particles were removed by filtration and dried; m.p. 306° dec.

Anal. Calcd. for $C_8H_{15}IN_2O$: C, 34.06; H, 5.39; N, 9.94. Found: C, 35.84; H, 5.50; N, 9.06.

When the reaction mixture in another run was filtered after becoming turbid, a tan solid, melting at 295° dec., was obtained. The compound crystallized from 47% hydroiodic acid as yellow crystals, m.p. 297° dec. The melting point appeared to vary with the rate of heating.

Anal. Found: C, 35.05; H, 5.18; N, 9.60.

Conversion of N-Styrylmorpholine to N-β-Phenylethylmorpholine.—A sample of N-styrylmorpholine in methanol was reduced using Adams' platinum oxide catalyst in a Parr apparatus. The N-β-phenylethylmorpholine which was obtained as an oil after catalyst and solvent had been removed was converted to a picrate by treatment with ethanolic picric acid. The compound crystallized from 95% ethanol as yellow needles, m.p. 165–166°.

Anal. Calcd. for $C_{18}H_{29}N_4O_8$: C, 51.43; H, 4.76; N, 13.33. Found: C, 51.16; H, 4.81; N, 12.80.

The compound did not depress the melting point of an authentic sample of N-β-phenylethylmorpholine picrate prepared by the following sequence of reactions: N-phenylacetylmorpholine prepared from phenylacetyl chloride and morpholine was reduced with lithium aluminum hydride. The N-β-phenylethylmorpholine obtained as a light brown oil was converted to the picrate with ethanolic picric acid. The picrate crystallized from 95% ethanol as yellow needles, m.p. 165–166°.

Conversion of *N*-Styrylmorpholine to α,γ-Diphenylcrotonaldehyde.—To 2.0 g. (0.0105 mole) of N-styrylmorpholine was added dropwise with stirring 10 ml. of 98–100% formic acid.[17] The mixture was cooled in an ice bath during the addition and until all solid had dissolved. The clear orange solution was warmed on a steam bath for 30 min., cooled, diluted with 10 ml. of 3 *N* hydrochloric acid, and extracted with 50 ml. of ether. The ether extract was re-extracted with 10 ml. of 3 *N* hydrochloric acid and concentrated to obtain a brown oil. The oil was distilled to obtain 663 mg. (56.8%) of α,γ-diphenylcrotonaldehyde as a light yellow oil, b.p. 152° (*ca.* 2 mm.).[11]

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.28; H, 6.45.

The oil yielded an orange 2,4-dinitrophenylhydrazone, m.p. 194–195° after crystallization from 95% ethanol.

Anal. Calcd. for $C_{22}H_{18}N_4O_4$: C, 65.66; H, 4.51; N, 13.92. Found: C, 65.63; H, 4.86; N, 13.8.

The compound did not depress the melting point of the 2,4-dinitrophenylhydrazone obtained from a sample of α,γ-diphenylcrotonaldehyde prepared by the method of Lindermann.[18]

Preparation of 1-(Iodoethynyl)cyclohexanol.—To the morpholine-iodine complex formed from 28 g. (0.11 mole) of iodine and 40 g. (0.46 mole) of morpholine in 200 ml. of methanol was added 13.6 g. (0.11 mole) of 1-ethynylcyclohexanol. After the mixture had stood at room temperature for 2 days, it was evaporated to half its volume and diluted with ether. The solid which precipitated was removed by filtration, washed with ether, and dried to obtain morpholine hydroiodide as light yellow needles, m.p. 212–213° dec. The filtrate was concentrated by evaporation to obtain a thick red oil. The oil was triturated in water and the mixture allowed to stand at room temperature while the oil solidified. The solid was removed by filtration and dried to obtain 25 g. (91.2%) of crude 1-(iodoethynyl)cyclohexanol. The product crystallized from petroleum ether (b.p. 65–110°) as colorless needles, m.p. 88–89°.

Anal. Calcd. for $C_8H_{11}IO$: C, 38.42; H, 4.43. Found: C, 38.69; H, 4.35.

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[17] The reaction conditions were those recommended by P. de Benneville and J. Macartney, *J. Am. Chem. Soc.*, **72**, 3073 (1950) for reduction of enamines. In this case little reduction apparently occurred, and hydrolysis followed by aldol condensation was promoted.

[18] H. Lindemann, German Patent 554,785 (January 13, 1931); *Chem. Abstr.*, **26**, 6080 (1932).

2-Fluorocyclohexanol

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Although 2-fluorocyclohexyl acetate has been prepared[2] by acetylation of 2-chlorocyclohexanol and subsequent treatment with potassium fluoride, the literature reveals no record of the parent substance, 2-fluorocyclohexanol. Several unsuccessful attempts were made in this laboratory to prepare the fluoro alcohol. One such experiment involved treatment of 2-chlorocyclohexanol with potassium fluoride as described by Knunyants and co-workers[3] for ethylene chlorohydrin. It was also shown[4] that the action of anhydrous hydrogen fluoride under various conditions resulted in chain polymerization of ethylene oxide to yield polyethylene glycols and polyethylene fluorohydrins. However, in their attempts to minimize polymerization by adding a large amount of ethyl ether as a solvent, they obtained ethylene fluorohydrin in 40% yield.

Various epoxides in the steroid series have been converted to the corresponding fluorohydrins in good yields by treatment with anhydrous hydrogen fluoride in tetrahydrofuran and chloroform.[5,6]

According to some of these workers tetrahydrofuran behaves as a base, increasing the effective concentration of fluoride ion without inhibiting completely the acid catalysis necessary for epoxide ring opening. It therefore seemed quite possible that sodium bifluoride would behave in a similar manner and that heating an epoxide such as cyclohexene oxide, with this reagent being a controlled source of anhydrous hydrogen fluoride, the corresponding fluorohydrin would be produced. The

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[1] Present address: Hazel-Atlas Glass, Plainfield, Illinois.

[2] E. Gryszkiewicz-Trochimow, A. Sporzynski, and J. Wnuk, *Rec. trav. chim.*, **66**, 413 (1947).

[3] I. L. Knunyants, O. V. Kil'dasheva, and E. Bukovskaya, *J. Gen. Chem. USSR*, **19**, 93 (1949).

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[5] R. F. Hirschmann, R. Miller, J. Wood, and R. E. Jones, *J. Am. Chem. Soc.*, **78**, 4956 (1956).

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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]

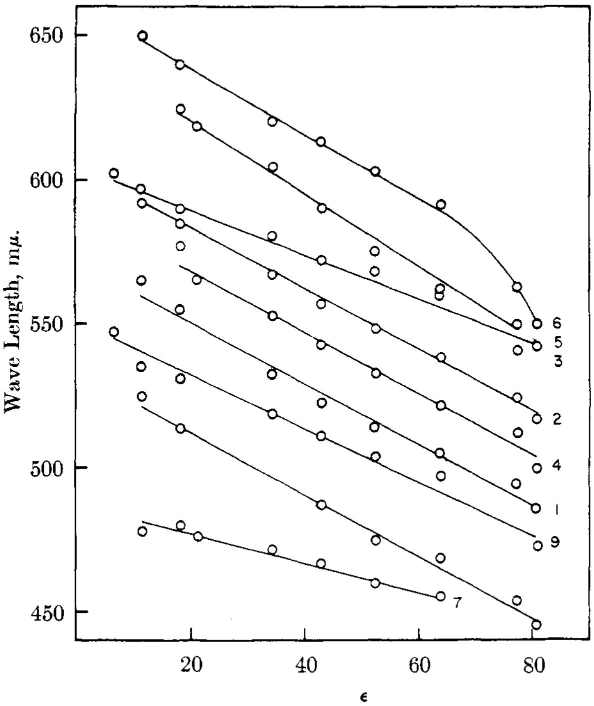

Fig. 1.—Wave length of maximum absorbance of merocyanines as a function of dielectric constant in water–dioxane mixtures (see Table I for identification of compound numbers).

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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