($MgSO_4$) and distilled to give 0.80 g (54%) of 4 at 96–100° (16 mm) (by ^1H nmr, 80% cis, 20% trans).

Reduction of 1-Methyl-3-phospholanone (1) with Sodium and Ethanol. Sodium sand (2.0 g, 87 mmol) in 100 ml of toluene at 5–10° was treated with 3.36 g (29.2 mmol) of ketone 1 in 4.0 g (87 mmol) of absolute ethanol at such a rate as to keep the temperature below 10°. After 2.5 hr at 10°, 15 ml of water was cautiously added. The toluene layer was removed, and the aqueous layer was extracted with two 40-ml portions of benzene. The organic fractions were combined and dried ($MgSO_4$); distillation gave 0.41 g (12.7%) of 4 containing a trace of starting ketone 1. The ^1H nmr spectrum showed the composition 79% *cis*- and 21% *trans*-1-methyl-3-phospholanol (3).

Thermal Equilibration of 1-Methyl-3-phospholanol Isomers. A neat specimen (78.7% cis, 21.3% trans) was heated in an oil bath maintained at 135°. The specimen was then placed in benzene and its ^1H nmr spectrum was recorded for determination of the isomer composition by the PCH_3 signal size. After 35 hr, the composition was 67% cis, 33% trans. After an additional 107 hr, the composition of the dark material was 51% cis, 49% trans. Further heating caused tar formation, and the experiment was terminated.

1-Methyl-3-acetoxyphospholane 1-Oxide (5) and 1-Methyl-3-acetoxyphospholane (6). Ten grams (75.8 mmol) of 1-methyl-3-phospholanone 1-oxide (2) was hydrogenated as above. The product was dissolved in 35 ml of pyridine, cooled to 0°, and treated with 5.86 g (74.7 mmol) of acetyl chloride. After 2 hr, the mixture was warmed to room temperature and the precipitated pyridine hydrochloride was filtered off. The filtrate was evaporated to dryness, placed in 30 ml of 1 *N* HCl, and extracted with six 50-ml portions of $CHCl_3$. The extracts were dried ($MgSO_4$) and distilled, giving 6.6 g (50.5%) at 126–128° (0.17 mm) which solidified on standing. The product was a mixture of cis (34%) and trans (66%) isomers: nmr ($CDCl_3$) δ 2.16 (d, $^2J_{PH}$ = 13.5 Hz, cis PCH_3), 2.22 (d, $^2J_{PH}$ = 13.5 Hz, trans PCH_3), 2.38–3.12 (complex m, ring CH_2), 2.51 and 2.54 (s, CH_3CO), 5.34–6.25 (complex m, OCH). The oxide mixture is very hygroscopic and difficult to purify. Analytical results are only partly satisfactory.

Anal. Calcd for $C_7H_{13}O_3P$: C, 47.71; H, 7.44. Found: C, 46.91; H, 7.75.

The oxide mixture was deoxygenated as described previously with trichlorosilane–triethylamine. Distillation gave 3.46 g (82.8%) of colorless liquid at 105–110° (12 mm); nmr ($CDCl_3$) δ 1.44 (d, $^2J_{PH}$ = 2.92 Hz, PCH_3 of cis isomer, 34%), 1.58 (d, $^2J_{PH}$ = 2.80 Hz, PCH_3 of trans isomer, 66%), 1.79–2.92 (complex m, ring CH_2), 2.44 and 2.45 (s, CH_3CO), 5.84 (m, OCH); ir (neat) $\nu_{C=O}$ 1740, ν_{CO} 1240 cm^{-1}. Various attempts to form quaternary salts for analysis of the isomer mixture have so far given only intractable oils.

Registry No.—**1**, 49849-35-6; **2**, 21229-61-8; **3a**, 51015-54-4; **3b**, 51015-55-5; 3 methiodide, 51015-53-3; **4a**, 51015-58-8; **4b**, 51015-59-9; **5a**, 51015-60-2; **5b**, 51015-61-3; **6a**, 51015-62-4; **6b**, 51015-63-5.

References and Notes

(1) Taken from the Ph.D. Dissertation of R. C. Stocks, 1973. Supported by Public Health Service Research Grant CA-05507 from the National Cancer Institute. The National Science Foundation provided funds toward the purchase of the Bruker spectrometer (Grant No. GP 10301).
(2) (a) A. T. McPhail, J. J. Breen, and L. D. Quin, *J. Amer. Chem. Soc.*, **93**, 2574 (1971); (b) A. T. McPhail, J. J. Breen, J. H. Somers, J. C. H. Steele, Jr., and L. D. Quin, *Chem. Commun.*, 1021 (1971); (c) A. T. McPhail, P. A. Luhan, S. I. Featherman, and L. D. Quin, *J. Amer. Chem. Soc.*, **94**, 2126 (1972).
(3) L. D. Quin and J. H. Somers, *J. Org. Chem.*, **37**, 1217 (1972).
(4) S. I. Featherman and L. D. Quin, *J. Amer. Chem. Soc.*, **95**, 1699 (1973).
(5) S. I. Featherman and L. D. Quin, *Tetrahedron Lett.*, 1955 (1973).
(6) L. D. Quin and R. C. Stocks, in press.
(7) L. D. Quin and J. A. Caputo, *Chem. Commun.*, 1463 (1968).
(8) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Oxford, 1969, p 234.
(9) H. E. Shook, Jr., and L. D. Quin, *J. Amer. Chem. Soc.*, **89**, 1841 (1967), first reported that at 60 MHz the separate signals were observable only in the presence of benzene. In more recent work (L. D. Quin and S. O. Lee, unpublished), it has been found that the signals are observable at 100 MHz in a nonaromatic solvent (CD_3COCD_3), with separation of 7 Hz.
(10) P. V. Demarco and L. A. Spangle, *J. Org. Chem.*, **34**, 3205 (1969).
(11) (a) P. Haake, J. P. McNeal, and E. J. Galbraith, *J. Amer. Chem. Soc.*, **90**, 715 (1968); (b) R. H. Cox and M. G. Newton, *ibid.*, **94**, 4212 (1972); (c) R. H. Cox, B. S. Campbell, and M. G. Newton, *J. Org. Chem.*, **37**, 1557 (1972); (d) K. Bergesen and T. Vikane, *Acta Chem. Scand.*, **26**, 2153 (1972).
(12) (a) K. Bergesen, M. Bjoroy, and T. Gramstad, *Acta Chem. Scand.*, **26**, 3037 (1972); (b) J. P. Albrand, D. Gagnaire, J. Martin, and J. B. Robert, *Org. Magn. Resonance* **5**, 33 (1973); (c) S. C. Peake, M. Fild, R. Schmutzler, R. K. Harris, J. M. Nichols, and R. G. Rees, *J. Chem. Soc., Perkin Trans. 2*, 380 (1972).
(13) (a) K. Bergesen, M. Bjoroy, and T. Gramstad, *Acta Chem. Scand.*, **26**, 2156 (1972); (b) K. Bergesen and M. Bjoroy, *ibid.*, **27**, 357 (1973).
(14) Y. Y. Samitov, M. A. Pudovik, A. I. Khayarov, and L. K. Kibardina, *Zh. Obshch. Khim.*, **43**, 46 (1973).
(15) (a) Y. Kawazoe, Y. Sato, M. Natsume, H. Hasegawa, T. Okamoto, and K. Tsuda, *Chem. Pharm. Bull.*, **10**, 338 (1962); (b) R. F. Zürcher, *Helv. Chim. Acta*, **46**, 2054 (1963).
(16) B. Fuchs and R. G. Haber, *Tetrahedron Lett.*, 1323 (1966).
(17) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience, New York, N. Y., 1965, p 202.
(18) R. G. Haber and B. Fuchs, *Tetrahedron Lett.*, 1447 (1966).
(19) M. Christl, H. J. Reich, and J. D. Roberts, *J. Amer. Chem. Soc.*, **93**, 3463 (1971).
(20) J. J. Breen, J. F. Engel, D. K. Myers, and L. D. Quin, *Phosphorus*, **2**, 55 (1972).
(21) I. O. C. Ekejiuba and H. E. Hallam, *J. Chem. Soc. B*, 209 (1970).
(22) J. C. Richer and C. Gilardeau, *Can. J. Chem.*, **43**, 3419 (1965).
(23) L. D. Quin and R. C. Stocks, unpublished work.
(24) Melting points were taken on a Mel-Temp apparatus and are corrected; boiling points are uncorrected. All manipulations of phosphines were conducted in a nitrogen atmosphere in a glove bag. Proton nmr spectra were taken with a Varian A-60 spectrometer; chemical shifts are relative to external TMS. ^{31}P nmr spectra were recorded on a Bruker HFX-10 system at 36.43 MHz with proton noise-decoupling; chemical shifts are relative to 85% H_3PO_4. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

The Stereochemical Elucidation of the Birch Reduction Product of [2.2]Paracyclophane[1a]

James L. Marshall* and Ban-Huat Song[1b]

Department of Chemistry, North Texas State University, Denton, Texas 76203

Received December 5, 1973

The tetrahydro Birch reduction product of [2.2]paracyclophane is shown to be the *dl* stereoisomer (**2b**), with the olefins of the upper deck only partially overlapping with the olefins of the lower deck. This stereochemical elucidation is accomplished primarily by means of a complete proton nmr analysis of the tetraepoxide derivative 3. The *dl* stereochemistry is in agreement with CNDO calculations performed on likely carbanion intermediates.

It has been recently shown[2,3] that the Birch reduction of [2.2]paracyclophane (1) gives the tetrahydro product 2 in which reduction has gone 2,5 in each deck. Although the structure elucidation of each deck of 2 was straightforward,[2,3] it was not possible to establish the overall stereochemistry of 2, *i.e.*, whether the product was meso (**2a**) with each olefin in the upper deck overlying a corresponding olefin in the lower deck, or was *dl* (**2b**) with the olefins

Table I
Proton Nmr Parameters of the ABC Pattern Observed for 3[a,b]

δ_A[c]	δ_B	δ_C	J_{AB}[d]	J_{AC}	J_{BC}
3.03	2.49	1.95	6.79 ± 0.06	1.35 ± 0.06	−16.99 ± 0.06

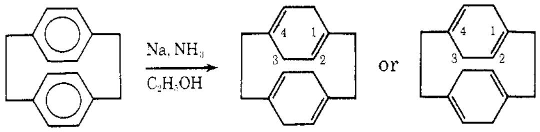
[a] For the partial structure which was assigned for these parameters, see 4. [b] The RMS error for this analysis was 0.09 Hz Probable errors as generated by the analysis are included in Table I. [c] In parts per million. [d] In hertz.

Table II
Proton Nmr Parameters of the AA'BB' Pattern Observed for 3[a]

δ_A[b]	δ_B	$J_{AA'}$[c]	$J_{BB'}$	$J_{AB'} = J_{A'B}$	$J_{AB} = J_{A'B'}$
2.34	1.35	12.11 ± 0.09	1.56 ± 0.08	6.48 ± 0.09	−14.94 ± 0.10

[a] The RMS error for this analysis was 0.10 Hz. Probable errors as generated by the iterative method are included in the Table. [b] In parts per million. [c] In hertz.

partially overlapping, or was a mixture of both isomers **2a** and **2b**. This paper describes the successful determination of the geometrical structure of 2 and discusses the probable mechanism for the reduction reaction.

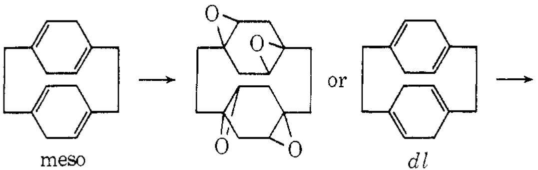


1 2a 2b

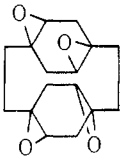
Structure Elucidation. The first step in elucidating the geometrical structure of 2 was to determine that 2 was only one isomer. The carbon magnetic resonance spectrum of 2 exhibited two olefin signals (at δ_{TMS} 137.4 and 125.6) and two aliphatic signals (at δ_{TMS} 44.0 and 38.0), consistent with either **2a** or **2b**. Since the carbon chemical shifts in **2a** and **2b** should be quite different for the respective methylene (C-3 and C-6) and olefin (C-2 and C-5) carbons,[4] it was evident that one isomer was preponderant.

It was reasoned that, if the geometry of 2 were meso (**2a**), then the two olefin pairs would be in a position ready for a [2 + 2] intramolecular cycloaddition.[5] However, photolysis of 2 under a variety of conditions resulted either in recovered starting material or in an untractable tar. Thus, indirect evidence was obtained that the geometry of 2 was *dl* (**2b**).

Next, a proton nmr study was conducted. Since the proton nmr of 2 could not differentiate between the two possible isomers **2a** or **2b** (see Experimental Section), a derivative of 2 was sought that would be amenable to a complete nmr analysis. It was found that epoxidation of 2 with excess peracid under carefully controlled conditions resulted in an isolable tetraepoxide derivative 3, whose proton nmr was remarkably soluble for such a large molecule. The 100-MHz spectrum of 3 exhibited an ABC pattern with an AA'BB' pattern partially overlapping (see Figure 1). The ABC pattern was easily recognized as being generated by four equivalent systems in the two puckered rings, with $|J_{BC}| > |J_{AB}| > |J_{AC}|$, corresponding to an approximately eclipsing H_A-H_B pair and an approximately orthogonal H_A-H_C pair (see 4). The AA'BB' pattern, caused by two equivalent $-CH_2CH_2-$ bridges, was partially obscured by the ABC pattern, but, since more than one complete half of the AA'BB' pattern was openly visible and since an AA'BB' pattern is perfectly bilateral,[6] a complete analysis of this pattern was possible. The ABC and AA'BB' patterns were analyzed separately by the iterative method[7] to give the parameters listed in Tables I and II. Recombination of the computed ABC and AA'BB' patterns gave the simulated spectrum shown in Figure 2.[8]



meso 2a 3a *dl* 2b



3b

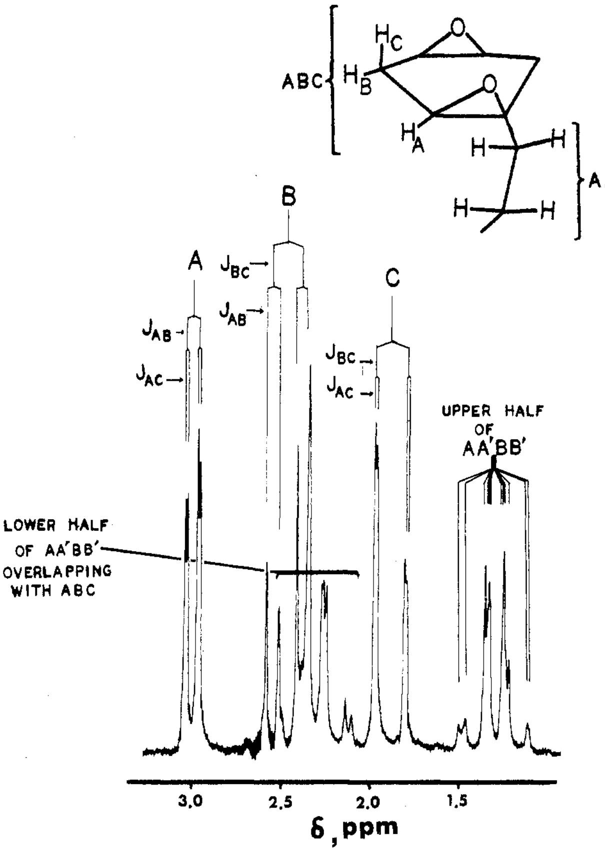
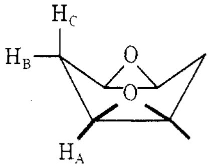


Figure 1. 100-MHz pmr spectrum of 3.



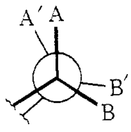
4

Table III
CNDO Calculations of the Radical Anions 12a and 12b with Varying Degrees of Puckering of the 1,4-Cyclohexadiene Ring[a]

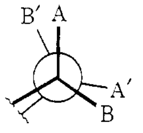
	Degree of Puckering, θ			
	0°	10°	20°	30°
12a (meso)	−0.0155 (−9.72)	−0.1051 (−65.92)	−0.1173 (−73.57)	−0.1039 (−65.17)
12b (*dl*)	0.0000 (0.00)	−0.1076 (−67.49)	−0.1228 (−77.02)	−0.1117 (−70.06)

[a] Values are given in atomic units (kilocalories in parentheses).

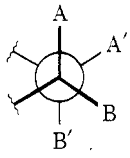
Although analysis of the ABC parameters gave in a straightforward manner the geometry of the involved nuclei (see 4) and was independent of the stereochemistry of the overall compound, a corresponding analysis of the AA′BB′ parameters was more complex and proved ultimately to involve the overall stereochemistry and conformation of the complete molecule **3**. First in this analysis of the AA′BB′ parameters was the realization that the $-CH_2CH_2-$ bridge must be in a particular conformation. A consideration of the four possible eclipsed and staggered conformations (see the Newman projections **5a–d**)[9] clearly favored **5d**, in which A and A′, which were diaxial, coupled with a large J value. The quite different values of $J_{BB'}$ and of $J_{A'B}$ indicated that this staggered conformation was actually skewed somewhat (**5e**) so that the dihedral angle of H_B and $H_{B'}$ approached 90° while the dihedral angle of H_A and $H_{B'}$ and of $H_{A'}$ and H_B approached 0°.[10] Of all the possible overall structures and conformers of **3** (see **6a–f**), the only choice fitting this particular AA′BB′ disposition was **6f**, the *dl* isomer with the two $-CH_2CH_2-$ bridges staggered so as to give the molecule D_2 symmetry; all other possibilities (**6a–e**) could be ruled out. Structures **6a** and **6d** were eliminated because they would have the eclipsed arrangement of the AA′BB′ nuclei. Structure **6b** would not fit any of the AA′BB′ arrangements, since with all of its protons having different chemical shifts an ABCD pattern would result. Structure **6e** would have *two different* AA′BB′ patterns (the protons being disposed differently about the epoxide in the two bridges, the chemical shifts of the protons in the two bridges would differ). Finally, structure **6c** could be removed as a possibility because H_A and H_B would be diaxial (*i.e.*, **5c**).[11] Thus, the only remaining possibility was **6f**, the D_2 conformer of the *dl* staggered isomer.[12]



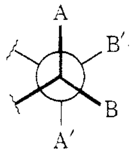
5a



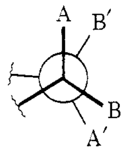
5b



5c



5d



5e

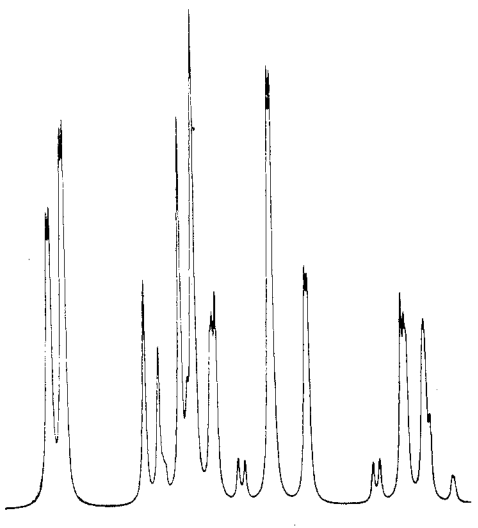
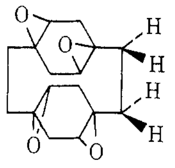
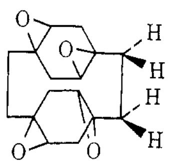


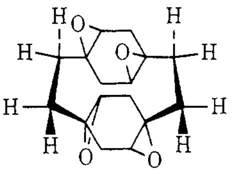
Figure 2. Computer-simulated spectrum of 3.


meso, eclipsed, C_{2h}

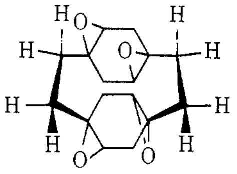
6a


dl, eclipsed, D_2

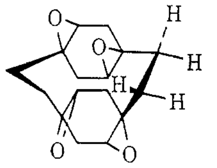
6d


meso, staggered, C_i

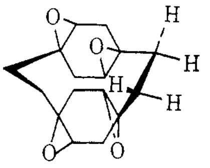
6b


dl, staggered, C_2

6e

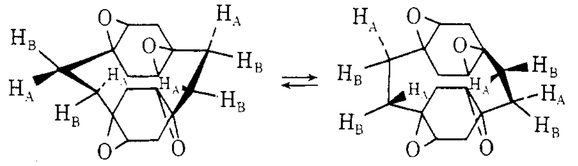

meso, staggered, C_2

6c


dl, staggered, D_2

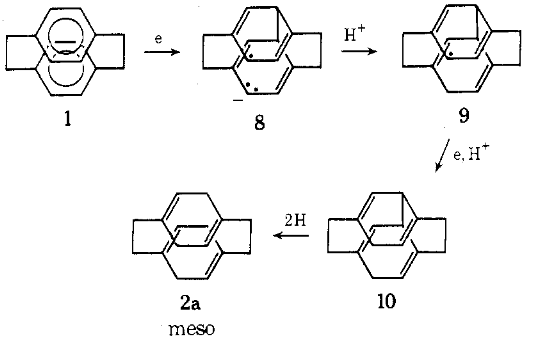
6f

A brief consideration was made of the possibility of rapidly equilibrating conformers (*e.g.*, **7a** ⇄ **7b**),[13a] but this possible complication was ruled out by three compelling arguments. (1) The time-averaged spectrum of two rapidly equilibrating conformers would never have a large apparent J approximating J_{180} ; at best the largest apparent J would be $J = \frac{1}{2}J_{60} + \frac{1}{2}J_{180}$. In fact, $J_{AA'}$ (see Table II) was clearly approximating J_{180}.[13b] (2) A time-averaged spectrum of two conformers would give rise to a higher order of identity in the parameters; for example, equilibrating **7a** and **7b** would give an apparent AA′BB′ system in which $J_{AA'} = J_{BB'}$, $J_{A'B} = J_{AB'}$, and $J_{AB} =$



7a 7b

Scheme I



$J_{A'B'}$. (3) It was observed that the proton nmr spectrum of 3 was unchanged down to −50°.

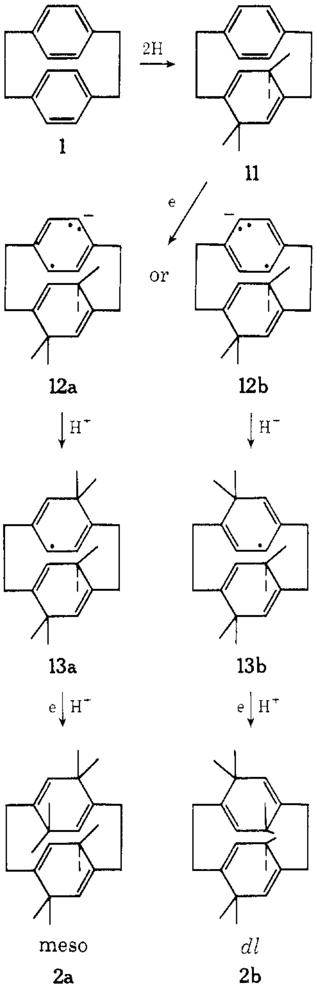
Thus, the proton nmr study of the tetraepoxide 3 indicated that the correct structure was *dl* (**3b**), thereby giving conclusive evidence that the structure of the Birch reduction production of [2.2]paracyclophane is *dl* (**2b**).

Two points are worthy of further discussion concerning the nmr analysis of **3**. First, the $J_{AA'}$ value corresponding to a diaxial arrangement of A and A′ (**5d**) is at first sight perhaps surprisingly large for two nuclei which are in fact somewhat skewed (**5e**).[14] However, there is evidence[15] that an electronegative substituent *vicinal* to a proton involved in vicinal coupling *increases* the J value. Thus, the observed $J_{AA'}$ is actually just about right for the proposed conformation.[16]

The second matter deserving comment concerns precisely in what D_2 conformation (**7a** or **7b**) the tetraepoxide 3 exists. Although it appeared certain that the isomer and conformer was the D_2 staggered *dl* structure, it was not immediately obvious whether the conformer was **7a**, with H_A of the $-CH_2CH_2-$ bridge lying away from the epoxide ring, or **7b**, with H_A lying over the face of the epoxide ring. It was frustrating to realize that in fact the complete nmr analysis, though resolving a number of vital questions, could not choose between two quite different conformers. The chemical shifts of H_A and H_B were left as the only means to decide between **7a** and **7b**, but unfortunately the literature is not settled concerning the magnetic anisotropy of the epoxide ring.[17,18] A tentative assignment, however, was made in favor of **7b** by means of the following argument. First, H_B (of AA′BB′) was assigned as the upfield proton at δ 1.35, because its geometrical relationship with the epoxide in either **7a** or **7b** was the same as H_C (of ABC) with the similar chemical shift of δ 1.95; *viz.*, these protons eclipsed the C-O bond of the epoxide ring.[19] Next, it was recognized that in **7a** the H_A proton (of AA′BB′) was in a geometrical relationship similar to that of H_B (of ABC) with the epoxide groups. It was further reasoned that, since H_B (of ABC) next to two epoxides is deshielded somewhat from H_C, then H_A (of AA′BB′) of **7a**, which is next to only one epoxide, should be deshielded but somewhat less. As a matter of fact, H_A (of AA′BB′) is deshielded much *more* than H_B (of ABC). On the other hand, in the other conformer **7b**, H_A (of AA′BB′) is quite close to the face of the epoxide ring, which might explain the large downfield shift. It was concluded, therefore, that the correct conformer was **7b** with H_A (of AA′BB′) over the face of the epoxide with the recognition that this conclusion rested upon the assumption that the face of the epoxide was a deshielding region.

Mechanism. Proposed mechanisms for the Birch reduction of [2.2]paracyclophane (1) involving classical formulations lead to faulty conclusions, *i.e.*, that the meso product **2a** should be produced. A reasonable mechanism involving such classical formulations with σ-bond participation between the two decks during the stepwise reduction of 1 is outlined in Scheme I. According to this scheme, an electron is first added to 1 to give the radical anion 8 with a σ bridge between the two decks. A proton is then added at the carbanion to give the radical **9**. A subsequent addition of an electron and a proton gives the bridged intermediate **10**; at this point, the geometry of the ultimate product has been determined to be meso. Addition of two more electrons and two more protons would reduce the σ bridge to give the final meso product **2a**.

Scheme II



A theoretical approach not involving such σ-bridge participation, however, is in agreement with the assigned structure **2b**. The most reasonable mechanism is outlined in Scheme II. According to this scheme, first one ring is reduced to give **11**. Then reduction of the second ring commences by the usual addition of an electron to give the radical anion **12**. At this point it is necessary to inquire whether C-2 or C-3 has the higher electron density[20] (represented by **12a** and **12b**, respectively), because the next step in the mechanism—the addition of a proton to give **13**—fixes irrevocably the geometry of the final product. Thus, a study was conducted on the anion **12** to see if theoretical considerations would support the contention that **12b** (which would ultimately lead to the observed final product **2b**) is more important than **12a**. This study involved the CNDO/2 calculations[21] of the relative stabilities of **12a** and **12b**, in which the upper deck was held flat and the lower deck was puckered. The degree of this puckering was varied from $\theta = 0°$ to 30° (θ was the dihedral angle of the two planes defined by the $CH-CH_2-CH$ bonds and the two olefin bonds of the lower deck). Table III reports the results. The data suggest that the bottom deck is puckered with $\theta \cong 20°$ and that in this conformation the *dl* radical anion **12b** is in fact more significant than the meso radical anion **12a**.[22]

Experimental Section

Melting points were determined by a Thomas-Hoover melting point apparatus. Infrared spectra were recorded on a Perkin-Elmer 237 grating infrared spectrophotometer. Nuclear magnetic resonance spectra were recorded on a Jeolco JNM-MH-60 (Minimar) and a Jeolco JNM-PS-100, with tetramethylsilane as an internal reference. Elemental analyses were performed by C. F. Geiger, Ontario, Calif.

[2.2]Paracyclophane (1) was obtained from Aldrich Chemical Co., Milwaukee, Wis.

***dl*-Tricyclo[8.2.$2^{1,10}$.$2^{4,7}$]hexadeca-4,10,1(13),7(16)-tetraene (2b) (Tetrahydro[2.2]paracyclophane).** To a 1000-ml, three-necked flask cooled in a Dry Ice-acetone mixture and purged with nitrogen was added 1.424 g (0.00684 mol) of [2.2]paracyclophane (1), 400 ml of anhydrous tetrahydrofuran, 200 ml of distilled liquid ammonia, and 10.0 ml of anhydrous ethanol. Over a period of 1.5 hr, 2.3 g of sodium was added in small pieces while 10.0 ml more of anhydrous ethanol was added dropwise. The blue color persisted for 0.5 hr and the reaction mixture was quenched by the careful addition of 30 ml of water. After 20 min of stirring, the reaction mixture was allowed to warm to room temperature and to stand overnight. The organic layer was separated and the aqueous layer was extracted with 100 ml of ether. The combined organic layers were dried (anhydrous magnesium sulfate) and concentrated to give 1.393 g of crude **2b.** Sublimation of the product (100°, 30 mm) gave 1.316 g (93%) of **2b:** mp 121.0–123.5°; ir ($CHCl_3$) 794 cm^{-1}; proton nmr ($CDCl_3$) δ 2.3 (m, 16, methylene) and 5.3 (m, 4, olefin); carbon nmr δ_{TMS} 137.4, 125.6, 44.0, 38.0; mass spectrum *m/e* 212 (P).

Anal. Calcd for $C_{16}H_{20}$: C, 90.50; H, 9.49. Found: C, 90.44; H, 9.52.

Attempted Photolysis of 2. Photolysis of 2 by a number of different methods[23-26] resulted in either an untractable tar, unreacted starting material, or a mixture of both. Sublimation of the product gave no volatile material except unreacted 2, with trace amounts (<5%) of [2.2]paracyclophane (1). Nineteen runs were executed.

Tetraepoxide of 2b (3b). Over a period of 1.5 hr, a solution of 2.20 g (0.0128 mol of 85% assay) of *m*-chloroperbenzoic acid in 50 ml of chloroform was added dropwise to a vigorously stirring mixture of 0.500 g (0.00235 mol) of **2b** in 15 ml of chloroform. The mixture was stirred and refluxed for 3 hr and then worked up in the usual manner.[27] The crude product was crystallized from carbon tetrachloride to give 0.420 g (65%) of white crystals, mp 287.0–289.5° dec, mass spectrum *m/e* 276 (P), nmr (see Tables I and II).

Anal. Calcd for $C_{16}H_{20}O_4$: C, 69.54; H, 7.29. Found: C, 69.32; H, 7.31.

Acknowledgments. We are indebted to the Robert A. Welch Foundation (Grant B-325) and to North Texas State University Faculty Research for financial support of this work.

Registry No.—**1,** 1633-22-3; **2b,** 50921-78-3; **3b,** 50978-09-1.

References and Notes

(1) (a) Presented in part at the 166th National Meeting of the American Chemical Society, Chicago, Ill., Aug 26–31, 1973. (b) Robert A. Welch Predoctoral Fellow, 1971–1973.

(2) W. Jenny and J. Reiner, *Chimia,* **24,** 69 (1970).

(3) J. L. Marshall and T. K. Folsom, *Tetrahedron Lett.,* **No. 10,** 757 (1971).

(4) In **2a** the C-2 carbon of the upper deck should be shielded by the underlying olefin while in **2b** the C-3 carbon of the upper deck is shielded by the underlying olefin: F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N. Y., 1969, pp 72–73.

(5) R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.,* **87,** 2046 (1965).

(6) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon Press, New York, N. Y., 1965, pp 399–415.

(7) A. A. Bothner-By and S. M. Castellano, "Computer Programs for Chemistry," Vol. 1, D. F. DeTar, Ed., W. A. Benjamin, New York, N. Y., 1968, p 10.

(8) To confirm the nmr parameters of Tables I and II, the spectrum of **3** was recorded and simulated also at 60 MHz. In this way several other possible combinations of the nmr parameters were conclusively ruled out.

(9) There are other degenerate possibilities with the A's and B's interchanged with no change in the bilateral AA′BB′ pattern. All possibilities, however, must have two hydrogens of equal chemical shift on vicinal carbons; there is no conformation of **3a** or **3b** (see **6a–f**) in which chemically equivalent protons are geminal.

(10) M. Karplus, *J. Amer. Chem. Soc.,* **85,** 2870 (1963).

(11) These arguments hold when all the conformers **5a–d** are skewed. The critical feature of this analysis is that the largest vicinal coupling constant is of protons with the *same* chemical shift ($J_{AA'}$) and that the corresponding $J_{BB'}$ is very small. This realization eliminated all meso possibilities.

(12) Even when **6f** is skewed, the point group is still D_2.

(13) (a) In passing from **7a** to **7b,** the labels have been reversed; *e.g.,* the protons labeled as H_A in **7a** become labeled as H_B in **7b**. This is done so that the H_A's are always diaxial. (b) S. Sternhell, *Quart Rev., Chem. Soc.,* **23,** 236 (1969).

(14) For [2.2]metacyclophane, whose $-CH_2CH_2-$ bridge appears to be almost perfectly staggered, the diaxial J = 12.3 Hz: H. S. Gutowsky and C. Juan, *Discuss. Faraday Soc.,* **34,** 52 (1962).

(15) A. D. Cohen and T. Schaeffer, *Mol. Phys.,* **10,** 209 (1966).

(16) Further consideration of the probable influence of the electronegative epoxide groups rationalizes the observed geminal coupling constants J_{BC} (of the ABC) and $J_{AB} = J_{A'B'}$ (of the AA′BB′). The former J value is expected to be lower (more negative) because of two epoxides vicinal to each geminal pair of protons (see ref 13).

(17) K. Tori, K. Kitahonoki, Y. Takano, H. Tanida, and T. Tsuji, *Tetrahedron Lett.,* **No. 11,** 559 (1964).

(18) P. R. Jefferies, R. S. Rosich, and D. E. White, *Tetrahedron Lett.,* **No. 27,** 1853 (1963).

(19) Because H_C (of ABC) eclipses two epoxides while H_B (of AA′BB′) eclipses one epoxide, this assignment presumes that the epoxide in this geometrical arrangement has little effect or is slightly deshielding. This assumption, however, is reasonable, because, if the anisotropic effect of the epoxide in this arrangement of the AA′BB′ protons were shielding, then H_B (of AA′BB′) should be downfield and must be accordingly assigned as the downfield signal at δ 2.34, which is an incredibly lowfield signal for a *shielded* proton.

(20) In the Birch reduction the addition of a proton to the intermediate carbanion is kinetically controlled and is directed to the carbon atom with the highest electron density: R. B. Bates, S. Brenner, C. M. Cole, E. W. Davidson, G. D. Forsythe, D. A. McCombs, and A. S. Roth, *J. Amer. Chem. Soc.,* **95,** 926 (1973).

(21) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.

(22) Boekelheide has tentatively assigned as *dl* the stereochemistry of the Birch reduction product of [2.2.2](1,3,5)cyclophane: V. Boekelheide and R. A. Hollins, *J. Amer. Chem. Soc.,* **95,** 3201 (1973).

(23) H. G. Cuts, E. N. Cain, H. Westberg, and S. Masamune, *Org. Photochem. Syn.,* **1,** 83 (1971).

(24) N. J. Turro, C. D. DeBóer, P. Wyatt, and G. S. Hammond, *J. Amer. Chem. Soc.,* **86,** 2532 (1964).

(25) P. G. Gassman and D. S. Patton, *J. Amer. Chem. Soc.,* **90,** 7276 (1968).

(26) W. G. Dauben and R. L. Cargill, *Tetrahedron,* **15,** 197 (1961).

(27) L. A. Paquette and J. H. Barrett, *Org. Syn.,* **49,** 62 (1969).