported that the reaction between tetracyclone and chloromaleic anhydride in bromobenzene gives 75 per cent. of tetraphenylphthalic anhydride.<sup>4</sup> This elegant procedure was duplicated here<sup>5</sup> and it suggested the application to the synthesis of the desired esters.

Three hitherto undescribed esters of chloromaleic acid—the *n*-propyl, *n*-butyl<sup>6</sup> and *n*-amyl—were prepared in from 58–66% yield by reaction of the chosen alcohol with chloromaleic anhydride in the presence of *p*-toluenesulfonic acid (Table I). An excess of each of these esters was refluxed with tetracyclone at atmospheric pressure. In each case carbon monoxide and hydrogen chloride were eliminated and colorless, crystalline esters of tetraphenylphthalic acid were obtained in from 67–76% yield<sup>7</sup> (Table II).

(1) Taken from a thesis submitted for the Bachelor of Science degree, Polytechnic Institute of Brooklyn, June, 1951.

(2) W. Dilthey, I. Thewalt and O. Trösken, *Ber.*, **67**, 1959 (1934).

(3) C. F. H. Allen and L. J. Sheps, *Can. J. Research*, **11**, 171 (1934).

(4) M. E. Synerholm, *THIS JOURNAL*, **67**, 1229 (1945).

(5) John A. Romano, thesis submitted for the Bachelor of Science degree, Polytechnic Institute of Brooklyn, June, 1949.

(6) *n*-Butyl chloromaleate has been mentioned by C. H. Fisher and W. C. Mast (*Ind. Eng. Chem.*, **40**, 107 (1948)), but its preparation and properties were not given.

(7) Preliminary experiments with methyl chloromaleate and ethyl chloromaleate had given the already known methyl and ethyl esters of tetraphenylphthalate (see ref. 5).

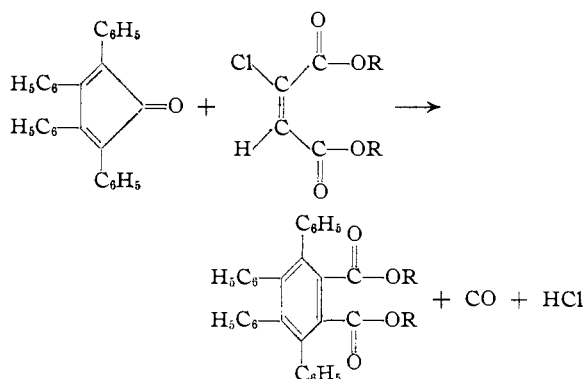


TABLE I

ESTERS OF CHLOROMALEIC ACID			
	$n\text{-C}_3\text{H}_7$	$n\text{-C}_4\text{H}_9$	$n\text{-C}_5\text{H}_{11}$
Yield, %	66	60	58
B. p., °C.	89–90	150	47
M. p., °C.	1	11	0.6
$d^{25}_4$	1.108	1.072	1.028
$n^{20}_D$	1.4571	1.4566	1.4559
Formula	$\text{C}_{10}\text{H}_{15}\text{ClO}_4$	$\text{C}_{12}\text{H}_{19}\text{ClO}_4$	$\text{C}_{14}\text{H}_{23}\text{ClO}_4$
Carbon, %	Calcd. 51.18 Found 51.23	54.85 54.63	57.82 57.47
Hydrogen, %	Calcd. 6.44 Found 6.48	7.29 7.02	7.97 7.80
Chlorine, %	Calcd. 15.11 Found 15.14	13.50 13.27	12.20 12.01

TABLE II

ESTERS OF TETRAPHENYLPHTHALIC ACID			
R is	$n\text{-C}_3\text{H}_7$	$n\text{-C}_4\text{H}_9$	$n\text{-C}_5\text{H}_{11}$
Yield, %	76	70	67
M. p., °C.	196.5–197.5	193–194	190–191.5
Formula	$\text{C}_{38}\text{H}_{34}\text{O}_4$	$\text{C}_{40}\text{H}_{38}\text{O}_4$	$\text{C}_{42}\text{H}_{42}\text{O}_4$
Carbon, %	Calcd. 82.28 Found 82.21	82.49 82.25	82.59 82.22
Hydrogen, %	Calcd. 6.18 Found 5.93	6.57 6.17	6.93 6.73

It is interesting to report that recrystallization of the *n*-propyl ester from ethanol gave the ethyl ester. This was established by melting point, mixed melting point with known ethyl tetraphenylphthalate and analysis for carbon and hydrogen. This facile *trans*-esterification is unusual in view of the failure of the methyl or ethyl ester of tetraphenylphthalic acid to hydrolyze and also of the failure to synthesize either of these esters from the acid and the alcohol.<sup>2,3</sup>

### Experimental

**Starting Materials.**—Chloromaleic anhydride was supplied by the Allied Chemical and Dye Corporation and was redistilled before use, b. p. 89° (14 mm.),  $n_D^{20}$  1.5021. *n*-Propanol, *n*-butanol and *n*-pentanol were refluxed with potassium hydroxide, dried and distilled. Tetracyclone was prepared according to Johnson and Grummitt<sup>8</sup> and melted at 219–220°.

**Esters of Chloromaleic Acid.**—The three esters were prepared in similar fashion. The following description for the di-*n*-propyl ester is representative.

A mixture of 62 g. (0.50 mole) chloromaleic anhydride, 67 g. (1.1 mole) *n*-propanol, and 0.5 g. *p*-toluenesulfonic acid monohydrate was refluxed for 3.5 hours. The solution was diluted with 150 ml. of ether, extracted with cold saturated sodium bicarbonate solution until neutral, dried over anhydrous magnesium sulfate and filtered. After distilling the ether and discarding a small forerun (7.3 g., b. p. 80–89° (1 mm.)), the major product (77 g., 0.33 mole) distilled at 89–90° (1 mm.).

The esters are unsaturated with respect to potassium permanganate in acetone. They are soluble in absolute ethanol, acetone, methyl ethyl ketone, dioxane, ethyl ether, chloroform, carbon tetrachloride, benzene, toluene, petroleum ether (b. p. 60–70°), and acetic acid. They show limited solubility in ethylene glycol, and formic acid (87%) and are insoluble in water.

**Esters of Tetraphenylphthalic Acid.**—A 1 × 6 in. Pyrex side-arm test-tube was fitted with a condenser to which was attached by means of 5-mm. glass tubing a series of vials. Starting at the condenser these were (1) an empty vial serving as a trap, (2) a vial containing a 1–2 ml. 0.1 *N* silver nitrate solution, (3) another trap, and (4) a vial containing 1–2 ml. of 0.01% solution of palladium(II) chloride solution to test for carbon monoxide. A slow stream of nitrogen was led into the side arm throughout an experiment.

A mixture of 0.38 g. (1.0 mmole) of tetracyclone and 7.0 g. (0.03 mole) of di-*n*-propyl chloromaleate was refluxed over a free flame until the intense purple color of the tetracyclone had changed to brown. During this time the effluent gases turned blue litmus red, the vial holding the silver nitrate solution deposited a curdy white precipitate (silver chloride) and the vial holding palladium(II) chloride solution deposited a black precipitate. The reaction mixture was dissolved in 4 ml. of acetic acid, diluted with water to incipient crystallization and extracted with warm (40–45°) petroleum ether (b. p. 60–70°). Concentration of the petroleum ether gave 0.42 g. (0.76 mmole) of colorless crystals, m. p. 196.5–197.5°, which subsequent recrystallizations did not raise.

The esters are saturated with respect to potassium permanganate in acetone.

When the recrystallization of the *n*-propyl ester was attempted from ethanol, the substance melted over a wide range. Three recrystallizations gave a compound melting at 205–206° (reported<sup>2,5</sup> 205–206°) which showed no depression in a mixed melting point with authentic di-ethyl tetraphenylphthalate.

*Anal.* Calcd. for C<sub>26</sub>H<sub>30</sub>O<sub>4</sub>: C, 82.10; H, 5.74. Found: C, 81.93; H, 5.62.

(8) J. R. Johnson and O. Grummitt, *Org. Syn.*, **23**, 92 (1943).

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### Isotope Exchange Reaction of Chloroform-*d* with Bromoform

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This note reports an infrared spectrophotometric investigation of the deuterium exchange reaction  $\text{CCl}_3\text{D} + \text{CBr}_3\text{H} \rightleftharpoons \text{CCl}_3\text{H} + \text{CBr}_3\text{D}$ .

The isotope exchange was studied in the liquid phase at 30 and 105°, and in the vapor phase at 105°. The influence of organic bases such as *n*-butylamine and piperidine on the rate of the exchange was observed.

The CCl<sub>3</sub>D and CBr<sub>3</sub>D were prepared by the reaction of sodium deuteroxide with chloral and bromal, respectively. These products contained as impurities CCl<sub>3</sub>H and CBr<sub>3</sub>H, to the extent of approximately 10% and 5%, respectively, as determined by infrared and mass spectrometric analysis. The CBr<sub>3</sub>H, *n*-butylamine and piperidine were C.P. products which were further purified by fractional distillation under reduced pressure.

The experimental procedure consisted in weighing out small portions (ca. 200 mg.) of the reactants, CCl<sub>3</sub>D and CBr<sub>3</sub>H, and the desired quantity of base into several ampoules of about 2–4 ml. volume. These were then outgassed several times at –78° and sealed *in vacuo*. After suitable times of reaction in the absence of light at the appropriate temperature the contents were cooled to –78° and held frozen until subsequent analysis. In several experiments no visible decomposition occurred during the course of the reaction. However, in certain cases the solution appeared yellow or dark after an experiment. The volatile contents of the ampoule were then distilled *in vacuo* into another storage ampoule kept at –78°. The residue seldom exceeded 5% (by weight) of the original mixture. In one experiment (15) a special 300-ml. reaction vessel was used; it was large enough to ensure that the reactants as well as the base were completely in the vapor state during the entire reaction. At the conclusion of the experiment, all products were frozen down and analyzed in the usual manner.

The infrared absorption spectra of the mixtures were obtained with a Perkin-Elmer Model 12C spectrophotometer with rocksalt optics, using a 0.027 mm. NaCl cell. The extent of the reaction was determined by measuring the concentration of CBr<sub>3</sub>D in the mixtures. The strong doublet at 848 and 864 cm.<sup>-1</sup>, characteristic of CBr<sub>3</sub>D<sup>1</sup> was chosen for the analysis. The extinction coefficient for CBr<sub>3</sub>D was obtained using as a calibration standard a 10 mole % solution of CBr<sub>3</sub>D in chloroform.

The results reported are based on absorption measurements at 848 cm.<sup>-1</sup>. In certain of the experiments in the presence of fairly high concentrations of piperidine, interference at 864 cm.<sup>-1</sup> due to this molecule was significant. The 864 cm.<sup>-1</sup> band was, however, used as a rough check on the analysis, and also served to indicate the extent of decomposition of the piperidine.

The rates of disappearance of CCl<sub>3</sub>D and formation of CCl<sub>3</sub>H were followed by observing the

(1) S. M. Ferigle, F. F. Cleveland, W. M. Boyer and R. B. Bernstein, *J. Chem. Phys.*, **18**, 1073 (1950).