added, and the solution was stirred at 0° for 3 hr. Alkaline peroxide oxidation, work-up in the usual manner, distillation of the solvent, and distillation of the residue at temperatures up to 140° gave crude 3-hexanol (**12**) contaminated by traces of **4**. Chromatography on alumina (80–200 mesh) in pentane, elution with ether, and distillation (kugelrohr, 125–140°) of the eluate gave 0.90 g (32% yield) of **12**, $n^{20}\text{D}$ 1.4158, $[\alpha]^{24}\text{D}$ $-1.47°$ (neat) (lit. $n^{20}\text{D}$ 1.4167,[67] $[\alpha]^{20}\text{D}$ $+7.09°$ (neat)[47]). Glpc analysis (6-ft 10% column of Carbowax 4000, at 130°, helium flow rate 30 cc/min) indicated the presence of 3-hexanone (*ca.* 3%), of an unidentified impurity (*ca.* 2%), and of **12**, with retention times of 2.8, 3.6, and 4.4 min, respectively.

In a separate experiment, $BH_3 \cdot THF$ (56 mmol) and (+)-**4** (7.62 g, 56 mmol) were allowed to react at 0° for 0.5 hr and the solution was then kept at room temperature for 21 hr. *cis*-3-Hexene (2.352 g, 28 mmol) was added and the solution stirred at room temperature for 3 hr. Work-up and purification, as above, gave 0.70 g (24.5% yield) of **12**, $n^{20}\text{D}$ 1.4162, $[\alpha]^{24}\text{D}$ $+0.76°$ (neat). Glpc analysis, as above, indicated that **12** was contaminated with *ca.* 1% each of 3-hexanone and the unidentified contaminant.

Circular Dichroism of (+)-Dimethyldibenzsuberone. The sample used had the following properties: $[\alpha]\text{D}$ $+617.7°$ (*c* 1.4, benzene), uv in isooctane solution $\lambda_{\max}$ mμ (ε) 317 (263), 307 (584), 297.5 (752), 289 (746); CD in isooctane solution (*c* 0.0464 g/100 ml at $\lambda >$ 260 mμ, *c* 0.00464 g/100 ml at $\lambda <$260 mμ) $\lambda_{\max}$ ([θ]) 335 (0), 316 ($+5.5 \times 10^4$), 306.5 ($+11.2 \times 10^4$), 296.5 ($+12.5 \times 10^4$), 289.5 ($+9.3 \times 10^4$), 280 sh ($+4.3 \times 10^4$), 245 (10×10^4) [lit. $[\alpha]^{23}\text{D}$ $+617°$ (*c* 1.65, benzene);[55] uv[55] 317 (257), 307 (575), 297.5 (759), 289.5 (759); CD[10a] 296 ($+10.8 \times 10^4$), 245 ($+9.65 \times 10^4$).

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[67] R. Lespieau and R. Lombard, *Bull. Soc. Chim. Fr.*, **2**, 369 (1935).

Stereochemistry of 9-Dimethylamino-9,10-dihydro-4,5-dimethylphenanthrene[1,2]

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Abstract: In an asymmetric transfer reaction, two optically active diastereomers of 9-dimethylamino-9,10-dihydro-4,5-dimethylphenanthrene (**1**) are formed by Stevens rearrangement of an optically active bridged biphenyl azepinium bromide (**2**). The isomers, which differ in the chirality of the biphenyl moiety but share the same chirality at the asymmetric carbon atom (C-9), interconvert by torsion around the biphenyl pivot bond axis, and are isolated in crystalline forms which arise by second-order asymmetric transformations. First-order rate constants of mutarotation, the equilibrium constant between the isomers, and the Arrhenius and the transition-state parameters for the interconversion have been determined. From an analysis of the optical rotatory dispersion and nmr spectra of the products of rearrangement of (+)-(*S*)-**2**, the *S* configuration has been assigned to C-9 in both diastereomers and the *R* and *S* configurations to the biphenyl moieties in (−)-**1** and (+)-**1**, respectively. These results are in consonance with current views on the mechanism of the Stevens rearrangement. In connection with the configurational and conformational analysis, a brief discussion is offered on the limitations and applicability of the Wood–Fickett–Kirkwood method for determining thermodynamic parameters from the temperature dependence of physical properties.

Optically active 9-dimethylamino-9,10-dihydro-4,5-dimethylphenanthrene (**1**) is obtained as a basic oil when optically active 1,1,4′,1′′-tetramethyl-2,7-dihydro-3,4,5,6-dibenzazepinium bromide (**2**) is treated with phenyllithium in ether.[3] This reaction involves an asymmetric transfer, in which an asymmetric carbon atom (at C-9 of **1**) is generated in a Stevens rearrangement[4] from a compound having only biphenyl chirality.[5] In our hands, the rearrangement of (+)-**2** yielded **1** which eventually crystallized; the material thus obtained was dextrorotatory, (+)-**1**. Subsequent crystallizations of the *same* basic oil yielded the levorotatory form, (−)-**1**. Evidently the two crystalline forms (+)-**1** and (−)-**1** arise by second-order asymmetric transformations,[6] the separation of the crystalline phase displacing the equilibrium between the two diastereomers in the supernatant solution. As will be discussed in further detail below, both (+)-**1** and (−)-**1** were found to mutarotate in toluene to give the same equilibrium mixture, whose sign of rotation was found to be temperature dependent; the rate of mutarotation was found to follow strict first-order kinetics.

Reaction of (+)-**2** with potassium amide in liquid ammonia gave as the major products 4,5-dimethylphenanthrene (**3**) and 9,10-dihydro-4,5-dimethylphenanthrene (**4**), the ratio of **3**:**4** decreasing with increasing reaction time. For example, the ratio of **3**:**4** was 0.012 after 1-hr reaction time, and 17.6 after 1 week. After a reaction time of 8 months, only **4** could be observed. With weaker bases, such as potassium hydroxide in liquid ammonia, **1** was produced. It thus appears that when the reactant is potassium hydroxide, the reaction stops largely at the rearrangement stage, whereas reaction with potassium amide removes a benzylic hydrogen from C-10 of the

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[1] This work was supported by the Air Force Office of Scientific Research under Grant No. AF-AFOSR-1188-67 and by the National Science Foundation under Grant No. GP-3375.

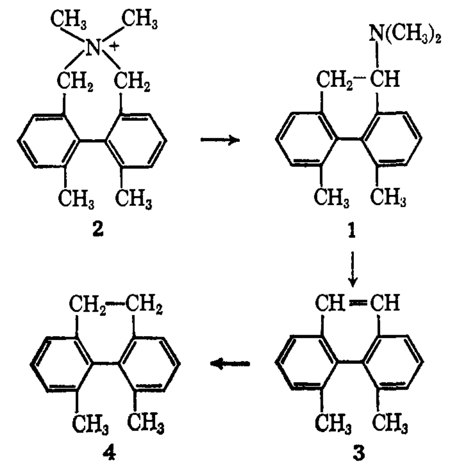
[2] For a preliminary account of portions of this work, see K. Mislow and H. Joshua, *J. Amer. Chem. Soc.*, **87**, 666 (1965).

[3] G. Wittig and H. Zimmermann, *Chem. Ber.*, **86**, 629 (1953).

[4] Transfer of asymmetry from nitrogen to carbon in a Stevens rearrangement has recently been described by R. K. Hill and T. Chan, *J. Amer. Chem. Soc.*, **88**, 866 (1966).

[5] The reverse, generation of biphenyl chirality by asymmetric transfer from a system having only central chirality, is illustrated by the phenyldihydrothebaine synthesis (R. Robinson, *Nature*, **160**, 815 (1947)).

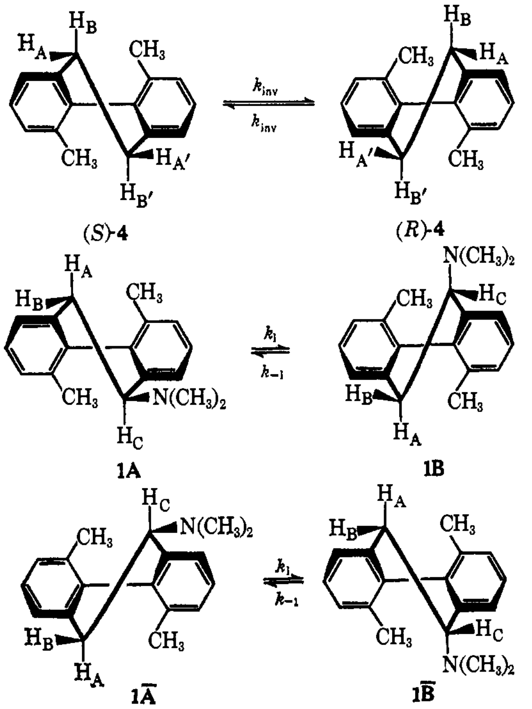
[6] E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 42 ff.

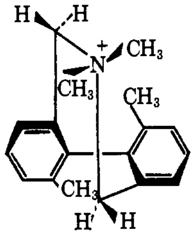


produced **1** to cause elimination of dimethylamine, giving **3**.[7] The latter is then slowly hydrogenated on C-9 and C-10 to give **4**; the details of the hydrogen transfer are unknown. In support of this proposed sequence of events, it was found that reaction of **1** and **3** for 1 week with potassium amide in liquid ammonia afforded **4** in 68 and 82% yields, respectively. When **1** was treated with potassium amide under the same conditions but for a shorter period of time (1 hr), **3** was obtained as the major product, in *ca.* 64% yield.

It had previously been demonstrated[8] that at the temperatures for which mutarotation of **1** is observed, the parent compound, **4**, racemizes by a process involving the interconversion of the two conformational enantiomers (see Chart I). In each enantiomer of **4**, there are two equivalent sets of diastereotopic[9] protons, H_A and H_B (or $H_{A'}$ and $H_{B'}$). Replacement of H_A (or $H_{A'}$) and H_B (or $H_{B'}$) by a dimethylamino group affords diastereomers of **1**, as indicated in Chart I. Thus, replacement of H_A or $H_{A'}$ in (*S*)-**4** gives **1A**, replacement of $H_{B'}$ or $H_{B'}$ in (*S*)-**4** gives **1$\bar{\mathrm{B}}$**, replacement of H_A or $H_{A'}$ in (*R*)-**4** gives **1$\bar{\mathrm{A}}$**, and replacement of H_B or $H_{B'}$ in (*R*)-**4** gives **1B**. Diastereomers **1A** and **1B**, and similarly diastereomers **1$\bar{\mathrm{A}}$** and **1$\bar{\mathrm{B}}$**, can interconvert by torsion around the biphenyl pivot bond axis, thus accounting for the mutarotation as well for the second-order asymmetric transformation. In the interconversion process, although the configuration of the asymmetric C-9 atom remains unchanged, the disposition, quasi-axial (**1B** and **1$\bar{\mathrm{B}}$**) or quasi-equatorial (**1A** and **1$\bar{\mathrm{A}}$**), of the dimethylamino group changes. Finally, it is to be noted that the **1A**/**1B** system arises from rearrangement of one enantiomer of **2**, while the **1$\bar{\mathrm{A}}$**/**1$\bar{\mathrm{B}}$** system arises from rearrangement of the other. The absolute configuration of (+)-**2** is known to be *S*.[10] The purpose of the present work was in part to establish the absolute configurations of the diastereomers and thus to describe more completely the stereochemistry of the rearrangement reaction.

Chart I





(+)-(*S*)-**2**

Conformational Equilibria and Barriers to Interconversion of Diastereomeric 9-Dimethylamino-9,10-dihydro-4,5-dimethylphenanthrenes. The thermodynamic parameters K, $\Delta H°$, and $\Delta S°$ for the equilibrium between (+)-**1** and (−)-**1** in solution are of interest primarily for two reasons. First, while K for the equilibrium between the enantiomeric conformers of **4** in an achiral solvent is necessarily unity, the extent of the effect on K of substitution by the dimethylamino group might be appreciable, particularly so since in one diastereomer of **1** the substituent group is in a quasi-axial position, whereas in the other it is in a quasi-equatorial position. Second, knowledge of these parameters is needed for the evaluation of the activation energy barriers for the forward and reverse reactions indicated by k_1 and k_{-1} in Chart I; these rate constants are necessarily the same in the analogous interconversion of (*S*)-**4** and (*R*)-**4** and are indicated by k_{inv} in Chart I.

Two independent approaches were taken to determine the desired quantities, one involving measurements of the temperature dependence of optical rotation, the other measurement of the temperature dependence of nmr signal intensities; these will be discussed separately below.

Equilibrium Constants from Optical Rotations. Mutarotations of (+)- and (−)-**1** gave excellent first-order

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[7] Professor G. Wittig has informed us of experiments in his laboratory (Dr. M. Jautelat) which indicate that elimination occurs only in the presence of a molar excess of potassium amide (as in the above experiments). We thank Professor Wittig for permission to cite these results in the present context. *Cf.* also D. M. Hall and T. M. Poole, *J. Chem. Soc.*, 268 (1963).

[8] K. Mislow and H. B. Hopps, *J. Amer. Chem. Soc.*, **84**, 3018 (1962).

[9] K. Mislow and M. Raban in "Topics in Stereochemistry," Vol. 1, N. L. Allinger and E. L. Eliel, Ed., John Wiley and Sons, Inc., New York, N. Y., 1967, Chapter 1.

[10] K. Mislow, *Angew. Chem.*, 70, 683 (1958), and references cited therein.

Table I. Mutarotation of (+)-**1** and (−)-**1** to the Equilibrium Mixture in Toluene

Temp,[a] °C	Concn, g/100 ml	$(\alpha_t - \alpha_e)$ at t_i[b]	No. of points[c]	$k_M \times 10^4$, sec^{-1}	$[\alpha_0]_{435}$, deg[g]
25.0	1.54	−14.50	17 (*2*)	1.24 ± 0.09[d] (−1.0000)[f]	
25.0	1.48	−17.20	16 (*2*)	1.22 ± 0.09 (−0.9999)	−570
32.8	3.64	−37.79	34 (*5*)	3.4 ± 0.2 (−0.9997)	−590
32.8	3.73	−1.75	18 (*4*)	3.2 ± 0.2 (−0.9996)	
32.8	3.73	−1.59	16 (*6*)	2.4 ± 0.2 (−0.9586)	
32.8	2.42	+1.48	16 (*6*)	3.7 ± 0.3 (−0.9960)	
32.8	3.22	+28.48	38 (*4*)	3.3 ± 0.2 (−0.9999)	+566
32.8	1.76	+19.76	27 (*2*)	3.2 ± 0.2 (−0.9999)	+607
32.8	2.65	−0.69	12 (*4*)	3.3 ± 0.2 (−0.9978)	
32.8	3.77	+34.39	25 (*6*)	3.3 ± 0.2 (−1.0000)	+596
40.4	1.63	−13.84	25 (*3*)	7.8 ± 0.6 (−1.0000)	−561
42.3	1.74[e]	+0.64	12 (*7*)	10.1 ± 0.7 (−0.9947)	

[a] The temperatures are considered accurate to within 0.2°. [b] α_t is the observed rotation (l 2 dm) at time t and α_e is the equilibrium rotation, both taken at 435 mμ, in degrees; t_i is taken as the time of the initial (first) measurement. [c] Period of measurement in half-lives is given parenthetically in italics. [d] Probable errors from the least-squares regression line. [e] In benzene. [f] Correlation coefficient for the plot of $\ln(\alpha_t - \alpha_e)$ against time. [g] Extrapolated specific rotation.

rate constants (k_M) which are collected in Table I. In some runs values of the specific rotation at zero time, $[\alpha_0]$, were calculated by extrapolation; the resulting specific rotations of the pure diastereomers (absolute rotations) are collected in Table I.[11] It is noted that the $[\alpha_0]_{435}$ values of (+)- and (−)-**1** are opposite in sign and roughly equal in magnitude, indicating a negligible contribution of the chiral center at C-9 to the over-all rotation; *i.e.*, as will be discussed in the section dealing with configurational and conformational aspects of this problem, the diastereomers act as quasi-enantiomers.

A clue that the free energies of the diastereomers are nearly equal comes from the observation that the rotation of the equilibrium mixture of (+)- and (−)-**1** is small, typically $[\alpha]^{32.8}_{435}$ +30° (toluene), compared to the $[\alpha]^{32.8}_{435}$ values of *ca.* ±570° (toluene) for the absolute rotations of the pure diastereomers. A quantitative estimate is obtained by the following method.

For the equilibrium between two mobile conformers, A and B, the equilibrium constant K (= [B]/[A]) is given by

$$K = \frac{P_A - P_M}{P_M - P_B} \qquad (1)$$

where P_A and P_B refer to an intensive property of A and B, in this case the absolute rotations of the diastereomers, which have been set equal to the extrapolated values ($[\alpha_0]_{435}$) for (+)-**1** and (−)-**1**, respectively, and P_M is the property of the equilibrium mixture at a given temperature, in this case the equilibrium value of $[\alpha]_{435}$ given in Table II. Using the expression

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \qquad (2)$$

ΔH° and ΔS° are obtained from the slope and intercept of the plot of ln K *vs.* $1/T$.[12]

Table II. The Temperature Dependence of the Equilibrium Specific Rotation of the Diastereomers of **1** in Toluene

Temp,[a] °K	$[\alpha]_{435}$,[b] deg
323.2	+10.6
328.2	+5.3
333.2	+0.1
338.2	−4.8
343.2	−10.0
348.2	−15.5
353.2	−21.0

[a] The temperatures are considered to be accurate to within 0.2°. [b] These rotations were measured on a Cary 60 spectropolarimeter and have been corrected for the increase in volume of the solvent with increase in temperature. Estimated deviations are ±0.2°.

Since values for the extrapolated rotations ($[\alpha_0]_{435}$) of (+)-**1** and (−)-**1** are somewhat scattered, though within reasonably narrow limits (see Table I), eq 1 and 2 were solved for various combinations of P_A in the range 540–620° and P_B in the range −540 to −620°, in intervals of 10°.[13] For the 81 combinations of P_A and P_B which bracket the extrapolated rotations given in Table I, ΔH° was within the rate of 760–880 cal/mol and ΔS° within the range of 2.2–2.7 eu. These ranges of ΔH° and ΔS° are subject to the assumption that the extrapolated specific rotations fall within the assumed ranges, and that the specific rotations of (+)-**1** and (−)-**1** (*i.e.*, P_A and P_B) are temperature independent over the small temperature range given in Table II.

An alternative method of computing ΔH° and ΔS°, which does not rely on the extrapolated rotations of (+)-**1** and (−)-**1**, was also investigated. This method was first employed by Wood, Fickett, and Kirkwood,[14] who used it to calculate K for the equilibrium between conformers of 1,2-dichloropropane and to estimate the rotatory power of the conformers. Subsequently this approach (hereafter referred to as the "WFK method") has been widely employed to studies of equilibria by nmr spectroscopy[15–28] and by circular dichroism.[29]

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(11) It is assumed for the purpose of this discussion that the rearrangement is completely stereospecific and that the enantiomerically pure starting material, (+)-**2**, gives rise to enantiomerically pure product, *i.e.*, **1A**/**1B** uncontaminated by $\overline{\textbf{1A}}/\overline{\textbf{1B}}$, or *vice versa*. Although this assumption is not an essential one for the calculations of equilibrium and activation parameters, it is reasonable on the basis of arguments to be adduced below.

(12) For a recent discussion on the reliability of this method as applied to conformational analysis, see J. C. Celotti, J. Reisse, and G. Chiurdoglu, *Tetrahedron*, 22, 2249 (1966).

(13) These calculations were carried out on an IBM 7094 computer using a FORTRAN IV program. We are indebted to the Princeton University Computer Center and its staff for their assistance. This work made use of computer facilities supported in part by National Science Foundation Grant NSF-GP579.

(14) W. W. Wood, W. Fickett, and J. G. Kirkwood, *J. Chem. Phys.*, 20, 561 (1952).

(15) R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **39**, 39 (1961).

(16) H. S. Gutowsky, G. G. Belford, and P. E. McMahon, *J. Chem. Phys.*, **36**, 3353 (1962).

In the WFK method, the experimental data, P_M and T, are substituted in eq 3, according to which a linear plot of P_M *vs.* $(1 + \exp[(-\Delta H°/RT) + (\Delta S°/R)])^{-1}$ gives $P_A - P_B$ as the slope and P_B as the intercept for the best choice of $\Delta H°$ and $\Delta S°$. In practice, the linear least-squares line corresponding to the smallest sum of the residues, Σ_{Res}, for different trial values of $\Delta S°$ and $\Delta H°$ gives the slope $(P_A - P_B)$ and the intercept (P_B). Equation 3 can be derived from eq 1 by solving for P_M and substituting $\exp[(-\Delta H°/RT) + (\Delta S°/R)]$ for K.[30]

$$P_M = \frac{P_A - P_B}{1 + \exp[(-\Delta H°/RT) + (\Delta S°/R)]} + P_B \quad (3)$$

Solutions to eq 3 have been obtained by plotting procedures,[14,15,17] but due to the time-consuming nature of the calculations, use of computer programs is preferable.[16,18–20,22–27] In the present work, the data in Table II were processed by the WFK method, employing a FORTRAN IV computer program (FIBO).[31] However, the computations did not reveal a true minimum between $\Delta S° = -10$ and $+10$ eu when $\Delta S°$ was allowed to vary in 0.1-eu increments between these limits.[32] For the data in Table II, as $\Delta S°$ changed from -3.0 to $+3.0$ eu, P_A changed from 119 to 105°, P_B changed from $-10{,}078$ to $-907°$, and $\Delta H°$ changed from 1940 to 2430 cal/mol. In the entire range of $\Delta S°$ considered (-10 to $+10$), the Σ_{Res} was considerably smaller than the sum of the squares of the deviations in the measurement of P_M, indicating that the derived parameters are unreliable.[27] Because of the experimental errors in P_M, neither the four-parameter ($\Delta S°$, $\Delta H°$, P_A, and P_B) eq 3 nor a simplified three-parameter ($\Delta H°$, P_A, and P_B) equation[15] yields physically meaningful results.

In view of the importance of the WFK method in conformational analysis, we briefly describe hereunder some ancillary observations which bear on its applicability and general usefulness. Details may be found elsewhere.[31]

In order to determine the effect of precision in the data on the accuracy of WFK solutions, synthetic P_M values obtained for various values of $\Delta H°$ and $\Delta S°$ in a temperature range often used in the application of this method were processed by FIBO. It was found that P_M values good to five or more significant figures gave computed parameters ($\Delta S°$, $\Delta H°$, P_A, and P_B) in excellent agreement with the parameters used to calculate the synthetic data, but that as fewer significant figures in the synthetic P_M data were used, poorer agreement was obtained; $\Delta H°$ and the property parameter of the predominant component survive this treatment best. Computer experiments with synthetic data also showed that errors in T must be smaller for systems in which $\Delta H°$ is low if acceptable parameters are to be obtained. Errors larger than 1° can have appreciable effects on the computed parameters.

Experimental data to five significant figures are hard to obtain at present; however, at the price of reducing the number of variable parameters from four to three, the WFK method may be successfully employed using data of a lower order of precision. Most frequently, $\Delta S°$ is the parameter which is removed as a variable, by equating it to zero; alternatively, a fixed value may be assigned to one of the property parameters (P_A or P_B) in order to remove it as a variable.[34,35] Although this approach may introduce a systematic error into the computed parameters, it is far more reliable than the four-parameter WFK method if the property parameter corresponding to the less populated isomer is the invariant quantity. For systems in which a fixed value of $\Delta S°$ (including zero) has to be assigned, computer experiments on synthetic data show that the parameters $\Delta H°$, P_A, and P_B are extremely sensitive to deviations from the correct value of $\Delta S°$. Here, too, $\Delta H°$ and the property parameter of the predominant component are the least sensitive. When $\Delta S°$ is assigned to within *ca.* 0.1 eu of the true value, acceptable parameters may be obtained with P_M data good to three to four significant figures, provided that errors in T are negligible (<1°) and that a large temperature range (*ca.* 150°) is employed. Further reduction of the four-parameter eq 3 to a two-parameter equation, by assigning reasonable values (by direct measurement, from theory, or by analogy with structurally related compounds) to P_A and P_B, yields the method used in the beginning of this section.

Equilibrium Constants from Nuclear Magnetic Resonance Spectra. Since the rate at which (+)-**1** and (−)-**1** interconvert is slow compared to the time scale of nmr, it was possible to obtain superposition spectra for the equilibrium mixture at temperatures between 305.3 and 376.9°K. The relative populations of (+)-**1** and (−)-**1** were equated to the relative peak heights of the signals due to the dimethylamino group in each of the diastereomers.[36] These signals will be referred

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(17) R. W. Fessenden and J. S. Waugh, *J. Chem. Phys.*, 37, 1466 (1962).

(18) H. S. Gutowsky, *Pure Appl. Chem.*, 7, 93 (1963).

(19) J. B. Lambert and J. D. Roberts, *J. Amer. Chem. Soc.*, **85**, 3710 (1963); **87**, 3884 (1965).

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(21) P. E. McMahon and W. C. Tincher, *J. Mol. Spectrosc.*, **15**, 180 (1965).

(22) J. Jonas and H. S. Gutowsky, *J. Chem. Phys.*, **42**, 140 (1965).

(23) D. F. Koster, *J. Amer. Chem. Soc.*, **88**, 5067 (1966).

(24) G. M. Whitesides, J. P. Sevenair, and R. W. Goetz, *ibid.*, **89**, 1135 (1967).

(25) J. R. Cavanaugh, *ibid.*, **89**, 1558 (1967).

(26) T. D. Alger, H. S. Gutowsky, and R. L. Vold, *J. Chem. Phys.*, **47**, 3130 (1967).

(27) G. Govil and H. J. Bernstein, *ibid.*, **47**, 2818 (1967).

(28) D. Wendisch, *Z. Naturforsch.*, **22b**, 1227 (1967).

(29) A. Moscowitz, K. Wellman, and C. Djerassi, *J. Amer. Chem. Soc.*, **85**, 3515 (1963).

(30) In using eq 3, Wood, Fickett, and Kirkwood[14] made the following assumptions. (1) There exist only two narrow potential minima so that the problem may be treated as one involving an equilibrium between only two conformers. (2) $\Delta G°$ can be treated as a constant, independent of temperature, *i.e.*, $\Delta S° = 0$. These assumptions are common to most investigations using this method. Gutowsky, Belford, and McMahon[16] have given a detailed derivation of eq 3 for use of coupling constant and chemical shift data and provide a discussion of some of the assumptions inherent in the method. Questions as to the validity of the method have been raised and certain experiments have shown that parameters obtained at low temperatures, where the individual conformers are frozen out, are at variance with results obtained by use of eq 3.[27]

(31) R. Gans, Ph.D. Dissertation, Princeton University, 1968.

(32) A routine processing by FIBO of data obtainable in the literature[14–20,22,23,27,29,33] also revealed no meaningful minimum. For those cases where a minimum was obtained, $\Delta S°$ fluctuated by more than 5.0 eu when the experimental errors in P_M and T were included into the computations.

(33) Thanks are due to the following investigators who made available their temperature-dependent data in a numerical form or who helped us locate pertinent data in the literature: Professors J. B. Lambert, J. S. Waugh, L. H. Sutcliffe, K. Schlögl, and A. Moscowitz.

(34) R. J. Abraham, *Mol. Phys.*, **4**, 369 (1961).

(35) D. Jung and A. A. Bothner-By, *J. Amer. Chem. Soc.*, **86**, 4025 (1964).

(36) In toluene-d_8 the line shapes and half-line widths of the two peaks were found to be the same; this solvent was used in order to permit com-

to as $NMe_2{}^A$ and $NMe_2{}^B$,[37] respectively. The equilibrium constant was calculated from eq 4.

$$K = \frac{\text{height of the NMe}_2{}^\text{B}\text{ peak}}{\text{height of the NMe}_2{}^\text{A}\text{ peak}} \qquad (4)$$

Values for $\Delta H°$ (620 ± 40 cal/mol)[38] and $\Delta S°$ (1.8 ± 0.1 eu)[38, 39] were obtained by fitting the data obtained from eq 4 to eq 2. These values are in reasonable agreement with those independently estimated for $\Delta H°$ (760–880 cal/mol) and for $\Delta S°$ (2.2–2.7 eu) on the basis of optical rotation data, as described in the beginning of the preceding section. However, there are several factors in the nmr method, as applied here, that can cause sizeable errors in the thermodynamic parameters: (1) the change in peak heights is small over the temperature range employed; (2) the temperature fluctuates; (3) the height of the $NMe_2{}^A$ peak is affected by overlapping peaks of aromatic methyl and methylene protons. The first two errors were minimized somewhat by taking up to ten spectra at each of 20 temperatures in the 71.6° range and using the average for the computations. The errors due to the overlapping of peaks cause an apparent decrease in $\Delta H°$ and $\Delta S°$, and correction for this effect would bring the results into even better consonance with those of the previous section. No attempt was made to estimate this correction quantitatively.

Since the first of the two experimental methods of estimating the conformer populations (previous section) was felt to be somewhat more reliable, values of $P_A = 580°$, $P_B = -570°$, $\Delta S° = 2.5$ eu, and $\Delta H° = 820$ cal/mol were chosen for subsequent calculations (see below). This selection was based on the data in Tables I and II and on the processing of those data by use of eq 1 and 2. Independent calculations show that this set of parameters, though somewhat arbitrary within the narrow limits set by the data, is fairly insensitive to changes within the range given above; *i.e.*, the kinetic parameters calculated below are not significantly changed by a slightly different choice of thermodynamic parameters.

It remains to be pointed out that the difference in free energy between the two diastereomers, $\Delta G°$, is quite small; typically, at 25°, if $\Delta H° = 820$ cal/mol and $\Delta S° = 2.5$ eu, $\Delta G° = 75$ cal/mol. As seen by inspection of Table II, the relative order of stability of the two diastereomers is inverted within the temperature range studied, and $\Delta G°$ is calculated to be zero at 55° for the above values of $\Delta H°$ and $\Delta S°$, close to the experimentally found temperature of *ca.* 60° (Table II, assuming $P_A \cong -P_B$). The isomer (+)-**1** (derived from (+)-**2**)) has the lower enthalpy and the lower entropy, compared to (−)-**1**. Both $\Delta H°$ and $T\Delta S°$ terms are small, and evidently the substitution of a dimethylamino group on C-9 of **4** has little effect on the relative stability of the conformers in the temperature range studied.

Activation Energy Barriers for Conformational Interconversions. Mutarotation studies on (+)-**1** and (−)-**1** are summarized in Table I. The rate constant fits the Arrhenius equation $k_M = 10^{12.6 \pm 0.6} \exp(-22.5 \pm 0.8/RT)$ sec^{-1}; enthalpies and entropies of activation are $\Delta H^{\ddagger} = 21.9 \pm 0.8$ kcal/mol and $\Delta S^{\ddagger} = -2.8 \pm 0.2$ eu.[38] Combination of the equilibrium constants $K = k_1/k_{-1}$ (calculated from the $\Delta H°$ and $\Delta S°$ values given in the previous section) and the mutarotation rate constants $k_M = k_1 + k_{-1}$ (listed in Table I) yields $k_1 = 10^{12.6 \pm 0.6} \exp(-23.0 \pm 0.8/RT)$ sec^{-1} and $k_{-1} = 10^{12.0 \pm 0.6} \exp(-22.1 \pm 0.8/RT)$ sec^{-1}. The transition-state parameters for the forward reaction are $\Delta H^{\ddagger} = 22.4 \pm 0.8$ kcal/mol and $\Delta S^{\ddagger} = -3.0 \pm 0.2$ eu, and for the reverse reaction are $\Delta H^{\ddagger} = 21.5 \pm 0.8$ kcal/mol and $\Delta S^{\ddagger} = -5.5 \pm 0.2$ eu. The values of these parameters, especially those for the forward reaction, are similar to the values of $k_{inv} = 10^{12.5} \exp(-23.1/RT)$ sec^{-1}, $\Delta H^{\ddagger} = 22.4$ kcal/mol, and $\Delta S^{\ddagger} = -3.6$ eu found for the racemization of **4**[5] (Chart I).[40] It follows from these findings that the transition state for mutarotation strongly resembles that for racemization, and that substitution of the dimethylamino group on C-9 has a negligible effect on the structure of the transition state,[41] assuming that the ground states of (+)-**1** and (−)-**1** do not both happen to be equally displaced relative to the ground state of (+)- or (−)-**4** (in addition to the differential in $\Delta H°$ and $\Delta S°$ already discussed).

Configuration and Conformation of 9-Dimethylamino-9,10-dihydro-4,5-dimethylphenanthrene. A discussion of the stereochemistry of **1** is conveniently subdivided, from the structural point of view, into two parts. The first part deals with the sense of twist of the biphenyl moiety, and the second with the chirality of the center at C-9. Given the interrelationship of (+)-**1** and (−)-**1** as diastereomers differing only in biphenyl chirality, a fact established by the observations of mutarotation and second-order asymmetric transformations, the pair of isomers belong either to the **1A**/**1B** or the $\mathbf{1\bar{A}}/\mathbf{1\bar{B}}$ system, depending on whether the chirality of the center at C-9 is *S*, as in **1A** and **1B**, or *R*, as in $\mathbf{1\bar{A}}$ and $\mathbf{1\bar{B}}$. Within each system, the chirality of the biphenyl may be *R*, as in $\mathbf{1\bar{A}}$ and **1B**, or *S*, as in **1A** and $\mathbf{1\bar{B}}$. These questions are disposed of in the following sections.

Chirality of the Biphenyl Moiety. The observation that the absolute rotations of (+)-**1** and (−)-**1** are almost equal as well as opposite indicates that the contribution of the chiral center at C-9 to the total rotation is of minor importance, *i.e.*, that the chirality of the inherently dissymmetric biphenyl moiety is the dominant factor determining sign and magnitude of the optical rotation. As was remarked in the first section, (+)-**1** and (−)-**1** may be regarded as quasi-enantiomers. Another indication that the contribution of the center at C-9 is minor is the similarity in magnitude between the initial rotation observed for **4** (*i.e.*, $[\alpha_0]^{28.1}_{435}$ −609° (benzene))[42] and the extrapolated values found for (+)-**1**

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parison of the results obtained by this method with those obtained from the rotation data (preceding section).

[37] The superscript denotes the diastereomer of 1 (**A** or **B**) in which the group or atom is located, without distinction between enantiomers (since enantiotopic protons[9] are isochronous in achiral solvents). For example, $\underline{\mathrm{H}}_{\mathrm{C}}{}^{\mathrm{A}}$ refers to the enantiotopic protons labeled C in structures IA and $1\bar{A}$ (Chart I). The chemical shifts in toluene-d_8 at 29° are δ 2.19 and 1.94 for $NMe_2{}^A$ and $NMe_2{}^B$, respectively. The reason for this assignment will be discussed below.

[38] Unless otherwise noted, the errors are the probable errors.[39]

[39] L. G. Parratt, "Probability and Experimental Errors in Science," John Wiley and Sons, Inc., New York, N. Y., 1961, pp 173–174.

[40] It should be noted that $k_{inv} = 0.5k_{rac}$ and that the parameters for **4** therefore refer to inversion, not racemization.

[41] The transition state for the racemization of **4** has been discussed in another connection: *cf.* K. Mislow, R. Graeve, A. J. Gordon, and G. H. Wahl, Jr., *J. Amer. Chem. Soc.*, **86**, 1733 (1964).

[42] Calculated from the data in ref 5.

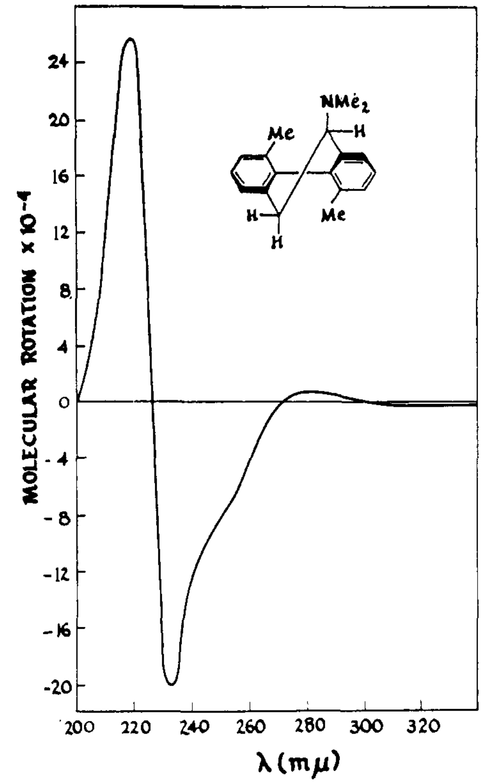

Figure 1. ORD curve of (−)-**1** (≡ **1B**) in isooctane.

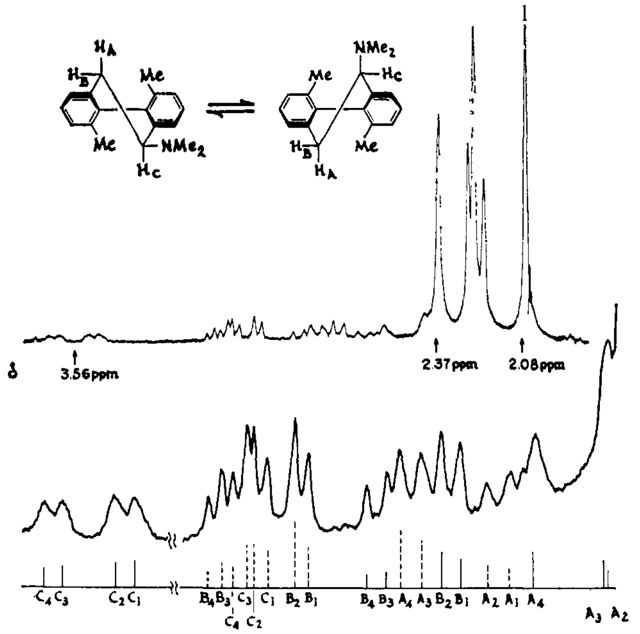

Figure 2. Portions of the experimental and calculated 100-MHz nmr spectrum of equilibrated **1** [(+)-**1** (≡ **1A**), solid lines; (−)-**1** (≡ **1B**), dashed lines] in CDCl$_3$ at 25°. The A$_1$ transition of the H$_A$^{A} proton at δ 2.28 ppm is not shown.

and (−)-**1** (Table I). Since **4** was prepared from optically pure precursor, this comparison lends weight to the assumption made above[11] that the $[\alpha_0]_{435}$ values of **1** are also absolute rotations.

It has been pointed out that 2,2′-bridged biphenyls which lack extraneous chromophores and which have the *S* configuration have strong positive rotations in the visible region.[43] The chiralities of the biphenyl components in (+)-**1** and (−)-**1** might therefore be tentatively assigned as *S* and *R*, respectively. These conclusions are placed on firm grounds by the ORD measurements on (−)-**1** (Figure 1):[44] a high-intensity positive Cotton effect near 260 mμ, corresponding to the biphenyl conjugation band, is superimposed on the long-wavelength tail of an even stronger negative Cotton effect located near 225 mμ. This behavior, which is typical of similar 2,2′-bridged biphenyls,[8,45] unequivocally signalizes the *R* configuration for the biphenyl moiety in (−)-**1**, and consequently the *S* configuration for the biphenyl moiety in (+)-**1**.[46]

The Chiral Center at C-9. Granted the above assignments, the remaining problem is to decide between $\overline{\mathbf{1A}}$ and **1B** for the structure of (−)-**1** and between **1A** and $\overline{\mathbf{1B}}$ for the structure of (+)-**1**.

Crucial information is obtained from the values of the proton vicinal coupling constants in the methine methylene portion of the diastereomers. Thus, if (−)-**1** and (+)-**1** have the structure given by $\overline{\mathbf{1A}}$ and **1A**, respectively, one would expect to observe one large and one small vicinal coupling constant ($J_{AC} \approx$ 8–14 Hz (*trans*) and $J_{BC} \approx$ 1–7 Hz (*gauche*), respectively),[47] whereas, if **1B** and $\overline{\mathbf{1B}}$ were the correct structures, two small vicinal coupling constants ($J_{AC} \approx J_{BC} \approx$ 1–7 Hz (both *gauche*))[47] would be observed.

The chemical shifts of equilibrated **1** (derived from (+)-**2**) in CDCl$_3$ (Figure 2) fall into three regions: a methyl region, δ 2.08–2.37, a methine methylene region, δ 2.43–3.56, and a complex aromatic region, δ *ca.* 6.9–7.5 ppm (not shown). The insert in Figure 3 shows the ABC spin pattern of the methine methylene portion of (−)-**1**, and the bottom of Figure 2 the corresponding patterns for the equilibrium mixture of (+)- and (−)-**1**. By elimination, the ABC spin pattern for (+)-**1** can be identified. The vicinal coupling constants for (−)-**1** in the mixture were determined by using the ABX approximation to yield approximate values of the parameters and then employing these values as a starting point for an iterative ABC treatment.[48] In the ABC pattern of (+)-**1** only ten transitions were observed. Irradiation of each half of the quartet centered at δ 3.56 made it possible to identify transitions due to H$_B$ and to demonstrate that J_{AB} and J_{AC} have opposite signs.[49] For this diastereomer the ABC analysis was performed by first using a first-order AMX approximation to yield values of the parameters which were then

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(43) D. D. Fitts, M. Siegel, and K. Mislow, *J. Amer. Chem. Soc.*, **88**, 480 (1958); K. Mislow, *Angew. Chem.*, **70**, 683 (1958).

(44) At the temperature (0°) used for the ORD measurement, the interconversion of (+)- and (−)-1 was slow enough so that consecutive determinations showed negligible changes in the amplitude of the curve. We thank Dr. P. Laur for these measurements.

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

(46) No material was available for the measurement of ORD of (+)-1. However, there can be little doubt that this isomer would have a negative Cotton effect centered at the biphenyl conjugation band.

(47) N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, p 51.

(48) A modified version of the computer program LAOCOON II [S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, **41**, 3863 (1964)] was kindly provided by Dr. L. G. Alexakos (Mobil Oil Corp., Research Department, Paulsboro, N. J.). Helpful discussions with Dr. L. G. Alexakos and Dr. R. C. Hirst (Socony Mobil Oil Co., Inc., Research Department, Princeton, N. J.) are gratefully acknowledged.

(49) R. Freeman, K. A. McLauchlan, J. I. Musher, and K. G. R. Pachler, *Mol. Phys.*, **5**, 321 (1962).

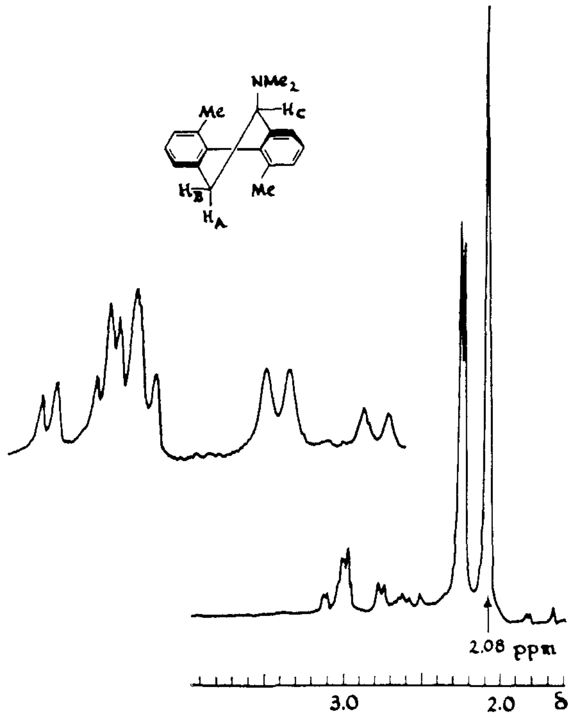

Figure 3. Partial 100-MHz nmr spectrum of (−)-**1** (≡ **1B**) in CDCl$_3$ at 0°.

used as a starting point in the iterative ABC treatment. The multiplicity of solutions was reduced and the relative signs of the coupling constants were partially predetermined since only some solutions gave an energy level diagram[50] consistent with the decoupling experiments. In the analysis of (−)-**1** and of (+)-**1**, only one solution gave a fit that was consistent with spectra taken at 60 and 100 MHz.[49] In the lower part of Figure 2 are shown the assignments that result. The chemical shifts and coupling constants[51] computed for both diastereomers are collected in Table III.

Table III. Chemical Shifts and Coupling Constants for the Diastereomers of **1**[a]

	(−)-**1** ≡ **1B**	(+)-**1** ≡ **1A**
δ_A	2.706 ± 0.001 ppm	2.432 ± 0.001 ppm
δ_B	3.021 ± 0.001 ppm	2.745 ± 0.001 ppm
δ_C	3.049 ± 0.001 ppm	3.556 ± 0.001 ppm
J_{AB}	−15.4 ± 0.2 Hz	−13.19 ± 0.09 Hz
J_{AC}	3.5 ± 0.2 Hz	13.23 ± 0.09 Hz
J_{BC}	2.6 ± 0.2 Hz	3.21 ± 0.09 Hz

[a] These parameters refer to the spectrum shown in Figure 2.

The vicinal coupling constants decide the absolute configuration at C-9; thus for (+)-**1**, structure **1A** is consistent with one large and one small vicinal coupling constant (J_{AC} = 13.23 Hz and J_{BC} = 3.21 Hz) whereas **1B** is not. Similarly, for (−)-**1** the result of the two small vicinal coupling constants (J_{AC} = 3.5 Hz and J_{BC} = 2.6 Hz) is only consistent with structure **1B**. Therefore C-9 is *S* in the two diastereomers (−)-**1** and (+)-**1**, which are obtained from (+)-**2**.

The three center peaks of the methyl region at δ 2.26, 2.23, and 2.20 (Figure 2) can be assigned to the aromatic methyl groups by comparison with the chemical shift reported[52] for the methyl groups in **4** (δ 2.25 in CDCl$_3$).[53] The remaining two signals at δ 2.37 and 2.08 therefore belong to the NMe$_2$ groups in the two diastereomers. As seen by a comparison of Figures 2 and 3, the signal at 2.37 ppm, which is present in the nmr spectrum of the equilibrium mixture (Figure 2), is absent in the spectrum of pure (−)-**1**. It follows[37] that the signal at 2.37 ppm is due to (+)-**1**, and therefore NMe$_2$^{A}, and that at 2.08 to the (−) isomer, and therefore NMe$_2$^{B}. This assignment supports the identification of the isomers. Since the NMe$_2$^{B} group occupies a quasi-axial position and thus resides in the shielding zone of the biphenyl, the corresponding signal is expected[54] to appear upfield relative to that of the NMe$_2$^{A} group.

Stereochemistry of the Stevens Rearrangement. The preceding results have some bearing on the mechanism of the Stevens rearrangement. There is strong evidence that this rearrangement is cleanly intramolecular[55,56] and involves either a concerted cyclic process or a tight ion pair. In the rearrangement of (+)-**2**, the initial step, removal of one of the two protons on the carbon adjacent to the nitrogen atom,[57,58] is followed or accompanied by migration of one methylene carbon to the carbanionic center created on the other. The rearrangement is highly stereospecific, since optically pure (+)-**2** leads to a product (**1A**/**1B**) which is optically pure or nearly so, to judge from the previously discussed comparison of the extrapolated rotations[59] of the diastereomers of **1** with the absolute rotation of the parent compound, **4**. Transfer of biphenyl dissymmetry in **2** to C-9 asymmetry in **1** thus appears to be essentially complete.[4] It is readily seen that if the rearrangement is concerted, (*S*)-**2** leads directly to **1A** ((+)-**1**), which has the same biphenyl chirality (*i.e.*, *S*) as the starting material and has the *S* configuration at C-9. This isomer would then undergo conformational equilibration to the **1A**/**1B** mixture actually obtained. If the rearrangement involves an ion-pair intermediate, the initially formed product, **5**, is a tetra-*ortho*-substituted biphenyl which is expected to be optically stable under the conditions of rearrangement.

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[50] E. F. Friedman and H. S. Gutowsky, *J. Chem. Phys.*, **45**, 3158 (1966); W. A. Anderson, R. Freeman, and C. A. Reilly, *ibid.*, **39**, 1518 (1963); R. Freeman and W. A. Anderson, *ibid.*, 37, 2053 (1962).

[51] The absolute signs of these coupling constants have been assigned by analogy to other ethanelike fragments: *cf.* L. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon Press, Inc., New York, N. Y., 1965, pp 172–174.

[52] K. Mislow, M. A. W. Glass, H. B. Hopps, E. Simon, and G. H. Wahl, Jr., *J. Amer. Chem. Soc.*, **86**, 1710 (1964).

[53] Diastereomers (+)-1 and (−)-1 should each show two aromatic methyl proton signals. Accidental coincidence of two of these produces the large center peak.

[54] C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

[55] D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, pp 223–229.

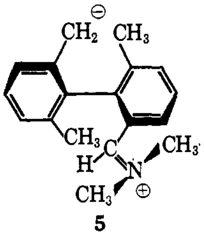
[56] E. Grovenstein, Jr., and G. Wentworth, *J. Amer. Chem. Soc*, **89**, 1852 (1967), and references cited therein.

[57] Although the rates of abstraction of the two diastereotopic protons on each methylene group differ in principle,[58] this circumstance need not be implicated in the stereochemistry of the rearrangement since abstraction of the more labile proton does not necessarily lead to the lower energy pathway for rearrangement. Similarly, in a stepwise mechanism the initially formed pyramidal carbanion may suffer configurational inversion which is rapid compared to the rate of rearrangement.

[58] *Cf.*, for example, P. T. Lansbury, J. F. Bieron, and A. J. Lacher, *J. Amer. Chem. Soc.*, **88**, 1482 (1966); I. S. Wolfe and A. Rauk, *Chem. Commun.*, 778 (1966).

[59] This comparison depends on the assumption that the crystalline material, on which the rotational values for 1 are based, has not undergone major optical enrichment in the process of crystallization.

Collapse of this ion pair also leads to **1A**. However, given time for torsion (*ca.* 180°) around the phenyl–enammonium bond prior to collapse, conformation **6** of the ion pair could obtain, which on collapse would lead to $\mathbf{1\bar{B}}$ (and hence to the conformational mixture $\mathbf{1\bar{A}}/\mathbf{1\bar{B}}$). To the extent that the product (**1A**/**1B**) is uncontaminated by the enantiomeric set, *i.e.*, to the extent that optical purity is maintained in the rearrangement, this pathway is excluded, and it follows that if an ion pair is the intermediate in the rearrangement, it cannot have an appreciable degree of conformational mobility, *i.e.*, it must be described as "tight." These conclusions are in excellent accord with present views of the mechanism of the Stevens rearrangement.[56]



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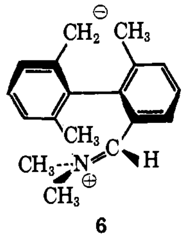

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Experimental Section[60]

9-Dimethylamino-4,5-dimethyl-9,10-dihydrophenanthrene (1).[3] A. Phenyllithium in ether (8.5 ml, 0.95 *N*, 8.07 mmol) was added (hypodermic syringe) to a magnetically stirred suspension of (+)-**2**[3,62] (2.10 g, 6.04 mmol, mp 278–280° dec, $[\alpha]^{25}\text{D}$ +30.3° (*c* 1.28, methanol)) in 12 ml of ether, under a nitrogen atmosphere. Within 0.5 hr the reaction mixture turned from white to creamy yellow and ultimately turned to a dark red clear solution. After 1 week the red color was discharged and the reaction mixture was hydrolyzed by the slow addition of 65 ml of water. The mixture was extracted with 50 ml of ether, and the ether layer was extracted with 6 *N* HCl. The precooled acid extracts were neutralized (litmus blue) with aqueous sodium hydroxide, the basic solution was extracted with ether, the ethereal solution was dried over anhydrous sodium sulfate, and the solvent was removed, yielding a yellow viscous oil, which was distilled (kugelrohr). The distillate, bp 110–130° (0.07 mm) (lit.[3] bp 116.5–117.5° (0.01 mm)), was a clear colorless oil, 1.175 g (4.67 mmol, 74%), $[\alpha]^{25}\text{D}$ +14.28° (equilibrated solution, *c* 1.26, benzene) (lit.[3] $[\alpha]^{20}\text{D}$ +14.1° (*c* 1.420, benzene)). The absorption spectrum had $\lambda_{\max}^{\text{isooctane}}$ 254 mμ (ε 10,300), $\lambda_{\max}^{95\%\ \text{ethanol}}$ 261.5 mμ (ε 10,700) (lit.[61] $\lambda_{\max}^{95\%\ \text{ethanol}}$ 260 mμ (ε 10,600)). The base peak in the mass spectrum, *m/e* 207, corresponded to the molecular weight of **1** (*m/e* 251, which was not observed) less the mass of the dimethylamino group (*m/e* 44).

The oil crystallized slowly at room temperature. One month after the first crystals were observed in the oil, crystallization was not yet complete. The crystals were removed and triturated repeatedly with methanol to give colorless crystals of (+)-**1**, mp 83–84.5°. Vpc analysis of the amine crystals and amine washings on a 6 ft × 0.25 in. column packed with 10% Carbowax 20M on Chromosorb P at 250°, helium flow 160 cc/min, showed the following: for the amine crystals, one peak at 7.5 min; for the mother liquor, two peaks at 6.0 and 7.5 min, in the ratio of *ca.* 1:3. The uv spectrum of crystalline (+)-**1** had $\lambda_{\max}^{\text{isooctane}}$ 251 mμ (ε 11,700) and that of the mother liquor the same shape as that of the amine oil.

Subsequent crystallizations of the oil afforded colorless crystals of (−)-**1**, mp 71–82.5°. Recrystallization from methanol gave crystals, mp 85–90°, $\lambda_{\max}^{\text{isooctane}}$ 258.5 mμ (ε 12,800). The ORD is given in Figure 1. Tlc of (−)-**1** crystals (dissolved at −20° in $CHCl_3$) on silica gel with 9:1 benzene–methanol as eluent (also at −20°) gave a single spot (with I_2), R_f 0.32. When the same solution of (−)-**1** was heated for 5 min at 60° and then similarly chromatographed, two spots of R_f 0.32 and 0.57 for (−)-**1** and (+)-**1**, respectively, were obtained. On heating the chromatography plate, followed by elution in the other dimension by the same solvent mixture, each of these spots in turn partitioned into two spots, R_f 0.32 and 0.57.

Extrapolated specific rotations for (+)- and (−)-**1** are given in Table I. Nmr spectra of both compounds are discussed in the section dealing with the configuration at C-9. The ultraviolet spectrum of the equilibrated mixture of **1** had $\lambda_{\max}^{\text{isooctane}}$ 254.5 mμ (ε 11,900).

Anal. Calcd for $C_{18}H_{21}N$: C, 86.01; H, 8.42; N, 5.57. Found for oil of **1**: C, 86.00; H, 8.63; N, 5.70. Found for crystals of (+)-**1**: C, 85.96; H, 8.48; N, 5.31. Found for crystals of (−)-**1**: C, 86.24; H, 8.69; N, 5.72.

B. A mixture of (+)-**2**[3,62] (0.34 g, 1.03 mmol), *ca.* 12 ml of liquid anhydrous ammonia, and 0.55 g (9.7 mmol) of powdered potassium hydroxide was shaken in a sealed tube at room temperature for 20 hr. The color of the solution had become light yellow at the end of this period. The contents were poured into water and the aqueous layer was extracted with ether. The amine was worked up as described under A to give a colorless, clear viscous liquid (115.8 mg, 45% yield), which was crystallized as described above. The (−)-**1** thus obtained had mp 82.5–90°.

Reaction of (+)-2 with Potassium Amide in Liquid Ammonia. Potassium metal was added to *ca.* 30 ml of liquid anhydrous ammonia contained in a Carius tube, followed by catalytic amounts of anhydrous ferric chloride (sublimed, Fisher). After discharge of the characteristic purple color, (+)-**2** was added and the tube was sealed. The mixture was shaken at room temperature for 1 hr, the tube was opened, and the contents were poured into water. The aqueous layer was extracted with ether, and the combined ethereal solutions were extracted with 4 *N* HCl. The ether layer containing neutral products was worked up as described below. The hydrochloric acid extracts were neutralized with sodium hydroxide solution and extracted several times with ether. These ether extracts were dried over anhydrous sodium sulfate and filtered, and solvent was removed. No **1** could be detected in the small quantities of basic residues.

Removal of solvent from the ethereal solution containing the neutral products, followed by chromatography on alumina (Woelm neutral, activity grade I) with 1:1 hexane–benzene eluent, gave the product distribution indicated for run 1 in Table IV. Results for other reaction times (runs 2–4) are also collected in Table IV.

Table IV. Neutral Product Distribution in the Reaction of (+)-**2** with Potassium Amide

	Run no.			
	1	2	3	4
Reactants				
(+)-**2**, g	0.545	0.512	0.521	0.984
Potassium, g	0.489	0.438	0.478	1.062
Reaction time	1 hr	24 hr	1 week	8 month
Total chromatographed neutral products,[a] g	0.2647	0.2144	0.1792	0.454
% **4** (2.2)[b]	1.1	59.4	87.0	96.7
% **3** (5.1)[b]	92.5	32.0	5.0	...
% unknown 1 (6.0)[b]	5.7	3.3	...	...
% unknown 2 (12.5)[b]	0.7	5.3	8.0	3.3

[a] Analyzed by vpc, using a 6 ft × 0.25 in. o.d. 10% silastic on Chromosorb P column, helium flow rate of 175 cc/min in a column temperature of 200°. [b] Retention times (minutes) in parentheses; authentic samples[3] of 4,5-dimethylphenanthrene (**3**) and 4,5-dimethyl-9,10-dihydrophenanthrene (**4**) gave the same retention times.

Reaction of Potassium Amide in Liquid Ammonia with 1 and 3. Runs were carried out as described in the preceding section. Reaction conditions and product distribution are collected in Table V.

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(60) Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Unless otherwise noted polarimetric measurements were taken on a Schmidt and Haensch polarimeter adapted with a Rudolph photoelectric attachment. Mass spectra were taken on a CEC Type 21-103C instrument operated at 70 eV. ORD measurements were obtained with a Cary 60 recording spectropolarimeter. Unless otherwise specified, chemical shifts are reported in parts per million on the δ scale and refer to 10–20% (w/v) solutions with internal tetramethylsilane, as determined either on a Varian A-60A or Varian HA-100 spectrometer. We thank the National Science Foundation and the National Aeronautics and Space Administration for providing the funds for the purchase of the HA-100 instrument. Work on the HA-100 was supported in part by Biochemical Sciences Support Grant FR-07057.

(61) Estimated from the plot in ref 3.

Table V. Neutral Product Distribution in the Reaction of **1** and **3** with Potassium Amide

	Run no.		
	1	2	3
Reactants			
1, g	0.093	0.2524	...
3, g	...	...	0.065
Potassium, g	0.174	0.413	0.196
Reaction time	1 week	24 hr	1 week
Total chromatographed neutral products,[a] g	0.0523	0.1344	0.0558
% **4** (3.75)[b]	100	...	100
% **3** (10.0)[b]	...	80	...
% unknown (12.4)[b]	...	20	...

[a] Analyzed by vpc using a 6 ft × 0.25 in. o.d. 10% Carbowax 20M on Chromosorb P column, helium flow rate 158 cc/min, column temperature 250°. [b] Retention times (minutes) in parentheses; authentic samples[3] of **3** and **4** gave the indicated retention times.

Mutarotation of 1. Optical rotations were measured in toluene at 435 mμ using a 2-dm semimicro jacketed polarimeter tube. The temperatures were kept constant at ±0.05° by using a circulating bath. The change of rotation with time was followed by conventional methods. The first reading was normally taken *ca.* 10 min after dissolution. The rate constants of mutarotation were obtained using the integrated first-order rate law expression for the process of unimolecular mutarotation. These rate constants were used to calculate the extrapolated rotation ($[\alpha_0]$), taken to be the rotation at the time of dissolution. The results are collected in Table I.

Nmr Spectroscopy. Temperature-dependent spectra were run on a Varian A-60A spectrometer equipped with a variable-temperature probe. Samples were prepared as 0.072–0.268 g/ml solutions of (−)-**1** in toluene-d_8. Within experimental limits, the relative peak heights of $NMe_2{}^A$ and $NMe_2{}^B$ (*i.e.*, K) of equilibrated **1** were found to be independent of the concentration. Temperatures were measured using Varian ethylene glycol, which was placed in the inner tube of a coaxial cell; the outer tube was filled with sample. The use of this cell allowed the simultaneous measurement of the ethylene glycol peak separation and the NMe_2 peak heights over the temperature range of 305–377°K. Probable accuracies are estimated to be ±3° with a stability at any one temperature of ±1.5°. The correlation coefficient for the plot ln K against $1/T$ was −0.9303.

Decoupling experiments were carried out in the frequency sweep mode of the HA-100 with the aid of a Hewlett-Packard 200 CD audio oscillator. Samples were prepared as $CDCl_3$ solutions. The root-mean-square error for fitting the observed spectra to the computed spectra[48] was somewhat high (for (−)-**1**, 0.16; for (+)-**1**, 0.09) due to uncertainties in the measurement caused largely by the use of peak positions as frequencies.[62] In order to ascertain the effect of these uncertainties on the results, seven spectra were computed of (−)-**1** taken under different conditions, *i.e.*, of field strength (60 and 100 MHz), solvent (deuteriochloroform, toluene-d_8, and benzene), and temperature (0, 25, and 35°). The computed coupling constants were in the following ranges: J_{AB} = −15.04 to −15.54 Hz, J_{AC} = 3.3–3.7 Hz, and J_{BC} = 2.4–2.6 Hz. Thus, even though the root-mean-square errors were relatively high, the results may be considered good.

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(62) Peak positions do not always correspond to line positions, because of the overlap of lines of various widths.

The Stereochemistry and Mechanism of the Photochemical Interconversion of *cis*- and *trans*-5,6-Diphenylbicyclo[3.1.0]hexan-2-ones. Mechanistic Organic Photochemistry. XXXII[1]

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Abstract: Photochemical conversion of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one to the *cis* isomer **2** and 3,4- and 4,4-diphenylcyclohex-2-en-1-ones (**4** and **3**) was shown to involve the triplet excited state of reactant, but not of product. The stereochemical course of the *trans–cis* isomerization involved only cleavage of the C-1 to C-6 (external) bond, with retention of stereochemistry at C-5; overlap control appeared determining. A rate constant of 4.6 × 10^8 sec^{-1} was measured for rearrangement of the triplet. The photochemical isomerization of *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one to the *trans* isomer **1** and to 3,4-diphenylcyclohexenone was also investigated. The *cis–trans* isomerization involved fission of both the external (86%) and internal (14%) bonds. Strikingly, no 4,4-diphenylcyclohexenone was found. Microscopic reversibility was shown to be inapplicable, and the *cis–trans* and *trans–cis* mechanisms must not have potential energy surfaces which cross efficiently. The reasons for the different stereochemical behavior of the *cis* and *trans* ketones **1** and **2** are discussed. A triplet state was shown to be the most likely species involved in the *cis–trans* stereoisomerization. Reductive degradation of *cis*- and *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-ones with lithium–liquid ammonia and the relation of this reaction to the photochemistry are discussed in terms of stereoelectronic control. In the course of this research, a general method for resolution of ketones and oxidation of tertiary amines to ketones was developed.

The present problem began with the observation by Wilson and Zimmerman[2] that the photochemical *trans–cis* interconversion of *trans*- and *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-ones (**1** and **2**) accounted for the increasing proportion of the *cis* isomer **2** formed with increasing time in irradiations of 4,4-diphenylcyclohex-

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(1) For paper XXXI, note H. E. Zimmerman and K. G. Hancock, *J. Am. Chem. Soc.*, **90**, 3749 (1968).

(2) H. E. Zimmerman and J. W. Wilson, *ibid.*, **86**, 4036 (1964).