pure components. The results indicated that at least some exchange occurred.

Terpinyl Methyl Ether from α-Pinene.—α-Pinene, 150 g. (1.1 moles), was added to a stirred solution of 15.7 g. of concd. sulfuric acid in 141 g. (4.4 moles) of methanol at 35°. No external heat was applied. Within one hour the temperature of the reaction mixture rose to about 50°, then began to fall. Stirring at room temperature was continued overnight. The reaction mixture, heterogeneous at room temperature, was diluted with its own volume of water. The organic layer was separated and washed with 10% sodium hydroxide solution, then several times with water. In two experiments the crude reaction product was washed with sodium bicarbonate solution instead of sodium hydroxide; attempted distillation in these cases led to decomposition and isolation of no terpene ether. The product was dried over sodium sulfate and fractionally distilled through the helix-packed column to give: (I) g., b. p. 55-70° (20 mm.), (II) 54 g., b. p. 70-95° (20 mm.), and (III) 70 g., b. p. 95-107° (20 mm.). Most of cut I boiled 55-60° (20 mm.) and represents recovered α-pinene; cut II boiled mostly at 70-85° (20 mm.) and represents monocyclic terpene hydrocarbons. Redistillation of cut III through the helix-packed column gave 56 g. (30.1%) of terpinyl methyl ether, b. p. 106-107.5° (20 mm.), n^{25}_{D} 1.4647, d^{25}_{4} 0.9007. No attempt was made to improve the yield in this reaction.

Acknowledgment.—The author is indebted to the Emory University Research Committee and to the Research Committee, University Center in Georgia, for grants-in-aid toward the purchase of equipment and to Mr. A. E. Robinson, Jr., for determination of the densities reported in this paper.

Summary

d-Limonene reacts readily with primary alcohols in the presence of sulfuric acid to give terpene ethers. Evidence is presented that these ethers are principally of the α-terpinyl structure, although isomers may be present. The preparation and properties of the ethers derived from eight primary alcohols are described. Secondary alcohols do not react with *d*-limonene under the conditions used in this work. The nature of the reaction, an equilibrium complicated by concurrent isomerization of *d*-limonene, is discussed.

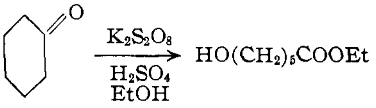
EMORY UNIVERSITY, GEORGIA
RECEIVED DECEMBER 2, 1948

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

Reactions of Per Acids. II. The Reaction of Perbenzoic Acid with Simple Cyclic Ketones. Kinetic Studies

BY S. L. FRIESS

In an extension of the previously reported work[1] on the reaction of perbenzoic acid with simple alicyclic and aromatic methyl and ethyl ketones, the present study deals with the action of this peracid on the ketopolymethylenes cyclopentanone, cyclohexanone and cycloheptanone in chloroform solution. Previous investigators, notably Baeyer and Villiger[2] and Robinson and Smith,[3] have touched upon the over-all reaction of these ketones with inorganic peracids in aqueous medium. Baeyer and Villiger found that treatment of cyclohexanone or suberone with Caro's acid in aqueous sulfuric acid solution resulted in monomeric lactones of the ω-hydroxy acids, and pointed out a rather formal analogy between this reaction and the Beckmann rearrangement of oximes. They found further that the presence of alcohol in the reaction mixture led directly to the ω-hydroxy esters in yields as high as 40%, by the reaction



Robinson and Smith modified this procedure somewhat by first forming the lactone from the cyclic ketone and persulfuric acid in aqueous solution at about 15°, followed by refluxing of the crude lactonic product in ethanolic aqueous sulfuric acid to yield the ω-hydroxy ethyl esters in comparable yields. The latter workers also included cyclopentanone in their series of reactants, and were able to isolate ethyl δ-hydroxyvalerate in approximately 45% yield, but they were unable to obtain a lactone from 4-methylcyclohexanone.

In the present work, the reactions of three representative ketopolymethylenes with perbenzoic acid in moist chloroform have been carried out. The lactonic products of the reactions were characterized by conversion to the known, crystalline ω-hydroxy acid hydrazides, and the kinetics of the reactions briefly investigated to obtain some insight into the relative rates of reaction for the different members of the series, as well as the mechanism of the ring expansion involved in lactone formation.

Experimental[4]

Stock solutions of perbenzoic acid in moist chloroform were prepared according to the procedure of Braun.[5]

In the first part of the work, where products were isolated and investigated, a typical reaction with one of the cyclic ketones involved thorough mixing of 0.10 mole of the ketone with 0.12 mole of perbenzoic acid in 250-300 ml. of moist chloroform. The reaction mixture was kept in the dark at room temperature (22-25°), and occasionally swirled. Each reaction proved to be slightly exothermic. Aliquots of the reaction mixtures were removed at intervals and titrated iodimetrically in the nor-

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[1] For paper I of this series, see Friess, THIS JOURNAL, 71, 14 (1949).

[2] Baeyer and Villiger, *Ber.*, 32, 3625 (1899); 33, 858 (1900).

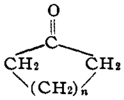
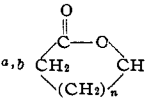
[3] Robinson and Smith, *J. Chem. Soc.*, 371 (1937).

[4] All melting and boiling points are corrected.

[5] Braun, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1947, p. 431.

TABLE I

KETONE REACTION WITH PERBENZOIC ACID IN CHLOROFORM AT ROOM TEMPERATURE (22–25°)

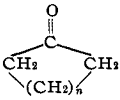
n	Ketone  B. p., °C.	$n^{25.5}_{D}$	Reaction time, hours	Moles peracid consumed by 0.10 mole ketone	Lactone product[a,b]  B. p. °C.	Mm.	ω-Hydroxy acid hydrazide, m. p. Observed	Lit. value	% Yield[g] of lactone
2	130	1.4352	28.1	0.096	145–146	40	105°	105–106[d]	78
3	155–155.8	1.4488	6.5	.098	102–104	7	114–115	114–115[e]	71
4	179.5–180.5	1.4592	405.0	.081	[c]		123	121–123[f]	97[h]

[a] Water-white liquids that gradually grew more viscous during distillation, and finally polymerized in the receivers. Converted to the ω-hydroxy acid hydrazides. [b] High-boiling residue in distillation flasks polymerized similarly. [c] Lactone converted directly to hydrazide, without distillation. [d] See reference 3. [e] Van Natta, Hill and Carothers, THIS JOURNAL, **56**, 455 (1934). [f] See reference 3. [g] Yield based on perbenzoic acid actually consumed. [h] Yield of hydrazide.

TABLE II

RATE RUNS

CYCLIC KETONES + PERBENZOIC ACID (BPA) IN CHLOROFORM SOLUTION

Run no.	Batch of stock PBA solution	Reaction Temp., °C.	Ketone 	Initial concentrations (molarities) ketone	PBA	General comment	k_2 l. mole^{-1} sec.$^{-1}$
1	A	26.96 ± 0.05	2	0.2519	0.3917	Moist solution	$1.73 \pm 0.12 \times 10^{-4}$
2	A	26.96 ± 0.05	3	.2513	.3917	Moist solution	$1.06 \pm 0.02 \times 10^{-3}$
3	A	26.96 ± 0.05	4	.2508	.3917	Moist solution	$1.69 \pm 0.05 \times 10^{-5}$
4	B	26.96 ± 0.05	2	.2524	.2914	Moist solution	$1.34 \pm 0.05 \times 10^{-4}$
5	B	26.96 ± 0.05	2	.2524	.1458	Moist solution	$1.01 \pm 0.16 \times 10^{-4}$
6	B	26.96 ± 0.05	2	.1514	.2944	Moist solution	$1.34 \pm 0.08 \times 10^{-4}$
7	B	26.96 ± 0.05	2	.2468	.2896	Solution 0.292 M in added benzoic acid	$2.62 \pm 0.10 \times 10^{-4}$
8	B	26.96 ± 0.05	2	.2539	.2979	No added benzoic acid	$1.27 \pm 0.06 \times 10^{-4}$
9	C	26.96 ± 0.05	2	.2529	.2956	Moist solution	$1.21 \pm 0.03 \times 10^{-4}$
10	C	26.96 ± 0.05	2	.2498	.2920	Solution 0.216 M in added acetic acid	$2.03 \pm 0.02 \times 10^{-4}$
11	C	26.96 ± 0.05	2	.2529	.2971	*Dried* solution	$1.44 \pm 0.03 \times 10^{-4}$
12	C	35.38 ± 0.05	2	.2529	.2972	Moist solution	$2.51 \pm 0.06 \times 10^{-4}$

The complete data for the course of two representative rate runs are given below as Tables III and IV.

mal manner[6] to determine the quantity of residual perbenzoic acid. In cases where the reaction was permitted to go to completion, the consumption of perbenzoic acid by ketone stopped sharply at one mole per mole of ketone.

After completion of the reaction, the benzoic and residual perbenzoic acids were extracted from the reaction mixture using dilute sodium bicarbonate solution, followed by a water wash of the resulting chloroform solution of the lactone. After drying and removal of the solvent, the reaction product was fractionally distilled under reduced pressure. The clear, colorless lactones slowly solidified to white amorphous solids, as formation of dimers, trimers, etc., occurred spontaneously in accordance with previous investigations[7] of these materials.

For more precise characterization of these polymeric lactones, portions of each were converted to the respective ω-hydroxy acid hydrazides by heating on the steam-bath for several hours with a slight excess of 100% hydrazine hydrate. The crude hydrazides were recrystallized from ethyl acetate as white, shiny needles.

A summary of results on yields and a description of reactants and products are found in Table I above.

Rate Runs

The course of the reaction could be followed quite easily by titrimetric determination of residual perbenzoic acid remaining in the reaction mixture at any given time. Each aliquot of reacting solution, upon addition to excess potassium iodide in dilute acetic acid solution, was instantly quenched by the quantitative reaction of perbenzoic acid to liberate iodine, which in turn was titrated with 0.1 N sodium thiosulfate solution.

The rate runs were begun by mixing the desired volume of moist chloroform solution of perbenzoic acid with the proper volume of purified chloroform as diluent, in a dark reaction flask suspended in a constant temperature bath. After attainment of temperature equilibrium, the addition of the necessary volume of cyclic ketone in chloroform solution started the reaction. Aliquots were withdrawn at timed intervals, and the iodimetric titrations made immediately.

A summary of all kinetic data obtained is to be found in Table II, with the last column giving the calculated values of second-order reaction rate constants.

Discussion

Products.—Inspection of the data of Table I indicates that the reaction of a cyclic ketone with

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(6) See ref. 5, p. 434.

(7) Stoll and Rouvé, *Helv. Chim. Acta*, **18**, 1087 (1935).

TABLE III

REACTION OF SUBERONE WITH PBA IN CHLOROFORM

Initial concentrations: a = (Ketone) = 0.2508 M; b = (PBA) = 0.3917 M; temp. 26.96 ± 0.05°; x = moles/l. of PBA consumed at time t

Time elapsed after mixing, seconds × 10^{-3}	$\log \frac{b-x}{a-x}$	$k_2 \times 10^5$ l. mole^{-1} sec.$^{-1}$
0.66	0.1942	
7.44	.2011	1.66
20.34	.2137	1.62
32.22	.2262	1.66
80.70	.2784	1.72
104.16	.3035	1.73
175.20	.3819	1.76
	Average	1.69 × 10^{-5}

Average deviation from the mean ±0.05 × 10^{-5}

TABLE IV

REACTION OF CYCLOPENTANONE WITH PBA IN CHLOROFORM

Initial concentrations: a = (Ketone) = 0.2524 M; b = (PBA) = 0.2914 M; temp., 26.96 ± 0.05°; x = moles/l. of PBA consumed at time t

Time elapsed after mixing, seconds × 10^{-3}	$\log \frac{b-x}{a-x}$	$k_2 \times 10^4$ l. mole^{-1} sec.$^{-1}$
0.33	0.0630	
1.53	.0656	1.29
3.60	.0700	1.28
5.82	.0752	1.31
8.58	.0814	1.32
11.82	.0899	1.38
14.13	.0966	1.44
	Average	1.34 × 10^{-4}

Average deviation from the mean ±0.05 × 10^{-4}

PBA in chloroform at room temperature is clean-cut, and leads to a single lactone product in yields of 70–97% in each case. These yields and the fact that uptake of PBA stops sharply at one mole make the reaction of preparative value. Since the monomeric lactones are unstable and spontaneously polymerize to non-distillable trimers, etc., it is probable that all yields in terms of percentage of over-all reaction to give ω-hydroxy acids could be boosted to the quantitative level by the procedure adopted for suberone, where the crude lactone mixture of monomer and higher forms is converted directly to the monomeric, easily purified ω-hydroxy acid hydrazide.

Rates.—The kinetic data of this study are best fitted by a second-order rate law for the reactions. Second order kinetics have been noted in many investigations of the velocity of reaction of organic peracids with organic compounds, including reaction with olefins to give epoxides,[8,9] reaction with thianthrene and its sulfoxides,[10] epoxidation of cyclenes[11] and reaction with unsaturated acids and esters.[12]

Since cyclopentanone has a convenient rate to follow at or near room temperature, it was taken as a representative member of the series to subject to varying reaction conditions. In Table II, inspection of runs 4–6 indicates the constancy of the second order rate constant as the initial concentrations of reactants are varied. No change in k_2 is observed as the ketone concentration is changed by almost a factor of two, but a slight drop in k_2 is noted when the initial PBA concentration is lowered. This drop in k_2 is associated with runs where a smaller aliquot of the stock solution of PBA was used in making the rate determination, and hence where a smaller amount of benzoic acid (always present in variable amounts in PBA preparations) was present in the initial reaction mixture. This decrease in the k_2 value would seem to indicate that decreasing the initial amount of benzoic acid present decreases the rate, and imply that benzoic acid is a catalyst for the reaction in chloroform.

The fact that such is the case is seen by a comparison of runs 7 and 8, which differed only in that additional benzoic acid was added to 7, beyond that amount already present from the PBA stock solution. The rise in rate constant from 1.27 × 10^{-4} to 2.62 × 10^{-4} l. mole^{-1} sec.$^{-1}$ is adequate evidence for the catalytic effect of benzoic acid. Another point of confirmatory evidence is the fact that in any given run, the rate constant slowly rises as the reaction progresses. Since benzoic acid is an end-product of the reaction, this effect on k_2 is quite reasonable, and is attributed to the increasing amount of catalyst produced during the course of the reaction. Because of this effect, all k_2 values tabulated are averages for the first 25–30% of the respective reactions.

This catalytic effect of benzoic acid on the rate of the reaction probably explains the literature statement[13] that the activity of various preparations of PBA varies with small changes in the method of preparation. It is apparent that as the technique of preparation varies, there will be variable amounts of benzoic acid accompanying the PBA, and if benzoic acid behaves catalytically in other peroxidation reactions, the activity of the peracid solution will be a function of the benzoic acid concentration.

For this reason, wherever comparisons of rates were to be made in this work, all rate runs in the comparison group were made by taking identical aliquots of peracid from the same batch of solution, in order to keep the benzoic acid concentration initially a constant, and make comparisons possible. However, small variations in benzoic acid concentration are permissible without too

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(8) Medvedev and Blokh, *J. Phys. Chem.* (*U. S. S. R.*), **4**, 721 (1933): *C. A.*, **29**, 6492 (1935).

(9) Böeseken and Stuurman, *Rec. trav. chim.*, **56**, 1034 (1937).

(10) Böeseken and van der Meulen, *ibid.*, **55**, 925 (1936).

(11) Böeseken and Sturrman, *Proc. Acad. Sci. Amsterdam*, **39**, 2 (1936); *C. A.*, **30**, 3304 (1936).

(12) Heinanen, *Ann. Acad. Sci. Fennicae*, **A59**, No. 13, 3 (1943); *C. A.*, **41**, 2370 (1947).

(13) Böeseken and Blumberger, *Rec. trav. chim.*, **44**, 90 (1925).

large a resulting effect on k_2 values, as is seen by comparing rate constants for runs 1, 4 and 9 in Table II, in which the differences in benzoic acid concentration of three batches of stock solution lead to a spread of k_2 values from 1.21 to 1.73 × 10^{-4} l. mole^{-1} sec.$^{-1}$.

To observe whether this acid catalysis of the reaction is specific for benzoic acid, or whether general acid catalysis is the rule in chloroform solution, the values in runs 9 and 10 can be compared. The addition of acetic acid to the chloroform solution raises the rate constant from 1.21 to 2.03 × 10^{-4} l. mole^{-1} sec.$^{-1}$, showing that acetic acid too is a catalyst for the reaction. These limited results would indicate general acid catalysis. Runs in buffered aqueous medium are contemplated to check the possibility of specific hydronium ion catalysis.

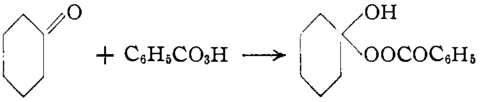
The effect of using moist *vs.* dry chloroform solution is seen by comparing runs 9 and 11. The difference in rate constants is small, and indicates that water has a slight decelerating effect on the reaction. Possibly this effect is exerted through an equilibrium involving formation of a slowly reacting ketone hydrate.

Perhaps the most striking comparison of all is to be found in runs 1, 2 and 3 in Table II, where under identical reaction conditions, the rates of reaction of cyclopentanone, cyclohexanone and cycloheptanone are compared. It is seen that the six-membered cyclic ketone reacts approximately ten times faster than the five, which in turn is ten times more reactive than the seven-membered ketone. In terms of the reaction mechanism to be postulated below, this is most probably attributed to differences in the velocities of addition of the peracid to the carbonyl group as the ring size changes. It is interesting to note in this connection that in the process of semicarbazone formation[14] in buffered solution at 25.10°, a reaction that is likewise subject to general acid catalysis,[15] the second order rate constants for cyclohexanone and cyclopentanone are in the ratio of 33.5:1.

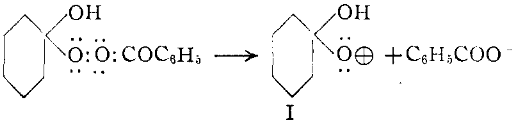
The data of runs 9 and 12 in Table II permit the calculation of a value for the Arrhenius energy of activation for the reaction of cyclopentanone over the temperature interval 27–35°. This value for E_a amounts to 15.9 kcal. per mole, which is of the same order of magnitude as the 14 kcal. found in the epoxidation of cyclohexene using organic per acids,[8] and the 15.1 kcal. and 15.6 kcal. found for the epoxidation of cycloheptene and cyclohexene, respectively, using peracetic acid[16] in acetic acid solvent.

Reaction Mechanism.—The nature of the reaction product and the fact that the reaction is clearly second order and subject to acid catalysis makes highly probable a mechanism suggested by Criegee for the reaction of ketopolymethylenes with Caro's acid, as inferred by analogy with his work on the rearrangement of esters of decalin hydroperoxide.[17]

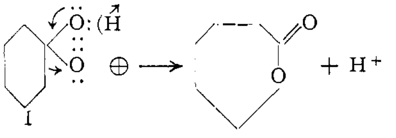
The first step in this scheme would be the slow, rate-controlling, acid-catalyzed addition of the peracid to the ketone group, similar to Criegee's postulation of the addition of Caro's acid


(1)

This would be followed by a sequence of rapid steps, involving first the cleavage to give a benzoate ion and the form I, which possesses an electron-deficient oxygen


(2)

and secondly a Whitmore type shift in I of a ring carbon to the positive oxygen, accompanied by simultaneous release of a proton

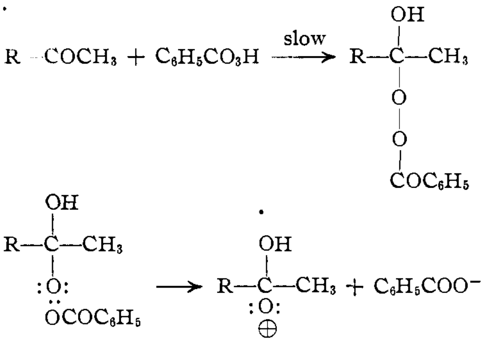

(3)

Actually, steps (2) and (3) might be part of a concerted process in which the benzoate ion leaves simultaneously with the Whitmore-type rearrangement to positive oxygen and release of the proton.

An alternate possibility for addition step (1) is the addition of $\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}{:}H^+$ directly from the reagent, which would eliminate the necessity for rapid step (2).

Criegee makes use of this concept of cationic oxygen to postulate reaction intermediates for such processes as the lead tetraacetate oxidation of glycols, and the decomposition of tetralin hydroperoxide.[17]

The above mechanism is probably the most reasonable one for the previously reported[1] reaction between methyl ketones and perbenzoic acid. Here, the steps could be formulated as



$$R{-}COCH_3 + C_6H_5CO_3H \xrightarrow{\text{slow}} R{-}\overset{\overset{\large OH}{|}}{\underset{\underset{\underset{\underset{COC_6H_5}{|}}{O}}{|}}{\underset{\underset{O}{|}}{C}}}{-}CH_3$$

$$R{-}\overset{\overset{OH}{|}}{\underset{\underset{\underset{OCOC_6H_5}{:\ddot{O}:}}{|}}{C}}{-}CH_3 \longrightarrow R{-}\overset{\overset{OH}{|}}{\underset{\underset{\underset{\oplus}{:\ddot{O}:}}{|}}{C}}{-}CH_3 + C_6H_5COO^-$$

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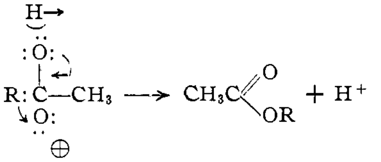
[14] Price and Hammett, This Journal, **63**, 2387 (1941).

[15] Conant and Bartlett, *ibid.*, **54**, 2881 (1932).

[16] Böeseken and Hanegraaff, *Rec. trav. chim.*, **61**, 69 (1942).

[17] Criegee, *Ann.*, **560**, 127 (1948).



Kinetic work on this reaction is in progress.

Summary

It has been found that by the reaction of perbenzoic acid in chloroform with the cyclic ketones cyclopentanone, cyclohexanone and suberone, the lactones of the corresponding ω-hydroxy acids are formed in 70–97% yields.

The kinetics of the reaction have been briefly investigated. The reaction is clearly second order, and subject to acid catalysis.

A reaction mechanism has been proposed which involves an electron-deficient oxygen in an intermediate molecule, and a Whitmore-type shift of a group from carbon to this oxygen.

ROCHESTER 3, N. Y. RECEIVED FEBRUARY 14, 1949

[DEPARTMENT OF PHYSICS, DUKE UNIVERSITY]

Vapor Pressures of the Isomeric Trichlorobenzenes in the Low Pressure Region[1a]

BY G. W. SEARS[1b] AND E. R. HOPKE

The vapor pressures of the isomeric trichlorobenzenes have been reported in the region 1–760 mm.[1c] Since, in studies of the ultraviolet absorption spectra of these compounds in the vapor phase, which have been carried out in this Laboratory, vapor pressures are rather low, it was desirable to extend the known data into the region 0.01–1.0 mm. The measurements were made with a Rodebush manometer.

Compounds.—A purified sample of 1,2,3-trichlorobenzene was obtained through courtesy of Dow Chemical Co., Midland, Mich. The sample was further purified by recrystallization from ethyl alcohol. It was dried for two hours at 45°. The melting point range was from 52.55° to 52.70°. The 1,2,4-trichlorobenzene was Eastman Kodak Co. white label product. The material was vacuum distilled and only the center fraction was used in this investigation. The melting point range of the sample was from 17.05 to 17.40°. The 1,3,5-trichlorobenzene was Eastman Kodak Co. white label product. The material was purified by recrystallization from methyl alcohol. It was dried for two hours at 50°. The melting point range of the sample was from 63.45 to 63.50°.

Experimental.—The vapor pressure measurements were made with a Rodebush gage of the type used by Rodebush and Henry.[2] The calibration has been described previously by Sears and Hopke.[3,4] In this investigation only 1,2,4-trichlorobenzene was sufficiently volatile to have a vapor pressure in the gage range below room temperature. The remaining two isomers were heated above room temperature by placing part of the apparatus in an asbestos box whose temperature was maintained about 30° higher than the temperature of the condensed sample. This procedure has been previously described by the authors.[5]

Temperatures were measured with a calibrated 0–50° mercury-in-glass thermometer. The smallest scale division was 0.1°. Although the temperature was read to 0.02°, the accuracy of the vapor pressure measurements did not necessitate temperature readings to closer than 0.1°.

The samples were outgassed after inserting them into the apparatus by melting the compound, freezing it, and then pumping out the evolved gases. This process was repeated four or five times. It was found that the outgassing necessary to remove the last traces of a volatile impurity was slower for the 1,2,3-compound than for the other isomers.

Results.—The vapor pressure of 1,2,3-trichlorobenzene was measured over the range 16 to 30°. The vapor pressures of 1,2,4- and 1,3,5-isomers were measured over the temperature ranges 6 to 25° and 9 to 28°, respectively. Each set of data was treated by the method of least squares to fit an equation of the form

$$\log_{10} P = -(A/T) + B \qquad (1)$$

where P is the pressure in microns, T is the absolute temperature, and A and B are constants The ice-point was taken as 273.2° K. Since the temperature range of 1,2,4-trichlorobenzene includes the melting point, it was necessary to set up two equations to represent the vapor pressure curve of the solid as well as the vapor pressure curve of the liquid. Table I gives the constants of Equation (1) for the respective compounds.

TABLE I

	A	*B*
1,2,3-Trichlorobenzene (sol.)	3440.2	13.662
1,2,4-Trichlorobenzene (sol.)	3254.0	13.445
1,2,4-Trichlorobenzene (liq.)	2452.3	10.682
1,3,5-Trichlorobenzene (sol.)	2956.0	12.176

[1a] This investigation was assisted by the Office of Naval Research under Contract N6ori-107, Task Order I, with Duke University.

[1b] Present address: General Electric Co., Schenectady, N. Y.

[1c] Stull, *Ind. Eng. Chem.*, **39**, 517 (1947).

[2] Rodebush and Henry, THIS JOURNAL, **52**, 3159 (1930).

[3] Sears and Hopke, *J. Phys. Chem.*, **52**, 1137 (1948).

[4] Hopke and Sears, THIS JOURNAL, **70**, 3801 (1948).

[5] Sears and Hopke, *ibid.*, **71**, 1632 (1949).