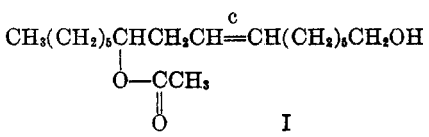

I

natural attractant, and all forms were equally attractive to male gypsy moths when tested in the field at 10^{-7} microgram/trap.[2]

Experimental

Preparation of the Acid Succinate of *dl*-I.—A mixture of 500 mg. of *dl*-I, 0.3 g. of recrystallized succinic anhydride, and 0.5 ml. of dry pyridine was heated at 100° in a sealed tube for 20 hr., cooled, poured into excess 5% hydrochloric acid, and extracted with several small portions of ether. The combined ethereal extract was washed free of mineral acid with water, extracted with 5% sodium carbonate, and the alkaline extract was acidified with 20% hydrochloric acid and extracted with ether. The ethereal extract was washed free of mineral acid with water, dried over sodium sulfate, and freed of solvent, giving 530 mg. of orange, viscous liquid that resisted repeated attempts at crystallization.

Preparation of the Brucine Salts.—A solution of the acid succinate in 4.5 ml. of acetone was heated to boiling on the steam bath, treated with 1 g. of L-brucine, heated an additional 30 sec., filtered, and cooled in an ice bath with scratching. The white solid that rapidly separated was recrystallized from acetone to give 273 mg. of insoluble brucine salt A, m.p. above 220°, $[\alpha]^{27}D$ −4.7° (*c* 2.0, chloroform).

The combined acetone filtrate and mother liquors were evaporated to dryness and the residue was taken up in ethyl acetate, washed with water, and dried over sodium sulfate. Removal of the solvent and crystallization of the white residue from 0.5 ml. of acetone at −50° gave 245 mg. of brucine salt B, $[\alpha]^{27}D$ −5.3° (*c* 2.0, chloroform).

Decomposition of the Brucine Salts.—Brucine salt A (270 mg.) was stirred at room temperature with 15 ml. of 20% hydrochloric acid, and the mixture was allowed to stand for 5 hr. and then extracted with ether. The ether extract was washed free of mineral acid with water, dried over sodium sulfate, and freed of solvent to give 246 mg. of the acid succinate of *d*-I as a pale yellow, viscous oil, $[\alpha]^{27}D$ +22.4° (*c* 2.0, chloroform), that failed to crystallize.

Decomposition of brucine salt B (240 mg.) in the same manner gave 219 mg. of the acid succinate of *l*-I as a pale yellow, viscous oil, $[\alpha]^{27}D$ −17.6° (*c* 2.0, chloroform).

Saponification of the Acid Succinates.—A solution containing 246 mg. of the acid succinate of *d*-I, 10 ml. of 10% sodium hydroxide, and 1 ml. of ethyl alcohol was heated on the steam bath for 2 hr., cooled, and extracted with ether, and the extract was washed with water, dried (sodium sulfate), and freed of solvent to give a yellow oil. This oil was dissolved in petroleum ether (b.p. 40–60°) and the solution filtered through a column of 10 g. of cellulose acetate and evaporated to dryness, giving 212 mg. of (+)-10-acetoxy-*cis*-7-hexadecen-1-ol as a colorless liquid, $[\alpha]^{27}D$ +7.8° (*c* 2.0, chloroform), identical with the natural gypsy moth attractant.[1]

In a similar manner, the saponification of 219 mg. of the acid succinate of *l*-I gave 179 mg. of (−)-10-acetoxy-*cis*-7-hexadecen-1-ol as a colorless liquid, $[\alpha]^{27}D$ −7.1° (*c* 2.0, chloroform), that solidified in the cold but melted again at room temperature. The infrared spectrum[3] was identical with those of *d*- and *dl*-I.

(2) These tests were carried out as described by J. M. Corliss, *Yearbook Agr.* (U.S. Dept. Agr.), 694 (1952). The assistance of E. C. Paszek, U.S. Department of Agriculture, Nashua, N. H., in carrying out these tests is gratefully acknowledged.

(3) Determined with a Perkin-Elmer Model 21 spectrophotometer, by means of sodium chloride optics and a 1% solution of the sample in carbon disulfide. Mention of trade names or proprietary products does not necessarily constitute endorsement by the Department of Agriculture.

The Bromination of Ethyl 4-Phenylphenyl Carbonate

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A number of esters of 4-phenylphenol have been brominated, and the results have been reported previously.[1] The chlorination[2] of 4-phenylphenyl acetate resulted in the formation of 4-(4-chlorophenyl)phenyl acetate, although bromination had given a product with the halogen atom at a position in the molecule *ortho* to the acyloxy group.[3] In an attempt to determine the behavior of another ester of 4-phenylphenol in which the acyloxy group is rather small and should have little steric effect at *ortho* positions, the bromination of ethyl 4-phenylphenyl carbonate[4] has been studied.

The results, which are shown in the Experimental, did not indicate that any bromination of the ester occurred *ortho* to the acyloxy group. Rather, substitution occurred in the ester at the most remote position in the biphenyl group, as had been observed in most of the previous investigations; there was evidence that some *ortho* substitution had occurred in free phenols, which were isolated from reaction mixtures. Compounds isolated from reaction mixtures were identified by mixed melting point procedures.

The bromination of ethyl 4-phenylphenyl carbonate proceeds more smoothly in carbon tetrachloride than in glacial acetic acid solution. An improved method for the preparation of 2,6-dibromo-4-(4-bromophenyl)phenol has been developed. Several new esters of bromine substituted 4-phenylphenols are reported.

Experimental

Bromine Substituted 4-Phenylphenols.—These compounds were prepared by methods that have been reported previously, except that 2,6-dibromo-4-(4-bromophenyl)-phenol[5] was prepared by a modification of a procedure[1] that had been used for the preparation of 2-bromo-4-(4-bromophenyl)phenol. 4-Phenylphenol (15 g., 0.088 mole) was suspended in 120 ml. of carbon tetrachloride, a trace of iron powder was added, and while the mixture was stirred and

(1) S. E. Hazlet and L. C. Hensley, *J. Am. Chem. Soc.*, **69**, 708 (1947) and earlier papers.

(2) C. M. S. Savoy and J. L. Abernethy, *ibid.*, **64**, 2219 (1942).

(3) S. E. Hazlet and H. A. Kornberg, *ibid.*, **61**, 3037 (1939).

(4) E. Baumgarten, H. G. Walker, and C. R. Hauser, *ibid.*, **66**, 303 (1944).

(5) F. Bell and P. H. Robinson, *J. Chem. Soc.*, 1131 (1927).

TABLE I
ETHYL 4-PHENYLPHENYL CARBONATE AND BROMINE SUBSTITUTED DERIVATIVES

Phenol used	Yield, %	Solvent	M.p., °C.	Formula	Bromine, % Calcd.	Found
4-Phenyl	86.9	Ethanol	75–76	$C_{15}H_{14}O_3$	[a]	
2-Bromo-4-phenyl[b]	38.8	Methanol	31–32.5	$C_{15}H_{13}BrO_3$	24.89	25.12
4-(4-Bromophenyl)[c]	51.3	Methanol	75.5–76.5	$C_{15}H_{13}BrO_3$	24.89	24.95
2,6-Dibromo-4-phenyl[b]	41.0	Methanol	61–62	$C_{15}H_{12}Br_2O_3$	39.95	39.88
2-Bromo-4-(4-bromophenyl)[d]	62.5	Methanol	52.5–54	$C_{15}H_{12}Br_2O_3$	39.95	40.07
2,6-Dibromo-4-(4-bromophenyl)	79.0	Methanol	103.5–105	$C_{15}H_{11}Br_3O_3$	50.5	49.80

[a] Reported m.p. 73.9–75°; see ref. 4. [b] See ref. 9. [c] S. E. Hazlet, *J. Am. Chem. Soc.*, 59, 1087 (1937). [d] See Ref. 1.

refluxed gently, 56.5 g. of bromine (0.353 mole) was added slowly during a period of 2 hr. The mixture was refluxed for an additional 2.5 hr. and cooled; excess bromine was removed by treatment with sodium bisulfite solution. The carbon tetrachloride solution was separated, treated with charcoal, filtered, and evaporated to small volume. Coarse needles separated; m.p. 154–158°, 15.75 g. (0.039 mole, 44% yield). Recrystallization from carbon tetrachloride yielded 11.3 g. (0.028 mole, 31.7%), m.p. 158–159.5° (lit.,[5] m.p. 159°).

Ethyl 4-Phenylphenyl Carbonate and Bromine Substituted Derivatives.—These compounds were prepared by the action of ethyl chloroformate on the appropriate phenol in the presence of a slight excess of pyridine with *p*-dioxane as diluent.[6] Results are shown in Table I.

Bromination of Ethyl 4-Phenylphenyl Carbonate. A. In Glacial Acetic Acid.—The ester (10 g., 0.041 mole) was suspended in 30 ml. of glacial acetic acid in a three-necked flask fitted with a reflux condenser, a stirrer, and a dropping funnel. A trace of iron powder was added, and 6.6 g. (0.041 mole) of bromine dissolved in 5 ml. of glacial acetic acid was introduced slowly during a period of 45 min. During the addition of the bromine and for 5 hr. thereafter, the mixture was stirred and heated in an oil bath (98–100°). The mixture was cooled, poured into 200 ml. of water, and neutralized with sodium bicarbonate solution. The neutral solution was extracted with ether; the ether extract was washed three times with 5% sodium hydroxide solution and then with saturated sodium chloride solution.

The **ether extract** was dried with anhydrous sodium sulfate in the presence of charcoal and filtered. The ether was removed by distillation. The residue[7] was a low-melting solid and weighed 7 g. Repeated fractional crystallizations from ethanol and from *n*-heptane resulted in the separation of two products: (a) 4-(4-bromophenyl)phenyl ethyl carbonate (from *n*-heptane), m.p. 74.5–75.5°, 2.19 g. (0.0068 mole, 16.6% yield); (b) ethyl 4-phenylphenyl carbonate (from *n*-heptane), m.p. 74–75°, 3.3 g. (0.0136 mole, 33% yield).

The **sodium hydroxide extract** was acidified with 5% hydrochloric acid. The precipitate weighed 4.5 g. Repeated fractional crystallizations from chloroform and from *n*-heptane resulted in the separation of three products: (a) 2,6-dibromo-4-(4-bromophenyl)phenol (from *n*-heptane), m.p. 156.5–158°, 1.39 g. (0.0034 mole, 8.3% yield); (b) 2,6-dibromo-4-phenylphenol (from *n*-heptane), m.p. 91–93.5°, 1.3 g. (0.00396 mole, 9.6% yield); (c) 4-(4-bromophenyl)phenol (from chloroform), m.p. 144–145.5° [converted to the benzoic ester (from methanol), m.p. 187.5–188.5°[9]], 0.4 g. (0.0016 mole, 3.9% yield).

B. In Carbon Tetrachloride.—The ester (10 g., 0.041 mole) was suspended in 50 ml. of carbon tetrachloride and treated with bromine (6.6 g., 0.041 mole) dissolved in carbon tetrachloride (10 ml.) in the presence of a trace of iron powder; oil-bath temperature, 115°; time, 3.5 hr. The reaction mixture was cooled and extracted twice with 5% sodium hydroxide solution. (Only a trace of phenolic material was obtained from the sodium hydroxide extract; this was not identified.) The carbon tetrachloride solution was dried with anhydrous sodium sulfate in the presence of charcoal; from it was obtained 11.4 g. of solid product. Recrystallizations from *n*-heptane gave 4-(4-bromophenyl)-phenyl ethyl carbonate, m.p. 72–74°, 8.65 g. (0.027 mole, 65.4% yield).

(6) S. E. Hazlet, L. C. Hensley, and H. Jass, *J. Am. Chem. Soc.*, **64**, 2449 (1942).

(7) In one experiment, the residue (8 g.) was hydrolyzed with 12% potassium hydroxide solution. After acidification of the reaction mixture with sulfuric acid, volatile acid was collected by distillation. On a portion of the distillate, Duclaux numbers were determined: 6.1, 6.6, 6.8.[8] The total volatile acid calculated as acetic acid was 0.0495 g.; this indicated that a small amount, approximately 2%, of the ester fraction following the substitution reaction was acetate.

(8) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed., J. Wiley and Sons, Inc., New York, 1956; p. 204; Duclaux numbers for acetic acid: 6.8, 7.1, 7.4.

(9) S. E. Hazlet, G. Alliger, and R. Tiede, *J. Am. Chem. Soc.*, **61**, 1447 (1939).

Benzo[*d*]thiazolo[2,3-*b*]quinazoline-11-one. The Action of Hot Sulfuric Acid on 2-Thio-3-phenyl-1*H*,3*H*-quinazoline-2,4-dione

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In 1930 Ghosh[1] heated 2-thio-3-phenyl-1*H*,3*H*-quinazoline-2,4-dione (I) with concentrated sulfuric acid at 125–130° for three to four hours and obtained a product to which he assigned the structure II. In the same paper,[1] he also reported that when 2-thio-3-allyl-1*H*,3*H*-quinazoline-2,4-dione (III) was heated with 12 *N* hydrochloric acid the product obtained was 2-allylaminobenzo[*d*][1,3]thiazine-4-one (IV). The latter report has previously been shown to be in error.[2]

As a part of a continuing study of aromatic heterocyclic compounds,[2,3] the author repeated the work of Ghosh.[1] The melting point of the product obtained from the acid-catalyzed rearrangement and oxidation of I agreed, although poorly, with

(1) T. N. Ghosh, *J. Indian Chem. Soc.*, **7**, 981 (1930).

(2) R. V. Ohmart, J. E. McCarty, and C. A. VanderWerf, *J. Org. Chem.*, in press. The correct structure was shown to be V.

(3) (a) B. A. Carpentier, J. E. McCarty, and C. A. VanderWerf, *ibid.*, **26**, 853 (1960); (b) J. E. McCarty, E. L. Haines, and C. A. VanderWerf, *J. Am. Chem. Soc.*, **82**, 964 (1960).