For the imidazole general base-catalyzed hydrolysis of the dichloroacetyl esters, there is seen to be no facilitation by a neighboring hydroxyl group. Inspection of Table III reveals that at 30° and 70° the same rate enhancement is obtained upon substitution of a *trans*-hydroxyl and *trans*-methoxyl group vicinal to the ester bond in cyclopentyl dichloroacetate. Neighboring hydroxyl group facilitation in the alkaline hydrolysis of cyclopentyl acetate is subject to a marked compensation in ΔS^* and ΔH^*. It would of course be quite conceivable that a neighboring hydroxyl group could participate in the imidazole general base-catalyzed hydrolysis of cyclopentyl dichloroacetate without altering ΔF^* significantly if any change in ΔH^* were completely compensated for by a change in $T\Delta S^*$. Inspection of Table IV reveals that all changes in ΔH^* and $T\Delta S^*$ amount to no more than 1 kcal. The apparent compensation in the present study could arise simply from a random error of 1 kcal. in ΔF^*. It may be noted that the values of ΔH^* for the imidazole general base-catalyzed hydrolysis of cyclopentyl dichloroacetate are comparable to that for hydroxide ion catalysis but that a much more negative ΔS^* is associated with the imidazole catalysis. This would be in accord with a greater solvent striction in the imidazole reaction.

Acknowledgment.—We wish to thank the National Institutes of Health and the National Science Foundation for the support of this research.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF NEW YORK UNIVERSITY, NEW YORK 53, N. Y.]

Optically Active 9,10-Dihydro-4,5-dimethylphenanthrene[1]

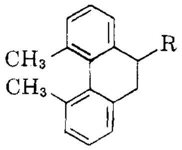
BY KURT MISLOW AND HARVEY B. HOPPS

RECEIVED APRIL 2, 1962

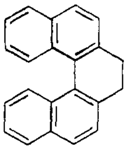
(−)-(R)-9,10-Dihydro-4,5-dimethylphenanthrene has been prepared. The optical stability and optical rotatory dispersion characteriscics are discussed.

Our interest in securing optically active 9,10-dihydro-4,5-dimethylphenanthrene (Ia) was stimulated by related work in these laboratories[2,3] and by the recorded failure of a previous attempt in the same direction.[4]

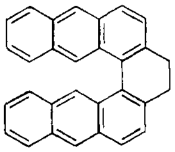
Precedent exists for stereoisomerism in cognate systems. Thus, the bridged binaphthyl[5] and bianthryl[6] analogs II and III are optically stable, the overcrowded aromatic compounds IV[7] and V[8] have been obtained in optically active, albeit optically unstable, form, and the separation of diastereomeric forms of Ib has been claimed.[4]



Ia, R = H
b, R = N(CH$_3$)$_2$



II



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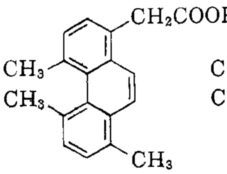

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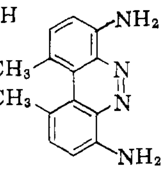

V

The desired compound was obtained by ring closure of (−)-(R)-2,2′-bis-(bromomethyl)-6,6′-dimethylbiphenyl with phenyllithium at ice-bath temperatures. In order to remove unreacted starting material, the crude product was treated with silver nitrate in aqueous acetone at 0–5°. Chromatography on silica gel at 0–5° gave a 30% yield of (−)-(R)-Ia, identical in every respect, other than rotation, with authentic racemic material.

Racemization studies on (−)-Ia are summarized in Table I. The rate constants follow the Arrhenius equation $k_1 = 10^{12.8} \exp(-23.1/RT)\text{sec.}^{-1}$. The Arrhenius parameters are of an order of magnitude frequently encountered in bridged biphenyls.[9]

TABLE I

RACEMIZATION OF Ia IN BENZENE

Temp., °C.	28.1	42.1	54.4
α_{435} at t_0[a]	−11.77°	−10.15°	−8.01°
$k_1 \times 10^4$, sec.$^{-1}$	1.07	5.87	23.6
$t_{1/2}$, min.	108	19.7	4.9

[a] c 0.986, l 2, t_0 taken as the time of the first measurement, usually about 3 minutes after the sample has been brought to the desired temperature.

The two methyl groups in Ia appear to be far less effective as blocking groups than the two benzo groups in II: the binaphthyl racemizes according to the expression[9] $k_1 = 10^{13.4} \exp(-30.8/RT)\text{sec.}^{-1}$. In the transition state the two methyl groups can bend out of the way more readily than the rigid aromatic framework in II; similar considerations have been advanced to account for the relative

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[1] Grateful acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research, and to the Alfred P. Sloan Foundation for fellowship support (K.M.).

[2] K. Mislow, *Angew. Chem.*, **70**, 683 (1958).

[3] K. Mislow, *Ann. N. Y. Acad. Sci.*, **93**, 457 (1962).

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

[5] D. M. Hall and E. E. Turner, *J. Chem. Soc.*, 1242 (1955).

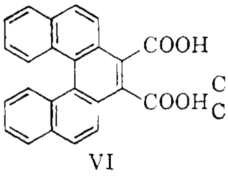
[6] G. W. Badger, P. R. Jefferies and R. W. L. Kimber, *ibid.*, 1837 (1957).

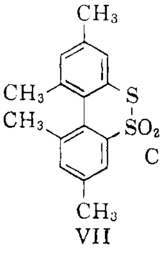
[7] M. S. Newman and A. S. Hussey, *J. Am. Chem. Soc.*, **69**, 3023 (1947).

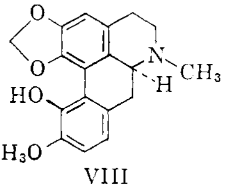
[8] W. Theilacker and F. Baxmann, *Ann.*, **581**, 117 (1953).

[9] D. M. Hall and M. M. Harris, *J. Chem. Soc.*, 490 (1960).

optical stabilities of certain unbridged biphenyls and binaphthyls.[10] The appreciable optical stability of III[6] may be similarly explained. Of interest also is the unexpected result that the calculated half-life of Ia at 24.8°, 2.8 hours, is of the same order of magnitude as the approximate half-life estimated for the aromatic counterpart IV from the data of Newman and Hussey,[7] 3–4 hours at 24.8°. In an analogous situation, II was found to have a significantly *higher* optical stability than the comparable pentahelicene derivative VI.[5]


VI


VII


VIII

Assuming no distortion of the biphenyl skeleton and neglecting torsional strain,[11] the energy barrier of racemization in Ia is seen to be almost entirely a reflection of the repulsive interaction between the two methyl groups in the transition state: the calculated activation energy for racemization of 9,10-dihydrophenanthrene is only about 2 kcal./mole.[12] This conclusion is supported by an analysis of the factors which contribute to the energy barrier (31 kcal./mole) of racemization[13] in VII. It may be assumed, by analogy with other sulfides and sulfones,[14] that the approximate bond distances and angles in VII have the values: C–S and C–SO_2, 1.81 Å.; S–SO_2, 2.10 Å.; $CSSO_2$ and SSO_2C, 105°. If the further assumption is made that the biphenyl skeleton remains essentially undistorted in the coplanar transition state, it can be shown that the above angles also remain virtually unchanged ($CCSO_2$ and SSO_2C, 103°) in the transition state, whereas the internal CCS angles suffer distortion from *ca.* 120 to 137°. Taking the angle bending energy for CCS to be the same as for CCC (*i.e.*, 17.5 cal./deg.^{2}/mole) and neglecting torsional and other non-bonding strains,[11] the energy requirement for distorting the bridge in the transition state is calculated to be 10 kcal./mole. The remaining 21 kcal./mole may thus be assigned to the non-bonded interactions of the methyl groups in the 6,6′-positions, an excellent if possibly fortuitous agreement with the estimate made for Ia. We add parenthetically that the optical stability of the aporphine alkaloids, exemplified by bulbocapnine (VIII), is not due to the blocking substituents but rather to the special feature of the bicyclic system, which is not present in the previously discussed cases (I–VII).

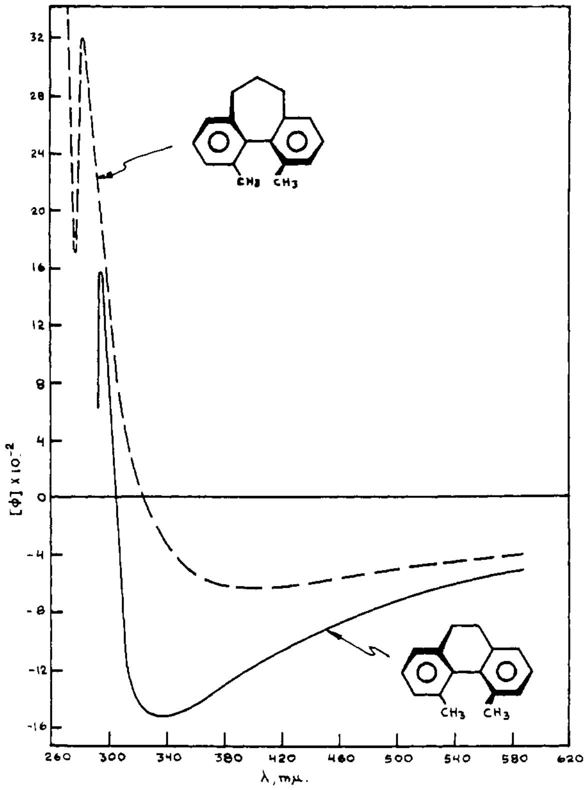


Fig. 1.

In previous preparations of Ia by the method employed in the present work, the product was isolated by distillation at 115–117° (0.2 mm.)[15] or at 97.5–98.5° (0.01 mm.).[4] At those temperatures, the half-life of racemization estimated by extrapolation from the data at lower temperatures is *maximally* a few seconds, and the reported isolation of racemic Ia from active dibromide[4] is thus accounted for. By the same token, the isolation[4] of separate diastereomers of Ib by distillation at elevated temperatures (116–119°) does not seem to us to be compatible with the demonstrated conformational instability of the parent system Ia.

The optical rotatory dispersion curve (Fig. 1) of Ia, determined at temperatures (0–1°) sufficiently low to ensure optical stability over the period of measurement, conforms in type to that of related bridged biphenyls.[16] As expected for the (R) configuration, a positive long-wave length extremum of low intensity is superimposed on a strong negative background rotation. There is considerable similarity between this portion of the curve and that of the homologous seven-membered ring bridged biphenyl[16] (Fig. 1). It has been shown[16] that a high-amplitude Cotton effect is centered at the conjugation band of 2,2′-bridged biphenyls and is an attribute of the inherently dis-

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[10] W. Theilacker and R. Hopp, *Chem. Ber.*, **92**, 2293 (1959).

[11] For a discussion of these and related assumptions, *cf.*, *e.g.*, K. Mislow, S. Hyden and H. Schaefer, *J. Am. Chem. Soc.*, **84**, 1449 (1962).

[12] K. E. Howlett, *J. Chem. Soc.*, 1250 (1955).

[13] W. L. F. Armarego and E. E. Turner, *ibid.*, 3668 (1956); M. M. Harris, in W. Klyne and P. B. D. de la Mare, "Progress in Stereochemistry," Vol. 2, Academic Press, Inc., New York, N. Y., 1958, p. 174.

[14] "Table of Interatomic Distances and Configuration in Molecules and Ions," published by The Chemical Society, London, 1958; G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955.

[15] E. D. Bergmann and Z. Pelchowicz, *J. Am. Chem. Soc.*, **75**, 2663 (1953).

[16] K. Mislow, M. A. W. Glass, R. E. O'Brien, P. Rutkin, D. H. Steinberg, J. Weiss and C. Djerassi, *ibid.*, **84**, 1455 (1962).

symmetric biphenyl chromophore. We are therefore confident that enantiomerically homogeneous material displays a Cotton effect of high amplitude, centered near 261 mμ, the λ_{max} of the conjugation band, and that the sign of that Cotton effect is positive for the configuration of (−)-Ia. A combination of circumstances unfortunately prevented the polarimetric exploration of this spectral region: the high extinction at the maximum (ε 16,800) appeared in this instance to be accompanied by relatively low rotations, the result of partial racemization. In the previous work[16] it had been found that Cotton effects could not be measured reliably under conditions of optical density much greater than unity. The concentration of the optically active component in our sample was apparently not sufficient to compensate for the intense absorption by a high enough optical rotation.

Experimental Part[17]

(−)-9,10-Dihydro-4,5-dimethylphenanthrene (Ia).—A filtered (under nitrogen) solution of phenyllithium (from 0.32 g. of lithium and 3.7 g. of bromobenzene) in 35 ml. of ether was added dropwise to a solution of (−)-2,2′-bis-(bromomethyl)-6,6′-dimethylbiphenyl (5.5 g., $[\alpha]^{24.5}\text{D}$ −49.8° (*c* 1.2, C_6H_6)) in 130 ml. of ether at ice-bath temperatures. The reaction mixture was stirred at 0–5° for 1 hour and hydrolyzed by addition of ice-cold dilute sulfuric acid. The ether layer was washed with ice-cold sodium bicarbonate solution and water, and the ether was removed under reduced pressure at 0–5°. The residue was stirred for 30 minutes at ice-bath temperatures with a solution of 5.0 g. of silver nitrate in 10 ml. of water and 30 ml. of acetone. The mixture was filtered, the filtrate was concentrated at 0–5° and extracted with ether, and the ether was removed at 0–5°. The residue, dissolved in hexane, was chromatographed on 100 g. of silica gel (100–200 mesh) which was kept at 0–5° through use of a jacketed column. Bromobenzene was eluted first, followed by Ia. The material obtained on evaporation of the solvent at 0–5° was a solid, m.p. 50–52°, λ_{max}^{EtOH} 261 mμ (ε 14,500), $\lambda_{max}^{isooctane}$ 261 mμ (ε 16,800); lit.[4,15] (estimated from the published graphs) λ_{max}^{EtOH} 260 mμ (ε, 16,000); O.R.D. in isoöctane (0–1°, *c* 1.1–0.006): $[\alpha]_{589}$ −242°, $[\alpha]_{340}$ −726°, $[\alpha]_{296}$ +774°, $[\alpha]_{293}$ +290°; see Fig. 1. The cyclization and isolation steps described above took about 7 hours altogether.

The product, as eluted off the column and used in subsequent rate studies, was at least 90% homogeneous by gas chromatography at 200° on a 6′ × 0.25″ column packed with Apiezon L, helium carrier at 30 p.s.i., retention time 15.3 min. Bromobenzene (amounting to a few per cent.) was identified among the small forerun of contaminants (retention times 2.3 min. or less). No biphenyl was detected.

For purposes of comparison, a sample of racemic Ia was prepared by the older procedure.[15] On scratching the oil, crystallization was induced. The solid melted at 51–53° after recrystallization from ethanol. The infrared spectra of (−)-Ia and of authentic (±)-Ia were identical.

A sample of (−)-Ia was distilled (with concomitant racemization) under high vacuum at 70° (bath temperature) for elemental analysis.

Anal. Calcd. for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.07; H, 7.92.

Racemization Experiments.—Thermostated 1% solutions of (−)-Ia in benzene were examined polarimetrically (2-dm. tube) over a period of at least 1 half-life. Readings were taken at 435 mμ and the results were plotted as log α_t *vs.* time. Excellent straight-line relationships resulted from the twelve or more readings which were obtained for each run. The values of *k* (and half-lives) obtained from the slopes of the curves are listed in Table I, as are the rotations observed at t_0. After a little less than 1 hour at 54.4°, or after heating 3 minutes near 100°, the rotation had become, and remained, zero.

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[17] Microanalysis by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. The rotatory dispersion was measured with an automatic recording Rudolph spectropolarimeter.

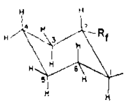
COMMUNICATIONS TO THE EDITOR

trans AND *cis* CONFORMATION ISOMERS OF 1-IODO-2-PERFLUOROALKYLCYCLOHEXANES AND THEIR NUCLEAR MAGNETIC RESONANCE SPECTRA

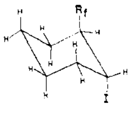
Sir:

Trans and *cis* isomers of 1-iodo-2-perfluoroisopropylcyclohexane and of 1-iodo-2-perfluoropropylcyclohexane have been prepared and characterized.[1] Evidence obtained to date strongly indicates that these products have chair structures Ia (R_f = $(CF_3)_2CF$–), Ib (R_f = $CF_3CF_2CF_2$–) and IIb (R_f = $(CF_3)_2CF$– and $CF_3CF_2CF_2$–).[2,3]

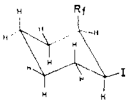
Free radical addition of heptafluoro-2-iodopropane to cyclohexene gave two adducts (*trans*, A and *cis*, B) which were separated by gas liquid phase chromatography.[4] Heptafluoro-1-iodopropane and cyclohexene gave two adducts[5] also, but



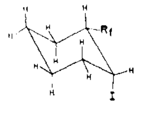
Ia



Ib



IIa



IIb

trans — A (Ia), C (Ib)

cis — B, D

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[1] N. O. Brace, to be submitted to the *Journal of the American Chemical Society*.

[2] A full exposition of the evidence will be given with an appropriate discussion in a later publication; space permits here only a summary of the salient points.

[3] For a review of the stereochemistry of cyclohexanes, see W. G. Dauben and K. S. Pitzer in M. S. Newman's "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956.

[4] Tricresyl phosphate on a firebrick column at 124°, 1.5 p.s.i. helium pressure, 6.0 flow rate with a Perkin–Elmer Vapor Fractometer was used in all cases. Preparative scale separation of adducts was done by John Robson. A [R_f = $(CF_3)_2CF$–] gave a retention time (R.T.) of 9.2 minutes; $n^{25}\text{D}$ 1.4373; $d^{25}{}_4$ 1.792. B [R_f = $(CF_3)_2CF$–] gave an R.T. of 12.6 min.; $n^{25}\text{D}$ 1.4378; $d^{25}{}_4$ 1.804. *Anal.* Calcd. for $C_9H_{10}F_7I$: C, 28.6; H, 2.67; F, 35.3; I, 33.6. Found: (A) C, 28.7; H, 2.9; F, 35.8; I, 33.0. (B) C, 28.9; H, 2.8; F, 35.7; I, 33.3.

[5] C (R_f = $CF_3CF_2CF_2$–) gave 7.9 R.T.; $n^{25}\text{D}$ 1.4310; $d^{25}{}_4$ 1.772. D (R_f = $CF_3CF_2CF_2$–) gave R.T. 15.5; $n^{25}\text{D}$ 1.4325; $d^{25}{}_4$ 1.784. *Anal.* Calcd. for $C_9H_{10}F_7I$: C, 28.6; H, 2.67; F, 35.3; I, 33.6. Found: (C) C, 28.8; H, 2.7; F, 35.3; I, 33.8. (D) C, 28.8; H, 2.7; F, 35.4; I, 33.8.