heat of vaporization or the change in the enthalpy function, becomes

$$\Delta H = \frac{\mathrm{d}p}{\mathrm{d}T}\frac{RT^2}{Mp}\sqrt{1 - \frac{Dp}{T^3}} \tag{3}$$

The vapor pressure of ethylbenzene has been measured from 0 to 60° by Guttman, Westrum and Pitzer,[2] and from 60 to 140° by Willingham, Taylor, Pignocco and Rossini.[3] The vapor pressure equation of the first group of observers is of the form

$$\log p = -\frac{a}{T} - b \log T + C \tag{4a}$$

that of the second group

$$\log p = -\frac{B}{C + t} + A \tag{4b}$$

Taking T_c = 619.6°K, p_c = 38.1 atm., ice-point = 273.16°K., mol. wt. = 106.160, R = 1.98647 (15° cal./deg. mole, for p in atm.),[4] and inserting the values of the constants as given by the authors, the heat of vaporization, in cal./g., becomes, respectively

$$\Delta H = (127.495 - 0.10853T)\sqrt{1 - \frac{Dp}{T^3}} \tag{5a}$$

$$\Delta H = \frac{61.1526T^2}{(T - 60.549)^2}\sqrt{1 - \frac{Dp}{T^3}} \tag{5b}$$

and the external work of vaporization, in cal./g.

$$-\Delta A = 0.018712T\sqrt{1 - \frac{Dp}{T^3}} \tag{6}$$

The equations are valid: (5a) from 0 to 60°; (5b) from 60 to 140°; (6) from triple point to critical point.

A comparison of calculated heats of vaporization and measured values is shown in Table I.

TABLE I

T, °K.	ΔH, cal./g. eq. (5a)	Measd.	Observer
294.01	95.47	95.62	Scott, Brickwedde[4]
298.16	95.00	95.08	Osborne, Ginnings[5]

Measured values in int. joules are converted through: 15° cal. = 4.1847 int. joules.[6]

Calculations of the heat and the external work of vaporization give the following values, in cal./g.: at 0° 97.81 and 5.109; at 50° 92.03 and 6.022; at 100° 85.35 and 6.839; at 140° 79.74 and 7.343. In this region the heat of vaporization decreases and the external work of vaporization increases with temperature.

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[2] L. Guttman, E. F. Westrum, Jr., and K. S. Pitzer, THIS JOURNAL, **65**, 1246 (1943).

[3] Ch. B. Willingham, W. J. Taylor, J. M. Pignocco and F. D. Rossini, *J. Research Natl. Bur. Standards*, **35**, 219 (1945).

[4] R. B. Scott and F. G. Brickwedde, *ibid.*, **35**, 501 (1945).

[5] N. S. Osborne and D. C. Ginnings, private communication in preceding article, p. 511.

[6] R. T. Birge, *Rev. Mod. Physics*, **13**, 233 (1941),

Bromination of 4-Phenylphenol and 4-Phenylphenyl Benzoate

BY STEWART E. HAZLET AND LEE C. HENSLEY

Repeated brominations of 4-phenylphenyl benzoate in glacial acetic acid in an attempt to improve the yield of 4-(4-bromophenyl)-phenyl benzoate led to results comparable to those reported previously.[1] Some "solvent effects" had been noted in other substitution reactions,[2] and, therefore, bromination of the benzoate was attempted in carbon tetrachloride. In this medium, a yield of 35.8% of pure 4-(4-bromophenyl)-phenyl benzoate was obtained, and, in addition, some 2-bromo-4-(4-bromophenyl)-phenyl benzoate was isolated. Although it was rather low, the yield of dibromo compound is sufficient to justify mention of the influence of the solvent.

The preparation of 2-bromo-4-(4-bromophenyl)-phenol by direct bromination of 4-phenylphenol in carbon tetrachloride is another case in point illustrating a "solvent effect." In certain solvents,[3] bromine substitutes in the phenol principally first in one *ortho*- and then in the other *ortho*- position with respect to the hydroxyl group.

Experimental

2-Bromo-4-(4-bromophenyl)-phenol. A.—This compound was prepared in approximately 10% yield according to the method of Bell and Robinson.[4]

B.—A considerably higher yield was obtained in the following manner. Ten grams of 4-phenlyphenol was suspended in 300 ml. of hot carbon tetrachloride, a trace of powdered iron was added, and 6.6 ml. (1.08 times the quantity necessary to produce a disubstituted product) of bromine in 35 ml. of carbon tetrachloride was introduced over a period of ninety minutes. Warming (just below boiling) and stirring were continued during this period of time, and after the addition of bromine was completed, the mixture was refluxed for one and one-half hours. The reaction mixture was treated with Norite and filtered, and the volume was reduced to about 25 ml. by distillation. After the oil which separated upon treating the residue with 30–60° ligroin solidified, it was dissolved in boiling 70–90° ligroin; the solution was treated with Norite, filtered and allowed to cool slowly. Long needles separated on cooling. They were recrystallized from the same solvent; m. p. 113–114.5°; yield 9.2 g. (47.6%).

No depression was observed when a mixed melting point determination was made with equal amounts of the material prepared in the two ways.

2-Bromo-4-(4-bromophenyl)-phenyl Benzoate.—Two and two-tenths grams of 2-bromo-4-(4-bromophenyl)-phenol was benzoylated in pyridine solution.[5] The crude product was obtained in almost quantitative yield, and after several crystallizations from 70–90° ligroin, colorless needles resulted; m. p. 147.5–148°.

Anal. Calcd. for $C_{19}H_{12}O_2Br_2$: Br, 36.99. Found: Br, 36.89.

Bromination of 4-Phenylphenyl Benzoate. A. In Glacial Acetic Acid ("Analytical Reagent").—This reaction was carried out as described previously,[1] and 4-(4-bromophenyl)-phenyl benzoate was the only product obtained.

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[1] Hazlet, Alliger and Tiede, THIS JOURNAL, **61**, 1447 (1939).

[2] Hazlet, Hensley and Jass, *ibid.*, **64**, 2449 (1942); Hensley and Hazlet, *ibid.*, **65**, 987 (1943).

[3] Ref. 1; *cf.* especially note 3 in that report.

[4] Bell and Robinson, *J. Chem. Soc.*, 1127 (1927).

[5] Hazlet, THIS JOURNAL, **59**, 287 (1937).

B. In Carbon Tetrachloride.—Twenty and eight-tenths grams of the ester was dissolved in 120 ml. of warm (the oil-bath temperature was 85°) carbon tetrachloride with stirring, a trace of powdered iron was added, and 4.8 ml. of bromine in 20 ml. of carbon tetrachloride was added dropwise over a period of thirty minutes. After the addition was complete, the heating and stirring were continued for three hours with the oil-bath temperature at 80–85°. The solvent was then distilled off on a steam-bath, and the residue was crystallized twice from glacial acetic acid. Nine and six-tenths grams (35.8%) of 4-(4-bromophenyl)-phenyl benzoate was obtained; m. p. 189–190°. The mother liquors from the crystallizations were combined, the volume was reduced to about 40 ml. by distillation, and the residue was poured into water. The aqueous mixture was extracted twice with 50-ml. portions of benzene; the extracts were combined and washed with 5% sodium hydroxide solution and then with water. The benzene was removed on a steam-bath, and after several crystallizations of the residue from 70–90° ligroin, 2.2 g. (6.7%) of material melting at 146–147.5° was obtained. This compound caused no depression in melting point when mixed with 2-bromo-4-(4-bromophenyl)-phenyl benzoate prepared as described above.

The same product was obtained in 7.9% yield (1.25 g.) after ten crystallizations from 70–90° ligroin when 10 g. of the ester was brominated in the same manner using 4.12 ml. (2.2 molecular proportions) of bromine.

Hydrolysis of 2-Bromo-4-(4-bromophenyl)-phenyl Benzoate.—A small sample (2.2 g.) of this ester, obtained by brominating 4-phenylphenyl benzoate in carbon tetrachloride as described above, was hydrolyzed in the same manner as described in earlier studies[1] for similar compounds. The phenolic hydrolysis product melted at 113.5–115°, and when it was mixed with an authentic sample of 2-bromo-4-(4-bromophenyl)-phenol, prepared according to the method of Bell and Robinson,[4] there was no depression of the melting point.

DEPARTMENT OF CHEMISTRY
STATE COLLEGE OF WASHINGTON
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The Insecticidal Component of *Eugenia Haitiensis* Identified as 1,8-Cineol

BY MARTIN JACOBSON AND H. L. HALLER

In the course of investigations to find new insecticides of vegetable origin, a sample of the essential oil distilled from the leaves of *Eugenia haitiensis* Krug. & Urb. (family *Myrtaceae*) was received through the American Embassy in Port-au-Prince, Haiti. *E. haitiensis* is a tree reported to grow only in Haiti, where a kerosene solution of the essential oil is used by natives as an insecticide against flies, mosquitoes and bedbugs.

When tested without dilution, the oil gave complete knock-down and high mortality of house flies and adult mosquitoes. However, in a 50% solution in refined kerosene (Deobase) the toxicity was low, although there was still complete initial knock-down.[1]

Fractional distillation of the oil under reduced pressure yielded three fractions, of which only the lowest boiling fraction was insecticidally active. This fraction, representing 86% of the oil, had the same order of toxicity as the original oil. Its physical properties checked closely with those of 1,8-cineol (eucalyptol), which has previously been reported as occurring to the extent of 78.5% in the oil distilled from the leaves of *Eugenia buxifolia* (Sw.) Willd. in Puerto Rico.[2]

The toxic fraction was shown to be identical with 1,8-cineol by preparation of the *o*-chlorophenol addition product and oxidation to *dl*-cineolic acid. A commercial sample of 1,8-cineol after purification by distillation, showed the same toxicity to house flies as the toxic fraction isolated from the essential oil.

It is of interest to note that an isomer of 1,4-cineol has been reported to have insecticidal value against flies, mosquitoes and chiggers.[3]

Experimental[4]

Fractional Distillation of the Essential Oil.—One hundred and twenty-two grams of the yellow essential oil was subjected to slow fractional distillation under reduced pressure using a Widmer column. At 15-mm. pressure two distinct fractions and a residue were obtained, as shown in Table I.

TABLE I

FRACTIONAL DISTILLATION OF THE ESSENTIAL OIL OF *Eugenia haitiensis*

Fraction	B. p., °C. 15 mm.	Yield, g.	%	$n^{20}D$
I	60–62	105	86	1.4579
II	95–99	10	8	1.4721
Residue		7	6	1.4971

Since only fraction I was insecticidally active, nothing further was done with the other fractions. Fraction I was a colorless liquid possessing a strong, camphor-like odor. When cooled in an ice–salt mixture, it crystallized in colorless needles, m. p. 1.5°. It boiled at 174–176° at atmospheric pressure, d^{20} 0.927, and was optically inactive. These properties, and those given for this fraction in Table I, are in close agreement with those of 1,8-cineol (b. p. 174.4°, 62.75° at 15 mm., m. p. −1°, d^{15} 0.930, $n^{15}D$ 1.45839).[5]

Anal. Calcd. for $C_{10}H_{18}O$: mol. refr., 45.62. Found: mol. refr., 45.39.

***o*-Chlorophenol Addition Product of Fraction I.**—Three grams of *o*-chlorophenol was dissolved in 10 g. of warm fraction I. When the solution was cool, a product separated which was filtered on silk, washed with petroleum ether, and dried in a vacuum desiccator. The yield was 5 g. (70%) of colorless prisms that melted at 57–58°. A mixed melting point with a sample of authentic 1,8-cineol-*o*-chlorophenol addition product, m. p. 57–58°, prepared according to Dodge,[6] gave no depression.

Oxidation of Fraction I to *dl*-Cineolic Acid.—Five and one-half grams of fraction I and 30 g. of potassium permanganate in 450 ml. of water were heated on the steam-bath with mechanical stirring till the solution was decolorized (*ca.* six hours). Unchanged fraction I was removed by steam distillation, and the precipitated manganese dioxide was filtered and washed thoroughly with several portions of hot water. The combined filtrate and washings were evaporated to dryness on the steam-bath, and the residue was digested with three 15-ml. portions of hot ethanol. The filtered alcohol extracts were evaporated to dryness, and the residue was taken up in about 10 ml. of water and made acid to congo with dilute sulfuric acid, whereupon a white, crystalline material

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[1] The tests against house flies and mosquitoes were made by W. A. Gersdorff and J. H. Fales, respectively, of this Bureau.

[2] N. G. Arrillaga, *Puerto Rico Agr. Expt. Sta. Ann. Report* 1939, 29 (1940).

[3] M. G. Austerweil, *Bull. soc. chim.*, [4] **45**, 862 (1929).

[4] All melting points are corrected.

[5] J. L. Simonsen, "The Terpenes," Vol. I, Cambridge University Press, Cambridge, 1931, p. 378.

[6] F. E. Dodge, *J. Am. Pharm. Assoc.*, **22**, 20 (1933).