or 6 impurities amounting to a total of 1–2%. The total amount of hydrocarbon recovered was 75.1 g.

(b) **With $AlBr_3$.**—A 20.4-g. sample of norbornane of m.p. 87.5–88.0° was refluxed with 4 g. of $AlBr_3$ and one drop of *sec*-butyl bromide.[26] Hydrogen bromide gas[26] was admitted to the reaction flask. After refluxing for 25 minutes a lower boiling substance, amounting to 0.3%, was present. After 60 hours, the product, 14.1 g., m.p. 84.0–85.8°, was distilled from the reaction flask. A residue of 5.8 g. remained behind. The product contained 0.4% of the impurity and traces of 2 or 3 other components.

It was concluded from these experiments that norbornane was quite stable to the action of the aluminum halides at the reflux temperature. At most, a very small amount of fragmentation and isomerization was observed, but it is possible that some or all of the new substances present in the product arose from impurities in the starting material.

Attempted Isomerization of Norbornadiene (IV).—A commercial sample of norbornadiene,[28] 46 g., n^{20}D 1.4705, was refluxed with 1.0 g. of silica–alumina catalyst for 1090 minutes. The starting material contained a large number of impurities present in very small amounts. Neither these impurities nor IV were altered by the acidic catalyst. The infrared spectra of the material before and after treatment were identical. After distillation there remained only a small amount of residue in the reaction flask.

To 17.5 g. of norbornadiene from the above attempted isomerization was added 0.6 g. of the silica–alumina catalyst. Refluxing was continued for 1280 minutes and then the product, 12.5 g., was distilled. The pot residue, a mobile oil, weighed 2.5 g. The product, n^{20}D 1.4709, was identical with the starting material employed initially, as determined by gas chromatography and infrared spectroscopy.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STANFORD UNIVERSITY]

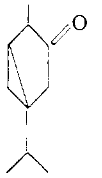
The Structure of Thujone Tribromide[1]

BY RICHARD H. EASTMAN, PHILLIP M. ILOFF, JR.,[2] AND HART ISAACS, JR.

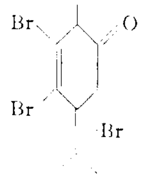
RECEIVED OCTOBER 28, 1957

Structures are proposed for thujone tribromide and its congeners on the basis of spectroscopic and chemical data.

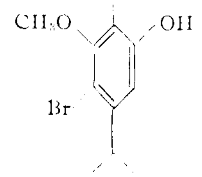
In a continuation of the study[3] of cleavage reactions of the bicyclo[3.1.0]hexane system we have turned our attention to the action of bromine on thujone (I) which was reported by Wallach[4] to produce a tribromide for which he proposed the structure II, and from which he obtained a substituted carvacrol, assigned the structure III, on treatment with sodium methoxide in methyl alcohol. We have repeated and confirmed his experimental observations, and extended the study to include ultraviolet and infrared spectroscopic examination of the tribromide and the carvacrol, as well as a chemical investigation of the latter.



I



II



III

The tribromide shows $\lambda_{\max}^{\mathrm{alc}}$ 243 mμ (ϵ 11,700), 337 mμ (ϵ 185) and bands at 5.93 and 6.17 μ in the infrared, which rule out II as a structural possibility and reveal the tribromide as a conjugated cyclohexenone carrying a single carbon substituent on the β-carbon atom of the olefinic linkage.[5] The phenolic character of the product of sodium methoxide treatment of the tribromide is confirmed by bands at 2.97 μ (OH) and 6.17, 6.32, 6.63 μ (benzenoid)[5a] in the infrared, and $\lambda_{\max}^{\mathrm{alc}}$ 283 mμ (ϵ 2030)[6] in the ultraviolet absorption spectra. The structural problem was thus reduced to locating the bromine and the methoxyl substituents in the carvacrol, and the distribution of three bromine atom substituents about a properly substituted cyclohexenone in the case of the tribromide itself.

Attachment of the methoxyl group to an *aliphatic* carbon atom in the carvacrol was evident when an attempted hydrobromic acid cleavage of the O–CH_3 bond presumed to be present resulted instead in the elimination of the elements of methyl alcohol and the formation of a dimeric species, $C_{20}H_{22}Br_2O_2$ (see below). The ease with which the elimination proceeded[7] indicated attachment of the methoxyl group to the benzylic carbon atom of the isopropyl substituent, and that such was the case was established by a proton nuclear magnetic resonance determination[8] on the methoxybromocarvacrol which showed three major peaks, A, B and C, exclusive of the aromatic proton signal. Peaks A and B were of equal area, A being assigned to the protons of the methoxyl group, and B to those of the single methyl group attached to the aromatic ring. The area of the third peak, C, was twice that of either A or B, and C is assigned to the six identical protons of the *gem*-dimethyl unit.

The infrared absorption (10% solution in chloroform, 1.0 mm.) of the methoxybromocarvacrol showed the pattern in the 5–6 μ region which is characteristic of the benzenoid system with substituents in the 1-, 2-, 3- and 5-positions,[9] thus lending weight

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[1] From the Doctoral Dissertation of P. M. Iloff, Jr., and the Senior Research Thesis of H. Isaacs, Jr., in the Department of Chemistry at Stanford University. Presented at the American Chemical Society Meeting in New York, N. Y., Sept. 13, 1957.

[2] Shell Fellowship recipient, 1949–1950.

[3] R. H. Eastman and A. Oken, THIS JOURNAL, **75**, 1029 (1953).

[4] O. Wallach, *Ann.*, **275**, 179 (1893); O. Wallach and J. T. Conroy, *ibid.*, **286**, 109 (1895).

[5] (a) Infrared assignments are from L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954. (b) The ultraviolet absorption is interpreted according to Woodward's rules as expressed by L. F. and M. Fieser, "Natural Products Related to Phenanthrene," Reinhold Publishing Corp., New York, N. Y., 1949, pp. 190 ff.

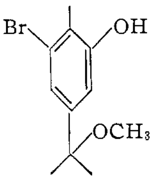
[6] L. Doub and J. Vandenbelt, THIS JOURNAL, **69**, 2714 (1947); **71**, 2414 (1949).

[7] The dimer, $C_{20}H_{22}Br_2O_2$, was the only product recovered from an attempted bromination of the methoxybromocarvacrol at −5°.

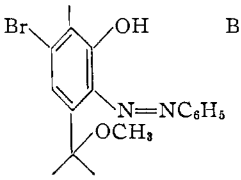
[8] By James N. Shoolery, Varian Associates, Palo Alto, Calif.

[9] C. W. Young, R. B. Duvall and N. Wright, *Anal. Chem.*, **23**, 709 (1951).

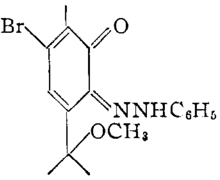
to structure IV for the compound. However, the infrared data in this case was felt not to be conclusive, and additional evidence was sought.



IV



V



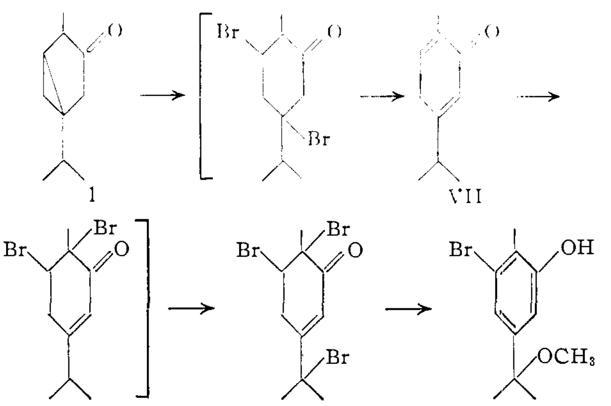
Va

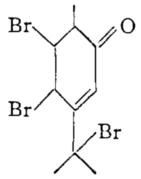
When treated with benzenediazonium sulfate in alkaline solution, the bromomethoxycarvacrol coupled smoothly to give a bright-orange product, $C_{17}H_{19}BrO_2N_2$, which was insoluble in 5% sodium hydroxide solution, and in whose infrared absorption spectrum the band characteristic of the OH group was absent. These properties are in accord with those reported[10,11] for *o*-hydroxyazo compounds which may exist in the tautomeric phenylhydrazone form, Va.[12] Formation of the bromine-containing, *ortho* coupling product (V or Va) ruled out the position *ortho* to the phenolic hydroxyl group for the bromine substituent.

The possibility that the bromine substituent was *para* to the phenolic hydroxyl was disposed of by applying the value of 12.6 mμ for the bathochromic shift of the long-wave length benzene band occasioned by *p*-bromo substitution in phenol[6] to the maximum for carvacrol (λ_{max} 277 mμ), giving a predicted λ_{max} for *p*-bromocarvacrol of 289.6 mμ, which is at a significantly longer wave length than that observed, 283 mμ, for the methoxybromocarvacrol from thujone tribromide.[13] The evidence against *o*- and *p*-bromo substitution taken with the infrared evidence for 1,2,3,5-substitution establishes structure IV, 3-bromo-5-(2-methoxy-2-propyl)-2-methylphenol, as most probable for the methoxybromocarvacrol.

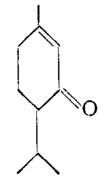
Attempts to degrade thujone tribromide to known compounds by oxidation failed, and structure VI, that of 3-(1-bromo-1-methylethyl)-5,6-dibromo-6-methyl-2-cyclohexenone, is proposed for the compound as satisfying the following requirements: 1. Formation by a reasonable sequence of reactions (I → VI) on treatment of thujone with bromine.

In accord with this scheme for formation of the tribromide is the racemic nature of the tribromide and Wallach's observation[4] that the same tribromide is obtained whether *l*-thujone or *d*-isothujone is treated with bromine. Both of these results would follow the intermediation of the symmetrical structure VII 2. Smooth conversion by sodium methoxide to the methoxybromocarvacrol IV. The alternative structure VIII would hardly be expected on treatment with base to retain the bromine substituent in the β-position to the carbonyl group. 3. That it be a conjugated cyclohexenone with a single β-substituent as required by the position of maximum absorption at 243 mμ in the ultraviolet.[5b] 4. That it have an equatorially oriented bromine substituent on the carbon atom α to the carbonyl group to account for the 0.08 μ hypsochromic shift of the carbonyl band (5.93 μ) from the position at 6.01 μ for the band in the similarly substituted piperitone (IX).[14]





VIII



IX

The Structures of the Dimers.—As pointed out earlier, when the methoxybromocarvacrol (IV) was treated with hydrobromic acid, a substance of the empirical formula $C_{10}H_{11}BrO$ was the result. The high melting point (221.5–222°) of the compound created the suspicion that it was actually a dimer of the substituted styrene (X), produced by the elimination of the elements of methanol from the methoxybromocarvacrol (IV), and its dimeric nature was confirmed by a Rast molecular weight determination (found 425, calcd. for $C_{22}H_{26}Br_2O_2$, 482) on the corresponding dimethyl ether derivative. The ultraviolet absorption spectrum of the dimeric phenol [λ^{alc}_{max} 285 mμ (ϵ 5500)] was very similar to that of the methoxybromocarvacrol [λ^{alc}_{max} 283 mμ (ϵ 2030)] and is taken to indicate that the dimer is of the saturated or indan, styrene dimer type.[15] Of the two possible structures, XI is preferred on the bases that the dimeric phenol was freely soluble in dilute sodium hydroxide solution, *i.e.*, was not cryptophenolic as might be expected of XII, and would result from ring closure to the position *para* to the activating OH group.

An analogous dimeric phenol, $C_{20}H_{24}O_2$, fortuitously resulted from attempted Raney alloy hydrogenolysis[16] of the bromine substituent in the methoxybromocarvacrol when the reaction mixture was decomposed with an excess of concentrated hydrochloric acid. The infrared and proton nuclear mag-

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(10) K. H. Saunders, "The Aromatic Diazo Compounds and Their Technical Applications," 2nd Ed., Edward Arnold and Co., London, 1949, p. 198.

(11) S. B. Hendricks, O. R. Wulf, C. R. Hilbert and U. Liddel, This Journal, **57**, 1997 (1936).

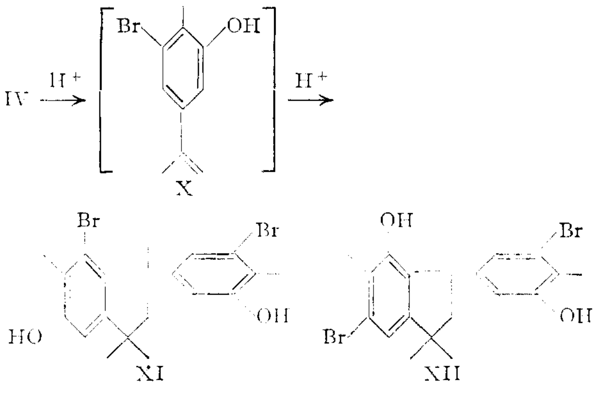
(12) A. Burawoy and A. R. Thompson, *J. Chem. Soc.*, 1443 (1953), and earlier papers.

(13) The values similarly calculated for *o*-bromocarvacrol and *m*-bromocarvacrol are respectively 284 and 282 mμ, so the ultraviolet data *per se* could not be used to distinguish *meta* from *ortho* bromine substitution in the methoxybromocarvacrol.

(14) Reference 5a, pp. 121 ff.

(15) W. Doering and J. Berson, This Journal, **72**, 1118 (1950).

(16) H. Hart, *ibid.*, **71**, 1967 (1949).



netic resonance spectra[7] of the dimers are in accord with the phenylindan structure.

Acknowledgments.—We wish to express our appreciation to the donors of the Shell Fellowship, held by P. M. I., and to Dr. James Shoolery for his assistance in measuring and interpreting the nuclear magnetic data.

Experimental

Thujone (I).—A commercial sample[17] of the leaf oil of *Thuja occidentalis* L. was fractionated in a 90 × 2.5 cm. glass helices column and the 47% of the oil boiling from 78–81° at 13 mm., of $n^{20}D$ 1.4505–1.4539, d^{25}_4 0.911–0.918, α_D −25 to +7° (1 dm., neat), was taken as a mixture of thujone isomers suitable for preparative work.

Thujone Tribromide (VI).—To 5 ml. of thujone in 30 ml. of petroleum ether (b.p. 30–60°), 5 ml. of bromine was added all at once. A violent reaction ensued and, when complete, the solution was poured on a watch glass and allowed to evaporate during two hours. The residue was triturated with 10 ml. of hexane followed by 20 ml. of methanol and then refrigerated (−5°) overnight. Filtration and washing with methanol produced 1.36 g. (12%) of white, crystalline tribromide of m.p. 120–122° dec.[18] Recrystallization from ethyl acetate gave a product of m.p. 122.5–124° (reported[4] 121–122°) which could be stored for months at −5° but decomposed within a week at room temperature. The compound was optically inactive in chloroform solution; spectra[19]: infrared, mineral oil suspension, 5.93 μ (C=O, conj.), 6.17 μ (C=C, conj.); ultraviolet, λ_{max}^{alc}, 243 mμ (ε 11,700), 337 mμ (ε 185).

Thujone tribromide was also prepared directly and in comparable yield (9%) from whole oil of Thuja, using 13 ml. of the oil in 60 ml. of petroleum ether, 10 ml. of bromine, and following the procedure described above for isolation.

Attempts to improve the yield of tribromide by the use of hexane or ethanol as solvent, moderating the reaction by cooling, or evaporating the petroleum ether solvent at the steam-bath failed to produce the tribromide. A Kuhn–Roth determination on the tribromide gave 1.82 moles of acetic acid per mole of compound.

3-Bromo-5-(2-methoxy-2-propyl)-2-methylphenol (IV).—To a solution of 24.8 g. of sodium in 700 ml. of absolute methanol was added 50 g. of thujone tribromide. The mixture was heated under reflux for three hours, then stored in the refrigerator overnight. The majority of the solvent was removed at reduced pressure, and the solid residue was taken up in 400 ml. of cold water. The resulting solution was made faintly acid to litmus with sulfuric acid, whereupon a tan crystalline mass formed. Filtration gave 37.3 g. of crude product which was crystallized from methanol (60 ml.) to yield 18.0 g. of white crystals, m.p. 156–157.5° (reported[4] 156–157°); spectra: infrared, 10% solution in $CHCl_3$, 2.97 (OH), 6.17, 6.32, 6.63 μ (benzenoid); ultraviolet, λ_{max}^{alc} 283 mμ (ε 2,030).

3-Bromo-5-(2-methoxy-2-propyl)-2-methyl-6-phenylazophenol (V).—To 2 g. of 3-bromo-5-(2-methoxy-2-propyl)-2-methylphenol (IV) dissolved in 12 ml. of 5% aqueous sodium hydroxide was added 10 ml. of water and then rapidly, with stirring, a solution of 1.7 g. of benzenediazonium sulfate[20] in 15 ml. of water. The resulting mixture was refrigerated for 24 hours, then filtered. The solid material was taken up in ether and extracted twice with 5% sodium hydroxide solution. Evaporation of the ether left an orange residue which yielded, after two crystallizations from alcohol, 0.6 g. of bright-orange crystals of m.p. 119.5–120.5°. This coupling product was insoluble in 5% aqueous sodium hydroxide and gave a strongly positive Beilstein test for halogen.

Anal. Calcd. for $C_{17}H_{19}BrO_2N_2$: C, 56.21; H, 5.27. Found[21]: C, 56.25; H, 5.08.

7-Bromo-5-hydroxy-1-(5-bromo-3-hydroxy-4-methyl-1-phenyl)-1,3,3,6-tetramethylindan (XI).—Ten grams of 3-bromo-5-(2-methoxy-2-propyl)-2-methylphenol (IV) was dissolved by heating in 130 ml. of glacial acetic acid, and to the solution 100 ml. of 42% aqueous hydrobromic acid was added. The solution was heated under reflux for two hours, allowed to stand for ten hours at room temperature, then refrigerated (−5°) for several hours and finally the crystalline product which had appeared was separated by filtration. Dilution of the mother liquor resulted in additional product which was combined with the first crop of crystals to provide 7.9 g. of crude product. This was dissolved in 50 ml. of hot glacial acetic acid, 7.8 ml. of water was added and on cooling and filtering 4.81 g. of material of m.p. 219–222.5° was received. Additional material (1.28 g.) was obtained on adding water to the mother liquors, and repeated crystallization from glacial acetic acid raised the melting point to 221.5–222°; spectra: infrared, mineral oil suspension, 3.06 (OH), 6.24, 6.35, 6.70[22] μ (benzenoid); ultraviolet, λ_{max}^{alc} 285 mμ (ε 5500).

Anal. Calcd. for $C_{20}H_{22}Br_2O_2$: C, 52.88; H, 4.88. Found: C, 52.68; H, 4.96.

The insolubility of the dimeric phenol precluded cryoscopic molecular weight determinations so the **dimethyl ether** was prepared by treating a solution of 3.0 g. of the dimeric phenol in 2.9 ml. of 20% aqueous sodium hydroxide with 1.7 ml. of dimethyl sulfate in two portions while shaking and maintaining the mixture at 100°. The mixture was worked up in the usual way after cooling, with alkali extraction to remove unmethylated material. Crystallization of the crude product from alcohol yielded 0.70 g. of the dimethyl ether.

Anal. Calcd. for $C_{22}H_{26}Br_2O_2$: C, 54.79; H, 5.43; mol. wt., 482. Found: C, 54.58; H, 5.45; mol. wt., 425 (Rast).

5-Hydroxy-1-(3-hydroxy-4-methyl-1-phenyl)-1,3,3,6-tetramethylindan.—To 2 g. of 3-bromo-5-(2-methoxy-2-propyl)-2-methylphenol (IV) dissolved in 20 ml. of alcohol was added 5.5 g. of Raney nickel alloy and then over a period of 25 minutes 55 ml. of 10% aqueous hydroxide was added dropwise.[16] The solid residue was filtered off, washed with 20 ml. of 10% aqueous sodium hydroxide and with 50 ml. of hot water and discarded. The combined filtrate and washings were cooled and poured into 100 ml. of concentrated hydrochloric acid. When the resulting solution was cooled to 10° a white, crystalline solid separated. The air-dried solid (1.21 g.) was crystallized repeatedly from aqueous methanol to yield 0.54 g. of white crystals, m.p. 175–176°; spectrum: ultraviolet, λ_{max}^{alc} 282 (ε 5650).

Anal. Calcd. for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16. Found: C, 80.90; H, 7.85.

The compound gave a negative Beilstein test for halogen, was soluble in 5% aqueous sodium hydroxide and produced strong colors when coupled with diazotized sulfanilic acid or benzidine.

STANFORD, CALIF.

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(17) Oil of Thuja from P. R. Dreyer and Co.

(18) Melting points are not corrected.

(19) Infrared spectra determined with Model 21 Perkin-Elmer instrument, ultraviolet with the Beckman DU instrument.

(20) H. Schoutissen, *Rec. trav. chim.*, **40**, 764 (1921).

(21) Analyses by Microchemical Specialties, Berkeley, Calif.

(22) In perchlorobutadiene suspension.