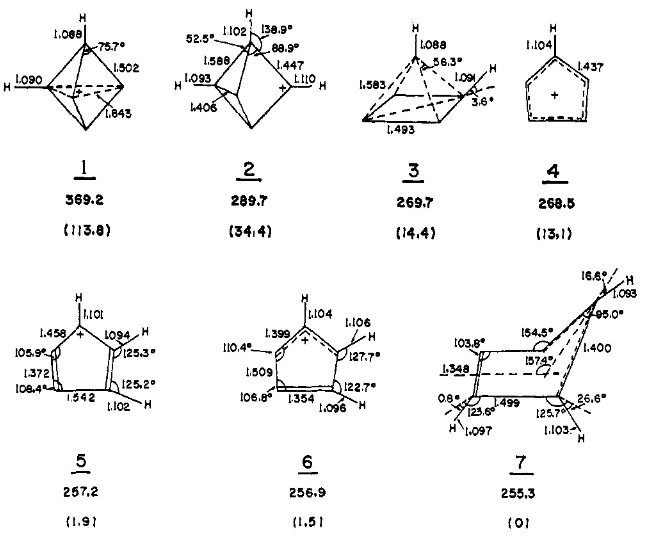

Figure 1. Geometries (bond lengths in Å), heats of formation (kcal/mol), and (in parentheses) relative energies (kcal/mol) of (CH)$_5^+$ isomers.

state, *i.e.*, a change in the angle ϕ (in **11**) from $<180°$ (in **3** and **7**) to $>180°$ in the vicinity of $\theta = 95°$. Our final estimate of the activation energy was 43 kcal/mol.

This high value suggests that **3**, once formed, should be quite a stable species. Since we predict **2** to rearrange spontaneously to **3**, **3** should be formed by solvolysis of compounds of the type **12**, but not **13**. Stohrer and Hoffmann[4] also predicted the rearrangement of **2**. However, we differ from them in predicting **7** to be not only stable but more stable than **3**. The available experimental evidence seems to be consistent with these predictions. Thus reaction of 5-iodocyclopentadiene with silver ion led[10] to products derived from **4** or some equivalent structure (*i.e.*, **5**, **6**, or **7**) while solvolysis of a dimethyl derivative of **12** in SO$_2$FCl–FSO$_3$H gave a cation whose nmr spectrum suggested that it was a dimethyl derivative of **3**.[12]

MINDO/3 calculations on protonated **14** and **15** (X = F), in which the fluorine leaves as HF, lead to the prediction that the solvolysis of **14** should give rise to **3**, whereas the solvolysis of **15** should lead to **7**. This is consistent with the observations of Schleyer and coworkers[13] on the reactions of analogous saturated systems. In the exo series, corresponding to **14**, concerted ring opening is forbidden. In the case of **14**, however, an alternative (concerted) process is available involving the double bond and is expected to lead to the formation of **3**.

We have also carried out similar calculations for (CH)$_5^-$ (Figure 2). Here, as one would expect, the most stable species by far is the planar aromatic anion **16**. The only other stable species seems to be the analog (**18**) of **2**. In this case the C_{4v} structure **19**, analogous to **3**, is unstable because it contains two electrons in an antibonding MO.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research through Contract F44620-71-C-0119 and by the Robert A. Welch Foundation through Grant F-126.

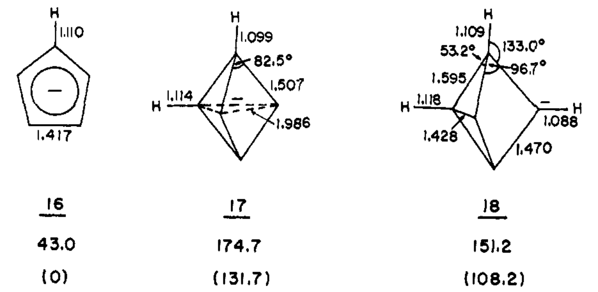

Figure 2. Geometries (bond lengths in Å), heats of formation (kcal/mol), and (in parentheses) relative energies (kcal/mol) of (CH)$_5^-$ isomers.

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Received February 28, 1973

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[12] S. Masamune, M. Sakai, and H. Ona, *J. Amer. Chem. Soc.*, **94**, 8955 (1972); S. Masamune, M. Sakai, H. Ona, and A. J. Jones, *ibid.*, **94**, 8956 (1972). See also H. Hart and M. Kuzuya, *ibid.*, **94**, 8958 (1972).

[13] P. R. Schleyer, G. W. Van Dine, U. Schöllkopf, and J. Paust, *ibid.*, **88**, 2868 (1966).

Cyclopentadienyl and Related (CH)$_5^+$ Cations

Sir:

The D_{5h} cyclopentadienyl cation (I) is antiaromatic[1] and should possess a triplet ground state. This is apparently true for the parent[2] and certain derivatives[3] but considerable evidence points to the existence of ground singlet states of highly substituted cyclopentadienyl cations.[3b,4,5] A theoretical study by Stohrer and Hoffmann[6] indicates that the singlet surface of (CH)$_5^+$ contains another minimum, of C_{4v} symmetry resembling cyclobutadiene complexed to CH$^+$ (IV).

The possibility of square pyramidal (CH)$_5^+$ has received experimental support.[7] Masamune and his coworkers[7a] recently recorded the proton and ^{13}C nmr spectra of what they believe is dimethyl (apical base) IV.

Semiempirical molecular orbital calculations[8] have not only provided evidence for IV but also indicate the existence of another (cyclopentadienyl type) singlet minimum. The two theoretical methods (CNDO[8a] and MINDO[8b]) disagree, however, as to which form is of lower energy.

Using *ab initio* molecular orbital theory[9] the lowest minimum on the singlet potential corresponds to planar

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[1] The singlet is a Jahn–Teller molecule and must distort to a lower symmetry.

[2] M. Saunders, R. Berger, A. Jaffe, J. M. McBride, J. O'Neill, R. Breslow, J. M. Hoffman, Jr., C. Perchonock, E. Wasserman, R. S. Hutton, and V. J· Kuck, *J. Amer. Chem. Soc.*, **95**, 3017 (1973); (b) R. Breslow, and J. M. Hoffman, Jr., *ibid.*, **94**, 2110 (1972).

[3] (a) R. Breslow, R. Hill, and E. Wasserman, *ibid.*, **86**, 5349 (1964); (b) R. Breslow, H. W. Chang, R. Hill, and E. Wasserman, *ibid.*, **89**, 1112 (1967).

[4] R. Breslow, H. W. Chang, and W. A. Yager, *ibid.*, **85**, 2033 (1963).

[5] R. E. Leone and P. v. R. Schleyer, *Angew. Chem., Int. Ed. Engl.*, **9**, 860 (1970).

[6] W. D. Stohrer and R. Hoffmann, *J. Amer. Chem. Soc.*, **94**, 1661 (1972).

[7] (a) S. Masamune, M. Sakai, H. Ona, and A. J. Jones, *ibid.*, **94**, 8956 (1972); (b) H. Hart and M. Kuzuya, *ibid.*, **94**, 8958 (1972).

[8] (a) H. Kollmar, H. O. Smith, and P. v. R. Schleyer, *ibid.*, **95**, 5834 (1973); (b) M. J. S. Dewar and R. C. Haddon, *ibid.*, **95**, 5836 (1973).

[9] The STO-3G basis[10] is used to locate energy minima; single 4-31G[11] calculations are then performed.

[10] W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).

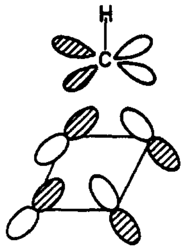
[11] R. Ditchfield, W. J. Hehre, and J. A. Pople, *ibid.*, **54**, 724 (1971).

Table I. Geometries and Energies of $(CH)_5^+$ Ions[a]

 I	 II	 III	 IV
$r(C_1C_2) = 1.428$	$r(C_1C_2) = 1.310$	$r(C_1C_2) = 1.604$	$r(C_1C_2) = 1.477$
	$r(C_2C_3) = 1.538$	$r(C_2C_3) = 1.348$	$r(C_1H_5) = 1.589$
	$r(C_3C_4) = 1.386$	$r(C_3C_4) = 1.464$	$r(OC_5)^b = 1.198$
	$\angle(C_1C_2C_3) = 107.5$	$\angle(C_1C_2C_3) = 107.5$	$\angle(HC_1O)^b = 174.6$
	$\angle(C_2C_3C_4) = 108.8$	$\angle(C_2C_3C_4) = 107.0$	
	$\angle(C_3C_4C_5) = 107.4$	$\angle(C_3C_4C_5) = 111.0$	
	$\angle(H_1C_1C_2) = 129.7$	$\angle(H_1C_1C_2) = 123.5$	
	$\angle(H_3C_3C_2) = 124.7$	$\angle(H_3C_3C_2) = 127.7$	
ΔE^c	20.6 (17.2)	21.4 (18.1)	44.8 (71.0)

[a] For I–III carbons (and associated hydrogens) numbered counterclockwise starting from lower left hand corner. For IV carbons 1–4 are basal, 5 is apical. The r values are in ångströms and the angles (L) are in degrees. [b] O is the midpoint of carbons 1–4. [c] Energies (kcal/mol) relative to triplet cyclopentadienyl cation I; STO-3G, 4-31G in parentheses.

cyclopentadienyl incorporating a solitary double bond (II); 0.9 kcal/mol higher (4-31G) lies a tautomer with two short bonds (II). We have not investigated nonplanar forms. A minimum corresponding to the square-based pyramid was indicated to lie 55 kcal/mol (4-31G, 23 kcal/mol at STO-3G) above the cyclopentadienyl forms. Since the energy of II and III *vs.* IV appears to be basis dependent, it will be desirable to perform 6-31G* level calculations.[12] A D_{5h} form of triplet cyclopentadienyl cation proved 17 kcal/mol more stable than the best singlet.[13] Theoretical geometries (STO-3G) and energies (STO-3G, 4-31G) for the four structures are given in Table I. The two singlet cyclopentadienyl cations are well represented by their respective valence structures (II and III). The basal hydrogens in the pyramidal form (IV) are directed *upward*, enabling a better orientation of the cyclobutadiene π system toward the apical CH^+.[16]



5-Bicyclo[2.1.0]pentenyl cation (V) collapses without activation toward pyramidal $(CH)_5^+$. Conversion of V to cyclopentadienyl requires considerable activation but we have not determined the precise needs. Ion VI, derived from homotetradrane, is also unstable with respect to IV, supporting Masamune's observations.[7a]

V

VI

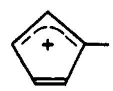
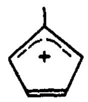
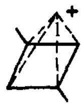
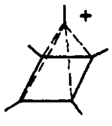
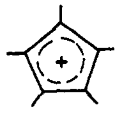
Effects of substituents in altering the energetics of the $(CH)_5^+$ surface can be evaluated by means of the *isodesmic*[17] reactions (Table II).

$$C_5H_4Me^+ + CH_4 \longrightarrow (CH)_5^+ + MeCH_3 \quad (1)$$

$$C_5H_4Ph^+ + CH_4 \longrightarrow (CH)_5^+ + PhCH_3 \quad (2)$$

Methyl substitution in singlet cyclopentadienyl cation shows high positional selectivity (VII–IX). Substitu-

Table II. Stabilization of $(CH)_5^+$ by Methyl and Phenyl Substituents (kcal/mol)[a]

Me Ph	 VII	9.8	 VIII	17.1 37.5	 IX	5.9
Me Ph	 X	12.1 17.1	 XI	10.5 15.9	 XII	11.4 40.0
Me	 XIII	23.8	 XIV	22.1		
Me	 XV	52.1	 XVI	53.7	 XVII	49.1

[a] STO-3G; geometries from parents, bond lengths: C–Me = 1.52 Å, C–Ph = 1.40 Å (VIII, XII), 1.50 Å (X, XI).

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(12) P. C. Hariharan, W. A. Lathan, and J. A. Pople, *Chem. Phys. Lett.*, **14**, 385 (1972).

(13) As the effects of correlation are ignored, energy comparison between species of different spin is unreliable. For example, the 4-31G basis suggests a singlet–triplet splitting in methylene of 37 kcal/mol,[14] 26 kcal/mol larger than that resulting when correlation is partially taken into account.[15]

(14) W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 808 (1971); W. A. Lathan, W. J. Hehre, L. A. Curtiss, and J. A. Pople, *ibid.*, **93**, 6377 (1971).

(15) C. F. Bender, H. F. Schaefer, III, D. R. F. Franceschetti, and L. C. Allen, *ibid.*, **94**, 6888 (1972).

(16) This has also been noted in isoelectronic B_5H_9: W. N. Lipscomb, *J. Chem. Phys.*, **22**, 985 (1954); W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963.

(17) W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 4796 (1970); L. Radom, J. A. Pople, and P. v. R. Schleyer, *ibid.*, **94**, 5935 (1972).

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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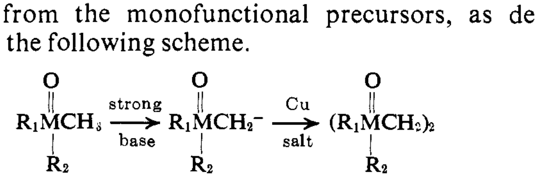
Received April 7, 1973

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.



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

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.