of a solution of sodium bisulfite (3.2 g.) and sodium hydroxide (2.1 g.) in 24 ml. of water to a hot solution of cupric sulfate hydrate (15.0 g.) and sodium chloride (3.9 g.) in 48 ml. of water, followed by washing of the precipitate. The tetrazotized solution was added to the cuprous cyanide mixture at 0–5°. The resulting precipitate was extracted with toluene, the organic solvent was removed, and the residue was distilled with steam to give an almost white solid (0.40 g.) suspended in 3 l. of distillate. Recrystallization from benzene–hexane afforded 0.10 g. (2%) of the desired product, m.p. 157–157.5°, $[\alpha]^{28}\text{D}$ +20° (*c* 1.9, tetrahydrofuran); the infrared spectrum (KBr wafer) exhibited the characteristically aciform and pronounced absorption at 2220 cm.$^{-1}$ (C≡N).

Anal. Calcd. for $C_{16}H_{12}N_2$: C, 82.7; H, 5.2; N, 12.1. Found: C, 83.0; H, 5.2; N, 12.1.

(−)-6,6′-Dicyano-2,2′-dimethylbiphenyl.[33]—Phosphorus pentachloride (6.5) was added to a mixture of (+)-6,6′-dimethyl-2,2′-diphenic acid[4] (2.1 g.) and *p*-toluenesulfonamide (2.8 g.) in a 50-ml. flask connected for distillation. The reaction started without external heating, but an oil-bath at 200–205° was now applied and heating continued until distillation was complete. Pyridine (6 ml.) and then water (28 ml.) was added to the residue. The resulting solid was collected by filtration and recrystallized from benzene–ligroin to give 0.70 g. (39%) of the desired product, m.p. 157–157.5°, $[\alpha]^{28}\text{D}$ −18° (*c* 5.6, tetrahydrofuran). The infrared spectrum was identical with that of the (+)-isomer.

Anal. Calcd. for $C_{16}H_{12}N_2$: C, 82.7; H, 5.2; N, 12.1. Found: C, 82.8; H, 5.4; N, 11.9.

Acknowledgment.—A portion of this work was supported by a grant from The Trubek Laboratories.

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[33] Patterned on the preparation of *p*-nitrobenzonitrile, C. S. Miller, in E. C. Horning, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 646. We are indebted to Dr. Alvin I. Kosak for bringing this elegant method to our attention.

[CONTRIBUTION FROM THE WM. H. NICHOLS LABORATORY, NEW YORK UNIVERSITY, AND CONTRIBUTION NO. 1451 FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

Conformation and Optical Rotation of Restricted Biphenyls. Configurational Correlation of Biaryls by Optical Displacement. The Absolute Configuration of Restricted 1,1′-Binaphthyls[1]

BY DONALD D. FITTS,[2] MAURICE SIEGEL AND KURT MISLOW

RECEIVED JULY 1, 1957

Values for the average interplanar angle (θ) of 6,6′-dichloro-2,2′-dimethylbiphenyl (I) have been calculated using the polarizability theory of optical activity; knowledge of the optical rotation and the absolute configuration of I permits an estimate of $\theta \sim 92°$. The difference in sign of 6,6′-dimethyl-2,2′-biphenyldiamine and 1,1′-bi-2-naphthylamine in aprotic and acidic solvents may be accounted for by a change in quadrant of θ. The *S*-configuration has been assigned to (+)-9,10-dihydro-3,4,5,6-dibenzphenanthrene and to (−)-1,1′-bi-2-naphthylamine. A general Optical Displacement Rule has been proposed which allows absolute configurational assignments in the biaryl series on the basis of characteristic rotational shifts accompanying 2,2′-bridge formation. The absolute configuration of 1,1′-bianthryls is discussed in the light of this rule.

The absolute configuration of 2,2′-dichloro-6,6′-dimethylbiphenyl (I) and of 6,6′-dimethyl-2,2′-biphenyldiamine (II) has been established as the result of work reported in the previous article of this series[3]; it has been concluded that (+)-I and (+)-II have the *R*-configuration. The purpose of this article is to calculate the specific rotations of I and II and relate the rotation to the average conformation of the molecule. We shall then be in a position to offer an interpretation of the change in sign of rotation of II in passing from aprotic to acidic solvents and to suggest the theoretical basis for a new indirect method of intercorrelating the configurations of optically active biaryls.[4]

According to the electromagnetic theory of optical rotatory power, the specific rotation $[\alpha]\text{D}$ is related to the molecular rotatory parameter g by

$$[\alpha]\text{D} = 4.930 \times 10^5 \frac{n^2+2}{3M} g \qquad (1)$$

where n is the refractive index of the solution, M is the molecular weight of the optically active substance, and g is expressed in Å.[4] The parameter g is related to the molecular conformation of the asymmetric molecules and is approximated by the polarizability theory of Kirkwood[5,6] as

$$\begin{aligned} g^{(0)} &= \frac{1}{6} \sum_{i<k=1}^{N} \alpha_i\alpha_k\beta_i\beta_k G_{ik} \mathbf{R}_{ik}\cdot(\mathrm{b}_i \times \mathrm{b}_k) \\ G_{ik} &= \frac{1}{R_{ik}^3}\left[\mathrm{b}_i\cdot\mathrm{b}_k - 3\,\frac{(\mathrm{b}_i\cdot\mathbf{R}_{ik})(\mathrm{b}_k\cdot\mathbf{R}_{ik})}{R_{ik}^2}\right] \qquad (2) \\ \mathbf{R}_{ik} &= \mathbf{R}_k - \mathbf{R}_i \end{aligned}$$

A typical asymmetric molecule is divided into N groups, each of which possesses a polarizability tensor of cylindrical symmetry. The mean polarizability of the i-th group is α_i and the anisotropy of the polarizability is β_i. The unit vector along the symmetry axis of group i is b_i. The summation in equation 2 extends over each pair of groups. The vector $\mathbf{R}_{ik}$ is the distance between groups i and k.

We now set up a right-handed Cartesian coördinate system in a molecule of 2,2′-diR-6,6′-dimethylbiphenyl as shown in Fig. 1. The phenyl ring

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[1] Configurational Studies in the Biphenyl Series. IV. Part III, preceding paper.

[2] National Science Foundation predoctoral fellow, 1954–1957.

[3] F. A. McGinn, A. K. Lazarus, M. Siegel, J. E. Ricci and K. Mislow, THIS JOURNAL, **80**, 476 (1958).

[4] The method of thermal analysis already has been successfully employed in the configurational intercorrelation of a number of optically active diphenic acids; M. Siegel and K. Mislow, THIS JOURNAL, **80**, 473 (1958).

[5] J. G. Kirkwood, *J. Chem. Phys.*, **5**, 479 (1937).

[6] W. W. Wood, W. Fickett and J. G. Kirkwood, *ibid.*, **20**, 561 (1952).

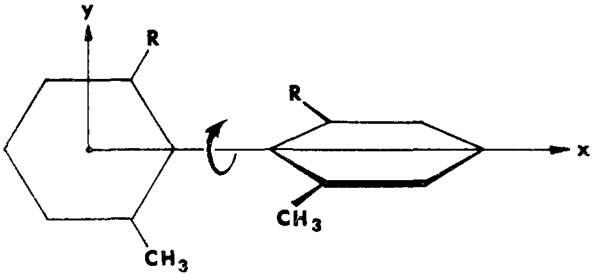

Fig. 1.—Chosen coördinate system for a 6,6′-disubstituted 2,2′-dimethylbiphenyl (a conformation corresponding to the *R*-configuration is shown).

on the left is held fixed and its center is chosen as the origin of the coördinate system. The positive x-axis extends along the phenyl–phenyl bond. The positive y-axis is selected in the plane of the left phenyl ring as shown in Fig. 1 and the positive z-axis is taken perpendicular to the phenyl ring and extending upward, out of the page. The unit vectors along the x, y and z axes are $\mathbf{i}$, $\mathbf{j}$ and $\mathbf{k}$, respectively.

The angle θ between the planes of the two phenyl rings is defined by rotating the right phenyl ring about the x-axis as shown in Fig. 1 from the reference position where the two phenyl rings are coplanar with both methyl groups extending in the same direction. We refer to the *cis* conformation when $\theta < 90°$, *i.e.*, when the two methyl groups are closer than they would be if the planes of the two rings were perpendicular, and to the *trans* conformation when $\theta > 90°$. The angle θ for each of these conformations is shown for II in the *R*- and *S*-configurations in Fig. 2.

Although steric interference between the substituent groups prevents the angle θ from taking on all values, the molecule is able to assume conformations corresponding to a range of values for the angle θ. In the following discussion we select a typical molecule whose interplanar angle θ is that for the minimum of the potential energy of internal rotation. We then speak of the average angle θ for the molecule. We assume that the deviations of θ from its average value are such that the optical properties of the molecules may be expressed in terms of the average value of the angle θ.

We now calculate the specific rotation of I as a function of the average interplanar angle θ. The molecule of I is divided into six groups: phenyl, phenyl′, methyl, methyl′, chloro and chloro′. The sum in equation 2 has, in this case, fifteen terms. The unit vector $\mathbf{b}_i$ for each phenyl group is directed normal to the ring. The unit vector for each methyl group is directed along the bond between the phenyl ring and the carbon atom of the methyl group. We assume that rotation about this bond is not restricted so that the methyl group may be regarded as cylindrically symmetrical. Similarly, the unit vector for each chloro group is directed along the bond between the ring and the chlorine atom.

The unit vectors $\mathbf{b}_i$ for the various groups are listed in Table I in terms of the coördinate system defined above. Since the unit vectors $\mathbf{b}_i$ of the phenyl and methyl groups are coplanar, the triple scalar product in equation 2 vanishes and the term involving the interaction between these two groups is zero. For this same reason, the terms in equation 2 involving the pairs phenyl′–methyl′, phenyl–chloro, phenyl′–chloro′, methyl–chloro and methyl′–chloro′ all vanish. The remaining nine terms vanish only if the two phenyl rings are coplanar, which they cannot be because of steric interference between the substituent groups.

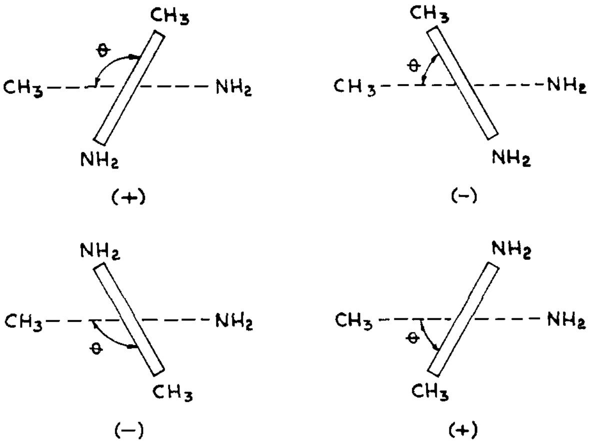

Fig. 2.—6,6′-Dimethyl-2,2′-biphenyldiamine: upper row, *R*-configuration, *trans* and *cis* conformations (left and right) corresponding to optical signs of (+) and (−), resp. Lower row: *S*-configuration, *trans* and *cis* conformations (left and right) corresponding to optical signs of (−) and (+), resp.

Table I

Unit Vectors for the Various Groups of I

Group	Unit vector
Phenyl	$\mathbf{k}$
Phenyl′	$\sin\theta\mathbf{j} + \cos\theta\mathbf{k}$
Methyl	$\frac{1}{2}\mathbf{i} - \frac{\sqrt{3}}{2}\mathbf{j}$
Methyl′	$-\frac{1}{2}\mathbf{i} - \frac{\sqrt{3}}{2}\cos\theta\mathbf{j} + \frac{\sqrt{3}}{2}\sin\theta\mathbf{k}$
Chloro	$\frac{1}{2}\mathbf{i} + \frac{\sqrt{3}}{2}\mathbf{j}$
Chloro′	$-\frac{1}{2}\mathbf{i} + \frac{\sqrt{3}}{2}\cos\theta\mathbf{j} - \frac{\sqrt{3}}{2}\sin\theta\mathbf{k}$

The calculated specific rotations of *R*-I in ethanol for values of the average interplanar angle θ ranging from 0 to 180° are presented in Fig. 3. The specific rotations of *S*-I are simply the negatives of those in Fig. 3. The calculated rotations of I in hexane are 1.01 times those of I in ethanol.[7] The molecule, of course, cannot assume values of θ near 0 and 180°, because of steric interference between the substituent groups. Comparison of the calculated values with the experimental[3] specific rotations of +33° in ethanol and +45° in hexane for *R*-I leads to the conclusion that the average angle θ is 92° in ethanol and 92.5° in hexane. Unfortu-

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[7] The distance between the centers of the two phenyl rings is 4.32 Å. The distances from the center of a phenyl ring to the carbon atom of a methyl group and to a chlorine atom on the same ring are 2.96 and 3.11 Å., respectively. The mean polarizabilities α of the methyl, chloro and phenyl groups are 2.25, 2.35 and 9.89 Å.^{3}, respectively. The anisotropy ratio β is 0.35 for the methyl and chloro groups and −0.58 for the phenyl groups. The indices of refraction for light of sodium D wave length are 1.3610 for ethanol and 1.3749 for hexane. The molecular weight of I is 251.15.

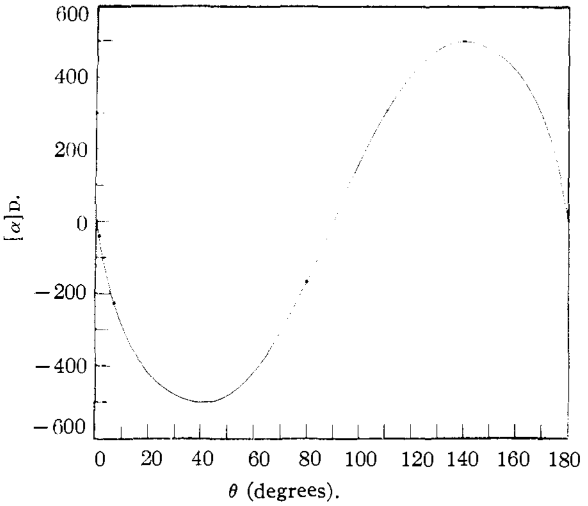

Fig. 3.—Calculated specific rotation of *R*-6,6′-dichloro-2,2′-dimethylbiphenyl in ethanol as a function of the interplanar angle θ.

nately, reliable estimates of the uncertainty of these calculated results are not available. In a calculation of the specific rotation of *trans*-2,3-epoxybutane,[6] whose internal structure is accurately known, the polarizability theory gave a specific rotation of +43°, to be compared with an experimental value of +59°. According to this calculation, the Fischer–Rosanoff convention is correct.[8]

For each of the interplanar angles between 45 and 135°, the term in equation 2 arising from the phenyl–phenyl′ interaction accounts for about 78% of the total calculated specific rotation. The four terms involving the interactions of the substituent groups with the two phenyl rings account for another 21% of the total calculated rotation. For the *R*-configuration, all five of these terms have the form

$$g^{(0)} = -K \sin 2\theta \qquad (3)$$

where K is a constant. As equation 3 readily shows, the contributions of these terms is negative for θ in the first quadrant and positive for θ in the second quadrant. The terms are identically zero when the planes of the two phenyl rings are perpendicular. That the specific rotation of I for incident plane-polarized light of sodium D wave length is zero for $\theta = 90°$ is due to cancellation of the remaining terms in equation 2. Here is an interesting case of a conformation which cannot be superimposed on (or converted into) its mirror image, yet for which the optical rotation at this wave length is zero. These five terms, moreover, vanish for $\theta = 90°$ at all wave lengths. Since the phenyl–phenyl′ term represents the dominant contribution to the optical activity, the qualitative features of the specific rotation as a function of the angle θ as represented in equation 3 remain valid despite any uncertainties in the numerical accuracy of the calculated specific rotations.

The specific rotation of II can be calculated in exactly the same manner as for I. However, the anisotropy ratio of the amino group is not known very accurately[5] and the parameters for the protonated amino group are not known at all. Since our calculations of the specific rotation of I indicate that the phenyl–phenyl′ term is the dominant contribution, we expect the specific rotation of II to possess the same qualitative behavior as I with respect to the angle θ. As illustrated in Fig. 2, the rotation for the *R*-configuration should be negative for θ in the first quadrant (*cis* conformation) and positive for θ in the second quadrant (*trans* conformation). The rotation for the *S*-configuration should be positive for the *cis* conformation and negative for the *trans* conformation. The angles where the signs change are exactly at 0 and 180° and approximately at 90°.

From the calculation of the specific rotation of I and the assignment[3] of the *R*-configuration to (+)-I and to (+)-II (aprotic solvents), we accordingly conclude that the average interplanar angle θ between the phenyl rings in I and II is between 90° and 180°; the actual value is probably fairly close to 90°. The observed change in sign of rotation of II with *p*H, discussed in the previous paper,[3] may then simply be accounted for by assuming a change in the quadrant of θ (from $\theta > 90°$ to $\theta < 90°$) as a result of protonation; by analogy with values of $[\alpha]_D$ for I, Fig. 3, a change of θ from 92 to 88° would result in a change of $[\alpha]_D$ of *S*-II from *ca.* −30° to *ca.* +30°. In aqueous dioxane, where a change in sign has been associated conclusively with formation of the monoprotonated species,[3] the change in quadrant may conceivably be a consequence of intramolecular hydrogen bonding between the amino and the ammonium groups; it is not unlikely that the same argument applies to similar reversals of sign in other solvent media.[9]

Multiplication of the unit vectors $\mathbf{b}_i$, given in Table I, for the two methyl groups by the dipole moment of the methyl group, μ_1, and for the two amino groups by the dipole moment of the amino group, μ_2, and addition of the resulting vectors yield for the dipole moment, μ, of the molecule

$$\mu = \mathbf{j}\,\frac{\sqrt{3}}{2}\,(\mu_2 - \mu_1)(1 + \cos\theta) - \mathbf{k}\,\frac{\sqrt{3}}{2}\,(\mu_2 - \mu_1)\sin\theta \qquad (4)$$

under the assumption that the dipole moment of the molecule is the sum of the dipole moments of the substituent groups. Forming the scalar product of μ with itself, we obtain a formula used by Bergmann and Engel[10] relating the interplanar angle θ to the magnitude of the dipole moment of the molecule

$$\cos\theta = \frac{2\mu^2}{3(\mu_2 - \mu_1)^2} - 1 \qquad (5)$$

The measured magnitude of the dipole moment of II is 1.66 D in benzene and the corresponding angle θ from equation 5 is 67°. While the assignment

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[8] The correctness of this convention has found independent and experimentally unambiguous corroboration in the work of J. M. Bijvoet, A. F. Peerdeman and A. J. van Bommel, *Nature*, **168**, 271 (1951).

[9] Under the assumption that *diprotonated* II has $\theta > 90°$ due to electrostatic repulsion between the ammonium groups, a second reversal of sign would be expected in going to this species. The data (ref. 3) were *permissive* of such an eventuality, although no conclusive inference could be made.

[10] E. Bergmann and L. Engel, *Z. physik. Chem.*, **15B**, 85 (1931).

of the average angle θ from dipole moment measurement differs in quadrant from the assignment based on the optical activity calculations using the polarizability theory, the assumption that the dipole moments of the substituent groups do not interact and therefore can be added vectorially to give the dipole moment of the molecule is only approximately valid for groups which are close together. Comparison of experimental and calculated magnitudes of the dipole moments for a number of disubstituted benzenes indicates that the above assumption is valid for *meta* and *para* compounds, but gives values which are too large for *ortho* compounds.[11] Two factors in this *ortho* effect are mutual induction and steric repulsion; both factors usually work in the same direction, although the effect of steric repulsion is often negligible. In the case of II, we may expect a large *ortho* effect, which would tend to increase the angle θ, *i.e.*, shift θ nearer to the second quadrant than 67°. Since equation 5 shows that the magnitude of the dipole moment is not a sensitive function of the angle θ, we do not believe that the assignment of θ in II based on dipole moment measurement is inconsistent with the assignment determined by optical activity calculations.

Surprisingly, a considerable body of evidence points to the *cis* conformation ($\theta < 90°$) as the stable one in 2,2′-disubstituted biphenyls.[12] Recent evidence reported by Beaven and Hall[13] indicates that the interplanar angle θ in 2,2′-dichlorobiphenyl is less than 90°. However, for I, the additional steric interference of the two methyl groups in the remaining *ortho* positions may be sufficient to change the quadrant of the angle θ. We do not believe, therefore, that the assignment of the *cis* conformation to 2,2′-dichlorobiphenyl affects our assignment of the *trans* conformation to I.

Optical Displacement Principle. Absolute Configuration of Hindered 1,1′-Binaphthyls.—An earlier attempt to correlate hindered 1,1′-binaphthyls with hindered biphenyls by the method of thermal analysis resulted in failure.[4] The success of this method depends on a similarity in size and shape of the comparison substances. In the hope of circumventing the restrictions imposed by this technique, we investigated the possibility that like shifts in rotation in related derivatives of biaryls having the same configuration might constitute the basis for a correlation method akin to Freudenberg's Displacement Rule (*Verschiebungssatz*) in the centrally asymmetric series of optically active compounds.[14]

Examination of the rotations of a large number of *S*-2,2′-diR-6,6′-diR′-biphenyls, including (−)-1,1′-binaphthalene-2,2′-dicarboxylic acid (III) derivatives (Table II), does not reveal a consistent over-all pattern. Thus, while carboxamides (methanol) (where investigated) and hydroxymethyl (benzene) derivatives are more levorotatory and methyl esters (methanol) more dextrorotatory than the parent dicarboxylic acids (methanol), taken as the standard, the corresponding bromomethyl and methyl derivatives show no such uniformity.[15] Again, while the acids and methyl esters become increasingly dextrorotatory in the series of 2,2′-disubstituted 6,6′-dinitrobiphenyl, 1,1′-binaphthyl, 6,6′-dichlorobiphenyl and 6,6′-dimethylbiphenyl, the same order is not maintained in the 2,2′-bis-(hydroxymethyl), 2,2′-bis-(bromomethyl) and 2,2′-dimethyl derivatives.

TABLE II

MOLECULAR ROTATIONS ([M]D) IN° OF SOME RESTRICTED *S*-BIARYLS[a]

R	Solvent	2,2′-DiR-6,6′-diR′-biphenyl, R′ =			2,2′-DiR-1,1′-binaphthyl
		$-NO_2$	$-Cl$	$-CH_3$	
$-COOH$	Acetone	−425	(3)	+ 41	−171
	Methanol	−422	− 22	+ 70	−116
	0.1 *N* NaOH	−850	− 43	+ 89	−287
$-CONH_2$	Methanol	−958[b]	−368[b]		
$-COOCH_3$	Et acetate	−408	− 40[b]	+118	− 96[b]
	Methanol	−346	− 20[b]	+128	− 67[b]
$-CH_2OH$	Benzene	−477	−400	−260	−352
	Et acetate	−197	−221	−119	−250
	Methanol	−179	−212	− 75	−175
	Dioxane	−261	−192	− 82	−144
$-CH_2Br$	Benzene	−266	−315	+173	−708[c]
	Dioxane	−198	−200	+165	−665
	Tetrahydrofuran	− 39	−159	+132	−655
$-CH_3$	Ethanol	− 68	− 83	0	+ 54[b]

[a] Except where noted all compounds or the corresponding enantiomers are described in refs. 3 and 4. [b] Experimental Part. [c] $[\alpha]^{29}_{546}$ −200° (C_6H_6); ref. 15 reports $[\alpha]^{23}_{546}$ −199° (C_6H_6).

It is possible, however, to assign the absolute configuration to III as follows. Since each of the naphthyl rings in a hindered 1,1′-binaphthyl is planar, we may apply the polarizability theory of optical activity in estimating the contribution of the naphthyl–naphthyl′ interaction to the specific rotation. Since the naphthyl–naphthyl′ term in the summation in equation 2 is much larger than the phenyl–phenyl′ term in the calculated rotation of I (because the polarizability of the naphthyl ring is greater than that of the phenyl ring), we may neglect interactions involving the substituent groups in forming a qualitative picture of the behavior of the specific rotation with internal conformation. The dominant contribution of the naphthyl–naphthyl′ term for the *R*-configuration is of

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[11] C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, pp. 331 ff.

[12] *Cf. e.g.*, L. L. Ingraham, in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 510; and G. H. Beaven, D. M. Hall, M. S. Lesslie and E. E. Turner, *J. Chem. Soc.*, 854 (1952).

[13] G. H. Beaven and D. M. Hall, *ibid.*, 4637 (1956).

[14] K. Freudenberg in "Stereochemie," Franz Deuticke, Leipzig, 1933, pp. 699 ff.

[15] There is some basis, nevertheless, for believing that an empirical *Ester-Amide Rule* may prove useful in assigning configuration to biaryl 2,2′-dicarboxylic acids. Configurationally related 4,5,6,4′,5′,6′-hexahydroxy-, hexamethoxy- and hexabenzyloxy- 2,2′-diphenic acids ([M]D +93°, +116° and −423° (methanol), resp.) are in turn related to methyl esters having [M]D +187° (methanol), +167° (ethanol) and −301° (acetone), respectively, and to amides having [M]D −113° (methanol), −432° (ethanol) and −1138° (ethanol), respectively (O. T. Schmidt and K. Demmler, *Ann.*, **586**, 179 (1954), the "D-Reihe"). 6,6′-Dimethoxy-2,2′-diphenic acid ([M]D +366° (ethanol)) gives a methyl ester with [M]D +415° (methanol) and an amide with [M]D +147° (methanol) (W. M. Stanley, E. McMahon and R. Adams, THIS JOURNAL, **55**, 706 (1933); the numerical data actually refer to the (−)-form which was obtained in a higher state of optical purity). The uniformity in the behavior of the various acids is impressive, and we therefore tentatively assign the *S*-configuration to all of the compounds listed above. Attempts to validate this conclusion are under way in this Laboratory.

the form given by equation 3. We therefore expect the same qualitative behavior of the rotation with respect to the interplanar angle θ as with I. (+) - 9,10 - Dihydro - 3,4,5,6 - dibenzphenanthrene[16] (IV) obviously has the *cis* conformation and is therefore assigned the *S*-configuration. Synthetic precursor[16] (−)-III therefore also has the *S*-configuration.[17]

We now turn to an examination of the rotations of some 2,2′-bridged biaryls of known absolute configuration. All bridged compounds (V–X, Chart I) prepared from *S*(−)-6,6′-dinitro- and *S*(−)-6,6′-dichloro-2,2′-diphenic acid[3] are strongly dextrorotatory. The bridged compounds (XI–XIII) prepared from *S*(+)-6,6′-dimethyl-2,2′-diphenic acid[3] are considerably more dextrorotatory than the parent acid and most of its unbridged derivatives (Table II). The bridged compounds (IV, XIV–XV) derived from *S*(−)-III are strongly dextrorotatory. It might have been anticipated that the change from an open to a bridged system, involving as it must a dramatic change in θ (including, possibly, quadrant), might be reflected in a characteristic manner in the sign and magnitude of the optical rotation. This expectation, arrived at through a qualitative interpretation of the polarizability theory, is borne out strikingly by the present data. We therefore propose the following general Optical Displacement Rule: *A symmetrically substituted hindered biaryl has the S-(resp. R-) configuration if, in going from an open to a bridged system, the optical activity suffers a marked shift in the positive (resp. negative) direction.*

An interesting application of the Displacement Rule involves restricted 2,2′-biaryldiamines. *R*-(+)-II gives strongly levorotatory bridged derivatives XVI and XVII (Chart I).[18] Similarly, (+)-1,1′-bi-2-naphthylamine (XVIII) yields the strongly levorotatory bridged derivative XIX (Chart I).[19] Further, the change in sign of both *R*(+)-II and (+)-XVIII in going from aprotic to acidic solvents[3,19] may be included in our generalized rule if, as noted above, intramolecular hydrogen bridging with concomitant change in quadrant of θ is responsible for the phenomenon. We conclude that (+)-XVIII has the *R*-configuration.

By the same token, we tentatively conclude that XX (Chart I), derived[20] from 4,6,4′,6′-tetramethylbiphenyl-2,2′-disulfonyl chloride ($[M]_{546}$ −385°), and XXI–XXIII (Chart I), related[21] to 1,1′-bi-2-thionaphthol ($[M]_{546}$ +213°) and to 1,1′-binaphthalene-2,2′-disulfonyl chloride ($[M]_{546}$ +115°), all have the *S*-configuration.

It is pertinent to speculate on the absolute configuration of the optically active 1,1′-bianthryls. Since the bridged derivatives[22] XXV and XXVI are far more dextrorotatory than the unbridged analogs[23,24] (XXIV) to which they have been configurationally related, we tentatively assign the *S*-configuration to all of these (dextrorotatory) compounds. Although (XXIVi) 1,1′-bi-2-anthroic acid and its methyl ester XXIVh have the same rotation, within experimental error, the derived 1,1′-bi-2-anthramide (XXIVc) is considerably more levorotatory, in harmony with our empirical rule[15] as applied to *S*-biaryls. On the other hand, 1,1′-bianthracene-2,2′-diamine (XXIVe) has[23] $[\alpha]_D$ −336.7° (chloroform) and −193.1° (0.1 *N* HCl). By analogy with *R*(+)-II and *R*(+)-XVIII, this diamine should have become *more*, rather than less, levorotatory in going from an aprotic to an acidic solvent. We hope to return to this problem in a future paper.

We believe that our rule represents a useful new working principle in biaryl stereochemistry. Its scope is not limited by the geometric requirements of the method of thermal analysis and it has, so far, yielded consistent results in every case. We do not believe, however, that it would generally be desirable to include compounds (such as IX and XIII) which contain asymmetric centers in a comparison series of optically active biphenyls. We would also hestitate at this time to come to *firm* conclusions unless the "marked shift" in our rule involved *both* a change in sign and a reasonably large change in magnitude of rotation.

Experimental Part[25]

(+)-6,6′-Dinitro-2,2′-biphenyldicarboxamide.—A mixture of (+)-6,6′-dinitro-2,2′-diphenic acid[26] (0.54 g., m.p. 228.5–230.5°, $[\alpha]^{26}_D$ +127° (methanol)), 5 ml. of thionyl chloride and 0.2 ml. of anhydrous pyridine was refluxed for 30 minutes. The solvent was removed and the residue (m.p. 147–153° after recrystallization from carbon tetrachloride) was treated with 2 ml. of concd. aqueous ammonia. The resulting solid, m.p. 204–211° after filtration, washing and drying, was recrystallized from methanol–hexane to give product, m.p. 217.5–218.5°, $[\alpha]^{28}_D$ +290° (*c* 0.92, methanol).

Anal. Calcd. for $C_{14}H_{10}N_4O_6$: C. 50.9; H, 3.1; N, 17.0. Found: C, 50.4; H, 3.5; N, 17.1.

(+)-6,6′-Dichloro-2,2′-biphenyldicarboxamide.—A mixture of (+)-6,6′-dichloro-2,2′-diphenic acid[27] (0.30 g., m.p. 263–265°, $[\alpha]^{24}_D$ +5.7° (methanol)), 5 ml. of thionyl chloride and 0.2 ml. of anhydrous pyridine was refluxed for 30 minutes. The solvent was removed and the residue (m.p. 132–135° after crystallization from carbon tetrachloride) was treated with 2 ml. of concd. aqueous ammonia. The resulting product, after recrystallization from chloroform, had m.p. 242–244°, $[\alpha]^{25}_D$ +119° (*c* 0.14, methanol).

Anal. Calcd. for $C_{14}H_{10}Cl_2N_2O_2$: C, 54.4; H, 3.3; N, 9.1. Found: C, 54.4; H, 3.4; N, 9.3.

(−)-2,7-Dihydro-4′,1″-dinitro-3,4,5,6-dibenzazepinium-1-spiropiperidinium Bromide (V).—A solution of piperidine (0.19 g.) in benzene was added to a solution of (+)-6,6′-dinitro-2,2′-bis-(bromomethyl)-biphenyl[28] (0.35 g., m.p.

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

(17) An attempt to confirm this conclusion by application of our general method of asymmetric synthesis (K. Mislow and P. Newman, THIS JOURNAL, **79**, 1769 (1957)) to the DBCH-6-one derivative of III is under way in this Laboratory.

(18) S. Sako, *Mem. Coll. Eng. Kyushu Imp. Univ.*, **6**, 263 (1932); *C. A.*, **26**, 3246 (1932). Chart I shows the other enantiomer.

(19) R. Kuhn and P. Goldfinger, *Ann.*, **470**, 183 (1929). Chart I shows the other enantiomer.

(20) W. L. F. Armarego and E. E. Turner, *J. Chem. Soc.*, **3668** (1956).

(21) W. L. F. Armarego and E. E. Turner, *ibid.*, **13** (1957).

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

(23) K. Lauer, R. Oda and M. Miyawaki, *J. prakt. Chem.*, **148**, 310 (1937).

(24) F. Bell and D. H. Waring, *J. Chem. Soc.*, 1579 (1949).

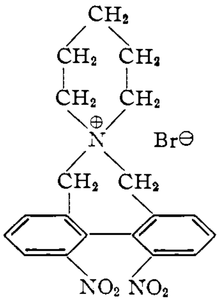
(25) Microanalyses by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

(26) A. W. Ingersoll and J. R. Little, THIS JOURNAL, **56**, 2123 (1934).

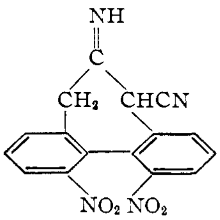
(27) G. H. Christie, C. W. James and J. Kenner, *J. Chem. Soc.*, 1948 (1923).

(28) P. Newman, P. Rutkin and K. Mislow, THIS JOURNAL, **80**, **465** (1958).

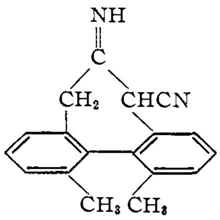
CHART I MOLECULAR ROTATIONS OF SOME BRIDGED *S*-BIARYLS



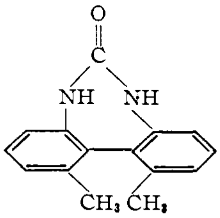
$[M]_D$ +2289°
$[M]_{546}$ +3474°
V^{a,b}



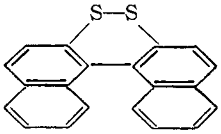
$[M]_D$ +2698°
IX^c



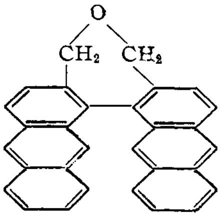
$[M]_D$ +1291°
XIII^e



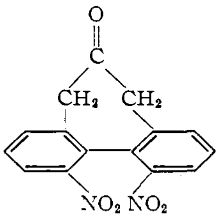
$[M]_D$ +151°
XVI^{g,b}



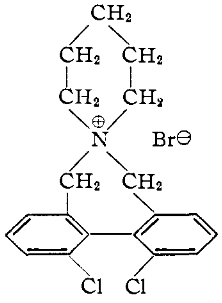
$[M]_{546}$ +2452°
XXI^j



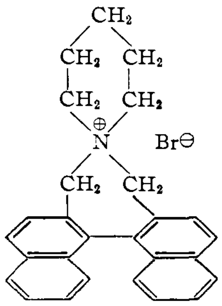
$[M]_D$ +6066°
XXV^{k,b}



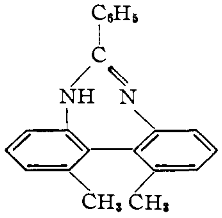
$[M]_D$ +650°
VI^c



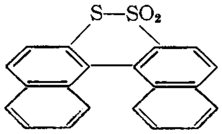
$[M]_D$ +343°
$[M]_{546}$ +347°
X^{a,b}



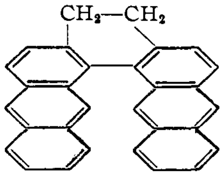
$[M]_{579}$ +1195°
$[M]_{546}$ +1362°
XIV^f



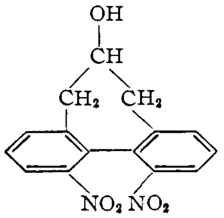
$[M]_D$ +2805°
XVII^{g,b}



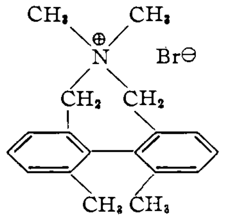
$[M]_{546}$ +592°
XXII^j



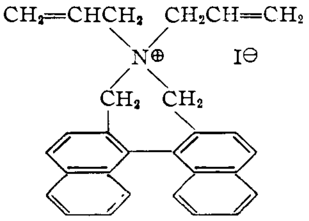
$[M]_D$ +7637°
XXVI^{k,b}



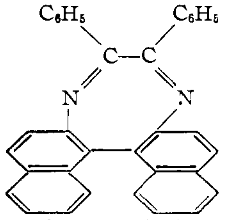
$[M]_D$ +2089°
VII^e



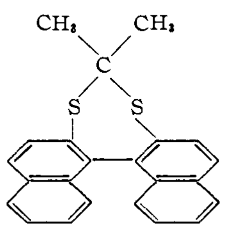
$[M]_D$ +101°
XI^e



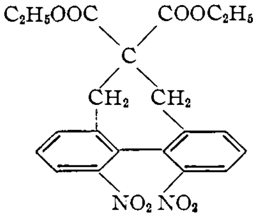
$[M]_{579}$ +917°
$[M]_{546}$ +1034°
XV^f



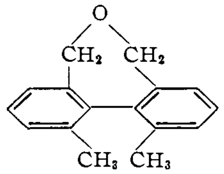
$[M]_D$ +8750°
XIX^{h,b}



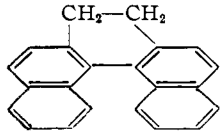
$[M]_{546}$ +1316°
XXIII^j



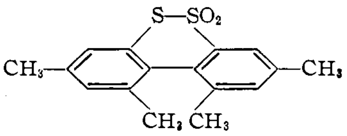
$[M]_D$ +1897°
VIII^{d,b}



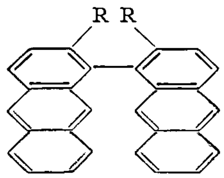
$[M]_D$ +256°
XII^e



$[M]_{579}$ +3651°
$[M]_{546}$ +4196°
IV^f



$[M]_{546}$ +770°
XX^i



XXIV^{kb,mb}
a,^{m} R = H, $[M]_{546}$ +783°
b, R = CH_2Br, $[M]_D$ +978°
c,^{l,b} R = $CONH_2$, $[M]_D$ +1194°
d, R = CH_2OAc, $[M]_D$ +1445°
e, R = NH_2, $[M]_D$ +1477°
f,^{m} R = Br, $[M]_{546}$ +1532°
g, R = CN, $[M]_D$ +1545°
h, R = $COOCH_3$, $[M]_D$ +1697°
i, R = COOH, $[M]_D$ +1708°

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[a] Experimental Part. [b] Other enantiomer actually used. [c] Ref. 28. [d] Dr. D. C. Iffland, private communication. [e] G. Wittig and H. Zimmermann, *Chem. Ber.*, **86**, 629 (1953). [f] Ref. 16. [g] Ref. 18. [h] Ref. 19. [i] Ref. 20. [j] Ref. 21. [k] Ref. 22. [l] Ref. 23; value corrected (ref. 24) to optical purity. [m] Ref. 24.

169–171°, $[\alpha]^{25}\text{D}$ +46° (dioxane)) in benzene. The yellow precipitate which formed overnight was dissolved in a minimum quantity of water. Addition of concd. aqueous potassium hydroxide precipitated an oil which solidified, m.p. 167–170° dec. The solid was dissolved in acetone and the mixture was filtered. The filtrate was evaporated to give product (0.10 g.), m.p. 168–169° dec., $[\alpha]^{25}{}_{546}$ −800°, $[\alpha]^{25}{}_{578}$ −637°, $[\alpha]^{28}\text{D}$ −527° (*c* 1.0, ethanol).

Anal. Calcd. for $C_{19}H_{20}BrN_3O_4$: Br, 18.4; N, 9.7. Found: Br, 18.0; N, 9.0.

(−)-2,7-Dihydro-4′,1″-dichloro-3,4,5,6-dibenzazepinium-1-spiropiperidinium bromide (X) was prepared from (+)-6,6′-dichloro-2,2′-bis-(bromomethyl)-biphenyl[3] (0.16 g., m.p. 70–71°, $[\alpha]^{29}\text{D}$ +77° (benzene)) and piperidine in the manner described for the synthesis of the 4′,1″-dinitro analog. Recrystallization from acetone afforded 0.08 g. of product, m.p. 297–298.5° dec., $[\alpha]^{27}{}_{546}$ −84°, $[\alpha]^{27}{}_{578}$ −84°, $[\alpha]^{27}\text{D}$ −83° (*c* 1.2, ethanol).

Anal. Calcd. for $C_{19}H_{20}BrCl_2N$: Cl, 17.2; N, 3.4. Found: Cl, 16.7; N, 3.4.

(−)-Methyl 6,6′-dichloro-2,2′-diphenate was prepared by reaction of (−)-6,6′-dichloro-2,2′-diphenic acid[27] (m.p. 261–262.5°, $[\alpha]^{29}\text{D}$ −7.2 (methanol)) with ethereal diazomethane in the usual manner. The product, after recrystallization from ethanol, had m.p. 104–105.5°, $[\alpha]^{27}\text{D}$ −5.8 (*c* 1.0, methanol), $[\alpha]^{27}\text{D}$ −11.5° (*c* 1.0, ethyl acetate).

Anal. Calcd. for $C_{16}H_{12}Cl_2O_4$: C, 56.7; H, 3.6. Found: C, 56.4; H, 3.5.

(−)-Methyl 1,1′-binaphthalene-2,2′-dicarboxylate was prepared by reaction of (−)-1,1′-binaphthalene-2,2′-dicarboxylic acid[16] (m.p. *ca.* 135° dec., $[\alpha]^{22}{}_{546}$ −123° (0.1 *N* NaOH)) with ethereal diazomethane in the usual manner. The product, after recrystallization from ethanol, had m.p. 154–155°, $[\alpha]^{29}\text{D}$ −18° (*c* 1.2, methanol), $[\alpha]^{27}\text{D}$ −27° (*c* 1.4, ethyl acetate).

Anal. Calcd. for $C_{24}H_{18}O_4$: C, 77.8; H, 4.9. Found: C, 77.9; H, 4.7.

(+)-2,2′-Dimethyl-1,1′-binaphthyl.—A mixture of 0.23 g. of (−)-2,2′-bis-(bromomethyl)-1,1′-binaphthyl[16] (m.p. 183.5–185.5°, $[\alpha]^{29}{}_{546}$ −200° (*c* 0.90, benzene)), 0.6 g. of lithium aluminum hydride and 45 ml. of ether was refluxed for one hour. The product, isolated in the usual way and recrystallized from a minimum quantity of ethanol, had m.p. 64–67°, $[\alpha]^{22}\text{D}$ +19° (*c* 1.3, ethanol).

Anal. Calcd. for $C_{22}H_{18}$: C, 93.6; H, 6.4. Found: C, 93.2; H, 6.4.

Acknowledgment.—We wish to express our appreciation to Professor J. G. Kirkwood of Yale University for his helpful discussions and advice.

NEW YORK 53, N. Y.
NEW HAVEN, CONN.

[CONTRIBUTION FROM THE WM. H. NICHOLS CHEMICAL LABORATORY, NEW YORK UNIVERSITY]

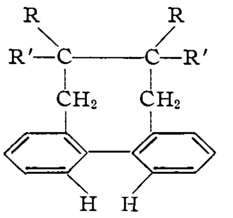
Stereochemistry of the 1,2,3,4-Dibenz-1,3-cycloöctadiene System[1]

BY LEO V. DVORKEN, R. BRUCE SMYTH AND KURT MISLOW[2]

RECEIVED JULY 1, 1957

The diastereomeric 1,2,3,4-dibenz-1,3-cycloöctadiene-6,7-dicarboxylic acids (α- and β-forms) have been prepared, resolved and identified as *trans* and *cis* stereomers by the fact that the enantiomeric forms of the former mutarotate while those of the latter racemize. The conformation of the bridge system has features closely resembling those of cyclohexane, the racemization of the *cis* compound corresponding to an interconversion of *aa*- and *ee*-isomers, and the mutarotation to an interconversion of *aa*- and *ee*-isomers. Rate constants of racemization and mutarotation in neutral and basic solvents have been determined; the *cis* isomer racemizes with $\Delta F^{\ddagger}$ 23 kcal./mole.

In connection with our work on the absolute configuration of hindered biphenyls, with particular reference to some members of the series containing substituents bridging the 2,2′-positions (preceding papers),[1] we had occasion to enquire into the resolvability of 1,2,3,4-dibenz-1,3-cycloöctadiene (Ia) or suitable derivatives.



I

Ia, R = R′ = H
b, R = R′ = $COOC_2H_5$
c, R = R′ = COOH
d, R = R′ = $COOCH_2C_6H_5$
e, R = H, R′ = COOH
f, R = H, R′ = $COOCH_3$

Optical resolutions have been reported for several biphenyls possessing 2,2′-bridges and no 6,6′-substituents other than hydrogen.[3] Judged[4] by the hypsochromic shift and attenuated extinction of the biphenyl maximum (K-band, configuration band) in Ia, Ib and If, the system of Ia and derivatives should be resolvable.[5]

Solution of the problem by optical activation of a suitable derivative of Ia not containing additional elements of dissymmetry resulted in failure: (a) no solid complex of Ib and TAPA[6] could be realized; (b) the 2′,3″-diamino derivative of Ib (IIb), prepared by the route IIIa → IIIb[7] → IIIc → IIa → IIb

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(1) Configurational Studies in the Biphenyl Series. V. Part IV, preceding paper.

(2) To whom correspondence regarding the article should be addressed.

(3) (a) F. Bell, *J. Chem. Soc.*, 1527 (1952); (b) I. G. M. Campbell and R. C. Poller, *ibid.*, 1195 (1956), and preceding papers; (c) D. C. Iffland and H. Siegel, *J. Org. Chem.*, **21**, 1056 (1956); (d) W. E. Truce and D. D. Emrick, THIS JOURNAL, **78**, 6130 (1956); (e) F. McCullough, Jr., and J. C. Bailar, Jr., *ibid.*, **78**, 714 (1956).

(4) For a summary of work relating absorption in the ultraviolet to hindered rotation, *cf.* E. A. Braude and E. S. Waight, in Klyne, "Progress in Stereochemistry," Academic Press, Inc., New York, N. Y., 1954, pp. 136 ff.; and ref. 3d.

(5) (a) G. H. Beaven, G. R. Bird, D. M. Hall, E. A. Johnson, J. E. Ladbury, M. S. Lesslie and E. E. Turner, *J. Chem. Soc.*, 2708 (1955); (b) A. C. Cope and R. D. Smith, THIS JOURNAL, **78**, 1012 (1956). An interplanar angle of 59° has been calculated (G. H. Beaven and D. M. Hall, *J. Chem. Soc.*, 4637 (1956)) for Ib and If; from the values given in (b) above and using the relationship $\cos^2\theta = \epsilon/\epsilon_0$ (E. A. Braude and W. F. Forbes, *J. Chem. Soc.*, 3776 (1955)), an interplanar angle of 44° is calculated for Ia. The average interplanar angle and the K-band shift might be considered measures, to a first approximation, of the free energy of racemization of simple bridged biphenyls.

(6) M. S. Newman and W. B. Lutz, THIS JOURNAL, **78**, 2469 (1956). A sample was kindly supplied us by Prof. Newman.

(7) This compound was prepared through the use of $CaCl_2$–$NaBH_4$ (J. Kollonitsch, P. Fuchs and V. Gábor, *Nature*, **173**, 125 (1954); **175**, 346 (1955)), which also proved a satisfactory reagent for the reduction of methyl 6,6′-dinitro-2,2′-diphenate to 6,6′-dinitro-2,2′-bis-(hydroxymethyl)-biphenyl, previously obtained by reduction with $LiAlH_4$–$AlCl_3$ (P. Newman, P. Rutkin and K. Mislow, THIS JOURNAL, **80**, 465 (1958)).