

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 studies¹ 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.

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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

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

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

Experimental⁴

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}^{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°, d_{20}^{20} 0.927 at 15 mm., m. p. –1°, d_{20}^{20} 0.930, n_{20}^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

(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).

separated. Filtration and recrystallization from water yielded 5.2 g. (68%) of colorless plates, m. p. 204–205°. A mixed melting point with an authentic sample of *dl*-cineolic acid, m. p. 204–205°, prepared by the method of Wallach and Gildemeister,⁷ gave no depression. (Wallach and Gildemeister report m. p. 196–197°, while m. p. 204–206° is reported by Rupe and Ronus⁸ for this compound. Wallach and Gildemeister undoubtedly had impure material, as can readily be seen from their reported values for carbon and hydrogen.)

Anal. Calcd. for C₁₀H₁₆O₂: mol. wt., 216.2. Found (titration): mol. wt., 216.6.

Solution of the acid in boiling acetic anhydride, followed by removal of the solvent and recrystallization of the residue from ligroin, gave a quantitative yield of cineolic anhydride, m. p. 77–78°.⁹

(7) O. Wallach and E. Gildemeister, *Ann.*, **246**, 268 (1888).

(8) H. Rupe and M. Ronus, *Ber.*, **33**, 3544 (1900).

(9) O. Wallach, *Ann.*, **258**, 320 (1890).

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The Catalytic Formation of Toluene from Benzene and Benzene-Methane at High Pressures

BY V. N. IPATIEFF AND G. S. MONROE

Berthelot¹ observed the formation of toluene, along with other products, when a mixture of benzene and methane was passed through a porcelain tube at red heat. When benzene alone was subjected to the same treatment no toluene was obtained.

In high pressure experiments (232 atm., 600°) over alumina-silica cracking catalyst (15 wt. % aluminum oxide), we obtained toluene in low yields (1.1%) from benzene alone and in somewhat higher yields (4.6%, based on the weight of benzene charged) from benzene-methane, with the mole ratio of methane:benzene at 9:1. The biphenyl yield in the two cases was 9.6 and 3.0%, respectively.

The results obtained over a nickel-silica hydrogenation catalyst² are given below:

TABLE I

CONVERSION OF BENZENE AND BENZENE-METHANE INTO TOLUENE OVER NICKEL-SILICA CATALYST AT 372°

Charge	Press., atm.	Yields ^b as wt. % benzene charge		% Recovered	
		Toluene	Carbon	Benzene	Methane
C ₆ H ₆	1	0.0	2.1	92.7	
C ₆ H ₆	410	12.3	2.4	79.3	
C ₆ H ₆	545	14.9	3.1	76.7	
C ₆ H ₆ + CH ₄	1	0.0	0.7	95.5	100.8
C ₆ H ₆ + CH ₄	410	15.3	1.0	83.0	98.0
C ₆ H ₆ + CH ₄	545	20.5	1.2	74.8	100.2

^a Hourly liquid space velocity, volume of liquid charged per unit volume of catalyst per hour. ^b Naphthalene was found in the residues obtained from the fractionation of the liquid product.

(1) Berthelot, "Les Carbures d'Hydrogene," Gauthier-Villiers, Paris, 1901.

(2) Ipatieff and Corson, *Ind. Eng. Chem.*, **30**, 1039 (1938).

Experimental

All experiments were made in continuous flow apparatus.³ The total amount of benzene charged, either alone or when methane was present, varied from 1 to 1.5 moles, depending on the length of the experiment. The yields are reported on a once-through basis. A fresh charge of catalyst was used for each run. The composition of the liquid product was determined by fractionation, the toluene in the fraction between the benzene and the toluene plateaux of the distillation curve being evaluated by the refractive index. The presence of toluene was confirmed by the preparation of the 2,4-dinitro derivative. The biphenyl and naphthalene remaining behind in the fractionation residues were identified by mixed melting point.

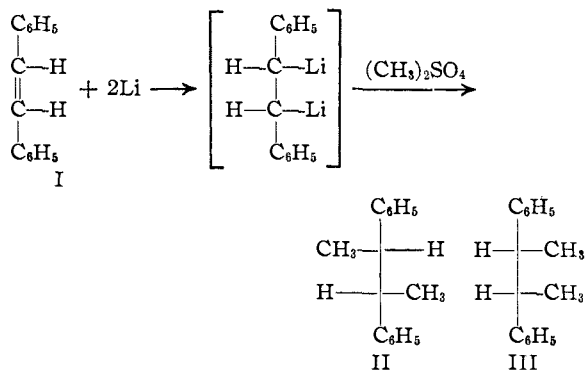
(3) Ipatieff and Monroe, *THIS JOURNAL*, **67**, 2168 (1945).

UNIVERSAL OIL PRODUCTS COMPANY
RESEARCH AND DEVELOPMENT LABORATORIES
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The Bonding in Dimetalated Diphenylethane

BY G. S. MYERS, H. H. RICHMOND AND GEORGE F. WRIGHT

In elaboration of previous work¹ it has been found that the same ratio (3:1) of *dd, ll*-2,3-diphenylbutane, II, to the *dl, dl*-diastereomer is formed with dimethyl sulfate whether the intermediate dimetalated diphenylethane, I, is formed from the reaction of either lithium or sodium with stilbene.



This ineffectiveness of the metal toward configuration of the reaction product II + III might suggest an ionic structure for I. Certainly the metal atoms are loosely bound. The list of reagents, like oxygen and methyl iodide, which will remove the metal entirely (stilbene being regenerated) has been extended in the present study by inclusion of sulfur and arsenic trichloride.

In spite of this evident loose bonding, no evidence of ion transport can be obtained after long electrolysis of disodiumdiphenylethane in glycol dimethyl ether solution between a mercury cathode and platinum anode. Although the conductance is quite low, the cathode contained no sodium after passage of fourteen coulombs. There was no observable migration of the color of the solution from either electrode. The solution reacted normally upon subsequent treatment with benzaldehyde.

(1) G. F. Wright, *THIS JOURNAL*, **61**, 2106 (1939).