

the structural assignment. The product reacts with oxygen in the matrix to give acenaphthoquinone (9)⁸ identified by IR comparison with an authentic sample. Warming to room temperature gives decacylene (10) which can be detected in the crude product and which has been isolated by HPLC and identified by comparison with authentic decacylene (mass spectrum, UV spectrum, and HPLC retention). Trace amounts of water trap acenaphthine giving acenaphthenone (11) which was isolated by HPLC and identified by comparison (mass spectrum, UV spectrum, and HPLC retention) with the authentic material and another compound (*m/e* 318) which corresponds to the hydrated dimer. The

(8) Krebs, H.; Kimling, H. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 509. *Tetrahedron Lett.* **1970**, 761. Leupin, W.; Wirz, J. *Helv. Chim. Acta* **1978**, *61*, 1663.

dimer of benzyne can be trapped in similar fashion with methanol.⁹ Larger amounts of water increase the yield of acenaphthenone and the hydrated dimer but also lead to premature reaction with cyclopropenone 7 giving the acid (12a, identified by its mass spectrum). Similar experiments with methanol (0.7% in argon) give the ester 12b (mass spectrum) and a trace (*M*⁺, 6% of the ester, base peak) of a product with *m/e* 182 corresponding to acenaphthine plus methanol.

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(9) Chapman, O. L. *Pure Appl. Chem.* **1974**, *40*, 511.

Additions and Corrections

Radical Anion and Radical Trianion of 1,4-Bis(dimethylphosphino)benzene [*J. Am. Chem. Soc.* **1978**, *100*, 6504]. W. KAIM and H. BOCK,* Institute of Inorganic Chemistry, University of Frankfurt, Frankfurt, West Germany.

The ESR spectra reported have been reassigned according to recent investigations:

i. The first species is not the radical anion of the title compound, but of its oxide R₂P(O)-C₆H₄-P(O)R₂, as has been proven by comparison:¹ phosphane oxides, even if present in only minimal amounts, are more easily reduced than the corresponding phosphanes.² The ESR spectrum of the unoxidized 1,4-bis(dimethylphosphino)benzene radical anion actually had been recorded and exhibits an unusual line width effect.³ Therefore, the correct interpretation could only be achieved by comparison with the ESR spectra of closely related radical anions.³

ii. The "radical trianion" of 1,4-bis(dimethylphosphino)benzene is in fact the radical anion of 4,4'-bis(dimethylphosphino)biphenyl, which is formed via P-aryl cleavage.⁴ The assignment has been confirmed by comparison with the ESR spectrum of the authentic species.³ The misinterpretation has been facilitated by the missing ESR coupling constant *a*_{H(3,3')} which must be smaller than 0.003 mT, and especially by the fact that different ESR data for this radical anion had been reported previously.⁵ That latter species,⁵ however, may be recognized as the corresponding phosphane oxide radical anion R₂P(O)-C₆H₄-C₆H₄-P(O)R₂⁻.³ A literature search⁶ suggests further confusion between radical anions of phosphanes and their oxides.³

(1) W. Kaim, *Z. Naturforsch., B*, **36**, 150 (1981).

(2) Cf. K. S. V. Santhanam and A. J. Bard, *J. Am. Chem. Soc.*, **90**, 1118 (1968).

(3) W. Kaim and H. Bock, *Chem. Ber.*, **114**, 1576 (1981).

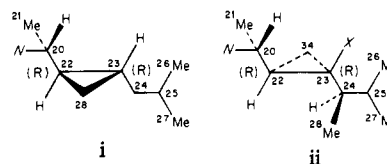
(4) Cf. K. Issleib and H. O. Fröhlich, *Z. Naturforsch., B*, **14**, 349 (1959).

(5) A. H. Cowley and M. H. Hnoosh, *J. Am. Chem. Soc.*, **88**, 2595 (1966).

(6) P. Schipper, E. H. J. M. Jansen, and H. M. Buck, *Top. Phosphorus Chem.*, **9**, 407 (1977).

Isolation and Structure Elucidation of 22(S),23(S)-Methylenecholesterol. Evidence for Direct Bioalkylation of 22-Dehydrocholesterol [*J. Am. Chem. Soc.* **1980**, *102*, 7113-4]. PIERRE-ALAIN BLANC and CARL DJERASSI,* Department of Chemistry, Stanford University, Stanford, California 94305.

Our continuing studies on steroidal cyclopropanes confirm that in this paper we correctly showed the absolute configuration of naturally occurring 22,23-methylenecholesterol (i) to be opposite to that (22(R),23(R),24(R)) of gorgosterol (ii, X = CH₃; N = cholesterol nucleus). Therefore, we referred to the natural material as the 22(S),23(S)-isomer. In fact this is a misapplication of the Cahn-Ingold-Prelog rules (*Angew. Chem., Int. Ed. Engl.* **1966**,



5, 385-415): even though of opposite absolute configuration, the natural 22,23-methylenecholesterol (i) should also be referred to as 22(R),23(R). This is so because the 22(R) indication in the related sterols gorgosterol (ii, X = CH₃) and demethylgorgosterol (ii, X = H) is based on a higher priority of C-23 over C-20, which is for demethylgorgosterol due to methyl substitution on C-24; 23(R) then results from the priority of C-22 over C-24. However, lack of the C-28 methyl group in 22,23-methylenecholesterol (i) leads to an inversion of the sequences around C-22 and C-23. Regarding the 22-carbon atom, C-20 now assumes priority over C-23, while the sequence around C-23 is H < C-24 < C-28 < C-22.

Complete Thermodynamic Analysis of the Hydration of Thirteen Pyridines and Pyridinium Ions. The Special Case of 2,6-Di-*tert*-butylpyridine [*J. Am. Chem. Soc.* **1979**, *101*, 7141]. EDWARD M. ARNETT* and B. CHAWLA, Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260.

Page 7144: The values for di-*tert*-butylpyridine (2,6-DTBP) in Table IV should be corrected as follows:

	reads	should read
$\Delta G^\circ \rightarrow \text{H}_2\text{O}$ (B)	3.87	0.40
$\delta \Delta G^\circ \rightarrow \text{H}_2\text{O}$ (B)	4.29	0.82
$\delta \Delta G^\circ \rightarrow \text{H}_2\text{O}$ (BH ⁺)	15.00	11.50
$\delta(T\Delta S_s^\circ)$ (B)	-5.99	-2.52
$\delta(T\Delta S_s^\circ)$ BH ⁺	-8.33	-4.8

Chiral Perturbation of Olefins by Deuterium Substitution. The Optical Activity and Circular Dichroism Behavior of (1S)-[2-²H]Norbornene and Deuterated Apobornenes [*J. Am. Chem. Soc.* **1980**, *102*, 7228]. LEO A. PAQUETTE,* CHRISTOPHER W. DOECKE, FRANCIS R. KEARNEY, ALEX F. DRAKE, and STEPHEN F. MASON, Department of Chemistry, The Ohio State University, Columbus, Ohio 43210 (L.A.P., C.W.D., and F.R.K.), and King's College, London WC2R 2LS, England (A.F.D. and S.F.M.).

Although the title and introduction to this paper carry the correct absolute configurational descriptors for the deuterated olefins, six examples of inadvertent transposition of the *R/S* notation can be found later in the text: