reaction of cyclohexene oxide with sodium bifluoride at 150–180° resulted in a 21% yield of 2-fluorocyclohexanol along with higher molecular weight fluoro alcohols in the residue. The fluorocyclohexanol had a tendency to release hydrogen fluoride over a long period of time at room temperature as well as in aqueous solution.

A number of unsuccessful attempts were made to synthesize 2-fluorocyclohexanol using sodium bifluoride and *trans*-2-chlorocyclohexanol as well as with cyclohexene oxide and anhydrous hydrogen fluoride. Solvents such as the dimethyl ether of diethylene glycol and dimethylformamide, respectively, were used in the above reactions. However, no fluorocyclohexanol was isolated in these latter cases.

Experimental

Preparation of 2-Fluorocyclohexanol.—A 1-l. stainless steel reaction vessel, which was fitted with a steel water condenser and a stirrer, was charged with 98 g. (1 mole) of cyclohexene oxide and 124 g. (2 moles) of sodium bifluoride. The reaction mixture was stirred rapidly and heated slowly to 150–180° and the temperature maintained overnight. The product was extracted with dry ether and filtered. The ether solution was dried over calcium sulfate. The ether was then distilled and the residue was fractionated under vacuum on an 18-in. Widmer column. A fraction boiling at 68–69°/8 mm., n^{30}_D 1.4446, m.p. 18–19°, was collected; yield 25 g. (21%).

The infrared analysis indicated the presence of —OH and —F groups. Periodic acid test was negative indicating the absence of diol. A negative bromine test indicated the absence of unsaturation.

Anal. Calcd. for $C_6H_{11}OF$: C, 61.1; H, 9.32; F, 16.1. Found: C, 61.3; H, 9.53; F, 15.7.

The α-naphthylurethane had a sharp decomposition point at 154°.

Anal. Calcd. for $C_{17}H_{18}NO_2F$: C, 71.0; H, 6.28; F, 6.63. Found: C, 70.9; H, 6.4; F, 7.0.

The residue from the above fractionation was distilled from a Claisen head at 0.25-mm. pressure. Three fractions were collected having boiling ranges in the neighborhood of 110, 150, and 160° and average molecular weights of 430, 510, and 718, respectively, according to the phthalic anhydride method for hydroxyl numbers as outlined by Siggia.[7] Infrared analysis indicated the presence of fluorine, hydroxyl, and ether linkages. Fluorine analysis on the polymers ranged from 10.55% for the 430 mol. wt., material to 6.26% for the one at 718.

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[7] S. Siggia, "Quant. Org. Anal. via Functional Groups," J. Wiley & Sons, 2nd ed., New York, 1954, p. 12.

Hydroxystyryl Derivatives of Quinoline and 5-Ethyl-2-methylpyridine as Solvatochromic Indicators

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Solvatochromic compounds—*i.e.*, substances having solution colors that depend strongly on solvent polarity—have been suggested as color indicators of solvent properties and of hydrogen bonding.[1,2] The merocyanines investigated in the present work are all negatively solvatochromic over most of the dielectric constant range examined—*i.e.*, the wave length of maximum absorbance increases with decreasing dielectric constant.[3]

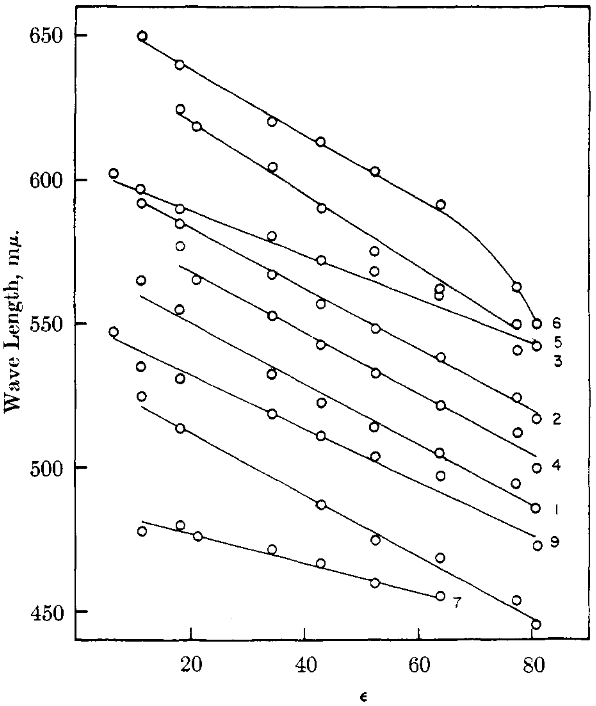

Fig. 1.—Wave length of maximum absorbance of merocyanines as a function of dielectric constant in water–dioxane mixtures (see Table I for identification of compound numbers).

Compounds of types I and II (see Table I for designation of Ar groups) were prepared by condensations of quinaldine or lepidine, respectively, with the appropriate hydroxyaldehyde in acetic anhydride, hydrolysis, and subsequent methylation with dimethyl sulfate. They were also prepared by methylation of quinaldine or lepidine followed by piperidine-catalyzed condensations with the aldehydes; this was also the only method used to obtain compounds of type III. The properties of I and II were the same by both methods and appeared to be those of the *trans* isomers; thus, the infrared spectra generally had a 10.4-μ *trans* band but lacked the strong bands at 10.88 and 12.4 μ supposed to be characteristic of the *cis* isomers.[4]

The ultraviolet and visible spectra of these compounds as first determined in 95% ethanol showed considerable variations from one compound to another, probably the result of partial merocyanine

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[1] L. G. S. Brooker, G. H. Keyes, and D. W. Heseltine, *J. Am. Chem. Soc.*, **73**, 5350 (1951).

[2] J. P. Saxena, W. H. Stafford, and W. L. Stafford, *J. Chem. Soc.*, 1579 (1959).

[3] S. Hünig and O. Rosenthal, *Ann.*, **592**, 161 (1955).

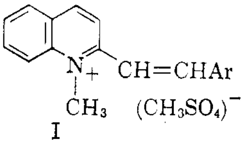
[4] D. F. DeTar and L. A. Carpino, *J. Am. Chem. Soc.*, **78** 475 (1956).

TABLE I

SPECTRA OF HYDROXYSTYRYL COMPOUNDS AND THEIR MEROCYANINES

Formula		Ar in formula	λ_{max} (log ϵ) in EtOH—HCl	Merocyanine λ_{max} in			
				C_6H_6	$CHCl_3$	95% EtOH	H_2O
1.	I	2-HOC_6H_4[a]	245(4.17), 300(3.63), 412(4.23)	640	613	555	490
2.	I	3,4-(MeO)(HO)C_6H_3[b]	250(4.24), 278s(4.02), 311(4.14), 445(4.85)	560	580	585	517
3.	I	2-HO—1-naphthyl	231(4.61), 273s(3.95), 325(3.95), 460(4.21)	605	595	600	552
4.	II	2-HOC_6H_4	242(4.16), 275s(3.95), 329(3.94), 427(4.33)	...	670	585	500
5.	II	3,4-(MeO)(HO)C_6H_3	242(4.33), 285s(4.04), 329(3.79), 460(4.20)	...	645	610	530
6.	II	2-HO-1-naphthyl	234(4.57), 322(4.17), 480(4.27)	635	670	618	560
7.	III	2-HOC_6H_4	300s(3.86), 374(4.17)	...	565	475	430
8.	III	3,4-(MeO)(HO)C_6H_3	275(3.43), 360s(3.39), 380(3.83)	...	570	510	445
9.	III	2-HO—1-naphthyl	282(3.96), 328(3.66), 392(3.79)	...	585	534	473

[a] Methiodide prepared by L. F. Werner, *J. Am. Chem. Soc.*, **42**, 2309 (1920). [b] Previously prepared by Phillips, Breese, and Barrall, *J. Org. Chem.*, **24**, 1104 (1959).



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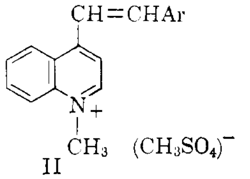
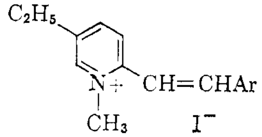


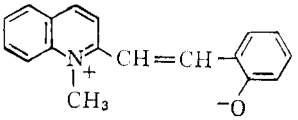
II



III

formation in the solutions. In the presence of hydrochloric acid (Table I) this cannot occur and very similar spectra are observed.

Complete conversion of the compounds into merocyanines is simply effected by adding base to the dissolved compound to ionize the phenolic hydroxyl—*e.g.*, IV is prepared from the N-alkylated 2-(*o*-hydroxystyryl)quinoline by adding sodium hydroxide to an aqueous solution.



IV

Merocyanine spectra were measured as functions of solvent dielectric constant over a range of water–dioxane mixtures[5] (0–90% dioxane) for which dielectric constants are available in the literature.[6] A family of graphs for the wave length of maximum absorption in the visible for each of the nine compounds studied (Fig. 1) shows that all appear fairly uniformly negatively solvatochromic in this range, with the most pronounced effect in those compounds having the most extensive chromophoric systems. The widest range of wave lengths for any compound in these solvents amounted to only about 100 mμ. For most of the compounds the colors faded rapidly at the higher dioxane concentrations; the discovery of dimerization of similar compounds[7] is a possible explanation.

A comparison of the maxima over a wider range of dielectric constant (Table I) was obtained by measuring spectra in benzene (ϵ 2.4), chloroform (ϵ 4.8), 95% ethanol (ϵ about 30), and water (ϵ 81), all containing small amounts of alkali. (Some were insufficiently soluble in benzene to allow determination.) Over this more extended range the solvatochromism is more pronounced but less uniformly negative for some of the compounds. Since specific solvent-solute interactions are probable in these varied solvents and since the use of dielectric constant as a suitable measure of solvent polarity is a moot question,[8,9] attempts to interpret these results are difficult.

It is interesting that relatively slight structural changes are needed to convert negative solvatochromism to positive. Thus the *p*-hydroxy isomer of compound 6 is said to be positively solvatochromic. A combination of this pair of reagents with a chart of their colors at various dielectric constant values could make a simple though relatively crude color test for solvent polarity.

Experimental

Condensations of quinaldine or lepidine with aromatic aldehydes were performed by refluxing 0.02-mole amounts with 2 ml. of acetic anhydride for 6 hr. The reaction mixture was then poured into water, 50 ml. of 20% sodium hydroxide added, and hydrolysis effected by heating for 1 hr. Acidification precipitated the products and 80–90% yields were obtained.

Quaternization of the above products to give compounds 1–6 (Table I) was accomplished by heating equimolar amounts of compound and dimethyl sulfate in nitrobenzene on a steam bath for a short time; after cooling the solution

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(5) E. G. McRae, *Spectrochim. Acta*, **12**, 192 (1958).

(6) C. A. Kraus and R. M. Fuoss, *J. Am. Chem. Soc.*, **55**, 21 (1933).

(7) J. L. R. Williams, *ibid.*, **84**, 1323 (1962).

(8) E. M. Kosower, *ibid.*, **80**, 3253 (1958).

(9) B. S. Neporent and N. G. Bakhshiev, *Opt. and Spectr.* (*USSR*) (*English Transl.*), **8**, 408 (1960).

TABLE II

MELTING POINTS AND ANALYSES OF HYDROXYSTYRYL COMPOUNDS

Compound[a]	M.p., °C.	Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
1.	176–178	61.12	5.13	3.75	60.73	4.99	3.70
2.	213–215 (dec.)	59.55	5.25	..	59.39	5.12	..
3.	204 (dec.)	65.25	5.00	3.31	64.90	4.85	3.86
4.	188–190	61.12	5.13	3.75	60.65	5.11	3.76
5.	227 (dec.)	59.55	5.25	3.47	59.13	5.02	3.05
6.	188–190	65.25	5.00	3.31	65.65	4.69	3.02
7.	160–161	52.33	4.94	3.81	52.39	5.35	3.96
8.	159–160	51.39	5.07	3.53	51.79	5.60	3.58
9.	227–229	57.56	4.83	3.36	57.32	4.80	3.66

[a] Numbers refer to Table I.

the precipitated methosulfates were filtered, washed with ether, and recrystallized three times from methanol.

Compounds 1–9 were also prepared by refluxing equimolar amounts of N-methylquinaldinium or N-methyllepidinium methosulfates or 5-ethyl-2-methylpyridinium iodide and the appropriate aldehyde in isopropyl alcohol for 1 hr. The precipitated products were washed with ether and recrystallized from methanol.

All ultraviolet and visible spectra were recorded with a Beckman DK-2 spectrophotometer. The water–dioxane mixtures were prepared by volume, and 0.2 ml. of a saturated solution of each compound in aqueous potassium hydroxide was added to 25 ml. of solvent. Infrared spectra of all compounds were obtained in potassium bromide pellets using a Baird AB-2 spectrophotometer.

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The Epoxidation of Allyl-Substituted Phenols and Ethers[1,2]

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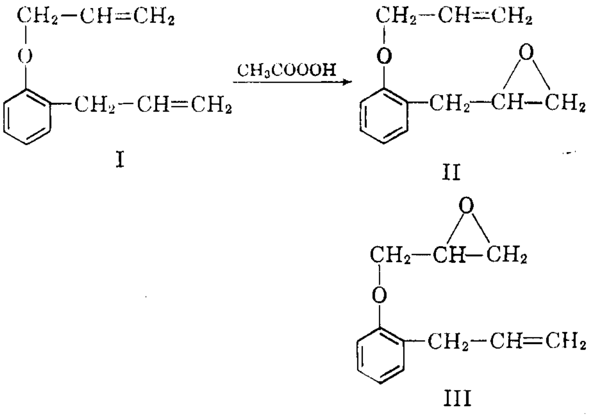
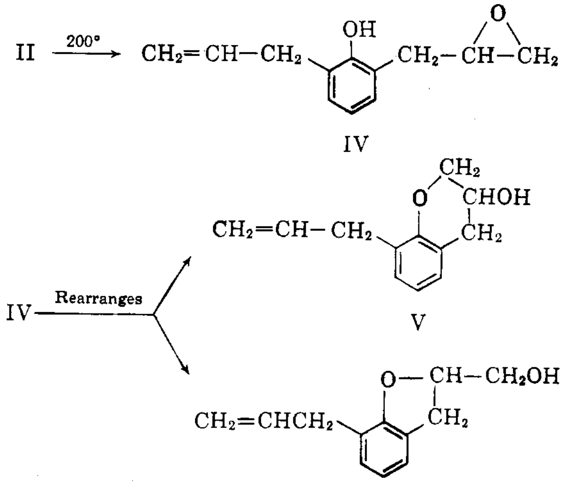
During the preparation of various polyepoxy compounds for testing as thermoset resins, the epoxidation of *o*-allylphenyl allyl ether (I) was carried out. It was found that although it was relatively easy to introduce one epoxy group, it was quite difficult to introduce two. Evidence indicated that the monoepoxy compound was *o*-glycidylphenyl allyl ether (II) rather than *o*-allylphenyl glycidyl ether (III). To check this the latter compound was prepared by treating *o*-allylphenol with epichlorohydrin. The physical properties—e.g., boiling point and refractive index of the product obtained by the epoxidation of I—were nearly identical to those of III and a mixture of them was not separated into two components in one trial by gas liquid chromatography.



It was decided to heat the compounds to 200° and note if any change occurred. The ether (II) should undergo the Claisen rearrangement whereas III should remain substantially unchanged. When this was done, it was found that the glycidyl ether (III) did not change appreciably; however, the compound obtained by epoxidizing I underwent a profound change.

The product was not the expected 2-glycidyl-6-allylphenol (IV), since it had no oxirane oxygen in it. It was reasoned that IV cyclized at the rearrangement temperature to give V or VI or a mixture of the two. Further work with the product indicated that it was largely one material.



Since V is a secondary alcohol and VI is a primary alcohol, a test frequently used in carbohydrate work for differentiating between primary and secondary alcohols was applied.[3] This test consists of warming an acetone solution of the tosyl ester of the alcohol with sodium iodide. The tosylates of primary alcohols forms the iodides and

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[1] Paper No. 240 Journal Series, Research Laboratories, General Mills, Inc.

[2] Part of a paper presented at the 136th Meeting of the American Chemical Society in Atlantic City, New Jersey.

[3] J. W. H. Oldham and J. K. Rutherford, *J. Am. Chem. Soc.*, **54**, 366 (1932).