

study of the optical rotatory dispersion (o.r.d.) of (+)-methyl *n*-butyl sulfoxide (I). A Cotton effect is found to be centered at the absorption maximum below 210  $m\mu$  whose solvent dependence (Figure 1) characterizes it as an  $n \rightarrow \pi^*$  transition<sup>3</sup>; in contrast, the shoulder near 215  $m\mu$  is relatively solvent insensitive.<sup>4</sup> We have found by vapor pressure osmometry<sup>5</sup> (v.p.o.) at 37° that, whereas I is monomeric in ethanol and acetonitrile, it is *dimeric* in cyclohexane; over the range from 0.018 to 0.055 *M* the dimerization appears to be essentially complete.<sup>6</sup> It has previously been reported that sulfoxides associate in solution.<sup>7,8</sup> We therefore cannot rule out at present the possibility that the absorption spectrum (and o.r.d.) of I in cyclohexane is that of the dimer or a composite of monomer and dimer.<sup>9</sup>

The previously proposed<sup>2</sup> classification of optically active dialkyl sulfoxide chromophores as "asymmetrically perturbed symmetric" was based on the presumption that this system could be usefully discussed from a viewpoint analogous to that employed in the treatment of saturated ketones.<sup>10</sup> In light of the unexpectedly high amplitude of the Cotton effect of I, this approach, which is eminently successful for aromatic sulfoxides,<sup>11</sup> may have to be modified in the case of dialkyl sulfoxides.

Sulfoxide I,  $[\alpha]_D +42^\circ$  (isooctane), was prepared by reaction of an excess of methylmagnesium bromide with a diastereomeric mixture of *l*-menthyl 1-butanesulfinates,  $[\alpha]_D -50^\circ$  (acetone), which was obtained by asymmetric synthesis from racemic 1-butanesulfinyl chloride.<sup>12</sup> *p*-Tolyl *n*-butyl sulfoxide,  $[\alpha]_D +88^\circ$  (acetone), was prepared by reaction of an excess of *p*-tolylmagnesium bromide with the same diastereomeric mixture. Since the ratio of diastereomers in the starting material equals the ratio of enantiomers in the product,<sup>12</sup> and since optically pure *p*-tolyl *n*-butyl sulfoxide has  $[\alpha]_D +187^\circ$  (acetone),<sup>12</sup> the optical purity of (+)-(I) is 47%. Assuming inversion in the Grignard reaction<sup>13</sup> and given the absolute configuration of

(3) H. McConnell, *J. Chem. Phys.*, **20**, 700 (1952).

(4) Further studies of this problem are in progress. For previous work on the absorption spectra of dialkyl sulfoxides see H. P. Koch, *J. Chem. Soc.*, 2892 (1950), and ref. 18.

(5) C. Tomlinson, *Microchim. Acta*, 457 (1961).

(6) In contrast, we find that aryl alkyl and diaryl sulfoxides are essentially monomeric in cyclohexane in that concentration range. The effect of structure on the association of sulfoxides is being investigated further.

(7) DMSO forms association polymers in the neat state (H. L. Schläfer and W. Schaffernicht, *Angew. Chem.*, **72**, 618 (1960)) and in benzene solution (J. J. Lindberg, J. Kenttämaa, and A. Nissema, *Suomen Kemistilehti*, B34, 98, 156 (1961)), and it appears to dimerize in carbon tetrachloride solution (C. D. Ritchie, unpublished observations; we are grateful to Professor C. D. Ritchie for informing us of his results prior to publication).

(8) 2-Thiaindan 2-oxide exists as a dimer in cyclohexane (R. F. Watson and J. F. Eastham, *J. Am. Chem. Soc.*, **87**, 664 (1965)).

(9) We find adherence to Beer's and Biot's laws in the spectrometrically accessible region over the concentration range of ca.  $10^{-2}$  *M* to ca.  $10^{-4}$  *M*. However, since the spectroscopic properties of monomeric and dimeric species may be similar, this result is in the nature of negative evidence. It is noteworthy that I has  $\lambda_{max}$  205  $m\mu$  and 193  $m\mu$  in the vapor phase, where it is presumably monomeric, whereas I in cyclohexane lacks the maximum at shorter wave lengths (as investigated down to 186  $m\mu$ ).

(10) A. Moscowitz, *Tetrahedron*, **13**, 48 (1961).

(11) Aryl alkyl sulfoxides have been discussed from the viewpoint of inherently dissymmetric chromophores<sup>2</sup>; diaryl sulfoxides may be profitably discussed from either point of view, depending on the structure (unpublished results).

(12) E. B. Fleischer, M. Axelrod, M. Green, and K. Mislow, *J. Am. Chem. Soc.*, **86**, 3395 (1964).

(13) K. K. Andersen, *Tetrahedron Letters*, No. 3, 93 (1962); *J. Org. Chem.*, **29**, 1953 (1964).

starting material,<sup>12</sup> the absolute configuration of (+)-(I) is (*S*).

Absolute configurations may now be assigned to other methyl alkyl sulfoxides by comparison of o.r.d. curves with that of I. Thus, the methyl alkyl sulfoxides studied by Klyne, *et al.*,<sup>14</sup> have negative plain curves which are tails of negative sulfoxide Cotton effects<sup>15</sup> centered near 203  $m\mu$  (acetonitrile); these compounds therefore have the (*R*)-configuration.<sup>16</sup> Similarly, since (–)-*L*-sulphoraphane<sup>17–19</sup> ( $\text{CH}_3\text{SO}(\text{CH}_2)_4\text{NCS}$ ) has a negative Cotton effect<sup>20</sup> and therefore has the (*R*)-configuration,<sup>16</sup> the arbitrary *D* and *L* nomenclature adopted for derivatives of this compound<sup>17</sup> may now be abandoned.

Our work on sulfoxides is continuing.

(14) W. Klyne, J. Day, and A. Kjaer, *Acta Chem. Scand.*, **14**, 215 (1960).

(15) As determined in these Laboratories on  $\text{CH}_3\text{SO}(\text{CH}_2)_5\text{NHCSNH}_2$ . We are indebted to Professor W. Klyne for a sample of this material.

(16) Professor A. Kjaer has kindly informed us that the same conclusion has been arrived at independently by X-ray analysis.

(17) H. Schmid and P. Karrer, *Helv. Chim. Acta*, **31**, 1497 (1948).

(18) P. Karrer, N. J. Antia, and R. Schwyzer, *ibid.*, **34**, 1392 (1951).

(19) We are indebted to Dr. Ž. Procházka for a sample of this material.

(20) As judged by the o.r.d. above 225  $m\mu$  (J. T. Melillo, Ph.D. Dissertation, New York University, 1964).

(21) N.I.H. Predoctoral Fellow, 1964–1965.

Kurt Mislow, Mark M. Green<sup>21</sup>

Peter Laur, Daniel R. Chisholm<sup>21</sup>

Department of Chemistry, Princeton University  
Princeton, New Jersey 08540

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## Diastereoisomerism in 9-Dimethylamino-9,10-dihydro-4,5-dimethylphenanthrene

Sir:

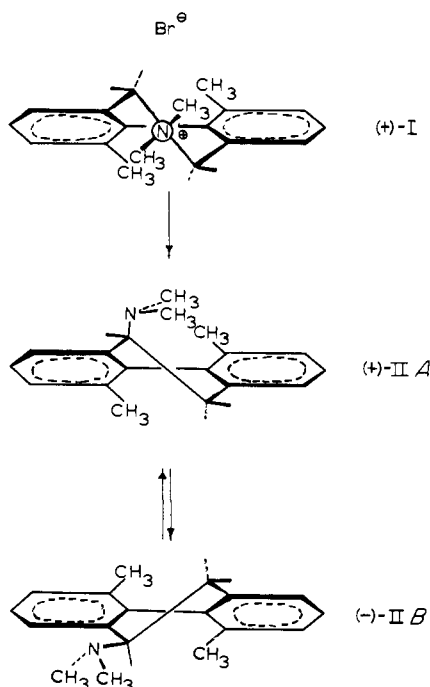
In 1953 Wittig and Zimmermann reported<sup>1</sup> the isolation of two diastereomers of amine II upon reaction of azepinium bromide I with phenyllithium in ether and with potassium amide in liquid ammonia, respectively. However, the claimed<sup>1</sup> isolation of the separate diastereomers of amine II by distillation at elevated temperatures (116–119°) is not compatible with the demonstrated optical instability of the 9,10-dihydro-4,5-dimethylphenanthrene system.<sup>2</sup> We have reinvestigated the work of Wittig and Zimmermann<sup>1</sup> and have obtained results which are at variance with their report and which confirm our earlier views.<sup>2</sup>

Reaction of (+)-(S)-I<sup>3</sup> with phenyllithium in ether gave II, a basic oil (74%, b.p. ca. 130° (0.07 mm)). The oil crystallized, neat or from methanol, to give a material (IIA, m.p. 82–85°; *Anal.* Found: C, 85.96; H, 8.48; N, 5.31) which mutarotated in toluene. The mutarotation followed strict first-order kinetics with  $k^{32.8} = 3.3 \times 10^{-4} \text{ sec}^{-1}$ . Extrapolation from three mutarotation experiments to zero time gave values for the initial rotation of  $[\alpha]^{32.8}_{435} +566$  to  $+607^\circ$ . In repetitions of this experiment starting from (+)-(S)-I, another crystalline substance was fortuitously obtained (IIB, m.p. 85–90°; *Anal.* Found: C, 86.24; H, 8.69; N, 5.72), which mutarotated in toluene with  $k^{32.8} = 3.4 \times 10^{-4} \text{ sec}^{-1}$ . However, extrapolation to zero

(1) G. Wittig and H. Zimmermann, *Chem. Ber.*, **86**, 629 (1953).

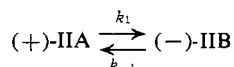
(2) K. Mislow and H. B. Hopps, *J. Am. Chem. Soc.*, **84**, 3018 (1962).

(3) K. Mislow, M. A. W. Glass, H. B. Hopps, E. Simon, and G. H. Wahl, Jr., *ibid.*, **86**, 1710 (1964).



time gave, in this case, values for the initial rotation of  $[\alpha]_{435}^{32.8} -561$  to  $-590^\circ$ . Evidently the crystalline forms of (+)-IIA and (-)-IIB arise by second-order asymmetric transformations; the separation of the crystalline phase displaces the equilibrium between the two diastereomers in the supernate. The same equilibrium rotation ( $[\alpha]_{435}^{32.8} \sim +25^\circ$ ) is obtained starting with either diastereomer.

The equilibrium rotation is temperature dependent and becomes negative above *ca.*  $60^\circ$ . Assuming the reasonable values<sup>4</sup> of  $\pm 570^\circ$  for  $[\alpha]_{435}$  of the pure diastereomers, equilibrium constants may be calculated from the temperature dependence of the equilibrium rotation, whence  $\Delta H^\circ$  is *ca.* 0.9 kcal./mole and  $\Delta S^\circ$  is *ca.* 2.7 e.u. for the equilibrium in toluene



Given these values of  $\Delta H^\circ$  and  $\Delta S^\circ$ , the temperature dependence of the rate constant of mutarotation ( $k_1 + k_{-1}$ ) yields  $k_1 = 10^{12.4} \exp(-22.7/RT) \text{ sec.}^{-1}$  and  $k_{-1} = 10^{11.8} \exp(-21.8/RT) \text{ sec.}^{-1}$ . The values of these rate constants are in consonance with the value of  $k_{\text{inv}} = 10^{12.5} \exp(-23.1/RT) \text{ sec.}^{-1}$  which was found for the configurational inversion ( $k_{\text{inv}} = 0.5k_{\text{rac}}$ ) of 9,10-dihydro-4,5-dimethylphenanthrene (III).<sup>2</sup>

The rotations of the diastereomers of II are effectively equal and opposite. It may therefore be concluded that the contribution of the asymmetric C-9 atom is essentially negligible and that the chirality of the inherently dissymmetric biphenyl moiety is the dominating factor determining sign and magnitude of the optical rotation. It has been shown that 2,2'-bridged biphenyls which lack extraneous chromophores and which have the (*S*) configuration have strong positive rotations in the visible.<sup>5</sup> The configurations of the biphenyl components in (+)-IIA and (-)-IIB are therefore (*S*) and (*R*), respectively. These conclusions are supported by preliminary o.r.d. results on (-)-IIB which

(4) Variations of less than 10% in the values assumed for  $[\alpha]_{435}$  do not significantly alter the calculated thermodynamic constants.

(5) K. Mislow, *Angew. Chem.*, **70**, 683 (1958).

are typical for such compounds;<sup>2,6</sup> the sign of rotation in the visible is dominated by the background rotation originating in an intense negative Cotton effect centered at short wave lengths (*ca.* 225  $m\mu$ ); a positive Cotton effect is interposed at the biphenyl conjugation band (near 260  $m\mu$ ). The absolute configuration at C-9 (arbitrarily shown as (*R*) in the drawing) is not yet firmly established and we are investigating this interesting problem which has direct bearing on the mechanism of the Stevens rearrangement. It should be noted at this time however that the transfer of dissymmetry (from biphenyl I to C-9 in II) appears to be essentially complete and that the reaction is therefore highly stereospecific.

Wittig and Zimmermann reported<sup>1</sup> that reaction of I with potassium amide in liquid ammonia gives an amine of structure II, and that this amine does not deaminate under the conditions of the reaction. In contrast we have found that the major products are 4,5-dimethylphenanthrene (IV) and III, the ratio of III:IV increasing with increasing reaction time (III:IV = 0.012 after 1 hr. and 17.6 after 1 week. After 8 months only III is observed). With weaker bases (potassium hydroxide) II is produced; this material is identical in every respect with the product of the phenyllithium reactions.

(6) K. Mislow, M. A. W. Glass, R. E. O'Brien, P. Rutkin, D. H. Steinberg, J. Weiss, and C. Djerassi, *J. Am. Chem. Soc.*, **84**, 1455 (1962).

(7) Correspondence should be addressed to the Department of Chemistry, Princeton University, Princeton, N. J. 08540.

Kurt Mislow,<sup>7</sup> Henry Joshua

Department of Chemistry, New York University  
New York, New York 10453

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## The Structure of Porphine<sup>1</sup>

Sir:

The crystal structures of several tetraphenylporphines have been determined recently by X-ray methods.<sup>2-4</sup> The space groups of these porphyrins all require some molecular symmetry. The structure of porphine is of interest because it is unaffected by phenyl substituents and has no molecular symmetry required by the space group. The results of an X-ray structure determination of this molecule are given here.

Porphine crystals are monoclinic, space group  $P2_1/a$ . Since there are four molecules per unit cell, there is no required molecular symmetry. The cell dimensions are  $a = 12.36 \pm 0.01$ ,  $b = 12.12 \pm 0.02$ ,  $c = 10.272 \pm 0.002$  Å.;  $\beta = 102.1 \pm 0.1^\circ$ . Cu  $K\alpha$  radiation was used to obtain 2421 nonzero structure factors, and the structure was solved by the probability methods of Hauptman and Karle.<sup>5,6</sup> The final conventional *R* factor including all 2421 reflections was 4.9%.

Twelve hydrogens at reasonable positions on the outside of the porphine ring and four "half-hydrogens"

(1) This research was supported by a grant from the Public Health Service.

(2) S. Silvers and A. Tulinsky, *J. Am. Chem. Soc.*, **86**, 927 (1964).

(3) M. J. Hamor, T. A. Hamor, and J. L. Hoard, *ibid.*, **86**, 1938 (1964).

(4) E. B. Fleischer, C. K. Miller, and L. E. Webb, *ibid.*, **86**, 2342 (1964).

(5) H. Hauptman and J. Karle, "Solution of the Phase Problem. I. The Centrosymmetric Crystal," A.C.A. Monograph, No. 3., Polycrystal Book Service, Brooklyn, N. Y., 1953.

(6) J. Karle and H. Hauptman, *Acta Cryst.*, **12**, 404 (1959).