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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AGRICULTURAL RESEARCH ADMINISTRATION
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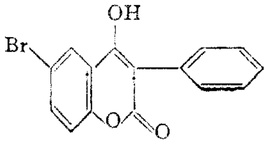
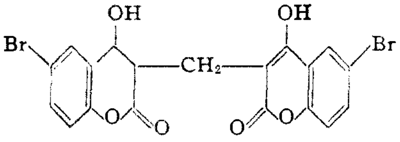
Brominated 4-Hydroxycoumarins

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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(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).

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) 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).

measured with a variable condenser which was carefully calibrated against a General Radio Precision Condenser (calibrated by the manufacturer at 1000 cycles per second). The cell was of the type described by Doborzynski[4] and the cell constant was obtained by measurements on purified samples of chlorobenzene, ethylene dichloride and benzene whose dielectric constants are known accurately (5.612, 10.36, 2.272 at 25°). Table I summarizes the results.

TABLE I

DIELECTRIC CONSTANTS AND DIPOLE MOMENTS OF ACETYLENIC ETHERS AND PHENYLACETYLENE

Compound, -acetylene	ϵ	M	$d^{25}{}_4$	$n^{25}{}_D$	MR_D obs.	$(n^2_\infty)^{25°}$	μ
Ethoxy-	8.05	70.1	0.7874	1.3785	20.53	1.853	1.98
Butoxy-	6.62	98.2	0.8078	1.4033	29.66	1.925	2.03
Phenoxy-	4.76	118.1	1.0088	1.5143	35.27	2.216	1.41
Phenyl-	2.98	102.1	0.9243	1.5461	34.99	2.231	0.78

Dipole moments were calculated by the Onsager equation[5,6] and phenylacetylene was included for comparison. The value is in reasonable agreement with 0.77–0.87 found by measurements in benzene solution.[7] The values of n^2_∞ were obtained by extrapolating the molecular refraction to infinite wave length as was done by Böttcher.[8] The observed molecular refractions for the acetyleneic ethers are in close agreement with the calculated values so that no error was introduced by using the latter. Phenylacetylene shows a rather large exaltation, but even here the values for the dipole moment obtained using calculated or observed molecular refractions were not greatly different (0.78 instead of 0.75).

Böttcher[8] has calculated the dipole moments of a number of compounds from the dielectric constants of the pure liquids using Onsager's equation. His results for unassociated substances are in excellent agreement with dipole moments obtained from measurements in solution or in the vapor state except for anisole and diethyl ether, and for these he believed that the equation failed. His calculations appear to be in error for anisole, and the corrected figure lies between values obtained in solution and in the vapor. We have calculated the moments for phenetole and diphenyl ether and found fairly close agreement, so that Onsager's equation appears to give reasonable results with simple aromatic ethers. The values for diethyl ether from the Onsager equation are high as Böttcher reported, but better agreement is found for di-*n*-propyl ether. Table II compares the calculated values for these ethers with values from measurements in solution or in the vapor.

TABLE II[a]

DIPOLE MOMENTS OF ETHERS

Compound	n^2	ϵ	Ref.	μCalcd.	μ_v	μ_s
Diethyl ether	1.798	4.376	9	1.47	1.18	1.2–1.3
Di-*n*-propyl ether	1.873	3.394[b]	10	1.31	1.18	1.16
Anisole	2.214	4.41	11	1.28	1.35	1.2
Phenetole	2.187	4.22	11	1.34	1.4	1.0
Diphenyl ether	2.388	3.686	11	1.17	1.14	1.13–1.17

[a] The values are at 20° unless otherwise stated. The calculated *MR*'s were used, but the exaltations are low with these compounds and μ is lowered but slightly by using *MR* obs. for the calculation. $\mu_{\text{calcd.}}$, μ_v and μ_s designate the dipole moments in Debye units from the calculations and from measurements in the vapor and in solution respectively. All μ_s values are in benzene except di-*n*-propyl ether which is in hexane. The values for the dipole moments in solution were taken from Landolt-Börnstein, "Physikalisch-chemische Tabellen," the second and third supplementary volumes, Julius Springer, 1931–1936. The values from measurements in the vapor phase are from Groves and Sugden, *J. Chem. Soc.*, 1779, 1782 (1937), except for diphenyl ether where their value of 1.35 appears less reliable than that found by Coop and Sutton, *J. Chem. Soc.*, 1869 (1938). [b] At 25.7°.

Despite the simplifying assumptions of symmetrical dipole configurations and non-association made in the derivation of the Onsager equation, the agreement between calculated and measured values is satisfactory in general and, as Wilson[6] has commented, the equation appears to be empirically useful. Certainly the values for acetylenic ethers are not in gross error. No interpretation of the moments of ethers can be made without knowledge of the —C—O— bond angles and these may be quite different in unsaturated ethers as compared with saturated. Nevertheless it is interesting that the dipole moment of phenoxyacetylene is only slightly larger than those of other aromatic ethers while the alkoxyacetylenes give figures which are significantly higher. One interpretation of this difference is that in the latter there is a considerable contribution from resonance forms of the type $R-\overset{+}{O}=C=\overset{-}{C}H$, an idea which is in accord with their greater rate of hydration.[12] An extended study of the dipole moments of vinyl and ethynyl ethers will be undertaken when more time and better equipment are available.

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[4] Doborzynski, *Z. Physik*, **66**, 657 (1930).

[5] Onsager, THIS JOURNAL, **58**, 1486 (1936).

[6] Wilson, *Chem. Rev.*, **25**, 377 (1939).

[7] Smyth and Dornte, THIS JOURNAL, **53**, 1296 (1931).

[8] Böttcher, *Physica*, **6**, 59 (1939); see ref. 6.

[9] LeFèvre, *Trans. Faraday Soc.*, **34**, 1127 (1938).

[10] Pyle, *Phys. Rev.*, **38**, 1057 (1931).

[11] Estermann, *Z. physik. Chem.*, **1B**, 134 (1928).

[12] Jacobs and Searles, THIS JOURNAL, **66**, May (1944).

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RECEIVED JANUARY 11, 1944

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p-Bromoaniline Salts of Monoaryl Sulfates

BY D. H. LAUGHLAND AND LESLIE YOUNG

It has been shown[1] that *p*-toluidine salts of a number of monoaryl sulfates can be prepared readily by allowing the alkali metal salt of the monoaryl sulfate to interact with the base hydrochloride in an aqueous medium. With bases which yield relatively insoluble salts of monoaryl sulfates, this reaction is of value in the isolation of monoaryl sulfates from the urine of animals dosed

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[1] A. D. Barton and Leslie Young, THIS JOURNAL, **65**, 294 (1943)