Resolution of Spiro[3.3]hepta-1,5-diene and a Prediction of Its Absolute Configuration

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Abstract: The resolution of the title compound (**1**) has been accomplished by two different methods. Both enantiomers of **1** were obtained by separation of the diastereomeric platinum(II) complexes containing three different types of optically active amines and by an asymmetric induction method using chiral diisopinocampheylborane. The highest observed value of the optical rotation of **1** was $[\alpha]^{25}\text{D}$ −26° in these resolution steps. An attempt has been made to predict the absolute configuration of spiro[3.3]hepta-1,5-diene (**1**). Application of three empirical rules suggests the *S* or 4*R* configuration for dextrorotatory **1**. Additional support for this assignment has been obtained from the reaction scheme of the asymmetric hydroboration of **1** with diisopinocampheylborane.

The resolution of asymmetric alkenes,[2] dissymmetric *trans*-cycloalkenes, and cycloalkadienes[3-6] has recently been accomplished by coordination with chiral platinum complexes. The olefins were resolved by separating the diastereomeric platinum(II) complexes $[(dl\text{-olefin})PtCl_2(\text{amine})]$ employing optically active α-methylbenzylamine or the *p*-nitro analog.[4] In particular, this method has been successfully utilized in the resolution of *cis,trans*-cycloocta-1,5-diene[3] and cyclonona-1,2-diene.[4] We have examined an extension of this method, namely the resolution of the dissymmetric spirene **1**.[7]

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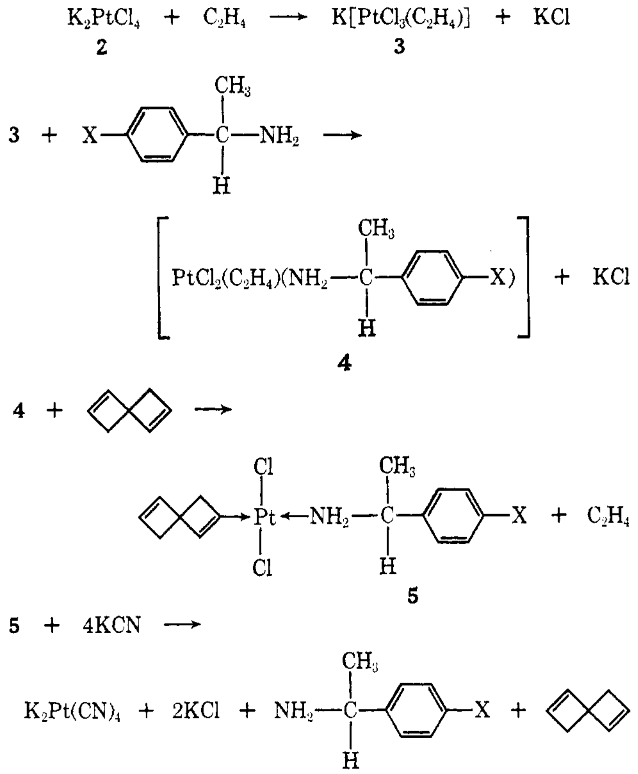
The resolution method mentioned above utilizes the principle of attaching both racemic spirocycle **1** and the optically active amine to the square planar platinum(II) to form a pair of diastereoisomers, separable by fractional crystallization. The optically active spiro hydrocarbon **1** can then be displaced from a diastereoisomer by treatment with aqueous sodium,[3a] potassium cyanide,[6] or triphenylphosphine.[3b] Evidence was obtained that spirene **1** could be partially resolved in this way. The chemistry involved in this resolution is outlined in Scheme I. Another satisfactory and potentially general method for the resolution of allenes and cyclic olefins has been developed,[8,9] based upon the method of asymmetric hydroboration described by Brown and his group.[8] Brown's kinetic resolution method rests upon the use of (+)-*sym*-tetraisopinocampheyldiborane, which has demonstrated to be a highly stereoselective hydroborating agent of unhindered cis alkenes and can be used to prepare certain optically active alcohols and alkenes of high optical purity.[10] Utilizing this reagent for the hydroboration of excess of spirene **1** we anticipated that the recovered spirocycle **1** would be enriched in one enantiomer, and this was confirmed by experiment (Scheme II).

Scheme I



a, X = (−)-H
b, X = (+)-H
c, X = (−)-NO_2

Cope's Resolution Method. Zeise's salt, potassium trichloro(ethylene)platinate(II) (**3**), was converted into

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[1] This paper represents a portion of the doctoral dissertation of L. A. Hulshof.

[2] R. Lazzaroni, P. Salvadori, and P. Pino, *Tetrahedron Lett.*, 2507 (1968).

[3] (a) A. C. Cope, K. Banholzer, H. Keller, B. A. Pawson, J. J. Whang, and H. J. S. Winkler, *J. Amer. Chem. Soc.*, **87**, 3644 (1965); (b) A. C. Cope, J. K. Hecht, H. W. Johnson, Jr., T. V. Van Auken, and H. J. S. Winkler, *ibid.*, **88**, 761 (1966).

[4] A. C. Cope, W. R. Moore, R. D. Bach, and H. J. S. Winkler, *J. Amer. Chem. Soc.*, **92**, 1243 (1970).

[5] (a) The partial resolution of a humulene complex by this method, see T. Chamberlain and M. A. McKervey, *Chem. Commun.*, 366 (1969); (b) A. Panunzi, A. de Renzi, and G. Paiaro, *Inorg. Chim. Acta*, **1**, 475 (1967).

[6] A. C. Cope, C. R. Ganellin, H. W. Johnson, Jr., T. V. Van Auken, and H. J. S. Winkler, *J. Amer. Chem. Soc.*, **85**, 3276 (1963).

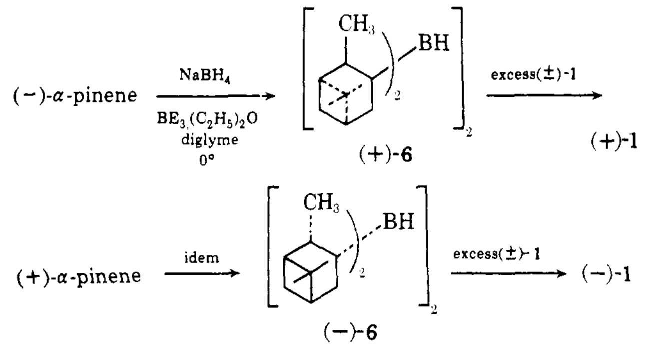
[7] See for synthesis and discussion of the spectroscopic properties of **1**: L. A. Hulshof and H. Wynberg, *J. Amer. Chem. Soc.*, **96**, 2191 (1974).

[8] G. Zweifel, N. R. Ayyangar, T. Munekata, and H. C. Brown, *J. Amer. Chem. Soc.*, **86**, 1076 (1964), and references cited therein.

[9] W. L. Waters, *J. Org. Chem.*, **36**, 1596 (1971), and ref 4 cited therein.

[10] H. C. Brown, N. R. Ayyangar, and G. Zweifel, *J. Amer. Chem. Soc.*, **86**, 397 (1964).

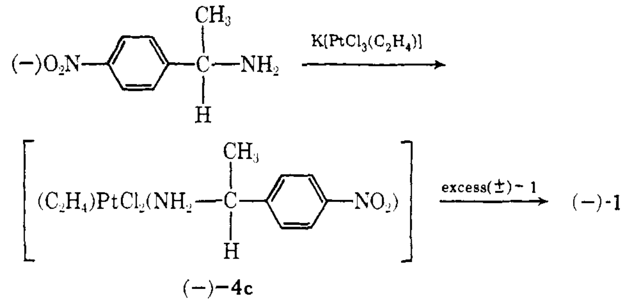
Scheme II



4a, (−)-*trans*-dichloro(ethylene)(α-methylbenzylamine)-platinum(II), according to the method described by Cope and coworkers.[6] This compound was generally obtained as a viscous oil, but purification of the complex by chromatography has occasionally been shown to give a crystalline material. Addition of racemic spirodiene **1** to a methylene chloride solution of the optically pure complex **4a** led to a hardly observable displacement of ethylene. However, evaporation of the solvent at 0° afforded the diastereomeric spirene complex **5a** as a yellow crystalline solid, even if the unpurified complex **4a** was used. The crude complex was crystallized from methylene chloride at low temperature (−70°) and from the same solvent at −80° by adding a few drops of petroleum ether until a slight turbidity set in. The crystallization was hampered by unfortunate crystallization properties. The odor of diene **1** could be detected now and then during warming up to room temperature suggesting thermal instability of the complex.[11] Consequently, the material could not be recrystallized exhaustively. Nevertheless, a change in rotation of the more and less soluble fractions was observed and decomposition of this material with aqueous potassium cyanide afforded optically active spirene **1**, $[\alpha]^{25}\text{D}$ −26° and $[\alpha]^{25}\text{D}$ +22° (CH_2Cl_2), respectively. Although $[\alpha]^{25}\text{D}$ −26° is the highest value of the optical rotation of **1** observed by this method, higher than that observed in the second method below, we feel that optically pure **1** should have a rotation of significantly greater absolute magnitude, the more so since higher specific rotations have been observed with other representatives of the rigid dissymmetric 1,4-diene class of compounds.[12]

Attempts to achieve a better resolution with complex **4b** gave only less partially resolved diene **1**. The complex **4b**, prepared from Zeise's salt and (+)-α-methylbenzylamine,[2] failed to give crystalline material. Displacement of ethylene by spirocycle **1** from this chiral complex **4b** in methylene chloride solution might have afforded a better separable complex in which both available ethylenic linkages of the diene formed a bond with two separate platinum atoms.[15] However, the fractional crystallization of the diastereomeric mixture was again thwarted by unfortunate crystallization properties as described above. Nevertheless, the more soluble fraction from the crystallization in methylene chloride containing petroleum ether at −70° furnished optically active **1** with $[\alpha]^{25}\text{D}$ +11°, $[\alpha]_{230}$ +704° (CH_2Cl_2, *n*-pentane, 1:1). From the less soluble fraction levorotatory spirene **1** could be recovered. Because of the difficulties encountered in the separation of the diastereoisomers above, another optically active amine containing platinum complex as resolving agent was chosen in an effort to obtain a more ready fractional crystallization and a broader range of more polar solvent systems.[4] For that reason, the usefulness of *p*-nitro-α-methylbenzylamine was investigated. Levorotatory *p*-nitro-α-methylbenzylamine[4] was converted to the corresponding platinum complex **4c**. A 5% excess over theory (for a 1:1 complex) of racemic spirene **1** was treated with complex **4c** in chloroform solution to give ultimately a mixture of diastereoisomers **5c**, $[\alpha]_{578}$ −39.9° (CH_2Cl_2). The reaction mixture was maintained at 0–2° for 3 days. The unreacted diene was recovered by distillation at low temperature (0–20°) giving levorotatory spirene **1** of specific rotation: $[\alpha]_{365}$ −4.2° ($CHCl_3$) as outlined in Scheme III. Dissolving the diastereoisomers in methylene chloride and repeated distillation of this mixture afforded again optically active diene **1**, $[\alpha]_{365}$ −9.5° (CH_2Cl_2). Repetition of this procedure did not furnish additional diene **1**. The total amount of the recovered olefin **1** being involved in this kinetic resolution process appeared to be the same as that derived from the theoretical quantity for a 2:1 complex **5c**.

Scheme III



Attempts to separate the residual diastereomeric mixture in order to obtain a higher optical purity of **1** than that of the kinetic resolution were again hampered by insufficient crystallization properties. However, crystallization from methylene chloride solution adding carbon tetrachloride and pentane as cosolvents until the cloud point was reached and storing at −30° gave a more and less soluble fraction from which optically active spiro olefin **1**, $[\alpha]_{365}$ +9.4° and $[\alpha]_{365}$ −1.2° (pentane), could be liberated with aqueous potassium cyanide. Thus, complete resolution of the diene *via* exhaustive recrystallization of **5** had reached an impasse, and obliged us to search after another resolving agent.

Brown's Kinetic Resolution Method. In a typical run, a suspension of (+)-**6** in diglyme was prepared from (−)-α-pinene and diborane (formed *in situ* from sodium borohydride and boron trifluoride etherate). A 25% excess (10.7 mmol) of racemic diene **1** was then added to the reaction mixture maintained at 0°. After 4 hr, the unreacted diene was recovered by evaporation and was purified by glc giving dextrorotatory

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[11] The separation of the diastereoisomers could not be followed by melting point variations. The various complexes of the diene 1 with platinum decomposed during the melting.

[12] Spiro[4.4]nona-1,6-diene[13] and 5-methylenebicyclo[2.2.1]hept-2-ene.[14]

[13] H. Gerlach and W. Müller, *Helv. Chim. Acta*, **55**, 2277 (1972).

[14] L. S. Foster, A. Moscowitz, J. G. Berger, and K. Mislow, *J. Amer. Chem. Soc.*, **84**, 4353 (1962); this compound is only differing from the mentioned spirodienes in the completely orthogonal position of the p orbitals.

[15] Compare the resolution of *cis,trans*-cycloocta-1,5-diene.[3]

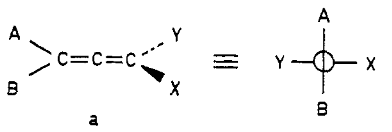


Figure 1.

diene **1** of specific rotation $[\alpha]_{436}$ +1.0°, $[\alpha]_{237}$ +30° (pentane).

In a repeated run, employing now (−)-**6** in diglyme as hydroborating agent (prepared from (+)-α-pinene and diborane) and adding a 25% excess (15.0 mmol) of *dl*-diene **1**, optically active **1** with a specific rotation $[\alpha]_{436}$ −4.9°, $[\alpha]_{365}$ − 14.6° (hexane) was recovered after 4 hr.

The level of asymmetric induction varied somewhat with the reaction conditions.[16] Running this reaction with an equivalent of *dl*-**1** and (+)-**6** on a different molar scale for 6 hr at 0° furnished enantiomeric diene **1** with $[\alpha]_{436}$ −2.2°, $[\alpha]_{365}$ −6.7° (pentane).

Improvement of this procedure[17] by consecutive asymmetric hydroboration of the optically active diene **1** to increase the rotation of **1** was not attempted since too little material was available.

The Absolute Configuration. Chiral molecules with C_2 symmetry (one twofold axis) are of interest because of their chiroptical properties (*i.e.*, rotation at the sodium D-line, ORD, and CD). Using the nature of these properties several examples of absolute configuration assignments to molecules of the chiral allene and spirane type possessing that symmetry have been described in recent years.[18] In most cases use was made of a suitable chemical correlation of the absolute configuration of the optically active C_2 symmetrical substrates with centrodissymmetric molecules of known chirality[18] and sometimes of a crystallographic method.[19,20]

Recently, Brewster[21] and Hill[22] made the assignment of the absolute configuration to the spiranes 1,1′-spirobiindan (**7**), 1,1′-spirobiindene (**8**), and 1,1′-spirobiindan-3-one (**9**) using empirical methods or deductions from chiroptical properties and relying on chemical correlation.[23] In addition, Gerlach[13] and Wagnière[24] established the absolute configuration of spiro[4.4]nona-1,6-diene (**10**) both by chemical correlation and by a combination of theoretical calculations and deductions of the rotational strength from the CD spectrum.

In this study we made an attempt to predict the chirality of spirene **1** by application of three generally accepted empirical rules and by use of the reaction scheme of an asymmetric induction pathway in a kinetic resolution step. All methods indicate a dextrorotation for the spirene with right-handed helicity.

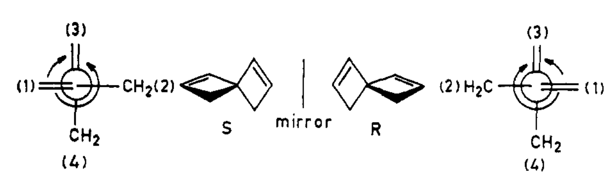
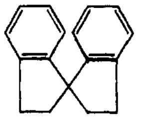


Figure 2. Application of Lowe's rule to (*S*)- and (*R*)-spiro[3.3]-hepta-1,5-diene.



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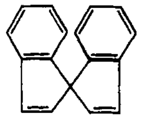

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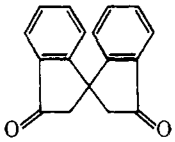

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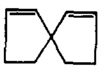

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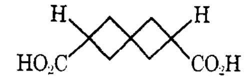

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S-(+)-**1**

R-(−)-**1**

Lowe's Rule. Lowe[25] pointed out that allenes (including those with C_2 symmetry) with the absolute configuration a (Figure 1) are dextrorotatory at the sodium D-line when A is more polarizable than B and X is more polarizable than Y. This rule has been useful in predicting the absolute configuration of a large number of chiral synthetic and natural allenes[18] with only one exception.[26] Lowe's rule is related to other models of optical activity, for example, Kirkwood's polarizability model[27] and Brewster's uniform conductor model[28] and should be in general applicable to helical systems including spiranes.[25,29,30] We have carefully examined the literature concerning Lowe's rule.[20–24,29–38] On the basis of the many failures of this rule when applied to spiranes **9**,[21,22] **10**,[13,24] **12**,[32] **13**,[35] several derivatives of **11**,[33,34] and a few of **14**[35] and **15**[20,36] we feel that no value should be attached without independent confirming evidence to the assignment of the *S* (old method)[39] or 4*R* (new method)[39] configuration to the dextrorotatory spirodiene **1** (Figure 2) with a screw pattern of right-handed helicity.

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[16] This phenomenon was also observed by W. L. Waters, W. S. Linn, and M. C. Caserio, *J. Amer. Chem. Soc.*, **90**, 6741 (1968), and by Brown, *et al.*[10]

[17] L. Porri, R. Rossi, and G. Ingrosso, *Tetrahedron Lett.*, 1083 (1971).

[18] (a) G. Krow, *Top. Stereochem.*, **5**, 31 (1970); (b) R. Rossi and P. Diversi, *Synthesis*, **5**, 25 (1973).

[19] L. A. Hulshof, A. Vos, and H. Wynberg, *J. Org. Chem.*, **37**, 1767 (1972).

[20] S. Hagishita, K. Kuriyama, K. Shingu, and M. Nakagawa, *Bull. Chem. Soc. Jap.*, **44**, 2177 (1971).

[21] J. H. Brewster and R. T. Prudence, *J. Amer. Chem. Soc.*, **95**, 1217 (1973).

[22] R. K. Hill and D. A. Cullison, *J. Amer. Chem. Soc.*, **95**, 1229 (1973).

[23] See also H. Falk, W. Fröstl, and K. Schlögl, *Tetrahedron Lett.*, 217 (1974).

[24] W. Hug and G. Wagnière, *Tetrahedron*, **28**, 1241 (1972).

[25] G. Lowe, *Chem. Commun.*, 411 (1965).

[26] P. Crabbé, E. Velarde, H. W. Anderson, S. D. Clark, W. R. Moore, A. F. Drake, and S. F. Mason, *Chem. Commun.*, 1261 (1971).

[27] J. G. Kirkwood, *J. Chem. Phys.*, **5**, 479 (1937); W. W. Wood, W. Fickett, and J. G. Kirkwood, *ibid.*, **20**, 561 (1952); H. Looyenga, Thesis, Leiden, 1955.

[28] J. H. Brewster, *Top. Stereochem.*, **2**, 1 (1967).

[29] J. H. Brewster and R. S. Jones, *J. Org. Chem.*, **34**, 354 (1969).

[30] J. H. Brewster and J. E. Privett, *J. Amer. Chem. Soc.*, **88**, 1419 (1966).

[31] H. Falk, W. Fröstl, and K. Schlögl, *Monatsh. Chem.*, **102**, 1270 (1971).

[32] G. Krow and R. K. Hill, *Chem. Commun.*, 430 (1968).

[33] H. Wynberg and J. P. M. Houbiers, *J. Org. Chem.*, **36**, 834 (1971).

[34] (a) L. A. Hulshof, A. Vos, and H. Wynberg, *J. Org. Chem.*, **38**, 4217 (1973); (b) L. A. Hulshof, H. Wynberg, B. van Dijk, and J. L. de Boer, manuscript in preparation.

[35] G. Haas, P. B. Hulbert, W. Klyne, V. Prelog, and G. Snatzke, *Helv. Chim. Acta*, **54**, 491 (1971).

[36] S. Hagishita, K. Kuriyama, M. Hayashi, Y. Nakano, K. Shingu, and M. Nakagawa, *Bull. Chem. Soc. Jap.*, **44**, 496 (1971).

[37] H. Gerlach, *Helv. Chim. Acta*, **51**, 1587 (1968).

[38] Compounds **16**, **17**, and **18** among others obey Lowe's rule.

[39] R. S. Cahn, C. Ingold, and V. Prelog, *Experientia*, **12**, 81 (1956) (old method); *Angew. Chem.*, **78**, 413 (1966) (new method).

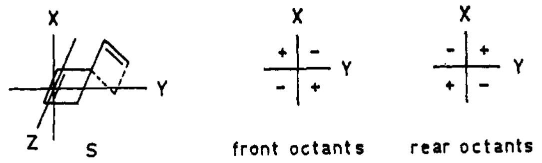
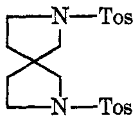


Figure 3. Octant diagram for (*S*)-spiro[3.3]hepta-1,5-diene and the corresponding octant signs (viewed along *Z* axis).



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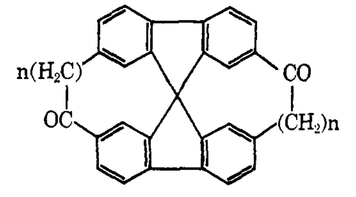

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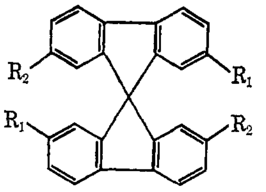

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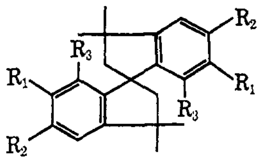

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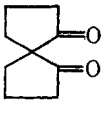

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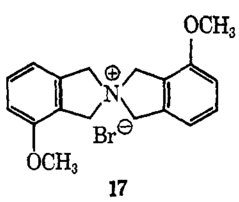

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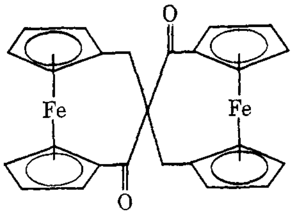

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Octant Rule. It has been shown that the CD data of a wide variety of chiral olefins are amenable to interpretation by an octant rule derived by Scott and Wrixon.[40] On the basis of a set of signs determined by this rule the absolute configuration of a considerable number of chiral olefins could be assigned, thus demonstrating that the sign of the Cotton effect of the principal $\pi-\pi^*$ transition near 200 nm may reflect the chirality about the olefinic chromophore. Assuming that the cyclobutene double bond in **1** behaves as an *isolated* olefinic linkage[41] and that the measured Cotton effect of **1** for the lowest energy optically active $\pi-\pi^*$ absorption is not interfered by inaccessible and dominating optically active higher energy transitions,[42] the octant rule predicts the *S* (or 4*R*)[39] configuration for the dextrorotatory spirene **1** (see Figure 3). As noted earlier,[44] it is important for this deduction that both olefinic bonds are considered to interact with light essentially independently.[45]

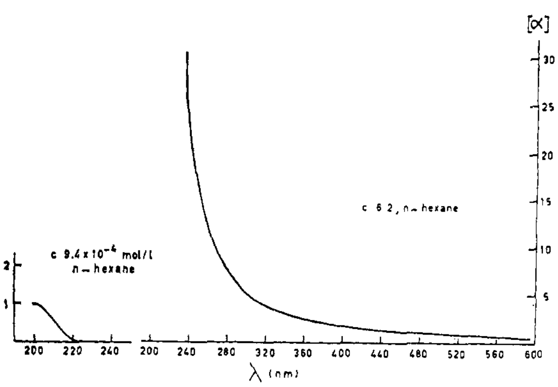

Figure 4. CD and ORD spectrum of **1**.

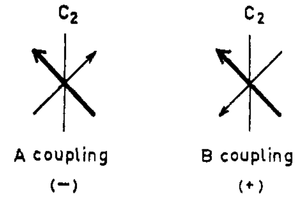

Figure 5. Modes of coupling of transition moments or polarizability axes in molecules with C_2 symmetry.

The fact that spirocycle **10** appeared to constitute an exception to this rule[13,24] might be regarded as an example that the higher energy Cotton effect is opposite in sign in the $\pi-\pi^*$ region and can control the optical activity at longer wavelengths.[46,48]

Consequently, Lowe's rule and the octant rule predict surprisingly the same chirality about the diene chromophore and are in agreement with the result of another theory of molecular rotatory power, *viz.*, the coupled oscillator theory.[28,51,52] The fact that for diene **1** a positive Cotton effect corresponds with a dextrorotation at the sodium D-line is depicted in Figure 4.

Coupled Oscillator Theory. Assuming that the two chromophores in **1** interact with one another under the influence of a light as oscillators coupled through dipole–dipole interactions,[28,51,52] then the absorption band would be split into two components corresponding to symmetrical (A) and antisymmetrical (B) modes of coupling of the transition moments (Figure 5) with Cotton effects of opposite sign. If the two modes are energetically different and this was confirmed by CNDO/2-CI calculations,[43] they will occur at different wavelengths. The situation for the cases shown in Figure 5 results in a B coupling that has the nature of a

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(40) A. I. Scott and A. D. Wrixon, *Tetrahedron*, **28**, 933 (1972), and earlier papers.

(41) A. I. Scott and A. D. Wrixon, *Chem. Commun.*, 1182 (1969).

(42) According to performed CNDO/2-CI calculations[43] the lowest energy transition is not obscured by additional discernible transitions.

(43) L. Flapper, L. A. Hulshof, and H. Wynberg, to be submitted for publication.

(44) J. A. Schellman, *J. Chem. Phys.*, **44**, 55 (1966); *Accounts Chem. Res.*, **1**, 144 (1968).

(45) If this is not the case with the two olefinic fragments then the same chirality is predicted by the concept of inherent dissymmetry.[43]

(46) Furthermore, other more complex spirodienes[47] having C_1 symmetry do not obey this rule either and this might be attributed to the existence of locally opposed senses of chirality[24] and/or to the sense of polarization of the allylic bonds.

(47) N. H. Andersen, C. R. Costin, D. D. Syrdal, and D. P. Svedberg, *J. Amer. Chem. Soc.*, **95**, 2049 (1973).

(48) In addition, the appearance of the twisted character of the double bonds in spirene **1** established by nmr spectroscopy[7] might cause the difference in chiroptical properties with spirocycle **10**.[49,50]

(49) M. Fetizon, I. Hanna, A. I. Scott, A. D. Wrixon, and T. K. Devon, *Chem. Commun.*, 545 (1971).

(50) M. Fetizon and I. Hanna, *Chem. Commun.*, 462 (1970).

(51) S. F. Mason, *Proc. Roy. Soc.*, *Ser. A*, **297**, 3 (1967).

(52) S. F. Mason, G. W. Vane, K. Schofield, R. J. Wells, and J. S. Whitehurst, *J. Chem. Soc. B*, 553 (1967), and earlier papers.

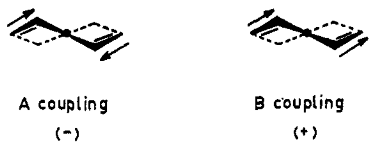

Figure 6. Coupling of long-axis transition moments or axes of polarizability in *S* (or 4*R*) spirene **1**. The twofold axis through the spiro C atom is perpendicular to the plane of the paper.

right-handed helix causing a positive Cotton effect and dextrorotation at the longest wavelength and in an A coupling with left-handed helicity producing a negative Cotton effect and levorotation.[24,28,51,52] The mode of coupling which is energetically preferable will be the one responsible for the longest wavelength Cotton effect.[24,28,51,52]

The features mentioned above have been of particular interest in attempts to correlate chirality with rotatory dispersion and circular dichroism by simple empirical relationships (the exciton model[51,52] if the interaction of the two fragments is relatively weak and the C_2-rule concept[24] if there is a strong coupling). Applying both concepts to the case of spirodiene **1**[53] its absolute configuration can be inferred. B coupling of the long-axis transition moments preferred over A coupling would give rise to a positive Cotton effect and dextrorotation at longer wavelengths for the diene **1** (see Figure 6) with right-handed helicity (*S* or 4*R* configuration). Similarly, the *S* (or 5*R*) configuration should be assigned to the dextrorotatory spirocycle **10** with right-handed helicity as well. The experiment, however, agrees well with a superposition of Cotton effects for which the rotational strength of the A transition dominates that of the B transition, thus leading to the *R* (or 5*S*) configuration for the dextrorotatory spirene **10**.[13,24]

Asymmetric Induction. The hydroboration of olefins with optically active organoboranes derived from the hydroboration of an optically active alkene in order to induce optical activity in the former olefin in a kinetic resolution step has been achieved in recent years.[56,57] The absolute configuration of **1** could in principle be deduced from the configuration of the transition state of the asymmetric hydroboration. A general scheme for the mode of asymmetric induction with (+)- and (−)-diisopinocampheylboranes **6** in reactions with cis olefins based upon the experiences of the group of Brown[58] was recently presented by Varma and Caspi.[59] From the structure and disposition in space of the various groupings in *d*- and *l*-borane **6** these authors could rationalize the reaction scheme and could predict correctly the configuration of the asymmetric products of the reaction. Evaluating their model for the case of spirodiene **1** (a cis olefin) with the assumption that attack of the borane on carbon 2 or 6,[60] which is more favorable because of steric reasons, and a four-membered transition state[61] are involved, we could make a distinction between the steric facility of both reacting configurations of the diene. A model[62] indicated that the transition state (as outlined in Figure 7) between the *S* (or 4*R*) configuration of diene **1** and *l*-borane **6** should be more favorable than the alternative case. From the observation that *d*-spirene **1** was obtained from the asymmetric induction with *d*-borane **6** prepared from *l*-α-pinene leaving behind the more reactive *l*-spirene and that *l*-spirene **1** was isolated from the reaction mixture with *l*-borane **6** leaving behind *d*-spirene, we conclude that *d*-spirene has the *S* (or 4*R*) configuration.

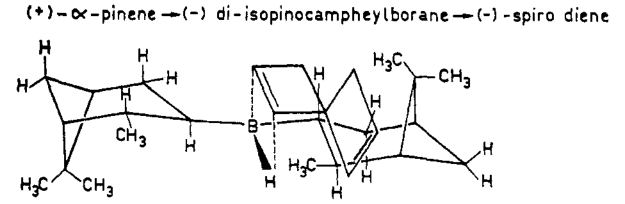

Figure 7. *S* (or 4*R*) spirene **1** reacts better with *l*-diisopinocampheylborane.

Although we feel that in general no conclusive evidence for an absolute configuration assignment is obtained by applying empirical relationships, the asymmetric induction scheme is in agreement with the assignment based upon the internally consistent rules and suggests that the assignment is correct. Furthermore, a quantum mechanical calculation[43] offers additional support for this analysis. More classical methods (*e.g.*, X-ray diffraction[63]) have to prove the present prediction, however.

Experimental Section

Boiling points are uncorrected. Melting points were determined on a Mettler FP_2 apparatus with microscope attachment at a warm-up rate of 0.2°/min. Infrared spectra were recorded on a Unicam SP 200 infrared spectrophotometer or on a Perkin-Elmer grating spectrophotometer (Model 125). Pmr spectra were recorded on a Varian A 60 instrument unless otherwise stated using tetramethylsilane as internal standard. Optical activity was measured on a Zeiss Lichtelektrisches Präzisionspolarimeter 005 or on a Perkin-Elmer Model 141 polarimeter using 1-dm or 5-cm cells. ORD spectra were taken on a Bendix Ericsson polarmatic 62, provided with a 150-W Xenon lamp and a 0.1-dm cell. Concentrations are given as grams/100 ml. The measurements were taken at room temperature. Ellipticity was measured with a Roussel-Jouan dichrograph II, provided with a deuterium lamp.

Zeise's Salt (3). Potassium trichloro(ethylene)platinate(II) (Zeise's salt) was prepared by treatment of an acidified solution of potassium tetrachloroplatinate(II) (**2**) with ethylene in a Parr apparatus according to a slightly modified procedure of Chatt and Searle.[64] **2** (10 g, 24 mmol) was dissolved in 10 ml of ethanol and 45 ml of water and acidified by 5 ml of concentrated hydrochloric acid. This solution was shaken in a Parr apparatus under 2 atm pressure of ethylene for a week. The yellow solution was filtered

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[53] The orientation of the transition moment of the separate olefinic moieties might be derived from that in styrene,[54] norbornadiene,[55] and cyclohexene.[55]

[54] (a) J. Tanaka, *Bull. Chem. Soc. Jap.*, **36**, 833 (1963); (b) S. F. Mason and G. W. Vane, *Tetrahedron Lett.*, 1593 (1965).

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and removal of solvent under reduced pressure at room temperature gave 9.5 g of a crude mixture of Zeise's salt and potassium chloride; pmr (D_2O) δ 5.35 (t, J = 34 Hz).

(−)- and (+)-*trans*-Dichloro(ethylene)(α-methylbenzylamine)platinum(II) (4a and 4b) were prepared according to Cope, *et al.*,[6] starting with 1-g runs of the crude mixture described in the preceding section and adding under analogous conditions 0.35 g (2.9 mmol) of freshly distilled (−)- and (+)-α-methylbenzylamine (Aldrich), respectively. In contrast to the work-up procedure of these authors, the precipitate at pH 5 was not filtered but the aqueous solution was extracted with methylene chloride. The organic layer was washed with water, dried on magnesium sulfate, and evaporated, yielding 0.98–1.04 g (85% with respect to the amine) of (−)- and (+)-*trans*-dichloro(ethylene)(α-methylbenzylamine)platinum (II) (**4a** and **4b**) as viscous oils, $[\alpha]_D$ varying from −12.5 to −16.8° (c 1.0, methylene chloride) and $[\alpha]^{21}_D$ +15.5 and 16.9° (c 1.0, methylene chloride), respectively. These platinum complexes were generally obtained as viscous oils. Purification of these compounds by chromatography over a silica gel column with methylene chloride gave only in one similar run a crystalline material with $[\alpha]_{578}$ −14.3°, $[\alpha]_{546}$ −16.6° (c 1.0, methylene chloride): mp 71.5–73.6°; pmr (CD_2Cl_2) δ 7.39 (s, 5 H), 4.62 (t, J = 30.5 Hz), 1.78 (d, J = 6.5 Hz, 3 H). The infrared spectra of the oils were, however, identical with that of this crystalline material.

(−)-*trans*-Dichloro(ethylene)(p-nitro-α-methylbenzylamine)platinum(II) (4c) was prepared according to a method described by Cope, Moore, Bach, and Winkler.[4] The N-acetyl derivative of (−)-α-methylbenzylamine (Aldrich) was prepared by this method in 97% yield: mp 100.5–102°; $[\Phi]_{578}$ −159.0° (c 13.1, acetone); pmr (CD_3COCD_3) δ 7.26 (s, 5 H), 5.03 (quintet, J = 7 Hz, 1 H), 1.87 (s, 3 H), 1.38 (d, J = 7 Hz, 3 H). Nitration afforded (−)-N-acetyl-p-nitro-α-methylbenzylamine in a yield of 91%: $[\Phi]_{578}$ −122.9° (c 10.9, acetone); pmr (CD_3COCD_3) δ 7.66 (AB quartet, J_{AB} = 8.5 Hz, 4 H), 4.95 (quartet, J = 7 Hz, 1 H), 1.92 (s, 3 H), 1.26 (d, J = 7 Hz, 3 H). The compound was hydrolyzed to give (−)-p-nitro-α-methylbenzylamine in an overall yield of 45% with respect to the starting amine: bp 115–117° (0.5 mm), $[\alpha]_{578}$ −16.1° (neat); pmr (carbon tetrachloride) δ 7.73 (AB quartet, J_{AB} = 8.5 Hz, 4 H), 4.19 (quartet, J = 7 Hz, 1 H), 1.43 (s, 2 H), 1.33 (d, J = 7 Hz, 3 H). To a cooled solution of 1.04 g (6.3 mmol) of p-nitro-α-methylbenzylamine, $[\alpha]_{578}$ −16.1° (neat), in 12.5 ml of water acidified with dilute hydrochloric acid was added to a cooled solution of 2.31 g of crude Zeise's salt (see **3** above) in 25 ml of 3% aqueous potassium chloride containing 0.5 ml of 10% hydrochloric acid. Work-up at pH 5 afforded 2.17 g (4.7 mmol or 75%) of **4c**: mp 93–99°; $[\alpha]_{578}$ −41.7° (c 2.5, methylene chloride); pmr (CD_2Cl_2) δ 7.92 (AB quartet, J_{AB} = 7 Hz, 4 H), 4.82 (quartet, J = 7 Hz, 1 H), 4.60 (t, J = 31 Hz), 1.78 (d, J = 7 Hz, 3 H) (lit.[4] mp 92–100°, $[\alpha]^{24}_D$ +40.7° (c 2.3, methylene chloride)).

***d*- and *l*-Spiro[3.3]hepta-1,5-diene (1) a. From (−)-*trans*-Dichloro(ethylene)(α-methylbenzylamine)platinum(II) (4a).** Racemic spirodiene **1** (1.32 g, 13.4 mmol) was added to a cooled solution of 3.06 g (7.4 mmol) of (−)-*trans*-dichloro(ethylene)(α-methylbenzylamine)platinum(II) (**4a**), $[\alpha]^{25}_D$ −12.5° (c 1.0, methylene chloride), in 30 ml of methylene chloride. The reaction mixture was stirred for 40 hr, while the color changed from yellow to orange. Evaporation of the solvent under reduced pressure and at ambient temperature afforded 3.64 g (7.4 mmol) of (−)-dichloro(spiro[3.3]hepta-1,5-diene)(α-methylbenzylamine)platinum(II) (**5a**) as a crystalline material: mp 129–135° dec; $[\alpha]^{25}_D$ −8.9° (c 1.0, methylene chloride); ir (KBr) had a band at 720 cm^{-1} (characteristic for cis olefin); pmr (Varian XL 100, CS_2 and CH_2Cl_2) δ 7.28 (s, aromatic protons), 6.08 (s, vinylic protons), 2.67 (d, J = 2 Hz, allylic protons), 4.50 (t, J = 32 Hz), 1.68 (d, J = 7 Hz). The fractional crystallization was carried out by dissolving the complex **5a** in methylene chloride at room temperature and storing this solution at −70° until crystallization occurred or by adding petroleum ether as cosolvent to a solution of the complex **5a** in methylene chloride at ambient temperature until the cloud point was reached and storing this solution at −70°. The laborious procedure was employed for several runs and was hampered by instability of the complex. Repeated recrystallization was therefore not attempted. After one crystallization the less soluble fraction was isolated $[\alpha]^{25}_D$ −11° (c 1.0, methylene chloride). The d enantiomer of spirene **1** was liberated by decomposition of this fraction with aqueous potassium cyanide at 0° and subsequent removal of the amine by extraction from the organic layer with acid at 0° in the way as described by Cope, *et al.*[6] The recovered diene **1** had a rotation of $[\alpha]^{26}_D$ +22° (c 0.3, methylene chloride) and was identified by comparison of its glc retention time. The concentration of **1** was determined by glc using n-heptane as an internal standard. The more soluble fraction with $[\alpha]_D$ −17.5° (c 1.0, methylene chloride) afforded the l enantiomer of spirene **1** in the same way as described above: $[\alpha]^{26}_D$ −26° (c 0.2, methylene chloride).

b. From (+)-*trans*-Dichloro(ethylene)(α-methylbenzylamine)platinum(II) (4b). Racemic spirene **1** (0.74 g, 8 mmol) was added to a cooled solution of 2.99 g (7.2 mmol) of (+)-**4b**, $[\alpha]^{21}_D$ +15.5° (c 1.0, methylene chloride), in 25 ml of methylene chloride. Employing a similar procedure as described in the preceding section a, 2.96 g (6.2 mmol) of (+)-**5b** was obtained with $[\alpha]^{23}_D$ +12.7° (c 1.0, methylene chloride), mp 90–110° dec. Crystallization of this yellow solid being hampered by unfortunate crystallization properties was performed as above resulting in a more soluble fraction with $[\alpha]_D$ +10.9° (c 1.0, methylene chloride), mp 95–100° dec. This fraction was decomposed with aqueous potassium cyanide and work-up as described above afforded dextrorotatory diene **1**: $[\alpha]^{25}_D$ +11°, $[\alpha]^{25}_{250}$ +704° (c 0.3, methylene chloride–pentane, 1:1). Recovery of levorotatory spirene **1** from the less soluble fraction with $[\alpha]^{23}_D$ +14.4° (c 1.0, methylene chloride–methanol, 1:1) was achieved by the same procedure. The specific rotation of this material was not determined.

c. From (−)-Dichloro(ethylene)(p-nitro-α-methylbenzylamine)platinum(II) (4c). Racemic spirene **1** (0.20 g, 2.2 mmol) was added to a cooled solution of 0.96 g (2.1 mmol) of **4c**, $[\alpha]_{578}$ −41.7° (c 2.5, methylene chloride), in 10 ml of chloroform. The reaction mixture was stirred for 3 days at 0–2°. Filtration of the solution and evaporation at ambient temperature gave 0.99 g of a yellow mixture of diastereoisomers, mp 100–120°, $[\alpha]_{578}$ −39.9° (c 2.3, methylene chloride). The yield of platinum complex **5c**, the absence of olefinic signals in the pmr spectrum, and lack of the infrared absorption at *ca.* 720 cm^{-1} suggest that both olefinic linkages are connected to two separate platinum atoms forming a bridged complex μ-(spiro[3.3]hepta-1,5-diene)tetrachloro-bis(p-nitro-α-methylbenzylamine)diplatinum(II).[3] From the distillate received at −180°, unreacted levorotatory diene **1** was obtained: $[\alpha]_{365}$ −4.2° (c 1.0, chloroform). Dissolving of the mixture of diastereoisomers in methylene chloride and repeated evaporation afforded additional diene **1** with $[\alpha]_{365}$ −9.5° (c 0.1, methylene chloride) to an aggregate amount of 1.05 mmol. Crystallizations from benzene and cyclohexane as cosolvent at −30°, from chloroform and carbon tetrachloride at −30°, and from acetone and pentane at −80° were not successful in achieving detectable quantities of optical active diene **1** after decomposition, as described above, of the partly separated mixture of diastereoisomers. However, crystallization from methylene chloride adding carbon tetrachloride and pentane as cosolvents until a slight turbidity set in and storing at −30° in a refrigerator gave a less and a more soluble fraction with $[\alpha]_{578}$ −45.1° (c 1.4, methylene chloride) and $[\alpha]_{578}$ −34.4° (c 1.8, methylene chloride), respectively. Decomposition of these fractions with aqueous potassium cyanide and careful distillation at 15 mm and ambient temperature furnished a methylene chloride solution, containing the spirene **1** with $[\alpha]_{365}$ −1.2° (c 3.3, methylene chloride) and $[\alpha]_{365}$ +9.4° (c 0.9, methylene chloride), respectively. l- and d-spirene **1** were identified by comparison of their glc retention time and the concentration of the diene in these fractions was determined by complete bromination at 0° to the tetrabrominated product; mass spectrum (70 eV) m/e 412; pmr (carbon tetrachloride) δ 5.1–4.0 (m, 4 H) and 3.9–2.2 (m, 4 H); $[\alpha]_{436}$ +0.2° (c 14.9, methylene chloride) and $[\alpha]_{436}$ −1.3° (c 3.9, methylene chloride), respectively.

***d*- and *l*-Spiro[3.3]hepta-1,5-diene (1). a. *d*-Spirene 1 from Asymmetric Induction with *d*-Diisopinocampheylborane (6).** The asymmetric hydroboration of **1** was carried out essentially by the method of Brown and coworkers.[8–10] Boron trifluoride etherate (freshly obtained by distillation) (1.22 g, 8.6 mmol) was added slowly to a stirred solution of 2.33 g (17.1 mmol) of (−)-α-pinene, $[\alpha]_D$ −47.0° (neat) (EGA), and 6.4 mmol of sodium borohydride (4% excess of theoretical) in 10 ml of diglyme (purified by distillation from lithium aluminum hydride) at 0°. After one night stirring under nitrogen atmosphere at 0°, 0.98 g (10.7 mmol) of racemic spirene **1** as a 30% solution in diglyme was added to the stirred borane mixture at −15°. After 4 hr of stirring at 0°, 1 ml of water was added and the volatile components were removed by evaporation at ambient temperature and 0.3 mm pressure. The distillate was received at −70 and −180° and contained spirene **1** and some unreacted α-pinene; 0.19 g (2 mmol or 38% recovery of theoretical excess) of dextrorotatory spirene **1** was obtained from purification by preparative glc with $[\alpha]_{536}$ +0.7° $[\alpha]_{237}$ +30° (c 6.2, n-pentane), CD $\Delta\epsilon$ + *ca.* 1 (200 nm) (c 9.4×10^{-4} mol/l., n-hexane). The residual organoborane was oxidized with alkaline hydrogen peroxide according to Brown and coworkers.[10] Attempts to isolate any possibly formed alcohols by extraction with ether were not successful. Gas chromatographic analysis of the residual mixture revealed that four new products were present which were not identified.

b. *l*-Spirene 1 from Asymmetric Induction with *l*-Diisopinocampheylborane (6). Asymmetric hydroboration of 1.34 g (15.0 mmol) of racemic spirene **1** in 10 ml of diglyme with a borane mixture prepared from 3.26 g (23.9 mmol) of (+)-α-pinene, $[\alpha]_{578}$ +48.4° (neat) (Aldrich), 0.35 g (9.0 mmol or 4% excess of theoretical) of sodium borohydride, and 1.70 g (12.0 mmol) of boron trifluoride etherate was performed as described above in section a for *in situ* hydroboration in diglyme and gave after purification by glc 14 mg of diene **1**, $[\alpha]_{578}$ −1.3°, $[\alpha]_{546}$ −2.5°, $[\alpha]_{436}$ −4.9°, $[\alpha]_{365}$ −14.6° (*c* 0.8, *n*-hexane). To the residual organoborane mixture 1 g (9 mmol) of *n*-oct-1-ene was added at 0°. After the mixture was stirred a further 3 hr at 0°, the volatile components were removed in the same way as described above furnishing 0.13 g of additional purified diene **1**, $[\alpha]_{565}$ −3.7° (*c* 8.4, methanol). Three reiterations of this procedure afforded 0.15 g of additional purified spirene **1**, $[\alpha]_{365}$ −3.5° (*c* 2.9, *n*-hexane). The total amount of recovered **1** was therefore 0.36 g or 54% of theoretical excess. Dextrorotatory diene **1** could not be isolated by this asymmetric hydroboration process. Asymmetric hydroboration of 0.87 g (9.4 mmol) of racemic spirene **1** in 8 ml of diglyme with a borane mixture prepared from 2.57 g (18.8 mmol) of (+)-α-pinene (Aldrich), 0.28 g of sodium borohydride, and 1.34 g (9.4 mmol) of boron trifluoride etherate was performed as described above and gave in the first instance 27 mg of diene **1**, $[\alpha]_{365}$ −6.7° (*c* 1.8, pentane). Repeated addition of 1 g of *n*-oct-1-ene afforded 0.99 g with $[\alpha]_{365}$ −6.0° (*c* 6.5, pentane), 0.03 g with $[\alpha]_{365}$ −5.8° (*c* 2.1, pentane), and 0.02 g with $[\alpha]_{365}$ −5.6° (*c* 1.6, pentane) of additional purified diene **1** to a total amount of 0.18 g or 42% of theoretical excess.

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Mechanisms of Elimination Reactions. XXII. Stereochemistry of Elimination Reactions of 3-Hexyltrimethylammonium Ion Promoted by Phenoxide Bases. The Role of Ion Pairing[1]

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Abstract: The *trans*-3-hexene from 3-hexyltrimethylammonium iodide and potassium phenoxide in mixtures of *tert*-butyl alcohol and dimethyl sulfoxide is formed *via* both syn and anti paths, the proportion of syn elimination ranging from 14% at 0% to 38% at 95% dimethyl sulfoxide. In contrast, the *cis*-3-hexene is the result of 94–98% anti elimination. With substituted phenoxides, the syn path for formation of *trans*-3-hexene ranges from 26% for *p*-MeO to 69% for *p*-NO_2 in 95% dimethyl sulfoxide. The cation of the metal phenoxide affects the proportion of syn elimination. In 20% dimethyl sulfoxide the syn → trans path ranges from 34% for potassium to 74% for lithium phenoxide. Temperature and base concentration also affect the proportion of syn elimination, but the effect of dicyclohexyl-18-crown-6 ether is negligible. These results are all compatible with a mechanism in which ion-paired metal phenoxide favors anti, but free, or more loosely ion-paired, phenoxide favors syn elimination. An ion-pair exchange equilibrium between the metal phenoxide and the quaternary ammonium salt fits these and other observations. The relative importance of free ions, solvent-separated ion pairs, and contact ion pairs is discussed.

The syn–anti dichotomy, in which E2 reactions give trans olefins partly or mainly by syn elimination and cis olefins almost entirely by anti elimination, is by now quite firmly established for eliminations from quaternary ammonium salts under a variety of conditions. It was first noticed with medium-ring compounds[2–5] but has also been found to occur with open-chain compounds.[6–12] A number of structural and environmental factors seem to be conducive to syn elimination, but one of the earliest to be implicated was base strength. The more strongly basic the medium, the greater is the propensity toward syn elimination.[5,7–9,11,13] While the qualitative correlation is quite clear, not only the base strength but also the solvent and the steric requirements of the base were varied in most of these studies. The present research

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