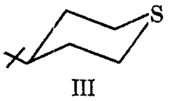
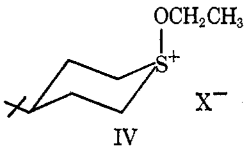
halogen oxidations is exhibited in the oxidation of 4-*t*-butylthiane (III) in ethanol solution by NBS followed by addition to silver tetrafluoroborate, or by *t*-butyl hypochlorite followed by addition of silver tetrafluoroborate or mercuric chloride. In each case salt IV (as the fluoroborate or trichloromercurate) was obtained as the major product.[9]



III



IV

Experimental Section

General Procedure for Preparation of *t*-Butoxy- and Isopropoxysulfonium Hexachloroantimonates.—To a solution of the sulfide (0.01 mole) in 20 ml of methylene chloride at −78° was added 1 equiv of alkyl hypochlorite (*t*-butyl hypochlorite was added neat; isopropyl hypochlorite was added as a methylene chloride solution maintained at −78°). After 15 min 1.28 ml (0.01 mole) of antimony pentachloride was added to the stirring solution. The solution was allowed to stir for another 10 min before addition of anhydrous ethyl ether to the cloud point. The solution was allowed to warm to 0°. The resultant precipitate was collected by filtration and recrystallized from methylene chloride–ethyl ether. The salts were dried in a vacuum desiccator unless they had been found to be unstable, in which case they were pressed dry on a sintered-glass Büchner funnel and stored immediately at 0°.

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[9] C. R. Johnson and D. McCants, Jr., unpublished results.

Spectroscopic Studies of Ketol–Enol Equilibria. XI. Optical Rotatory Dispersion in Aromatic Schiff Bases[1]

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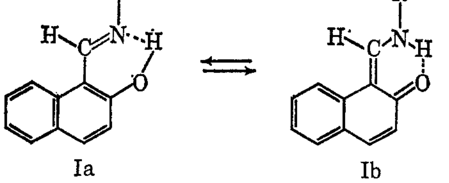
There is considerable influence of keto–enol equilibria (Ia $\rightleftarrows$ Ib) on the optical rotatory activity of Schiff bases



Ia Ib

derived from aromatic carbonyl compounds and optically active amines. In Figure 1, the complex optical rotatory dispersion (ORD) spectrum of a typical compound, I [R = (*S*)-(+)-α-phenylethyl] is depicted for three solvents.[2] The solvents were chosen, with reference to the pmr studies on similar systems,[1,4] to cover a range of associating ability. Above 320 mμ, the ORD curve is strongly solvent dependent with the curve in hexane differing markedly from the two for the hydrogen-bonding solvents, chloroform and absolute ethanol.

With compounds of this type, the proton can reside on either oxygen (Ia) or nitrogen (Ib) and this equilibrium has been extensively studied by means of proton resonance spectroscopy utilizing ^{15}N-labeled amines.[1,4] The pmr data indicate the equilibrium is toward Ia in nonpolar solvents, while in hydrogen-bonding solvents the equilibrium is shifted markedly toward Ib, the nonaromatic tautomer. In naphthols (1,2 substituted), the equilibrium is toward Ib, while in phenols the equilibrium is largely toward forms similar to Ia. Therefore the curves of Figure 1 are a result of the shift of the proton from oxygen to nitrogen as the solvent becomes more associating.[1] The dearomatization of the aromatic system accompanying the tautomer shift produces an extremum of the Cotton effect at considerably longer wavelengths.

The ultraviolet absorptions of the Schiff base (I, R = CH_3) consists of several solvent-dependent bands in the long wavelength region. One band at 350 mμ has been assigned to the aromatic tautomer Ia, while a pair at 408 and 420 mμ ($CDCl_3$ solution) has been assigned to the nonaromatic form, Ib.[1,5] The origin of the 318-mμ band (seen at 315 in salicylaldimines) is not known.[3] The band is not markedly solvent dependent, but does appear to involve the Schiff base chromophore.

From the ultraviolet spectrum of I in hexane solution, it can be determined that a small amount of Ib is present since the intensity of the 420-mμ band in hexane is 11% of its intensity in absolute ethanol. This is consistant with the data in Figure 1 and indicates that the ORD curve of Ia has no extremum beyond 350 mμ.

In their studies of optically active salicylaldimines, Smith and his colleagues[3] noted anomalies in the ORD curves of these Schiff bases as compared to the benzylidine derivatives. In particular, a new weak Cotton effect, centered at 420 mμ, appeared in ethanol solutions of the salicylaldimines. These authors discussed several possible explanations, and with the assistance of the ^{15}N pmr data, this anomaly clearly is the result of the presence of about 10% of the nonaromatic form (similar to Ib) in ethanol solution. The value for the molecular rotation [Φ] observed here is consistent with those reported by Smith, *et al.*,[3] if a correction is made for the amount of ketamine present in the solution.

With the results of the compound discussed here, which is a typical member of the naphthalene series, and the data of Smith on the phenols, it can be seen that the shift of the proton from one site to the other profoundly alters the electronic environment about the nitrogen. The reorganization most likely includes the aromatic system. The fact that the chromophore is quite disymmetric results in large rotations being observed.[6] If the integrated areas were used, the difference in rotatory power between Ia and Ib would be larger owing to the greater breadth of the 400-mμ bands compared with the 370-mμ band from Ia.

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[1] Part X: G. Dudek and E. P. Dudek, *Tetrahedron*, in press.

[2] For compatibility with the data of Smith, *et al.*,[3] the figure is given for the (+) isomer, although the (−) isomer was actually used.

[3] H. E. Smith, S. L. Cook, and M. E. Warren, *J. Org. Chem.*, **29**, 2265 (1964); M. E. Warren and H. E. Smith, *J. Am. Chem. Soc.*, **87**, 1757 (1965); H. E. Smith and R. Records, *Tetrahedron*, **22**, 813 (1966).

[4] G. Dudek and E. P. Dudek, *Chem. Commun.*, 464 (1965); *J. Am. Chem. Soc.*, **88**, 2407 (1966).

[5] There is a distinct inflection in the ORD curve at 415 mμ, corresponding to the minimum in the ultraviolet spectrum between the 408- and 420-mμ bands.

[6] *Cf.* P. Crabbe and B. Halpern, *Chem. Ind.* (London), 346 (1965).

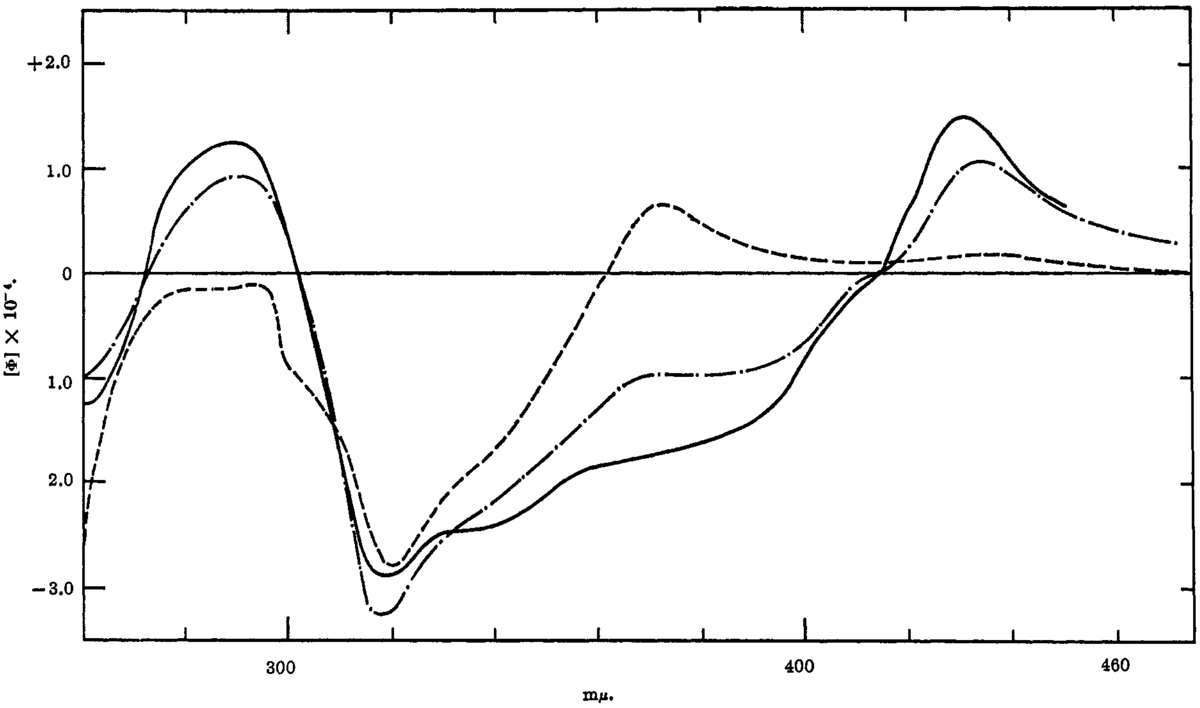

Figure 1.—The optical rotatory dispersion curve of 1-[(*S*)-(+)-α-phenylethylformimidoyl]-2-naphthol in - - - -, hexane; — · — chloroform; and ———, absolute ethanol.

Experimental Section

The compound, N-[(*R*)-(−)-α-phenylethyl]formimidoylnaphthol, was prepared by mixing (*R*)-(+)-α-phenylethylamine ([α] +39.4°) and 2-hydroxy-1-naphthaldehyde. After crystallization from benzene–hexane and then sublimation, it melted at 110.7–111.5°. *Anal.* Calcd for $C_{19}H_{17}NO$: C, 82.88; H, 6.22; N, 5.09. Found: C, 82.63; H, 6.06; N, 5.12.

It should be noted that the DL compound melted at about 82–85° and being a less tractable substance, the analytical data were obtained from the optically active material.

The ORD spectra were obtained from a Cary Model 60 recording spectropolarimeter using 1.0-mm cells. In all cases, ultraviolet spectra were taken of solutions used in the ORD studies to ensure optimum performance of the polarimeter. The solvents used were commercial spectra grade materials.

Registry No.—Ia [R = (*R*)-(−)-α-phenylethyl], 10349-22-1; Ia [R = (*S*)-(+)-α-phenylethyl], 10349-23-2; DL Ia, 10349-24-3; Ib [R = (*R*)-(−)-α-phenylethyl], 10349-25-4; Ib [R = (*S*)-(+)-α-phenylethyl, 10349-26-5; DL Ib, 10406-88-9.

Trimesate Esters by Formylation with Carbon Monoxide

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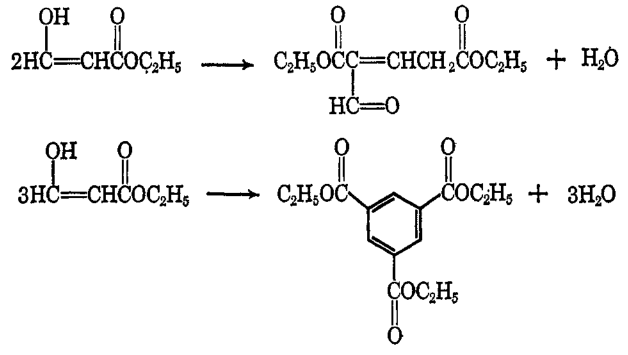
In 1887, Wilhelm Wislicenus first reported the condensation of ethyl formate and ethyl acetate through the action of sodium in ether or benzene.[1] A more thorough report was published in 1901.[2] The product, the sodium salt of formylacetic ester, when acidified gives ethyl formylacetate, which is, however, too unstable to isolate. It condenses with itself, forming ethyl formylglutaconate as the major product, along with small amounts of ethyl trimesate.



The first application of carbon monoxide under pressure in the formylacetic ester synthesis was reported in a patent by Beer and Halbig,[3] and later by Northey.[4] In these patents the usual condensation between a formate and acetate ester is effected, but under carbon monoxide pressure. The formate ester is prevented from decomposing, to an alcohol and carbon monoxide by the sodium alkoxide, and the alcohol that is normally formed in the reaction is converted to a formate ester. Neither of these patents, however, discussed the utility of using the formylacetic ester, obtained by acidifying the sodium salt, to prepare trimesate esters. The trimerization to trimesate esters was only mentioned in passing.

A mechanism for the reaction of carbon monoxide with an alkoxide ion and an alcohol to form a formate

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(1) W. Wislicenus, *Ber.*, **20**, 2930 (1887).

(2) W. Wislicenus and W. Bindemann, *Ann.*, **316**, 18 (1901).

(3) L. Beer and P. Halbig, German Patent 708,513 (1941).

(4) E. H. Northey, U. S. Patent 2,394,255 (1946).