the second ionization constant for deutero-carbonic acid may be calculated to be 1.42×10^{-11}. Thus K_H/K_D is equal to 3.95.

It should be pointed out that this value of K_H/K_D for the second ionization constant of carbonic acid agrees within 4% of that predicted by the curve of Rule and LaMer[4] and confirmed by Martin and Butler.[5]

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[4] Rule and LaMer, This Journal, **60**, 1974 (1938).

[5] Martin and Butler, *J. Chem. Soc.*, 1366 (1939).

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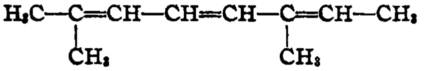
The Production of α- and β-Pyronene from *allo*-Ocimene

By L. A. Goldblatt and S. Palkin[1]

Among the products obtained in the pyrolysis of α-pinene in the vapor phase,[2,3,4] at about 375°, the acyclic terpene



$$H_3C{-}\underset{CH_3}{C}{=}CH{-}CH{=}CH{-}\underset{CH_3}{C}{=}CH{-}CH_3$$

(2,6-dimethyl-2,4,6-octatriene) is of the greatest interest, both from a practical and theoretical point of view. The simultaneous formation of the monocyclic hydrocarbons α- and β-pyronene was first observed by Dupont and Dulou, who postulated[3] that they were obtained from α-pinene by a simultaneous and independent reaction, namely, rupture of the four-membered ring in α-pinene, and not by further isomerization of either *allo*-ocimene or dipentene, other products of the pyrolysis. They later reported[5] that this hypothesis had been confirmed.

In the course of the work of the Naval Stores Research Division on the vapor phase thermal isomerization of terpene hydrocarbons, it was found that the pyronenes are in fact obtained by the recyclization of *allo*-ocimene.[6]

The apparatus used for the pyrolysis is shown in Fig. 1. This consists essentially of a pyrolysis tube, together with a suitable condensing and receiving system. Heat for the pyrolysis tube is supplied by means of a bath of "HTS" (a commercial mixture of sodium and potassium nitrate and nitrite). This in turn is heated by passage of an electric current through 25 feet (resistance, 16 ohms) of no. 20 Nichrome wire wound on asbestos-paper covering a suitable length of ordinary 1.5-inch iron pipe. Temperature was controlled by a variable voltage transformer and measured by a movable thermocouple in a glass well placed vertically in the center of the reaction tube. In normal operation the temperature generally did not vary more than 5° for about half the length of the pyrolysis tube, although the temperature was materially lower at both ends. *allo*-Ocimene was supplied to the pyrolysis tube by a Tropsch and Mattox pump[7] capable of supplying *allo*-ocimene at a definite rate varying from about 50 to 750 cc. per hour with a precision of 1%. Flow of *allo*-ocimene supplied by the pump was made more uniform by inserting a coil of glass tape just inside the spherical joint.

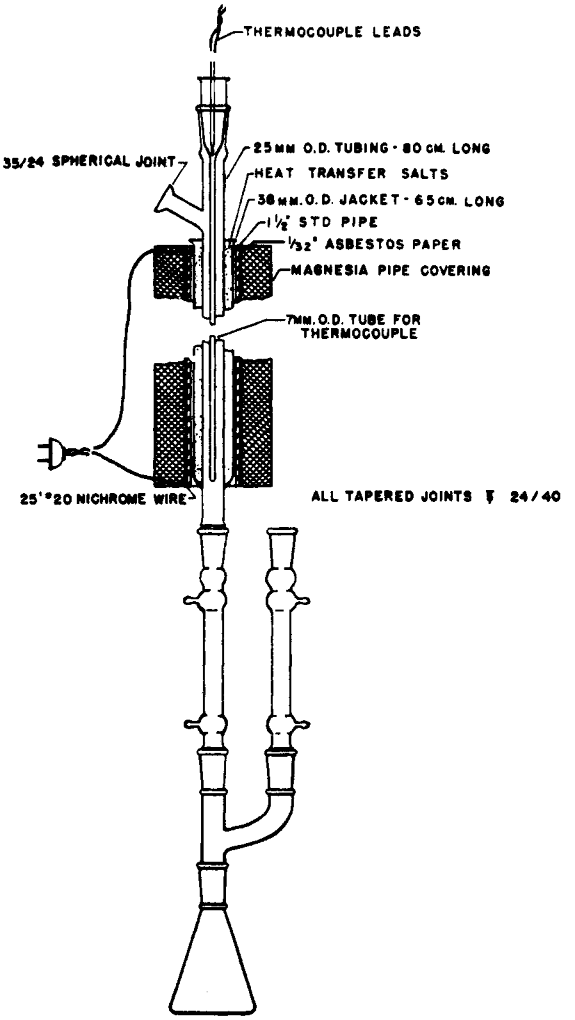


Fig. 1.—Pyrolysis unit.

Change in refractive index provides a convenient guide to the extent of isomerization. A sample of *allo*-ocimene having the characteristics

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[1] Died May 2, 1943.

[2] Arbuzov, *J. Gen. Chem.* (U. S. S. R.), **3**, 21 (1933); *Ber.*, **67B**, 563 (1934).

[3] Dupont and Dulou, *Compt. rend.*, **201**, 219 (1935).

[4] Goldblatt and Palkin, This Journal, **63**, 3517 (1941).

[5] Dupont and Dulou, *Atti. X° Congr. Intern. Chim.*, **2**, 127 (1939).

[6] Work of the Naval Stores Research Division on the vapor phase cyclization of *allo*-ocimene has been temporarily discontinued owing to preoccupation with problems more closely related to the war effort. Reporting of these preliminary results at this time is prompted by a communication from Dr. J. E. Hawkins and R. E. Fuguitt of the University of Florida, who have confirmed this observation from information obtained in the study of the thermal isomerization of α-pinene in the liquid phase, and who have generously undertaken to remove any question as to priority of this discovery in a forthcoming publication.

[7] Tropsch and Mattox, *Ind. Eng. Chem.*, **26**, 1338 (1934).

n^{20}D 1.5449 and d^{20}_4 0.8083, when pyrolyzed under optimum conditions (a temperature of 400° and a through-put of 250 g. per hour) gave a product of n^{20}D 1.4790. Considerable variations in through-put rate or pyrolysis temperature may be made without materially altering the extent of isomerization (as judged by change in refractive index).

A portion of the pyrolyzate obtained in this way (n^{20}D 1.4795; d^{20}_4 0.8358) when fractionally distilled *in vacuo* was found to contain about 30% of α-pyronene and about 45% of β-pyronene, together with some unchanged *allo*-ocimene, dimer, and other unidentified hydrocarbons. The fractions containing the highest concentrations of α- and β-pyronene had the following characteristics: α-pyronene, b. p. 54–56° at 20 mm., d^{20}_4 0.8272, n^{20}D 1.4672; β-pyronene, b. p. 62–64° at 20 mm., d^{20}_4 0.8481, n^{20}D 1.4800. From these fractions the characteristic maleic anhydride adducts of the respective pyronenes could be obtained in excellent yield.

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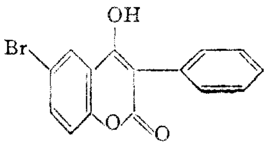
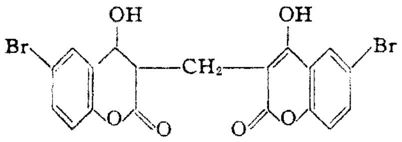
Brominated 4-Hydroxycoumarins

BY CHARLES F. HUEBNER AND KARL PAUL LINK

The synthesis of bromine-containing anticoagulants related to the original anticoagulant 3,3′-methylenebis-(4-hydroxycoumarin),[1] is described in this note. 3-Phenyl-4-hydroxy-6-bromocoumarin (I) was prepared by an intramolecular Claisen condensation[2] of methyl 2-phenylacetoxy-5-bromobenzoate. By the same type reaction, 4-hydroxy-6-bromocoumarin was prepared and by reaction with formaldehyde was converted to 3,3′-methylenebis-(4-hydroxy-6-bromocoumarin) (II).



(I)



(II)

Experimental

Methyl 2-Phenylacetoxy-5-bromobenzoate.—A mixture of 60 g. of phenylacetyl chloride and 90 g. of methyl 5-bromosalicylate[3] was heated under reflux on a steam-bath for four hours. Pyridine (30 ml.) was added and the heating was continued for four hours longer. The resulting oil was dissolved in ether and extracted successively with water, hydrochloric acid solution, and sodium carbonate solution. The ether solution was dried and the ester was crystallized by the addition of petroleum ether. After two recrystallizations from ethanol the product weighed 56 g., m. p. 68–70°. *Anal.* Calcd. for $C_{15}H_{10}O_3Br(OCH_3)$: OCH_3, 8.9. Found: OCH_3, 8.8.

3-Phenyl-4-hydroxy-6-bromocoumarin (I).—To a well-stirred melt of 20 g. of methyl 2-phenylacetoxy-5-bromobenzoate contained in a round bottom flask, 1.3 g. of sodium was added and the temperature was raised to 200°, at which point a spontaneous reaction occurred. External heating was discontinued and after thirty minutes the glassy mass was cooled and dissolved in water. The aqueous solution was acidified to *p*H 6, extracted with ether, and further acidified to *p*H 5. The product crystallizing between these two *p*H's was filtered and recrystallized twice from acetic acid. The yield was 8 g., m. p. 252–254°. *Anal.* Calcd. for $C_{15}H_9O_3Br$: C, 56.8; H, 2.8. Found: C, 57.0; H, 2.9.

Methyl 2-Acetoxy-5-bromobenzoate.—To 30 g. of methyl 5-bromosalicylate was added 80 ml. of acetic anhydride and 1 ml. of sulfuric acid. After thirty minutes the mixture was poured into ice water, the oil was washed with sodium carbonate solution, and crystallized from methanol–water. The yield was 20 g., m. p. 33–35°. *Anal.* Calcd. for $C_9H_6O_3Br(OCH_3)$: OCH_3, 11.4. Found: OCH_3, 11.3.

3,3′-Methylene bis-(4-hydroxy-6-bromocoumarin) (II)—4-Hydroxy-6-bromocoumarin was prepared in a manner similar to that described for 3-phenyl-4-hydroxy-6-bromocoumarin except that the reaction was run in kerosene and the final product was collected between *p*H 5.6 and 2.5. From 176 g. of ester, and 14.8 g. of sodium in 300 ml. of kerosene, 92 g. of crude 4-hydroxy-6-bromocoumarin was obtained. This crude product was refluxed in ethanol with an excess of formaldehyde. The methylenebis product which was extremely insoluble in alcohol crystallized after one hour. This product was filtered and recrystallized from cyclohexanone, yield 40 g., m. p. 326–327°. *Anal.* Calcd. for $C_{19}H_{10}O_6Br_2$: C, 46.2; H, 2.0. Found: C, 46.3; H, 2.3.

3,3′-Methylene bis-(4-hydroxy-6-bromocoumarin) dimethyl ether was prepared by the diazomethane technique. The ether was recrystallized from β-dichloroethyl ether, m. p. 218–220°. *Anal.* Calcd. for $C_{19}H_8O_4Br_2(OCH_3)_2$: OCH_3, 11.8. Found: OCH_3, 12.0.

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The Dielectric Constants and Dipole Moments of Acetylenic Ethers

BY THOMAS L. JACOBS, JOHN D. ROBERTS AND W. G. MACMILLAN

The dielectric constants of pure samples of ethoxy-, butoxy- and phenoxy-acetylene[1] were measured at 25° by the heterodyne beat method as described by Wood and Dickinson.[2]

The frequency of the standard circuit was adjusted to that of the carrier wave of radio station KFAC which broadcasts on a frequency of 1300 kilocycles,[3] and the increment of capacity was

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[1] Stahmann, Huebner and Link, *J. Biol. Chem.*, **138**, 513 (1941).

[2] Stahmann, Wolff and Link, THIS JOURNAL, **65**, 2285 (1943).

[3] Peratoner, *Gazz. chim. ital.*, **16**, 405 (1886).

[1] The acetylenic ethers were carefully refractionated samples prepared in connection with other investigations: Jacobs, Cramer and Hanson, THIS JOURNAL, **64**, 223 (1942); Jacobs, Cramer and Weiss, *ibid.*, **62**, 1849 (1940). The phenoxyacetylene was prepared by Dr. Wm. Penn Tuttle, Jr.

[2] Wood and Dickinson, *ibid.*, **61**, 3259 (1939).

[3] Otto and Wenzke, *Ind. Eng. Chem., Anal. Ed.*, **6**, 187 (1934).