tion by phenyl is vastly superior in stabilizing cyclopentadienyl ions, but not so much so in the pyramidal forms. Substitution at a base position in the pyramidal ions (X) is better than at the apex (XI). (1) and (2) may be generalized to several substituents. The more stable dimethyl IV has both substituents in basal positions (XIII) rather than one apical (XIV), consistent with the monomethyl species, but contradicting Masamune's observations[7a] and Hoffmann's extended Hückel calculations.[18] Pentamethyl substitution stabilizes all forms markedly, favoring the pyramidal ion (XVI) slightly over cyclopentadienyl (XV). The effect is not nearly enough to offset the large difference in stabilities of the parent ions, and XV is still of lower energy. The separation between singlet and triplet pentamethylcyclopentadienyl cations (XV *vs.* XVII) is smaller than that in the parents.

Acknowledgments. W. J. H. thanks the Centre de Recherches, Roussel Uclaf, for a generous fellowship. The work at Princeton was supported by grants from the National Science Foundation and Hoffmann-La Roche, Nutley, N. J.

(18) R. Hoffmann, private communication, cited in ref 7a.

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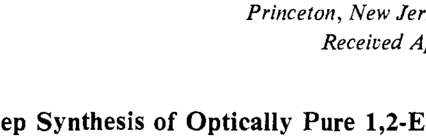
Received April 7, 1973

A One-Step Synthesis of Optically Pure 1,2-Ethano Bis Sulfoxides and Phosphine Oxides *via* the Copper-Promoted Oxidative Dimerization of Chiral Sulfinyl and Phosphinyl Carbanions

Sir:

Optically active ethano-bridged disulfoxides and diphosphine dioxides are useful as ligands in coordination chemistry and as key synthetic intermediates.[1] We have developed a practical and versatile one-step synthesis which furnishes either enantiomer of these substances in high enantiomeric purity.

The synthetic strategy consisted of assembling two subunits of these substituted ethanes, each containing a chiral center at sulfur or phosphorus, *i.e.*, the enantiomerically pure methyl-substituted sulfoxides or phosphine oxides. Our goal was realized by the copper-promoted oxidative coupling[2] of the α-carbanions derived from the monofunctional precursors, as depicted in the following scheme.



$$R_1\overset{\overset{O}{\|}}{\underset{\underset{R_2}{|}}{M}}CH_3 \xrightarrow[\text{base}]{\text{strong}} R_1\overset{\overset{O}{\|}}{\underset{\underset{R_2}{|}}{M}}CH_2^- \xrightarrow[\text{salt}]{\text{Cu}} (R_1\overset{\overset{O}{\|}}{\underset{\underset{R_2}{|}}{M}}CH_2)_2$$

M = S (R_2 = electron pair) or P

The practicality of this procedure stems from the ready availability of the precursors in a state of high enantiomeric purity,[3] and from the absence of significant loss of stereochemical integrity not only in the sulfinyl[3b,4] and phosphinyl[3a] carbanions, but also in the intermediate species present in the coupling reaction.

The present synthetic method represents a dramatic departure from and improvement over former approaches.[5,7,9] Our method circumvents the deficiencies inherent in the earlier methods and furthermore guarantees the absolute configuration of the products.[10]

A typical experimental procedure follows. A stirred solution of (+)-(*R*)-ethylmethylphenylphosphine oxide[3a] (2.51 g, 14.9 mmol), $[\alpha]^{27}D$ +24° (*c* 0.83, CH_3OH) (*ca.* 95% optically pure), in 60 ml of dry tetrahydrofuran was cooled to −78° and treated portionwise with *n*-butyllithium in hexane (16.4 mmol), under an inert atmosphere (N_2). After 25 min, dry copper(II) chloride (2.38 g, 17.7 mmol) was added. The mixture was kept at −78° for 15 min, allowed to warm (25°), and saturated with oxygen for 10 min. After hydrolysis (10% H_2SO_4), the mixture was extracted ($CHCl_3$), and the combined extracts were washed (dilute aqueous NH_3, then H_2O), dried (K_2CO_3), and evaporated. Distillation (Kugelrohr, 150° (0.02 Torr)) removed 300 mg of impure starting material. Chromatography of the residue on silica gel afforded 2.0 g of crude 1,2-bis(ethylphenylphosphinyl)ethane (**1**), upon elution with $CHCl_3$–EtOH. Treatment with acetone separated 85 mg (3%) of *meso*-**1**. Recrystallization (acetone–$CHCl_3$) provided an analytical sample,[11] mp 191–192°,

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(1) For example, see S. K. Madan, C. M. Hull, and L. J. Herman, *Inorg. Chem.*, **7**, 491 (1968); B. J. Brisdon, *J. Chem. Soc., Dalton Trans.*, 2247 (1972); S. S. Sandhu and R. S. Sandhu, *Inorg. Chim. Acta*, **6**, 383 (1972); F. Mani and M. Bacci, *ibid.*, **6**, 487 (1972).

(2) (a) T. Kauffmann and D. Berger, *Chem. Ber.*, **101**, 3022 (1968); (b) T. Kauffmann, M. Schönfelder, and J. Legler, *Justus Liebigs Ann. Chem.*, **731**, 37 (1970), and references cited therein.

(3) (a) O. Korpiun, R. A. Lewis, J. Chickos, and K. Mislow, *J. Amer. Chem. Soc.*, **90**, 4842 (1968); (b) J. Jacobus and K. Mislow, *ibid.*, **89**, 5228 (1967), and references therein. (c) For an extension of the scope of the Grignard synthesis[3a] of optically active phosphine oxides, see W. B. Farnham, R. K. Murray, Jr., and K. Mislow, *ibid.*, **92**, 5809 (1970).

(4) (a) G. Tsuchihashi, S. Mitamura, S. Inoue, and K. Ogura, *Tetrahedron Lett.*, 323 (1973); (b) G. Tsuchihashi, S. Iriuchijima, and M. Ishibashi, *ibid.*, 4605 (1972).

(5) Resolutions of racemates[6] have been reported for disulfoxides: (a) M. Cinquini, S. Colonna, and F. Taddei, *Boll. Sci. Fac. Chim. Ind. Bologna*, **27**, 231 (1969); (b) E. V. Bell and G. M. Bennett, *J. Chem. Soc.*, 1 (1930); (c) G. Farina, F. Montanari, and A. Negrini, *Gazz. Chim. Ital.*, **89**, 1548 (1959). Although there have been no reported resolutions of diphosphine dioxides, an ethano-bridged diphosphonium salt has been resolved: L. Horner, J. P. Bercz, and C. V. Bercz, *Tetrahedron Lett.*, 5783 (1966).

(6) This method furnishes materials of high optical purity but it is not general and provides no reliable information on absolute configuration.

(7) Asymmetric syntheses of disulfoxides by oxidation of bis-sulfides have been reported: (a) H. Nieuwenhuyse and R. Louw, *J. Chem. Soc., Perkin Trans. 1*, 839 (1973); (b) T. M. Sutliff, Ph.D. Dissertation, Case Western Reserve University, 1970.[8] This method is convenient and general but provides materials of low optical purity and of uncertain absolute configuration.

(8) We thank Professor A. L. Ternay, Jr., for bringing this work to our attention.

(9) It has recently been reported[7a] that optically active ethano-bridged disulfoxides may be prepared by a double Grignard reaction on bis(−)-menthyl ethane-1,2-disulfinate. Although this method is potentially useful for the preparation of the desired compounds, it must be emphasized that the diester, prepared by asymmetric synthesis from (−)-menthol and ethane-1,2-disulfinyl chloride, is capable of existing in three diastereomeric forms. Accordingly, the success of this method demands the separation and identification of these diastereomers; these criteria were not met.[7a] In the absence of an investigation of the optical properties of the unfractionated disulfoxides, and given the low yields of the purified products, the assignment of absolute configuration to the chiral centers on the basis of the direction of asymmetric synthesis is unwarranted.

(10) The present oxidative-coupling scheme is, of course, incapable of supplying optically active 1,2-bis(methylsulfinyl)ethane or any 1,2-bis(methyl-substituted phosphinyl)ethanes.

(11) All new compounds gave satisfactory elemental analyses and mass spectra in agreement with the assigned structures. Nmr spectra were recorded at 60 MHz.

$[\alpha]^{27}\mathrm{D}$ 0.0°, $[\alpha]^{27}{}_{400}$ 0.0° (c 0.70, $CHCl_3$); nmr ($CDCl_3$) δ 7.9–7.4 (m, 10 H), 2.4–1.6 (m, 8 H), 1.4–0.7 (m, 6 H). The residue from evaporation of the mother liquor was twice recrystallized (acetone–heptane) to furnish 0.85 g (34%) of analytically pure, hygroscopic (S,S)-**1**, mp 126–127°, $[\alpha]^{27}\mathrm{D}$ −18°, $[\alpha]^{27}{}_{400}$ −67° (c 0.33, $CHCl_3$);[12] nmr ($CDCl_3$) δ 7.8–7.2 (m, 10 H), 2.6–1.5 (m, 8 H), 1.4–0.7 (m, 6 H). The coupling reaction was also applied to optically pure (−)-(S)-methylphenyl-p-tolylphosphine oxide,[13] resulting in a 50% yield of (S,S)-1,2-bis(phenyl-p-tolylphosphinyl)ethane (**2**), mp 247–248°; $[\alpha]^{27}\mathrm{D}$ +6.9° (c 0.98, $CHCl_3$); nmr ($CDCl_3$) δ 8.0–7.1 (m, 18 H), 2.52 (apparent d, 4 H, separation 2.5 Hz), 2.38 (s, 6 H). Although we have been unsuccessful in measuring the enantiomeric purity of (S,S)-**1** or (S,S)-**2**, the small amounts of meso diastereomer conveniently confine the enantiomeric purity to $\geq 90\%$.

Enantiomerically pure (+)-(R)-methyl p-tolyl sulfoxide[14] was coupled using the above procedure, except for the necessary replacement of n-butyllithium by lithium diethylamide,[4] to afford (R,R)-1,2-bis(p-tolylsulfinyl)ethane (**3**) in 45% yield, after chromatography. The ^1H nmr spectrum was identical with that for authentic[15] *dl*-**3** and demonstrated the absence of any *meso*-**3**. Recrystallization (heptane–$CHCl_3$) supplied colorless needles (25%), mp 132–133°, $[\alpha]^{27}\mathrm{D}$ +278° (c 0.044, CH_3OH). The enantiomeric purity of (R,R)-**3** was confirmed at $\geq 97\%$ through the use of the chiral shift reagent tris(3-heptafluoropropylhydroxymethylene-(+)-camphorato)europium(III).[16]

The CD spectrum (CH_3OH) of (+)-(R,R)-**3** displays two Cotton effects centered at 242 nm, $[\theta]_{\max}$ +194,000°, and at 219 nm, $[\theta]_{\max}$ −218,000°. These optically active transitions closely resemble corresponding Cotton effects for (+)-(R)-methyl p-tolyl sulfoxide (CH_3OH), $[\theta]_{\max}$ +69,000° at 238 nm and $[\theta]_{\max}$ −95,000° at 215 nm. Consequently, there is no compelling evidence for intramolecular chromophoric coupling and hence no reason to suspect significant intramolecular association.[18,19]

Acknowledgment. This work was supported by the National Science Foundation (GP-30257).

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[12] The specific rotation of (S,S)-**1** is sensitive to moisture, and highly concentration and solvent dependent.

[13] R. D. Baechler and K. Mislow, *J. Amer. Chem. Soc.*, **92**, 3090 (1970).

[14] (a) K. Mislow, M. M. Green, P. Laur, J. T. Melillo, T. Simmons, and A. L. Ternay, Jr., *ibid.*, **87**, 1958 (1965). (b) The enantiomeric purity of this compound has been demonstrated by the use of a chiral shift reagent: H. Nozaki, K. Yoshino, K. Oshima, and Y. Yamamoto, *Bull. Chem. Soc. Jap.*, **45**, 3495 (1972).

[15] E. V. Bell and G. M. Bennett, *J. Chem. Soc.*, 3189 (1928).

[16] For racemic **3** in the presence of the chiral shift reagent[17] (0.5 mol equiv), one set of aromatic protons (presumably ortho) appeared as a pair of doublets centered at δ 9.67 ($\Delta\nu$ = 13.5 Hz, both $^3J_{HH}$ = 8 Hz), and the other set (presumably meta) appeared as an overlapping pair of doublets centered at δ 7.80 ($\Delta\nu$ = 2.5 Hz, both $^3J_{HH}$ = 8 Hz). Under the same conditions, the synthesized (+)-(R,R)-**3** exhibited only the high-field pairs of ortho and meta protons.

[17] R. R. Fraser, M. A. Petit, and M. Miskow, *J. Amer. Chem. Soc.*, **94**, 3253 (1972).

[18] Monosulfoxides have been reported to exhibit a tendency to self-associate (ref 14a and references cited therein).

[19] ^1H nmr spectral information on 1,2-ethano bis sulfoxides also suggests a lack of intramolecular association.[5a,7b,20]

[20] F. Taddei, *Boll. Sci. Fac. Chim. Ind. Bologna*, **26**, 107 (1968).

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Received June 30, 1973

*Book Reviews**

Carbon-13 NMR Spectra. By L. F. Johnson and W. C. Jankowski (Varian Associates). Wiley-Interscience, New York, N. Y. 1972. Unnumbered pp. $24.95.

This oversize volume consists principally of the nmr spectra of 500 selected compounds, displayed one to a page, with assignments of the signals. A name index and a code index allow one to find either a specific compound or a compound having specific structural features easily. The text consists of a seven-page preface that is primarily concerned with explaining the use of the code index. This is a useful reference work and a valuable adjunct to a textbook for those who are seriously engaged in learning about ^{13}C nmr.

Chemical Technology. An Encyclopedic Treatment. Volume 4. Petroleum and Organic Chemicals. Edited by L. W. Codd, K. Dijkhoff, J. H. Fearon, C. J. van Oss, H. G. Roeberson, and E. G. Stanford. Barnes and Noble, New York, N. Y. 1973. xxxi + 792 pp. $42.50 ($35.00 by series subscription).

This volume reminds one of a text on strictly "classical" organic chemistry, but brought up to date. Only four of its twenty chapters are closely connected with petroleum; the bulk of the book covers organic chemistry in systematic organization according to functional type or use (*e.g.*, dyes, explosives). The approach is strongly descriptive, with little concern for mechanism, structure, or correlations of reactivity. Specific compounds of industrial importance are emphasized, and their various uses, present and past sources or methods of production, and statistical data on manufacture and use are given in addition to succinct presentations of the general reactions of and synthetic routes to the various classes Short bibliographies, consisting largely of books, are given for each chapter. A substantial index increases the reference value of this volume independent of the others in the series.

Apart from its obvious utility to industrial chemists, Volume 4 could be a valuable source book for teachers of organic chemistry who wish to enrich their lectures by relating academic chemistry to the technology and society that support it.

Cooperative Phenomena near Phase Transitions. A Bibliography with Selected Readings. Edited by H. Eugene Stanley. MIT Press, Cambridge, Mass. 1973. xviii + 308 pp. $14.95.

This large-size (8½ × 11 in.), soft-bound, photo-offset volume consists of a bibliography of about 2500 articles current to June 1972, and reprints of 35 short experimental articles and the abstracts of 65 theoretical articles. It is intended to serve as a "companion" to the author's book "Introduction to Phase Transitions and Critical Phenomena" (Oxford University Press, 1971). Features of the bibliography that should make it especially useful are a list of the 61 journals utilized and a list of 50 relatively recent conference proceedings dealing with critical phenomena.

Developments in Inorganic Nitrogen Chemistry. Volume 2. Edited by C. B. Colburn (Auburn University). Elsevier Scientific Publishing Co., Amsterdam/London/New York. 1973. x + 228 pp.

The first volume of this work was published seven years ago.

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* Unsigned book reviews are by the Book Review Editor.