Chirality in Carbonium Ions, Carbanions, and Radicals

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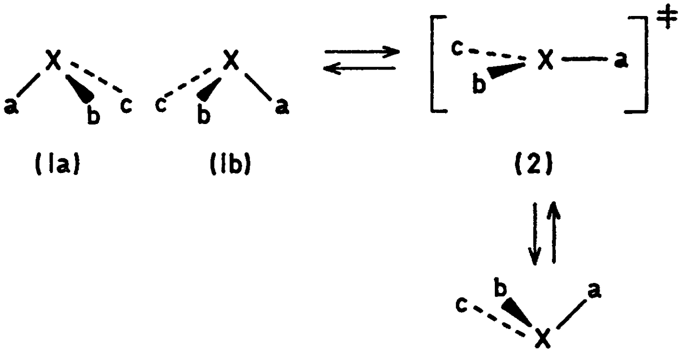
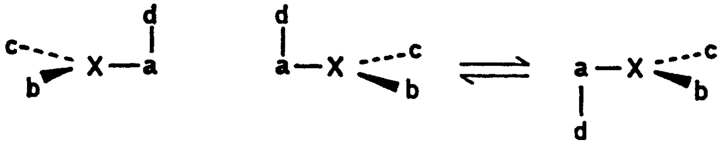
1 Introduction

In the absence of another chiral centre in the system, a carbonium ion, carbanion, or radical is chiral if either of two conditions is fulfilled. First, a system (1a) with a non-planar trisubstituted centre bonded to three different groups is non-superimposable on its mirror image (1b) and thus is chiral. Second, a system (4a) with a planar centre bonded to three different groups, one of which is not conically symmetrical, is non-superimposable on its mirror image (4b) and thus is chiral. The barrier to racemization in system (1) is the barrier to inversion of the central atom X through the a–b–c plane; *e.g.* (1b) inverts to structure (3) which is superimposable upon (1a), the enantiomer of (1b). The barrier to racemization in system (4) is the barrier to rotation about the a–X bond; *e.g.* (4b) rotates to structure (5), which is superimposable upon (4a), the enantiomer of (4b).



(1a) (1b) (2) (3)



(4a) (4b) (5)

Ab initio and semi-empirical calculations[1] of the geometries of methyl cation, anion, and radical all predict a planar carbonium ion and all but one[1b] predict a planar radical. All but one[1e] of the studies predict a non-planar carbanion. Although various geometries and inversion barriers have been predicted, the most acceptable result [1h] suggests an H—C—H angle of 106.8 ° and an inversion barrier of 5.2 kcal mol^{-1}. Carbonium ions[2a] and radicals[2b] were found in spectroscopic studies to be planar. Studies[3] of the reactivities of bridgehead carbonium ions, radicals, and carbanions suggest that carbonium ions have a strong preference for planarity, that radicals have a weak preference for planarity, and that carbanions have a strong preference for non-planarity. Thus chirality due to non-planarity of the trisubstituted centre is probably restricted to carbanion systems.

A barrier to racemization of at least 16–20 kcal mol^{-1} is necessary if a system is to be resolved at room temperature.[4] Thus unless the barrier to inversion (1b) → (3) can be raised above the usual 5 kcal mol^{-1} range or the barrier to rotation (4b) → (5) can be raised above the usual 3 kcal mol^{-1} range,[5] chiral carbonium ions, carbanions, and radicals will exist as racemic mixtures at room temperature. There are several systems in which such increased barriers have been observed. These systems and the mechanisms proposed to account for the increase in the inversion or rotation barrier of each are the topics of this review.

In some cases, the ability of an intermediate to retain its configuration has been measured directly, either by observing its racemization rate or by determining the barrier to the racemizing process by dynamic n.m.r. (d.n.m.r.).[6] However, in most studies, the optical activity of the intermediate has been detected by the product rotation method, *i.e.* by isolation of an optically active product from an optically active starting material. The observed rotation of the product of such a reaction reflects not only the ability of the intermediate to retain its configuration but also the stereoselectivities of the formation and capture reactions. Unless these reactions are 100% stereoselective, the net racemization observed in the product will be greater than the racemization of the intermediate during the reaction.

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[1] (*a*) V. Buss, P. von R. Schleyer, and L. C. Allen, submitted to *J. Amer. Chem. Soc.*; (*b*) W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, 1971, **93**, 808; (*c*) R. E. Kari and I. G. Csizmadia, *J. Chem. Phys.*, 1969, **50**, 1443; (*d*) M. J. S. Dewar and M. Shanshal, *J. Amer. Chem. Soc.*, 1969, **91**, 3654; (*e*) T. P. Lewis, *Tetrahedron*, 1969, **25**, 4117; (*f*) M. S. Gordon and H. Fischer, *J. Amer. Chem. Soc.*, 1968, **90**, 2471; (*g*) K. B. Wiberg, *ibid.*, p. 59; (*h*) P. Millie and G. Berthier, *Internat. J. Quantum Chem.*, 1968, **2S**, 67.

[2] (*a*) G. A. Olah, J. R. DeMember, A. Commeyras, and J. L. Bribes, *J. Amer. Chem. Soc.*, 1971, **93**, 459; (*b*) O. Simamura in 'Topics in Stereochemistry', ed. N. L. Allinger and E. L. Eliel, Interscience, New York, 1969, Vol. IV, pp. 1–37, and references therein.

[3] R. C. Fort, jun., and P. von R. Schleyer in 'Advances in Alicyclic Chemistry', ed. H. Hart and G. J. Karabatsos, Academic Press, New York, 1966, Vol. I, pp. 283–370; T. Kawamura, T. Koyama, and T. Yonezawa, *J. Amer. Chem. Soc.*, 1973, **95**, 3220.

[4] E. L. Eliel, 'Stereochemistry of Carbon Compounds', McGraw-Hill Book Co., New York, 1962, p. 156.

[5] M. Hanack, 'Conformation Theory', Academic Press, New York, 1965, pp. 22–41.

[6] G. Binsch in 'Topics in Stereochemistry', ed. N. L. Allinger and E. L. Eliel, Interscience, New York, 1968, Vol. III, pp. 97–192.

A recent review[7] of pyramidal atomic inversion points out the problems introduced into the study of inversion barriers in carbanions by the covalent nature of many carbon–metal bonds and by the existence of many organometallic compounds as molecular aggregates in solution. These factors also affect studies of barriers to racemization by bond rotation. Ion pairing introduces similar problems into the study of carbonium ions whereas reactions within the solvent cage introduce similar problems into the study of radicals. All these effects are solvent-dependent as was shown[8] for the stereochemistry of base-catalysed hydrogen–deuterium exchange *via* the carbanion, which varied from 99% net retention to 60% net inversion with changes in solvent composition. This review includes only systems for which there is reasonable evidence that barriers to racemization are independent of interactions with the solvent.

2 Cyclopropyl Anion and Radical

In the planar transition state (2) for inversion, and thus for racemization, of (1), the a—X—b angle is larger than in non-planar (1), hence the barrier to inversion can be raised by fixing one angle at much less than 120° by incorporating it into a small ring. *Ab initio* calculations[1a] on methyl cation, anion, and radical show that if one H—C—H angle of the carbanion is fixed at 120° the ion is non-planar with an inversion barrier of 4.6 kcal mol^{-1}. If the angle is fixed at 90°, however, the inversion barrier is increased to 19.9 kcal mol^{-1}. Similarly, with one angle fixed at 120°, the radical is planar; but when the angle is fixed at 90°, it is non-planar with an inversion barrier of 1.2 kcal mol^{-1}. For the carbonium ion, however, planarity is favoured in both cases and favoured more heavily with one angle fixed at 90°. *Ab initio* calculations on cyclopropyl anion predict a non-planar structure and a 20.85 kcal mol^{-1} inversion barrier.[9b] One[9a] of two semi-empirical calculations on the cyclopropyl system predicts a non-planar carbanion with a 14.2 kcal mol^{-1} inversion barrier. The other[1d] predicts a non-planar radical with a 4.8 kcal mol^{-1} inversion barrier and a non-planar carbanion with a 36.6 kcal mol^{-1} inversion barrier.[10]

In agreement with these calculations, experimental results imply a non-planar cyclopropyl anion with an inversion barrier high enough to prevent racemization at room temperature and a cyclopropyl radical which is either planar or non-planar with a low inversion barrier. The carbonium ion undergoes facile ring-opening to the allyl cation[12] and thus cannot be studied.

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[7] J. B. Lambert in 'Topics in Stereochemistry', ed. N. L. Allinger and E. L. Eliel, Interscience, New York, 1971, Vol. VI, pp. 19–105.

[8] D. J. Cram, J. L. Mateos, F. Hauck, A. Langemann, K. R. Kopecky, W. D. Nielsen, and J. Allinger, *J. Amer. Chem. Soc.*, 1959, **81**, 5774.

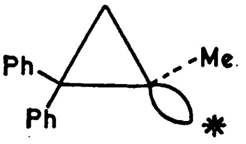
[9] (*a*) A. Rauk, J. D. Andose, W. G. Frick, R. Tang, and K. Mislow, *J. Amer. Chem. Soc.*, 1971, **93**, 6507; (*b*) D. T. Clark and D. R. Armstrong, *Chem. Comm.*, 1969, 850.

[10] Calculations[1b,11] indicate that the barrier to inversion of the cyclopropenyl carbanion should be higher than that of the cyclopropyl carbanion owing to the anti-aromatic nature of the planar transition state. However, there is no experimental evidence that this is the case.

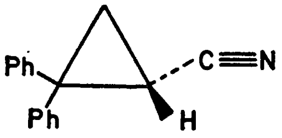
[11] D. T. Clark, *Chem. Comm.*, 1969, 637.

[12] R. Breslow in 'Molecular Rearrangements', ed. P. de Mayo, Interscience, New York, 1963, Part I, pp. 233–294.

The 1-methyl-2,2-diphenylcyclopropyl anion (6) has been produced with a variety of leaving groups in numerous solvent–base systems with reaction times up to 7.5 h. Net retention was 46—100%.[13] All comparable reactions in open-chain systems yielded racemized products except two reactions at low temperatures in hydrocarbon solvents.[14] Since many of the results on (6) were obtained at high temperatures in more dissociating ethereal solvents, the cyclopropyl anion must have a much higher barrier to inversion than the open-chain carbanion. However, since the solvents were not highly dissociating, the species involved was almost certainly not the free ion, so no estimate of the magnitude of the inversion barrier is possible.



(6) * = –
(7) * = •



(8)

Studies in more highly dissociating solvents reveal a type of solvent interaction other than ion-pair dissociation, which can complicate studies of carbanion chirality. Replacing the methyl group of carbanion (6) with groups capable of stabilizing the negative charge by resonance lowers the energy of the planar transition state for inversion. Thus the carbanion generated from 1-cyano-2,2-diphenylcyclopropane (8) racemized in less than 15 s; under the same conditions (6) showed high retention of configuration.[15b] However, (8) underwent base-catalysed hydrogen–deuterium exchange in methanol, t-butyl alcohol, or DMSO–methanol with 99.9—97.2% net retention.[15a] Unlike the order expected from a dissociation effect, retention was highest in methanol and lowest in DMSO–methanol.

The difference between the complete racemization observed in non-dissociating, aprotic solvents and the high net retention observed in dissociating, protic solvents is explained[15a] in terms of an increased barrier to inversion imposed by hydrogen bonding of the protic solvent with the charge-bearing sp^3 orbital, as observed in other systems.[7] The increase in racemization in t-butyl alcohol is due to the lesser ability of that solvent to form hydrogen bonds.[15a] DMSO cannot form hydrogen bonds with the carbanion but increased barriers to inversion due to the presence of non-hydrogen-bonded complexes are known.[7] Since hydrogen bonding does not seem to affect barriers to rotation,[7] this effect

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[13] J. B. Pierce and H. M. Walborsky, *J. Org. Chem.*, 1968, **33**, 1962; H. M. Walborsky, J. F. Impastato, and A. E. Young, *J. Amer. Chem. Soc.*, 1964, **86**, 3283; F. J. Impastato and H. M. Walborsky, *ibid.*, 1962, **84**, 4838.

[14] D. Y. Curtin and W. J. Koehl, jun., *J. Amer. Chem. Soc.*, 1962, **84**, 1967; R. L. Letsinger, *ibid.*, 1950, **72**, 4842.

[15] (*a*) H. M. Walborsky and J. M. Motes, *J. Amer. Chem. Soc.*, 1970, **92**, 2445; (*b*) H. M. Walborsky and F. M. Hornyak, *ibid.*, 1955, **77**, 6026.

should be much less in other chiral carbanion systems which racemize by rotation or simultaneous inversion–rotation mechanisms.

In the decomposition of (−)-(*R*)-1-methyl-2,2-diphenylcyclopropanoyl peroxide, all products of the 1-methyl-2,2-diphenylcyclopropyl radical (7) formed outside the solvent cage are racemic.[16] Within the solvent cage, 1-methyl-2,2-diphenylcyclopropane formed by the disproportionation of the two radicals to alkane and alkene shows 31—37% net retention. The rate constant for inversion of the cyclopropyl radical determined by e.s.r. is 10^8—10^{10} s^{-1}.[17] Since the disproportionation rate constant is probably not that high, much of the optical retention of the product is probably due to constraints placed on the radical by the solvent cage.

Both *cis*- and *trans*-1-bromo-2-methylcyclopropane react with n-butyllithium to yield 100% retained product after reaction with ethylene oxide and react with metallic lithium to yield partially racemized products with 8—38% retention of configuration.[18] The racemization with metallic lithium occurs at the intermediate radical formed in the first of two successive one-electron transfers. An interpretation[18] claiming that the observed retention is due to the intrinsic optical stability of that radical requires a much higher barrier to inversion than would be expected from the data on the reaction of (7). More likely, the retention is due to surface[19] and solvent-cage effects which hold the radical in such a position that the second electron transfer takes place on the same side of the cyclopropyl ring as the first.

3 Triarylmethyl Cations, Anions, and Radicals

Because overlap with the delocalized electrons of the aryl rings is greatest with *p*-orbitals, a planar structure for triarylmethyl carbanions and radicals will be greatly stabilized relative to the non-planar structures whose sp^3 orbitals overlap less well. Thus the ionic or radical centre of triarylmethyl anions and radicals is either planar or inverting so rapidly between its two non-planar conformers that it is effectively stereochemically planar. The structure of triphenylmethyl perchlorate has been determined by *X*-ray crystallography and the carbonium ion was planar.[20c] The structure of triphenylmethyl radical has been determined by electron diffraction in the gas phase[20b] and that of tri-*p*-nitrophenylmethyl radical has been determined by *X*-ray crystallography.[20a] In both cases, the radical centre was nearly planar with a bond angle of 118.0°. There have been no such studies of a triarylmethyl carbanion.

Since the three aromatic rings of triarylmethyl systems neither occupy the same plane as the three bonds to the central carbon (hereafter called the

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[16] H. M. Walborsky and J.-C. Chen, *J. Amer. Chem. Soc.*, 1971, **93**, 671.

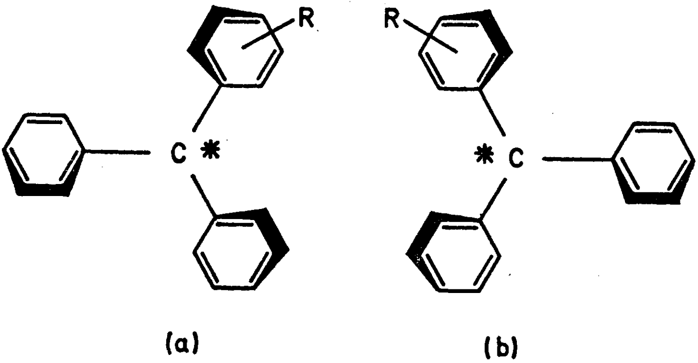
[17] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 1963, **39**, 2147.

[18] M. J. S. Dewar and J. M. Harris, *J. Amer. Chem. Soc.*, 1969, **91**, 3652.

[19] H. M. Walborsky and M. S. Aronoff, *J. Organometallic Chem.*, 1973, **51**, 55; H. M. Walborsky and A. E. Young, *J. Amer. Chem. Soc.*, 1964, **86**, 3288.

[20] (*a*) P. Andersen and B. Klewe, *Acta Chem. Scand.*, 1967, **21**, 2599; (*b*) P. Andersen, *ibid.*, 1965, **19**, 629; (*c*) A. H. Gomes de Mesquita, C. H. MacGillavry and K. Eriks, *Acta Cryst.*, 1965, **18**, 437.

reference plane) nor are perpendicular to that plane, but instead have propeller-like structures,[20] symmetrically substituted triarylmethyl anions, cations, and radicals can exist in the enantiomeric right- and left-handed propeller forms (9a) and (9b) which are interconvertible by rotation of the aryl groups through a transition state in which they are parallel or perpendicular to the reference plane.[21] Thus the barrier to these three simultaneous rotations is the barrier to racemization. For the substituted carbonium ion (10),[23] the barrier to interconversion of the enantiomers determined by d.n.m.r. is 12.5 kcal mol^{-1}. For the substituted radical (11),[24] the barrier to interconversion of the enantiomers determined by electron nuclear double resonance[25] is 5.5 kcal mol^{-1}.



(9) R = H, ✱ = +

(10) R = *m*, or *p*$-CF_2H$, ✱ = +

(11) R = *o*$-CH_2SMe$, ✱ = •

These barriers are too low to prevent racemization at room temperature. Substituents in the *ortho*-position are unlikely to have a dramatic effect on the barrier since the steric interactions that the substituents would impose on a transition state in which the *ortho*-substituted ring rotates through the reference plane can be avoided by a transition state in which the ring becomes perpendicular to the reference plane.[22] However, triaryl systems in which the three aryl groups are different and at least one aryl group has an *ortho*- or *meta*-substituent

[21] The possible mechanisms for interconversion of isomers in this and other triaryl systems have recently been analysed.[22] For a discussion of which mechanism actually operates, see ref. 23.

[22] D. Gust and K. Mislow, *J. Amer. Chem. Soc.*, 1973, **95**, 1535.

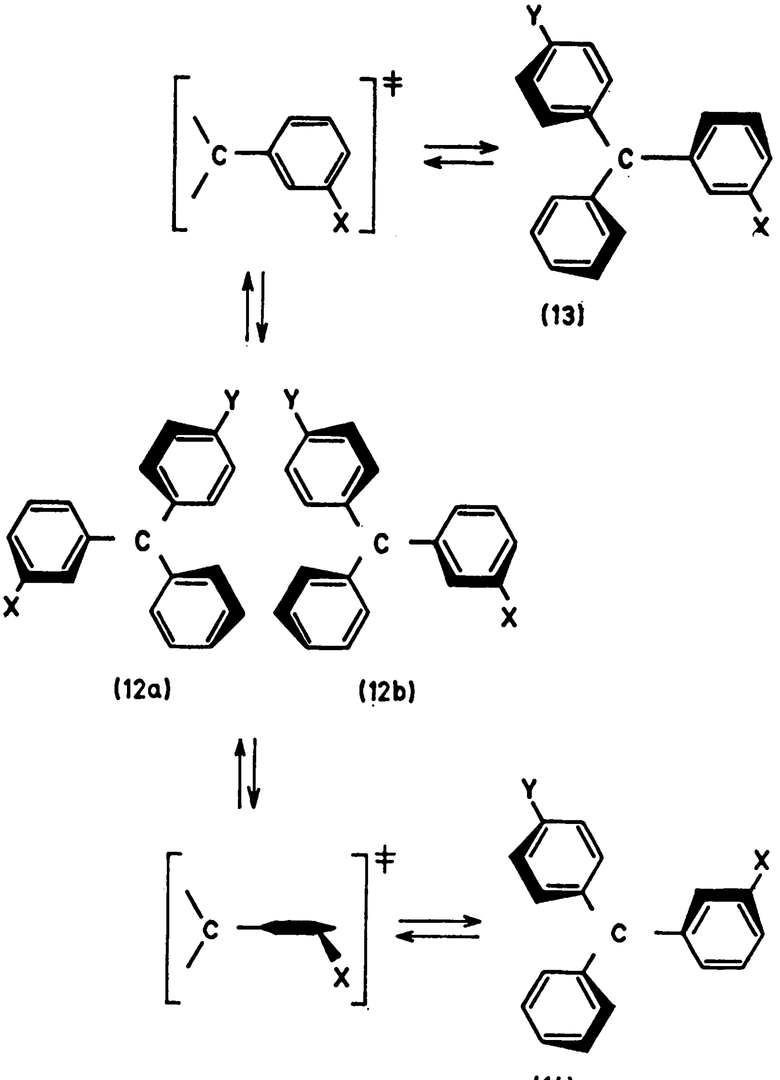
[23] J. W. Rakshys, jun., S. V. McKinley, and H. H. Freedman, *J. Amer. Chem. Soc.*, 1971, **93**, 6522.

[24] J. S. Hyde, R. Breslow, and C. DeBoer, *J. Amer. Chem. Soc.*, 1966, **88**, 4763.

[25] J. S. Hyde in 'Magnetic Resonance in Biological Systems', ed. A. Ehrenberg, B. G. Malström, and T. Vännård, Pergamon Press, Oxford, 1967, pp. 63–84; J. S. Hyde, *J. Chem. Phys.*, 1965, **43**, 1806.

possess an element of chirality separate from the propeller chirality described above.[22]

System (12a) is non-superimposable on its mirror image (12b). If (12b) undergoes rotation of the three aryl groups through a transition state in which the ring bearing the *meta*- (or *ortho*-) substituent is parallel to the reference plane, structure (13) results which is superimposable upon (12a), the enantiomer of (12b). However, if (12b) undergoes rotation of the three aryl groups through a



(13)

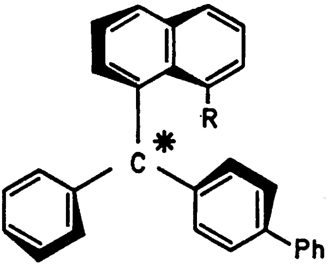
(12a)

(12b)

(14)

transition state in which the ring bearing the *meta*-substituent is perpendicular to the reference plane, structure (14) results, which is non-superimposable upon (12a) even though they have the same configuration in terms of propeller chirality; that is, (12a) and (14) are diastereomers. Thus (12) must racemize through a transition state in which a ring with an *ortho*- or *meta*-substituent becomes parallel to the reference plane, a transition state which should be more sensitive to steric hindrance to rotation than one in which the ring is perpendicular to the reference plane. It is clear that this chirality is independent of propeller chirality if we consider the case in which the three aryl rings of (12) are perpendicular to the reference plane. This destroys propeller chirality, yet (12a) is not superimposable upon (12b).

This element of chirality also operates in triaryl systems with four bonds to the central carbon,[22] and racemization barriers of greater than 26 kcal mol^{-1} have been observed[26] in such systems by d.n.m.r. However, the only triaryl systems with a trisubstituted centre for which this chirality has been found are phenylbiphenyl-α-naphthylmethyl cation (15)[27] and phenylbiphenyl-1-(8-methylnaphthyl)methyl cation (16)[28] and anion (17).[29]



(15) R = H, * = +
(16) R = Me, * = +
(17) R = Me, * = −

Observation of a mass-law effect shows that the hydrolysis of phenylbiphenyl-α-naphthylmethyl benzoate takes place through free dissociated ion (15). Yet the solvolysis of optically active benzoate yields alcohol with 33—52% net retention.[27] The barrier to racemization of ion (15) is the barrier to rotation of the naphthyl group.

However, the optical activity of the product depends not only on the rate of racemization of ion (15) but also on the ability of the starting material to form

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[26] S. V. McKinley, P. A. Grieco, A. E. Young, and H. H. Freedman, *J. Amer. Chem. Soc.*, 1970, **92**, 5900, and references therein.

[27] B. L. Murr and C. Santiago, *J. Amer. Chem. Soc.*, 1968, **90**, 2964; 1966, **88**, 1826.

[28] (*a*) B. L. Murr and L. W. Feller, *J. Amer. Chem. Soc.*, 1968, **90**, 2966; (*b*) L. W. Feller, Ph.D. Thesis, The Johns Hopkin University, 1968.

[29] J. W. Henderson, Ph.D. Thesis, The Johns Hopkin University, 1971.

one enantiomer stereospecifically and on the ability of the naphthyl group to direct the capturing reagent to only one face. Assuming that water attacks both faces of (15), the barrier to racemization is >9 kcal mol^{-1}.[27]

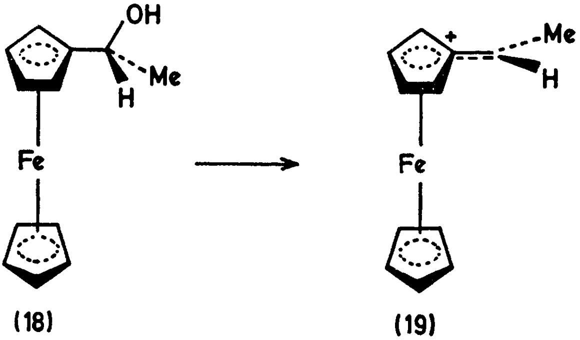
The substitution of a methyl group at position 8 of the naphthyl ring increases the barrier to rotation of the naphthyl group. Carbonium ion (16) is so optically stable that its rotation can be observed directly.[28] The carbonium ion produced by ionization of *d*-phenylbiphenyl-1-(8-methylnaphthyl)methanol in sulphuric acid showed $[\alpha]_{365}$ 1940°, $[\alpha]_{436}$ 3160° (1.24×10^{-5} mol l^{-1}). The ion showed no racemization after 2 h at −20 °C.

At room temperature in sulphuric acid, ion (16) underwent ring sulphonation to yield an ion with the opposite sign of rotation. However, once the reaction was complete, the rotation of the solution remained constant apparently indefinitely at room temperature.[28b] Thus the barrier to racemization of (16) is in the same range as that of compounds which are chiral by virtue of an asymmetric carbon.

A preliminary study[29] of phenylbiphenyl-l-(8-methylnaphthyl)methyl anion (17) indicates the presence of a similar but smaller barrier to racemization. Results on the stereochemistry of phenylbiphenyl-l-(8-methylnaphthyl)methyl radical are not yet available.

4 Ferrocenylmethyl Cation

In the formation of a carbonium ion α to a ferrocenyl group, the leaving group departs *anti* to the iron atom.[30] Thus (−)-(*R*)-1-ferrocenylethanol (18) ionizes stereospecifically in acidic solutions to form only enantiomer (19) of the chiral l-ferrocenylethyl cation. The barrier to racemization of (19) is the barrier to rotation about the carbon–ferrocenyl bond which is increased by resonance interaction with the ferrocenyl group. Ion (19) and its enantiomer show $[\alpha]^{25}_{587}$ = ± 395° (C = 0.1 in CF_3CO_2H) with a 24.5 kcal mol^{-1} barrier to racemization.[31]



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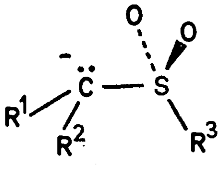
[30] G. W. Gokel, D. Marquarding, and I. K. Ugi, *J. Org. Chem.*, 1972, **37**, 3052; E. A. Hill and J. H. Richards, *J. Amer. Chem. Soc.*, 1961, **83**, 4216.

[31] T. D. Turbitt and W. E. Watts, *J.C.S. Chem. Comm.*, 1973, 182.

5 Carbanions α to Sulphur

Carbanions formed α to sulphonyl (20),[32] sulphinyl (21),[33] sulphenyl (22),[34] and sulphonium (23)[35] groups are capable of yielding optically active products under conditions which produce racemic products in other systems. In all these systems, the barrier to racemization is the barrier to C—S bond rotation if the carbanion centre is planar or the barrier to carbanion inversion with C—S bond rotation if the carbanion is non-planar.



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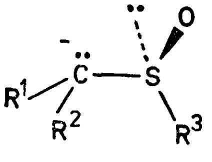

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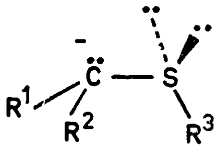

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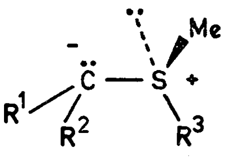

(23)

If the carbanion centre is planar, (24) is the only chiral staggered conformer. Racemization takes place *via* rotation about the C—S bond, (24a) → (24b). If

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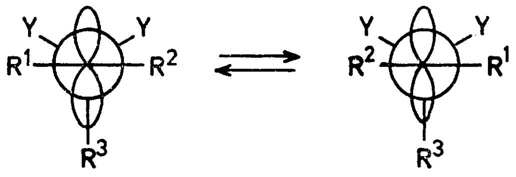
[32] (*a*) E. J. Corey and T. H. Lowry, *Tetrahedron Letters*, 1965, 803; (*b*) E. J. Corey and T. H. Lowry, *ibid.*, p. 793; (*c*) E. J. Corey and E. T. Kaiser, *J. Amer. Chem. Soc.*, 1961, **83**, 490; (*d*) J. N. Roitman and D. J. Cram, *ibid.*, 1971, **93**, 2225; (*e*) D. J. Cram, R. D. Trepka and P. St. Janiak, *ibid.*, 1966, **88**, 2749; (*f*) D. J. Cram, D. A. Scott, and W. D. Nielsen, *ibid.*, 1961, **83**, 3696; (*g*) M. D. Brown, M. J. Cook, B. J. Hutchinson, and A. R. Katritzky, *Tetrahedron*, 1971, **27**, 593; (*h*) R. R. Fraser and F. J. Schuber, *Chem. Comm.*, 1969, 1474.

[33] (*a*) R. Viau and T. Durst, *J. Amer. Chem. Soc.*, 1973, **95**, 1346; (*b*) T. Durst, R. Viau, and M. R. McClory, *ibid.*, 1971, **93**, 3077; (*c*) T. Durst, R. R. Fraser, M. R. McClory, R. B. Swingle, R. Viau, and Y. Y. Wigfield, *Canad. J. Chem.*, 1970, **48**, 2148; (*d*) R. R. Fraser, F. J. Schuber, and Y. Y. Wigfield, *J. Amer. Chem. Soc.*, 1972, **94**, 8795; (*e*) K. Nishihata and M. Nishio, *Tetrahedron Letters*, 1972, 4839; (*f*) K. Nishihata and M. Nishio, *J. C. S. Perkin II*, 1972, 1730; (*g*) R. Lett and A. Marquet, *Tetrahedron Letters*, 1971, 3255; (*h*) B. J. Hutchinson, K. K. Anderson, and A. R. Katritzky, *J. Amer. Chem. Soc.*, 1969, **91**, 3839; (*i*) J. E. Baldwin, R. E. Hackler, and R. M. Scott, *Chem. Comm.*, 1969, 1415; (*j*) E. Bullock, J. M. W. Scott, and P. P. Golding, *ibid.*, 1967, 168; (*k*) S. Wolfe and A. Rauk, *ibid.*, 1966, 778; (*l*) D. J. Cram and S. H. Pine, *J. Amer. Chem. Soc.*, 1963, **85**, 1096.

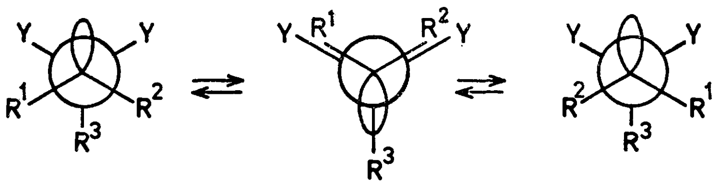
[34] (*a*) E. L. Eliel, A. Abatjoglou, and A. A. Hartman, *J. Amer. Chem. Soc.*, 1972, **94**, 4786; (*b*) A. A. Hartman and E. L. Eliel, *ibid.*, 1971, **93**, 2572; (*c*) E. L. Eliel, personal communication. See also R. T. Wragg, *Tetrahedron Letters*, 1969, 4959.

[35] (*a*) G. Barbarella, A. Gabesi, and A. Fava, *Helv. Chim. Acta*, 1971, **54**, 2297; (*b*) G. Barbarella, A. Gabesi, and A. Fava, *ibid.*, p. 341.

the carbanion centre is non-planar, all conformers are chiral. Racemization involves both carbanion inversion and C—S bond rotation, either simultaneously or stepwise. Stepwise racemization is shown for non-planar conformer (25).



(24a) (24b)



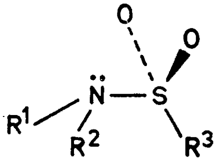
(25a) (25b)

If the first step in racemization is inversion, this structure is formed; if the first step is rotation, the structure with R^1 and R^2 reversed is formed.

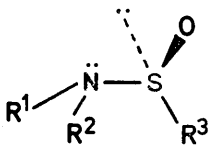
Y = O or an electron pair

Findings on the stereochemical properties of other systems which, like (20)–(23) have electron pairs or polar bonds on adjacent atoms have been generalized into two rules.[36] First, electron pair–electron pair, electron pair–polar bond, and polar bond–polar bond interactions significantly increase the rotation–inversion barrier in such systems. Second, the most stable conformer in such systems is the one which contains the maximum number of *gauche* interactions between the electron pairs or polar bonds.

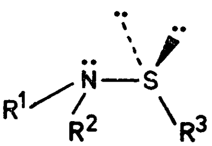
The first rule has been experimentally verified for numerous systems[36] including sulphonamides (26), sulphinamides (27), and sulphenamides (28), the isoelec-



(26)



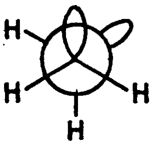
(27)



(28)

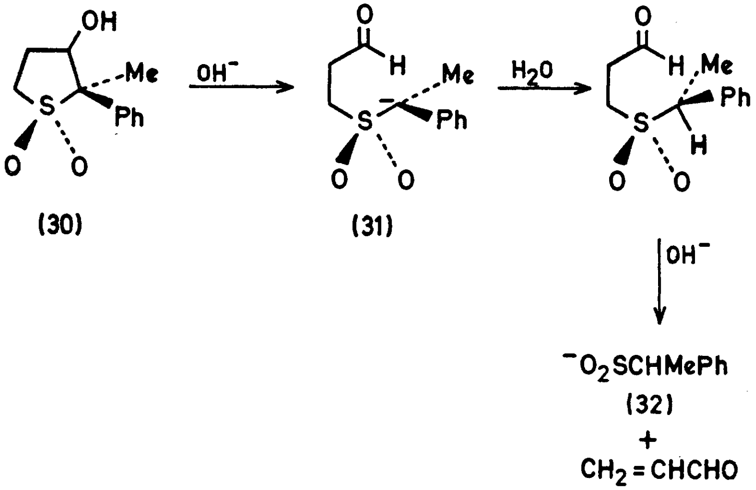
[36] S. Wolfe, A. Rauk, L. M. Tel, and I. G. Csizmadia, *J. Chem. Soc.* (*B*), 1971, 136, and references therein.

tronic nitrogen analogues of (20)—(22), respectively. The action of the second rule, known as the *gauche* effect,[37] can be seen in the preference[38] of hydrazine for conformer (29), the only conformer which contains an electron pair–electron pair *gauche* interaction. The barrier to rotation or rotation–inversion in (20)—(23) is undoubtedly the same as that found for (26)—(28) and other systems with electron pairs or polar bonds on adjacent atoms. A theoretical explanation of the nature of this barrier and of the interactions which produce the *gauche* effect has recently been provided.[37]



(29)

Ab initio calculations on α-sulphonyl,[39] α-sulphinyl,[40] and α-sulphenyl[41] carbanions predict that the most stable conformer in each case is that predicted by the *gauche* effect. The experimental verification of this predicted conformational preference is discussed below for each system.



(30) **(31)** **(32)**

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[37] S. Wolfe, *Accounts Chem. Res.*, 1972, **5**, 102.

[38] T. Kasuya and T. Kojima, *Proc. Internat. Symp. Mol. Struct. Spectroscopy*, Tokyo, 1962, C404; A. Yamaguchi, I. Ichishima, T. Shimanouchi, and S.-I. Mizushima, *J. Chem. Phys.*, 1959, **31**, 843.

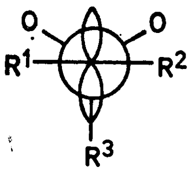
[39] S. Wolfe, A. Rauk, and I. G. Csizmadia, *J. Amer. Chem. Soc.*, 1969, **91**, 1567.

[40] A. Rauk, S. Wolfe, and I. G. Csizmadia, *Canad. J. Chem.*, 1969, **47**, 113.

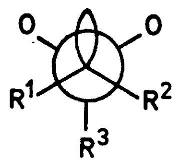
[41] S. Wolfe, A. Rauk, L. M. Tel, and I. G. Csizmadia, *Chem. Comm.*, 1970, 96.

A. α-Methylsulphonyl Anions.—Base-catalysed cleavage of 3-hydroxy-2-methyl-2-phenylthiolan 1,1-dioxide (30) *via* the sulphonyl carbanion (31) yielded 1-phenylethane sulphinate (32) of 90—100% inverted configuration.[32b] Base-catalysed cleavage in open-chain systems proceeded with 98—100% retention of configuration.[32a] This complete change in stereochemistry was taken[32b] as proof that the observed inversion in the reaction of (30) is not due to blocking of one face of the ion by the leaving group but reflects the preference of α-sulphonyl carbanions for a conformation in which the electron pair of the carbanion is directed along the bisector of the O–S–O angle, as predicted by the *gauche* effect.

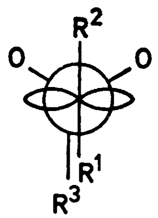
Planar conformer (33)[32c,f] and non-planar conformer (34),[39] both of which have their electron pair directed along the bisector of the O–S–O angle, have been proposed as the preferred conformer of the α-sulphonyl carbanion. *Ab initio* calculations[39] on the hypothetical hydrogen methyl sulphonyl anion (36)



(33)



(34)



(35)

(36): (33), (34), or (35), $R^1 = R^2 = R^3 = H$

predict that (34) with an H–C–H angle of 115° is 2.4 kcal mol^{-1} more stable than (33) but there is no experimental verification for this preference. Rather there is evidence[32a] that an increase in the planarity of an α-sulphonyl carbanion does not decrease its barrier to racemization. The rate of exchange of 1-phenylethyl phenyl sulphone (37) exceeds that of 2-octyl phenyl sulphone (38) by a factor of about 10^4, implying that the carbanion centre of (37) is more

$PhSO_2CHMePh$ (37)

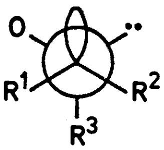
$PhSO_2CHMeBu^n$ (38)

nearly sp^2-hybridized to permit the favourable π overlap of the phenyl groups with the *p*-orbital. However, in spite of this increase in planarity, the barrier to racemization is slightly higher in the carbanion formed from (37) than in the carbanion formed from (38).

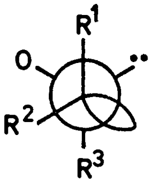
The difference between (33) and (34) is subtle and refers only to the conformation of the ion and not to the barrier to its racemization. The potential energy surface calculated[39] for (36) indicates that it 'racemizes' by simultaneous rotation and inversion *via* the same transition state (35) through which (33) racemizes.

Probably the hybridization at the carbanion centre in α-sulphonyl carbanion varies netween *sp*^{3} and *sp*^{2} depending on the nature of the substituents R^1 and R^2.

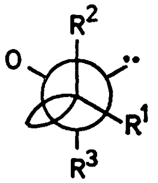
B. α-Methyl Sulphinyl Anions.—Since an α-sulphinyl carbanion contains a chiral sulphoxide group, α-sulphinyl carbanions with opposite configurations at carbon are diastereomeric rather than enantiomeric if the configuration at sulphur remains constant. This intrinsic diastereomerism makes them and the α-methyl sulphonium anions (see below) intrinsically different from the other systems covered by this article. They are included because of the close relationship of the barrier to interconversion of their diastereomeric carbanions with the barrier to interconversion of the enantiomeric carbanions of the sulphonyl and sulphenyl systems. All discussions[33,40] of the stability order of α-sulphinyl carbanions have been in terms of the three diastereomeric non-planar conformers (39)—(41). A strong argument[33d] has been made in favour of a non-planar carbanion centre rather than a planar one but there are no experimental data that cannot be explained in terms of either a planar or non-planar carbanion centre.



(39)



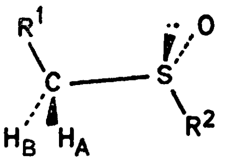
(40)



(41)

(42): (39), (40), or (41), $R^1 = R^2 = R^3 = H$

Ab initio calculations[40] on the hypothetical hydrogen methyl sulphinyl anion (42) are in agreement with the prediction of the *gauche* effect. Conformer (39), which experiences the maximum number of *gauche* interactions, is predicted to be 1.6 kcal mol^{-1} more stable than (40) and 12 kcal mol^{-1} more stable than (41), which represents an energy maximum. Experimental determinations of this stability order have centred on the study of compounds of type (43) by two approaches: measurements of the relative rates of base-catalysed hydrogen–deuterium exchange of H_A and H_B by n.m.r. and quenching with electrophilic reagents of the carbanions formed by the reaction of (43) with alkyl-lithium.



(43)

To interpret such results, several factors must be known:[36] (i) the absolute stereochemical relationship of the chiral centre at sulphur and the chiral centre created at carbon; (ii) the chemical shift assignments of H_A and H_B (in the n.m.r. experiments only); and (iii) the conformation in which the system reacts.

Although attempts have been made to determine the conformation through which (43) reacts in conformationally free systems, the most reliable results are expected to be those obtained on conformationally rigid systems in which the conformation in which (43) reacts is unambiguously known.[42] The experimentally determined relative stabilities of conformers (39)—(41) are shown in the Table along with the theoretical stability order.

Table *Relative stabilities of α-sulphinyl carbanions*

Method	*Solvent*	*Order*	*Ref.*
Theory	gas phase	(39) > (40) > (41)	40
H–D exchange	Bu^{t}OD	(41) > (40)[a]	33*d*
H–D exchange	Bu^{t}OD	(39) ~ (40) ~ (41)[a]	33*h*
H–D exchange	CD_3OD	(40) > (41)[a]	33*d*
H–D exchange	CD_3OD	(40) > (39) > (41)[a]	33*h*
H–D exchange	D_2O	(40) > (41),[a] (40) > (39)[a]	33*g*
H–D exchange	D_2O	(40) > (39) > (41)[a]	33*h*
H–D exchange	DMSO–CD_3OD	(39) ~ (40) ~ (41)[a]	33*h*
quenching	THF	(40) > (39) > (41)	33*e*
quenching	THF	(39) > (40) > (41)	33*a*

[a] Determined for conformationally rigid systems.

Some correlations among the results are discernible but they are not consistent and agreement with the theoretical order is rare, apparently because solvent effects, which are neglected in the theoretical calculations, are the predominant factor in the determination of the preferred conformation for α-sulphinyl carbanions. In one system,[33c] the ratio of the diastereomeric quenching products was reversed from 14.2 : 1 to 0.22 : 1 by changing the solvent. In another system,[33d] the relative stability of the carbanions was changed from (41) > (40) to (40) > (41) by a change of solvent.

Although the theoretically predicted stability order has not been confirmed experimentally, the predicted high angular dependence for α-sulphinyl carbanion stability has been verified.[33d] A difference of 40° in the orientation of two otherwise identical protons in a rigid system caused a thousand-fold difference in their exchange rates even though both of the resulting carbanions would formally be in conformation (39).

C. α-Methyl Sulphenyl Anions.—The *gauche* effect and *ab initio* calculations[41] on the hypothetical hydrogen methyl sulphenyl anion (46) predict that conformer (44) is preferred over conformer (45). This prediction has been verified experi-

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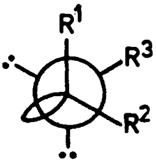
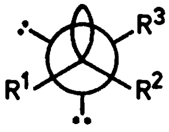
[42] Results in open-chain systems have, however, important applications in the synthesis of new chiral centres *via* optically active sulphoxides. See ref. 33*b*,*f*.



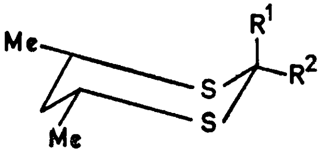
(44)



(45)

(46): (44), or (45), $R^1=R^2=R^3=H$

mentally by studies[34] on the ionization of the C-2-substituted *cis*-4,6-dimethyl-1,3-dithianes (47)—(52) with n-butyl-lithium followed by quenching with electrophilic reagents. In this system, the carbanion with the charge-bearing orbital equatorial is in conformer (44) (R^2 and R^3 being members of the six-membered ring) with respect to both sulphur atoms. The carbanion with the charge-bearing orbital axial is in conformer (45) with respect to both sulphur atoms.



(47) $R^1=R^2=H$

(48) $R^1=H$, $R^2=D$

(49) $R^1=R^2=D$

(50) $R^1=D$, $R^2=H$

(51) $R^1=H$, $R^2=Bu^t$

(52) $R^1=Bu^t$, $R^2=D$

Ionization of (47) followed by quenching with deuteriated hydrochloric acid yielded >99% equatorially deuteriated (48).[34b] Similarly, ionization of (49) yielded only (50) after quenching with hydrochloric acid.[34b] A lower limit can be set for the magnitude of the equatorial preference of the carbanion since ionization of the dithiane (51) with a t-butyl group in the equatorial position yielded, after quenching, over 99% (52) with the t-butyl group in the axial position.[34c] Since the equatorial preference of the t-butyl group at C-2 in a 1,3-dithiane is > 2.7 kcal mol^{-1},[43] the equatorial preference of the charge-bearing orbital must be at least 5 kcal mol^{-1} to account for the observed product distribution.[34c]

D. α-Methyl Sulphonium Anions.—The diastereotopic α-protons H_A and H_B in 1-methylthiolanium iodide (53) undergo base-catalysed hydrogen–deuterium

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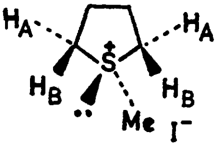
[43] E. L. Eliel and R. O. Hutchins, *J. Amer. Chem. Soc.*, 1969, **91**, 2703.

exchange in D_2O at relative rates of 30 : 1.[35b,34a] However, the conformational mobility of the system between the envelope and half-chair conformers does not allow unambiguous determination of the preferred conformation of the intermediate α-sulphonium carbanion. No rate difference was observed in the analogous six- and seven-membered ring systems.[35a]



(53)