15% ether in pentane; wt. 10.0 g. of colorless oil (VI), whose infrared spectrum exhibited no absorption in the O–H stretching region.

Anal. Calcd. for $C_{27}H_{34}O_6$: C, 71.77; H, 7.74. Found: C, 71.86; H, 7.99.

Attempted Acyloin Reactions of V and VI.—Application of the usual acyloin ring closure conditions[16] to V with sodium in refluxing xylene gave back about 23% of starting material, the rest being polymer. In a second attempt, a 7% recovery of starting material was obtained along with considerable polymer. A similar attempt with ether VI gave a 62% recovery of starting material in one run, and a 48% recovery in a second, the rest being polymer.

Chromic Acid Oxidations of [1.*n*]Paracyclophanes and Model I.—The procedure is illustrated as applied to [1.12]paracyclophane. The substance (2.98 g., 8.90 mmoles) was dissolved in 40 ml. of 97% glacial acetic acid–3% water. A solution of 1.0 g. of chromic acid (10 mmoles) in 45 ml. of 97% acetic acid–3% water was added over a 3-hr. period with stirring at 25°. The mixture was stirred for 24 hr. at 25°, poured into salt water, and the resulting mixture was extracted with ether. The ether layer was washed with saturated sodium bicarbonate solution, once with salt water, and was dried. Evaporation of the solvent deposited a waxy solid which was chromatographed on 25 by 2.5 cm. of activated alumina slurry packed in pentane. Starting material (1.0 g.) was washed from the column with 600 ml. of pentane. When treated with 300 ml. of 20% ether in pentane, the column yielded 0.75 g. (24%) of ketonic material, m.p. 78–85°. Recrystallization of this material from carbon tetrachloride gave 0.42 g. of ketone X, m.p. 89.8–90.5°. The substance in carbon tetrachloride solution exhibited bands at the wave lengths (μ): 3.44, 3.52, 5.96, 6.24, 6.62, 6.84, 6.93, 7.08, 7.90 and 8.46.

Anal. Calcd. for $C_{25}H_{32}O$; C, 86.15; H, 9.26. Found: C, 86.06; H, 9.25.

The same procedure applied to [1.10]paracyclophane gave 61% starting material and 8% of ketonic material, recrystallization of which gave VIII, m.p. 76.8–78.2°. The infrared spectrum of the substance in carbon tetrachloride gave bands at the wave lengths (μ): 3.44, 3.53, 5.98, 6.26, 6.64, 6.95 and 7.09.

Anal. Calcd. for $C_{23}H_{28}O$: C, 86.20; H, 8.81. Found: C, 85.94; H, 8.85.

The same procedure applied to [1.8]paracyclophane gave a 65% recovery of starting material and no ketonic material as shown by the absence of a ketonic carbonyl group in the total product before chromatography. Nothing but starting material was recovered from the chromatograph column.

(16) D. J. Cram and H. Steinberg, *J. Am. Chem. Soc.*, **73**, 5691 (1951).

The same procedure applied to 4,4'-diethyldiphenylmethane (I) gave 45% recovery of starting material, and 0.20 g. of ketonic product (VII), m.p. 43–44°, which when recrystallized from carbon tetrachloride gave m.p. 43–44°.

Anal. Calcd. for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.47; H, 7.87.

A somewhat different procedure was employed for oxidation of [1.11]paracyclophane to its corresponding ketone IX.[17] A mixture of 3.2 g. of [1.11]paracyclophane, 0.8 g. of chromium trioxide, 150 ml. of dry acetic acid and 7.5 ml. of concd. sulfuric acid was stirred for 20 hr. at room temperature. The reaction mixture was worked up by elution chromatography. The hydrocarbon fraction amounted to 2.10 g. (65%) while the ketonic material weighed 0.71 g. (25%), m.p. 82–84.5°. A small sample of this material was recrystallized from hexane to give white plates, m.p. 85–86°.

Anal. Calcd. for $C_{24}H_{30}O$: C, 86.10; H, 9.04. Found: C, 86.09; H, 9.05.

Ultraviolet Spectral Data on [1.10]-, [1.11]- and [1.12]Paracyclophanyl Ketones.[17]—Spectra were recorded on a Cary recording spectrophotometer model 11 PMS in 95% ethanol: 1-keto[1.10]paracyclophane, λ_{max} 258 mμ, log ϵ 4.08; 1-keto-[1.11]paracyclophane, λ_{max} 259 mμ, log ϵ 4.11; 1-keto[1.12]-paracyclophane, λ_{max} 259.5 mμ, log ϵ 4.16 mμ; acetophenone,[18] λ_{max} 242.5 mμ (ϵ 12,700), λ_{max} 279.5 mμ (ϵ 1050).

Hydrogen–Deuterium Exchange Reactions.—In a typical run (2), a carefully weighed portion of hydrocarbon (0.254 g.) was added to a clean, dry, heavy-walled Pyrex tube sealed at one end and constricted at the top. From a stock solution of 0.37 *N* potassium *tert*-butoxide in *tert*-butyl alcohol-OD[19] (99% of one gram atom of deuterium by combustion and falling drop method) was added by means of a fast draining automatic pipet 4.0 ml. of reaction medium. The resulting solution and tube were flushed with pure dry nitrogen, cooled to 0° and sealed. The tubes were never more than 50% full, since room for expansion of solvent is required. The tube was heated in a Woods metal-bath maintained at 195° for 10 hr., with the tube immersed only to the level of the liquid. The tube was cooled to 0° and opened. No pressure had developed. The solution was shaken with a mixture of 150 ml. of salted water and 100 ml. of pentane. The aqueous phase was extracted with two 50-ml. portions of pentane, and the combined pentane extracts were washed with three 150-ml. portions of salt water, dried and evaporated to give 0.218 g. of product. This material was dried at 25° under 2 mm. pressure and was submitted directly to n.m.r. analysis.

(17) The authors are indebted to Dr. M. F. Antar for this experiment and the ultraviolet spectral data.

(18) G. H. Beaven and E. R. Johnson, *J. Chem. Soc.*, 655 (1957).

(19) D. J. Cram and B. Rickborn, *J. Am. Chem. Soc.*, **83**, 2178 (1961).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES, LOS ANGELES 24, CALIF.]

Macro Rings. XXIX. Stereochemistry of a 1,6-Cycloaddition Reaction[1]

BY DONALD J. CRAM, CECILE K. DALTON[2] AND GRAHAM R. KNOX

RECEIVED NOVEMBER 2, 1962

The naphthalene analog of [2.2]paracyclophane ([2.2]paracyclonaphthane) has been synthesized in 3% yield by an elimination–cycloaddition reaction with 4-methyl-1-naphthyltrimethylammonium hydroxide as starting material. The same isomer was prepared by a 9-step sequence from [2.2]paracyclophane in 0.07% yield. By its nature, the latter synthesis led to the *anti* isomer of [2.2]paracyclonaphthane, a conclusion confirmed by nuclear magnetic resonance (n.m.r.) spectral comparisons. Production of the *anti* isomer in the 1,6-to-1,6-cycloaddition reaction indicates that unlike the Diels–Alder reaction, π–π interactions were minimized in the transition state. In the multistep preparation of [2.2]paracyclonaphthane, n.m.r. spectral evidence was obtained that the homoannular dibenzo derivative of [2.2]paracyclophane was produced as a by-product, although the substance was not obtained in a pure state due to its instability. Benzo[2.2]paracyclophane was also synthesized, and served as a model for n.m.r. and ultraviolet spectral comparisons.

One of the more important stereochemical generalizations of organic chemistry is that in the Diels–Alder reaction the predominant isomer is that whose transition state of formation maximizes π–π-interactions of the two components (Alder's *endo* rule).[3] Although of a different character, the Cope rearrangement assumes a steric course which minimized π–π interactions in the transition state which leads to the predominant product.[4] The present investigation is addressed to the problem of which isomer is formed (*syn*- or *anti*-II) when intermediate A dimerizes. The formally analogous question of whether *syn*- or *anti*-[2.2]metacyclophane (IV) is formed when dibromide III is treated with sodium has been answered in favor of the *anti* isomer.[5] On the other hand, synthesis of

(1) This work was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to donors of said fund.

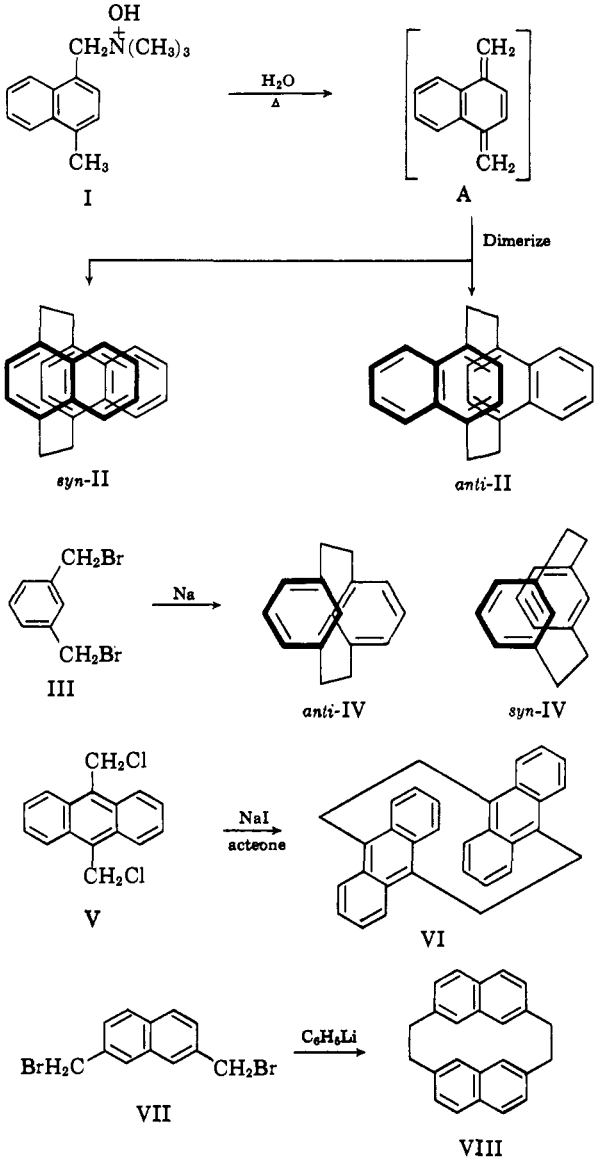
(2) N. S. F. Predoctoral Fellow, 1958–1959; du Pont teaching fellow, 1960–1961.

(3) (a) A. Wasserman, *J. Chem. Soc.*, 828, 1511 (1935); 432 (1936); 612 (1942); (b) J. A. Norton, *Chem. Rev.*, **31**, 319 (1942); (c) M. C. Kloetzel, *Org. Reactions*, **4**, 1 (1948); (d) R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959); for exceptions see: (e) J. A. Berson, Z. Hamlet and W. A. Mueller, *J. Am. Chem. Soc.*, **84**, 297 (1962), and references cited therein.

(4) W. E. Doering and W. R. Roth, *Tetrahedron*, **18**, 67 (1962).

tetrabenzo[2.2]paracyclophane (VI) from diiodide V has recently been reported,[6] presumably by a 1,6-to-1,6-cycloaddition reaction. Such a dimerization brings 3 sets of benzene rings face to face. The problem of which isomer is produced when dibromide VII is treated with phenyllithium[7] has not been solved to the authors' knowledge.

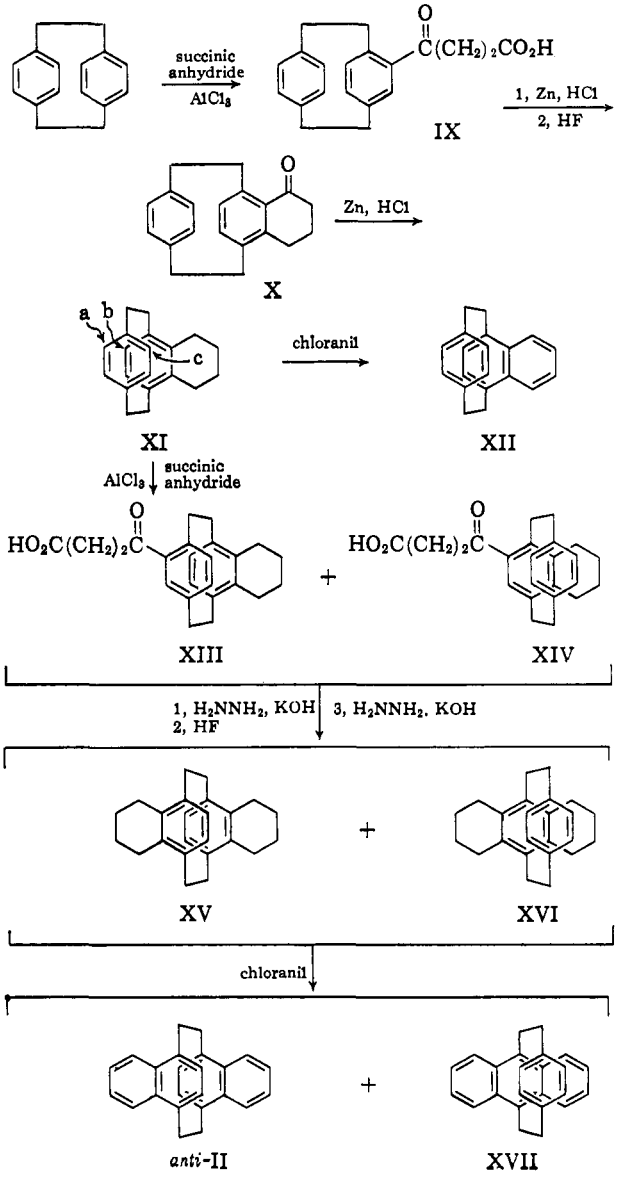
Syntheses.—In the present work, A was generated through a 1,6-elimination reaction analogous to that employed in the preparation of [2.2]paracyclophanes and their heterocyclic counterparts.[8] A 3% yield of a compound of either structure *syn*- or *anti*-II was produced, along with much polymer and 4-methyl-1-hydroxymethylenenaphthalene. To determine which structure applied, an unequivocal synthesis of the *anti* isomer was undertaken by the route outlined in the formulas. This approach was beset by one important but interesting uncertainty: the position of



succinoylation of XI. Of the three possible positions (see formula XI), attack at a would ultimately lead to *anti*-II, at b to the homoannular dibenzo[2.2]paracyclophane, and at c to *syn*-II. The last possibility (attack at c) can be ruled out on steric grounds. Molecular models indicate that the transannular methylene groups badly crowd position c. On an electronic basis, attack at b is preferred over a. The transannular ring is undoubtedly less activated by the methylene groups than the ring to which they are attached. Possibly a small steric factor favors attack at a over b.

In the event, substitution occurred at both a and b of XI, the latter predominating. The acylated products XIII and XIV and the subsequent sets of isomeric intermediates were not successfully separated one from the other, although satisfactory analyses of their mixtures were obtained. Homoannular dibenzo[2.2]-paracyclophane (XVII) was not isolated in a pure state due to its instability. Its presence in mixtures was demonstrated with n.m.r. spectra, and by the fact that it produced anthraquinone during recrystallizations. The extreme instability of XVII raises a question about the reported[6] stability of tetrabenzo[2.2]-paracyclophane. Pure specimens of *anti*-II made by the two routes proved to be identical in every respect.

The monobenzo[2.2]paracyclophane, compound XII, was prepared by aromatization of XI. Some of the structural features of *anti*-II and XVII are present in XII, and XII served as a model of unambiguous struc-



(5) C. J. Brown, *J. Chem. Soc.*, 3278 (1953).
(6) J. H. Golden, *ibid.*, 3741 (1961).
(7) W. Baker, J. F. W. McOmie and W. K. Warburton, *ibid.*, 2991 (1952).
(8) H. E. Winberg, F. S. Fawcett, W. E. Mochel and C. W. Theobald, *J. Am. Chem. Soc.*, **82**, 1428 (1960).

TABLE I

NUCLEAR MAGNETIC RESONANCE SPECTRAL DATA OF THE BENZO AND TETRAMETHYLENE DERIVATIVES OF [2.2]PARACYCLOPHANE[a]

Compound	Sets of aromatic hydrogens									Sets of aliphatic hydrogens					
	τ	No. H's	Mult.	τ	No. H's	Mult.	τ	No. H's	Mult.	τ	No. H's	Mult.	τ	No. H's	Mult.
[2.2]PCP[b]	3.63[b]	8	s	..	..	..	..	..	..	6.95	8	s	..	..	..
XII	2.44[c]	2	m	2.70[c]	2	m	3.38	2	s	6.30	2	m	6.81	2	[d]
XII	3.67	2	s	4.50	2	s	..	..	..	6.97	4	s	..	..	..
anti-II[b]	2.35[c]	4	m	2.67[c]	4	m	4.28	4	s	6.25[c]	4	m	7.00[c]	4	m
XVII[b]	2.10[c]	4	m	2.72[c]	4	m	4.50	4	s	6.14[c]	4	m	7.05[c]	4	m
XI	3.47	2	s	3.62	2	s	3.80	2	s	6.77	1	t	7.10	..[d]	s
XI	..	..	..	..	..	..	..	..	..	6.98	..[d]	s	7.20	..[d]	s
XI	..	..	..	..	..	..	..	..	..	7.15	..[d]	s	7.58[c]	4.5	m
XI	..	..	..	..	..	..	..	..	..	7.28	..[d]	s	8.34[c]	4	m
XV	3.75	4	s	..	..	..	..	..	.	7.13	8	s	7.60[c]	8	m
XV	..	..	..	..	..	..	..	..	..	8.37[c]	8	m	..	..	..
XVI	3.58	4	s	..	..	..	..	..	..	7.12	8	s	7.60[c]	8	m
XVI	..	..	..	..	..	..	..	..	..	8.37[c]	8	m	..	..	..

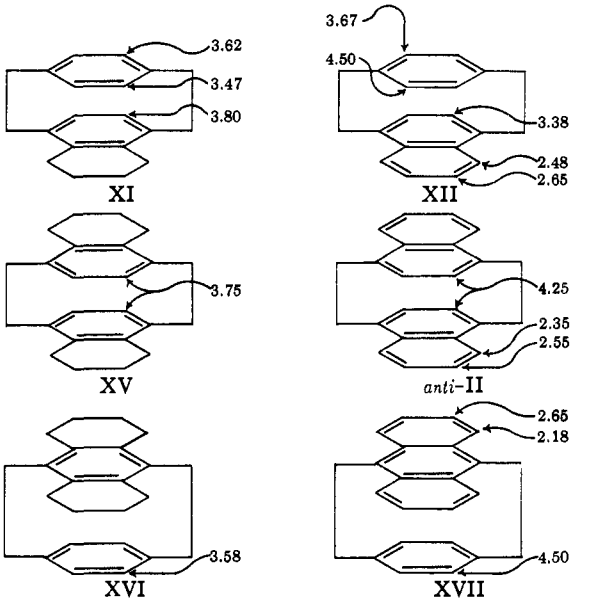
[a] Spectra taken in carbon tetrachloride solution (unless otherwise noted) with a Varian Associates model A-60 nuclear magnetic resonance spectrometer. [b] Spectra taken in deuterated chloroform. [c] Center of a multiplet. [d] Integration impossible due to overlapping peaks.

ture for n.m.r. and ultraviolet spectral comparisons (see next sections).

The above synthesis of *anti*-[2.2]paracyclonaphthane indicates that dimerization of intermediate A occurs by that transition state which *minimizes* π-π-interactions. This fact suggests that the usual repulsive forces between the two benzene rings of A were not disturbed in the transition state through conjugation with the exocyclic double bonds.[9]

Nuclear Magnetic Resonance Spectra.—Table I reports n.m.r. spectral data for [2.2]paracyclophane, monobenzo[2.2]paracyclophane (XII), *anti*-[2.2]paracyclonaphthane (*anti*-II), homoannular dibenzo[2.2]-paracyclophane (XVII), and their hydro derivatives XI, XV and XVI. Spectra of [2.2]paracyclophane, XI, XII and *anti*-II were taken on pure compounds, whereas spectra of XVI, XVII and XV were taken on mixtures. Compound XVII (84%) was mixed with *anti*-II (16%), and XV (35%) was mixed with (65%) XVI. The bands due to each component of the first of these two mixtures could be assigned unequivocally since the spectrum of the minor component (*anti*-II) in a pure state was available, and the absorption bands of the two compounds were well separated. The aromatic hydrogens of XV and XVI were well separated singlets, but the aliphatic hydrogens of the two compounds appeared to absorb in approximately the same places. The assignments of the band at τ 3.75 to XV and the band at τ 3.58 to XVI was made on the basis of intensity relationships. The approximate amounts of XV and XVI in the mixture were known from the relative proportions of XVII and *anti*-II produced on aromatization.

The assignment of bands to the various aromatic hydrogens are formulated, and are made on the following basis. In the benzo compounds (XII, *anti*-II and XVII), the two groups of peaks with the lowest τ-values are undoubtedly due to hydrogens on the carbons of the benzo nucleus. These hydrogens are all well away from the ring currents of the transannular rings, and therefore occur not far from their normal places. In naphthalene itself, the α-hydrogen absorbs at τ 2.3, and the β-hydrogen at 2.6, and therefore the β-hydrogens are assigned the higher values.[10] In monobenzo compound XII, the next lowest band (τ 3.38) is presumed to be naphthalenic (not benzenic), since naphthalenic hydrogens absorb at lower fields.[10]



The relatively high τ-value undoubtedly is due to the induced ring current of the transannular ring. In [2.2]paracyclophane itself, the aromatic hydrogens absorb at τ 3.63 due to this effect.[11] In the spectrum of XII, the hydrogens which absorb at τ 3.67 are closest to the value of 3.62 for [2.2]paracyclophane itself, and are therefore assigned to the hydrogens *anti* to the transannular benzo nucleus. The remaining two hydrogens are directly over the transannular benzo ring, and are shifted to very high field (τ 4.50), as might be expected. However, this value is less than the τ 5.73 observed for the two hydrogens *syn* to transannular benzene rings in *anti*-[2.2]metacyclophane (*anti*-IV).[12]

Assignments of bands in dibenzo compound XVII are: The singlet at τ 4.50 (4 hydrogens) is undoubtedly due to the 4 hydrogens on the benzene ring which are held in the field of the two benzo rings of the transannular anthracene nucleus. This band occurs at the same place as that found for the 2 high-field hydrogens of XII, a fact which suggests similar geometry for the two systems. The two multiplets (4 hydrogens each) which occur at lower fields are undoubtedly associated with the aromatic hydrogens of the anthracene nucleus.

(9) C. A. Coulson, D. P. Craig, A. Maccoll and A. Pullman, *Discussions Faraday Soc.*, **2**, 36 (1947).

(10) N.m.r. Summary Prepared by G. V. D. Tiers, Central Research Department, Minnesota Mining and Manufacturing Co., St. Paul 6, Minn., May, 1961.

(11) J. S. Waugh and R. W. Fessenden, *J. Am. Chem. Soc.*, **79**, 846 (1957).

(12) N. L. Allinger, M. A. Da Rooge and R. B. Hermann, *ibid.*, **83**, 1974 (1961).

Probably the multiplet centered at τ 2.18 is associated with the α- and that at τ 2.18 with the β-hydrogens. Two multiplets appear in the spectrum of 9-methylanthracene,[13] one centered at about 1.96 and a second at 2.63.

The substance *anti*-[2.2]paracyclonaphthane (*anti*-II) also has a 4-hydrogen singlet moved downfield to τ 4.28, which is clearly associated with the four hydrogens in the fields of transannular benzo rings. The fact that these hydrogens are less shielded than similarly situated hydrogens of XII and XVII arises out of their naphthalenic (in contrast to benzenic) character. Possibly by coincidence, the difference in chemical shift between this band and the benzenic band of XVII (0.22 τ) is close to the difference between the 3.38 band of XII and the 3.63 band of [2.2]paracyclophane (0.25 τ). The two multiplets (4 hydrogens each) of *anti*-II which occur at 2.35 and 2.67 are assigned to the α- and β-hydrogens of the naphthalene nucleus, respectively. The difference between these bands (0.28) is comparable to that observed (0.26) for similar hydrogens of XII. The spectrum of *anti*-II is inconsistent with what would be expected for *syn*-II. The latter compound would be expected to have the benzo hydrogens upfield and the remaining four hydrogens downfield from the observed absorptions.

Assignment of the aromatic hydrogens (4) of XVI is unequivocal, since only one kind is present. These hydrogens absorb at τ 3.58 (s), not far from those of [2.2]paracyclophane (τ 3.63). Compound XV also contains only one kind of aromatic hydrogen, which occurs further upfield (τ 3.75, 4 hydrogens as a singlet). The greater shielding is attributed to the electron-releasing character of the methylene groups.[14] For XI, the peak at highest field, τ 3.80, is associated with the aromatic hydrogens of the ring substituted with the methylene groups. This absorption is close to that of XV at 3.75. The other two assignments are more tenuous. The band at 3.62 is close to that of [2.2]-paracyclophane itself (3.63), and on that basis is provisionally assigned to the hydrogens *anti* to the transannular methylene bridge. This leaves the band at 3.47 for the hydrogens *syn* to the methylene bridge. This value is somewhat lower than the 3.58 observed for similarly situated hydrogens in XVI.

Ultraviolet Absorption Spectra.—The ultraviolet absorption spectra of [2.2]paracyclophane, monobenzo[2.2]paracyclophane (XII), *anti*-[2.2]paracyclonaphthane (*anti*-II) and 1,4-dimethylnaphthalene are recorded in Fig. 1. In previous correlations of spectra and structure of the paracyclophanes,[15] it was concluded that the abnormal positions of the longer wave length bands at 286 and 302 mμ in [2.2]paracyclophane were associated at least partially with benzene ring deformation, and the band at 244 mμ was most sensitive to transannular effects. On a similar basis, the longer wave length bands of XII (300 and 310 mμ) and of *anti*-II (310 mμ) are probably partly associated with the deformed benzene rings, whereas the shorter wave length bands of XII (232 mμ) and of *anti*-II (237 and 244 mμ) are most sensitive to transannular effects.

Experimental

1-Bromomethylene-4-methylnaphthalene.—From 1-bromonaphthalene was prepared[16] 1-methylnaphthalene in 60% yield, b.p. 182–184° (34 mm.). Bromination[17] of this material gave 1-bromo-4-methylnaphthalene in 79% yield, b.p. 190–198° (34 mm.), 97% pure by vapor phase chromatography. This compound was converted[18] to 1-carboxy-4-methylnaphthalene in 58% yield, m.p. 170–172°, literature[18] m.p. 175°. Reduction of this acid by the standard lithium aluminum hydride method produced 1-hydroxymethylene-4-methylnaphthalene in 74% yield, m.p. 68–71°, literature[17] 74–75°. This alcohol was converted to its corresponding bromide[17] in 93% yield, m.p. 78–79°, literature[17] m.p. 80°.

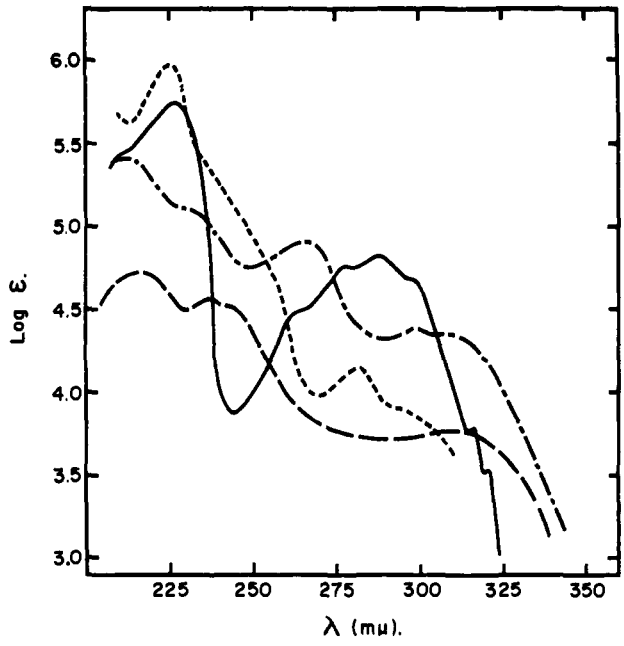


Fig. 1.—Ultraviolet absorption spectra in 95% ethanol, Cary recording spectrophotometer, model PMS 11. Curves are displaced 0.5 log ϵ unit upward on vertical axis from curve immediately below: ---, *anti*-[2.2]paracyclonaphthane (*anti*-II); - — - — benzo[2.2]paracyclophane (XII); ——, 1,4-dimethylnaphthalene; . . . ., [2.2]paracyclophane.

***anti*-[2.2]Paracyclonaphthane (II) from Quaternary Base I.**—A solution of 1-bromomethylene-4-methylnaphthalene (27.4 g.) in 500 ml. of benzene was treated with 15 g. of anhydrous trimethylamine (15 g.) at 0°. The white flocculent precipitate was collected and washed repeatedly with benzene and ether, and dried over phosphorus pentoxide to give 32.5 g. of I as a hygroscopic, microcrystalline solid, m.p. 232–234° dec.

The crude salt (31 g.) was dissolved in 200 ml. of water and stirred for 6 hr. with freshly prepared silver oxide (23.2 g.). The resulting mixture was filtered, and the filtrate was again treated with the same quantity of silver oxide for the same length of time and filtered. The clear, slightly yellow aqueous solution was mixed with 300 ml. of toluene and 0.1 g. of phenothiazine, and the water was removed by azeotropic distillation over a 14-hr. period. The toluene solution was concentrated to 50 ml., filtered, and cooled to produce slightly yellow hexagonal plates, m.p. 285–292° (sublimation and some decomposition), 0.441 g. (3.1%). Recrystallization of this material from 30% chloroform–70% carbon tetrachloride (300 ml.) followed by sublimation of the material at 0.1 mm. gave 0.296 g. of pure material, m.p. 299–301° (some decomp.).

Anal. Calcd. for $C_{24}H_{20}$: C, 93.46; H, 6.54. Found: C, 93.40; H, 6.65.

From the mother liquors was obtained 0.045 g. of addition material of inferior purity.

The extreme insolubility of [2.2]paracyclonaphthane in all solvents prevented the usual types of molecular weight determination. A molecular weight determined from crystal density and unit cell dimensions obtained from an X-ray crystal photograph gave 311 ± 4, compared to calculated 308.[19]

The final mother liquors were combined, evaporated to a small volume, and a small sample was submitted to vapor phase analysis on a 1-meter, 20% silicone rubber on firebrick column at 200° with helium as carrier gas. Only a trace of *anti*-II was detected

(13) N. S. Bhacca, L. F. Johnson and J. N. Shoolery, "High Resolution N.M.R. Spectra Catalogue," Palo Alto, Calif., 1962, spectrum 317.

(14) A movement upfield of the aromatic hydrogens of 4-ethyl[2.2]paracyclophane over that for the parent hydrocarbon was previously observed [L. A. Singer and D. J. Cram, *J. Am. Chem. Soc.*, **85**, 1080 (1963)].

(15) (a) D. J. Cram, R. H. Bauer, N. L. Allinger, R. A. Reeves, W. J. Wechter and E. Heilbronner, *ibid.*, **81**, 5977 (1959); (b) D. J. Cram and G. R. Knox, *ibid.*, **83**, 2204 (1961).

(16) V. Veselý and F. Sť rsa, *Coll. Czech. Chem. Comm.*, **4**, 139 (1932).

(17) R. Robinson and H. W. Thompson, *J. Chem. Soc.*, 2015 (1932).

(18) F. Meyer and A. Sieglitz, *Ber.*, **55**, 1839 (1922).

(19) The authors are indebted to Dr. K. N. Trueblood and Miss Linda Forrest for this determination.

on the column, and no other material of similar retention time (1.5 hr.) was observed. Control experiments with authentic samples demonstrated that about 95% of the total material put on the column was 1-hydroxymethylene-4-methylnaphthalene.

1,4-Dimethylnaphthalene.—A small sample of pure 1-hydroxymethylene-4-methylnaphthalene (1.0 g.) was converted to 1-bromomethyl-4-methylnaphthalene, which was reduced to 1,4-dimethylnaphthalene[20] with lithium aluminum hydride in refluxing tetrahydrofuran. The crude product (0.6 g.) was purified by preparative vapor phase chromatography on a 1-meter, 20% silicone gum on firebrick column at 200°, wt. 0.4 g.

β-[2.2]Paracyclophanoylpropionic Acid (IX).—To a mixture of 2.19 g. of anhydrous aluminum chloride and 10 ml. of pure dichloromethane cooled in an ice–salt bath (30 min.) was added 0.623 g. of succinic anhydride. The mixture was stirred for 30 min. and solid [2.2]paracyclophane (1.05 g.) was added. The solution turned a dark red color immediately. The mixture was stirred and cooled for 30 min., and poured onto a slurry of ice–concd. hydrochloric acid. The aqueous phase was extracted with methylene dichloride (twice), and the combined organic layers were washed with water until neutral. The solution was dried, evaporated, and concentrated to 1.78 g. of a crude semi-solid. This material was chromatographed over 60 g. of silica gel packed in 10% benzene in pentane. Starting material (0.224 g. or 21%) was first eluted from the column with 10% benzene in pentane, followed by keto acid IV, wt. 1.26 g. (81%), m.p. 145–147°.

Anal. Calcd. for $C_{20}H_{20}O_3$: C, 77.88; H, 6.54. Found: C, 78.04; H, 6.87.

Application of the same procedure (except that β-carbomethoxypropionyl chloride (18.68 g.) was substituted for succinic anhydride) to 21 g. of [2.2]paracyclophane (34.2 g. of aluminum chloride in 400 ml. of dichloromethane was employed) gave 26.0 g. (80%) of the methyl ester of IX, m.p. 60–61.5° (from ether).

Anal. Calcd. for $C_{21}H_{22}O_3$: C, 78.23; H, 6.88. Found: C, 78.23; H, 6.69.

δ-[2.2]Paracyclophanylbutyric Acid.—Mossy zinc (706 g.) was amalgamated with 70.5 g. of mercuric chloride, 1.2 l. of water and 30 ml. of concd. hydrochloric acid. The supernatant liquid was decanted. Water (435 ml.), 825 ml. of concd. hydrochloric acid and a solution of 39.2 g. (0.127 mole) of keto acid IX in 290 ml. of toluene were added to the amalgamated zinc in the order named. The reaction mixture was refluxed for 42 hr. during which time three 290-ml. portions of concd. hydrochloric acid were added. The reaction mixture was allowed to cool to 25°. The toluene layer was removed and the aqueous layer was diluted with 600 ml. of water. The aqueous phase was then extracted with three 500-ml. portions of benzene. The combined benzene–toluene extracts were washed with water until the wash water was neutral, dried and evaporated to dryness. The residue consisted of 48.1 g. of an orange semi-solid which exhibited no ketonic carbonyl absorption in the infrared. The crude product was chromatographed over 1.3 kg. of silica gel packed in benzene. Benzene eluted the desired acid, wt. 28.0 g. (75%). Recrystallization of a small sample from benzene gave white crystals, m.p. 123–124°.

Anal. Calcd. for $C_{20}H_{22}O_2$: C, 81.60; H, 7.54. Found: C, 81.52; H, 7.62.

Application of the same procedure to the methyl ester of keto acid IX gave a 65% yield of the above acid.

4,5-Tetramethylene-17-keto[2.2]paracyclophane (XI).—An 8-oz. polyethylene bottle containing 0.305 g. of acid IX was cooled to 0° on a balance. Anhydrous hydrogen fluoride was conducted into the bottle from a precooled tank through copper tubing until about 45 g. had collected. The bottle was stoppered and swirled. The solution became black immediately. After 16 hr. at 25° the bottle was opened and the hydrogen fluoride was allowed to vaporize at room temperature. The dark brown residue was dissolved in 50 ml. of ether, washed with 50-ml. portions of water, saturated sodium bicarbonate solution, and water until neutral. The solution was then dried and evaporated. The residue, 0.294 g. of a brown tar, was chromatographed on 15.8 g. of alumina. A light orange oil (0.204 g. or 71%) was eluted with ether–pentane (1:1). The oil crystallized to yield a colorless solid, m.p. 107–108°.

Anal. Calcd. for $C_{20}H_{20}O$: C, 86.91; H, 7.29. Found: C, 86.91; H, 7.01.

In a control experiment, 0.305 g. of [2.2]paracyclophane was dissolved in 67 g. of liquid hydrogen fluoride at 0°. After 2.5 hr., 0.285 g. of starting material was recovered unchanged.

4,5-Tetramethylene[2.2]paracyclophane (XI).—Mossy zinc (5.05 g.) was amalgamated with 0.565 g. of mercuric chloride, 2.5 ml. of concd. hydrochloric acid and 25 ml. of water. The amalgam was thoroughly washed with water, and 0.145 g. of ketone X in 4 ml. of toluene was added along with 8 ml. of absolute ethanol and 5 ml. of concd. hydrochloric acid. The mixture was heated at 105–110° for 51 hr., 0.6-ml. portions of concd. hydrochloric acid being added every 8 hr. Product was isolated in the usual way to give 0.157 g. of an orange oil, which was chromatographed on 8.2 g. of alumina. Product was washed from the column with pentane; wt. 0.138 g. (100%) of a light yellow oil. An analytical sample was crystallized and recrystallized from ether to give XI as a white solid, m.p. 119–120° (solidified and remelted at the same temperature).

Anal. Calcd. for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.39; H, 8.51.

Application of the usual Wolff–Kishner–Huang–Minlon reduction to ketone X gave a 56% yield of XI, m.p. 111–117°.

Benzo[2.2]paracyclophane (XII).—A mixture of 0.460 g. of pure chloranil, 0.240 g. of XI and 3 ml. of xylene was refluxed under helium for 20 hr. The mixture was cooled to 25° and 5 ml. of Skelly B was added. The mixture was filtered, and the filtrate was chromatographed on 13.7 g. of alumina. The product was eluted from the column with 10% benzene in pentane; wt. 0.055g. (24%). Recrystallization of the material from pentane gave broad, colorless needles, m.p. 114–115°. The infrared spectrum of this compound in dichloromethane exhibited bands (μ) at 6.30(m), 6.59(m), 6.65(m), 6.75(w), 6.85(w), 6.94(w), 7.06(m), 7.18(m), 7.32(w), 8.19(w), 8.43(w), 8.56(w), 8.67(w), 9.05(m), 9.59(w), 9.86(w), 10.18(w), 10.70(m), 11.22-(w), 11.45(s).

Anal. Calcd. for $C_{20}H_{18}$: C, 92.98; H, 7.02. Found: C, 93.10; H, 7.09.

Succinoylation of 4,5-Tetramethylene[2.2]paracyclophane (XI).—A mixture of 16.9 g. of anhydrous aluminum chloride, 5.23 g. of succinic anhydride and 100 ml. of dichloromethane was cooled in an ice–salt bath at −10°. A solution of 10.9 g. of XI was added, and the red solution was stirred for 25 min. at −10°. The mixture was then poured onto a slurry of ice and concd. hydrochloric acid. The aqueous layer was extracted with dichloromethane, the organic layers were combined, washed with water, dried and evaporated. The crude product, 15.95 g., was chromatographed on 820 g. of silica gel packed in benzene. Benzene washed from the column 4.40 g. (40%) of starting material. Keto acids XIII and XIV were eluted from the column with 8% ether in benzene; 9.97 g. (66%). This material was an oil, and as a whole was used in the next steps. However, some of the fractions crystallized from ether, and an analytical sample of one or the other isomer was obtained, m.p. 128–129°.

Anal. Calcd. for $C_{24}H_{27}O_3$: C, 79.51; H, 7.23. Found: C, 79.56; H, 7.04.

When compound XI was acylated (see procedure applied to [2.2]paracyclophane) with β-carbomethoxypropionyl chloride, 32.5% of starting material was recovered, along with 40% mono keto ester mixture (oil), and 22% of a diketo ester, a small amount of which crystallized from ether to give an off-white solid, m.p. 108–108.5°.

Anal. Calcd. for $C_{30}H_{32}O_6$: C, 73.75; H, 6.60. Found: C, 73.96; H, 6.96.

Reduction of 4,5-Tetramethylene-?-(β-carboxypropionyl)-[2.2]-paracyclophane.—A mixture of 7.12 g. of the mixture of keto acids XIII and XIV, 9.5 g. of potassium hydroxide, 2.0 ml. of 85% hydrazine hydrate and 200 ml. of diethylene glycol was refluxed for 3 hr. The condenser was removed, water and excess hydrazine were allowed to escape, and the mixture was allowed to reflux for an additional 3.5 hr. The reaction mixture was cooled and poured into excess 6 *N* hydrochloric acid. The solid that separated was collected, dried and chromatographed on 280 g. of silica gel packed in benzene. The desired acid free of ketone was eluted with 10% ether in benzene as a yellow oil; wt. 2.19 g. (33%). Ultraviolet and n.m.r. spectra of this material indicated the [2.2]paracyclophane nucleus to be intact. This material was used in the next step without analysis or further purification.

Attempts to reduce the keto acid mixture (XIII and XIV) by the Clemmensen procedure resulted in complete destruction of the [2.2]paracyclophane system, and creation of a methyl group (n.m.r. spectral evidence). Conversion of the keto acid mixture to the dimethylene thioketal followed by desulfurization with Raney nickel also destroyed the [2.2]paracyclophane system.

Ring Closure of 4,5-Tetramethylene-?-(γ-carboxypropyl)-[2.2]paracyclophane.—A solution of 2.0 g. of the substituted acid in 230 g. of anhydrous hydrogen fluoride was allowed to stand at 25° for 20 hr. The hydrogen fluoride was then allowed to evaporate, and the residue was dissolved in 400 ml. of dichloromethane. This solution was washed with water, saturated sodium bicarbonate solution, and then water. The solution was dried, evaporated, and the residue (1.96 g. of a brown glass) was chromatographed on 109 g. of alumina packed in benzene. A colorless oil (1.2 g., 63%) was eluted with benzene. The oil partially solidified to a tan solid, m.p. 79–139°.

Anal. Calcd. for $C_{24}H_{26}O$: C, 87.25; H, 7.93. Found: C, 86.95; H, 8.09.

(20) M. J. Kamlet, "Organic Electronic Spectral Data," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1960, p. 455.

Reduction of 4,5,?,?-Bis-tetramethylene-17-keto[2.2]paracyclophane to Mixture of XV and XVI.—A mixture of 1.21 g. of the above ketones was reduced by the Wolff–Kishner–Huang-Minlon procedure to give 1.14 g. of a tan solid. This material was chromatographed on 67 g. of alumina packed in benzene to give 0.968 g. (84%) of a white solid, m.p. 120–130°.

Anal. Calcd. for $C_{24}H_{28}$: C, 91.08; H, 8.92. Found: C, 91.26; H, 8.96.

Extensive attempts to separate XV and XVI at this stage through chromatography on silica gel failed to yield discrete compounds, although the mixture of XV and XVI were freed of minor amounts of impurities. Use of thin layer chromatography indicated that silica gel (Merck silica gel C) deactivated with 6% water packed in cyclohexane–isooctane (1:1) was the best system. The same solvent was used for elution purposes, 50-ml. fractions being collected. The first 105 fractions contained traces of a yellow oil. Fractions 109 to 119 were combined, as were 120 to 152, and 153 to 185. Fractions 109–119 consisted of 0.174 g. of material whose n.m.r. indicated it to be 96% of XVI (n.m.r. aromatic band at 3.58 τ) and 4% of a non-paracyclophane but aromatic impurity (n.m.r. band at 3.05 τ). Fractions 120–152 (0.430 g.) consisted of 87% XVI and 13% XV, the latter being identified by its n.m.r. band at 3.75 τ. Fractions 153 to 185 consisted of 65% XVI and 35% XV, wt. 0.123 g. Fractions 109–119 were used for n.m.r. data for XVI and fractions 153–185 for XV (Table I).

4,5,7,8-Dibenzo[2.2]paracyclophane (XVII).—Combined fractions 109–119 (0.174 g., see above) were dissolved in 10 ml. of *p*-xylene and treated with 0.564 g. of pure chloranil. The mixture was refluxed under helium for 21 hr., cooled and chromatographed on 25 g. of alumina packed in benzene. A yellow solid, 0.144 g. (85%), m.p. 130–170°, was eluted with benzene. Recrystallization of this material resulted in the substance becoming much more yellow. The substance was chromatographed on 152 g. of silica gel packed in 2.5% chloroform in carbon tetrachloride. Various mixtures of chloroform and carbon tetrachloride eluted oils. Dichloromethane eluted 0.026 g. of a yellow solid, m.p. 205–210° (sublimed). Recrystallization of this material from ether gave pale yellow needles, m.p. 284–286° (in a capillary tube), undepressed by admixture with an authentic sample of anthraquinone. The infrared spectrum of the substance was identical with that of anthraquinone.

Anal. Calcd. for $C_{14}H_8O_2$: C, 80.73; H, 3.87. Found: C, 80.72; H, 4.35.

***anti*-[2.2]Paracyclonaphthane (*anti*-II).**—Combined fractions 120–152 (0.430 g.) were treated with chloranil by the same procedure to give 0.358 g. of a yellow solid, m.p. 137–175°. Attempted recrystallization of this material from chloroform solution resulted in extensive decomposition. The total combined material was chromatographed on silica gel to give 0.017 g. of anthraquinone and 0.019 of *anti*-II, m.p. 294–296°.

Combined fractions 153–185 (0.123 g.) were aromatized by the same procedure to give 0.088 g. of a yellow solid, m.p. 139–159°. Again attempted crystallization of the material from chloroform resulted in extensive decomposition. The material was chromatographed over 106 g. of silica gel packed in 5% chloroform in carbon tetrachloride. Compound *anti*-II was eluted from the column with 5% chloroform in carbon tetrachloride; wt. 0.030 g., m.p. 298–300°, mixture melting point with *anti*-II prepared from I, 298–300°. The ultraviolet infrared and n.m.r. spectra of the two samples are identical (see spectra section of paper).

A sample of an isomeric mixture of compounds XV and XVI which had not been fractionated was aromatized. The n.m.r. spectrum of the product indicated the presence of 84% of XVII and 16% of *anti*-II. This material was used for the n.m.r. data of Table I for XVII.

An infrared spectrum of *anti*-II in KBr pellet exhibited bands (μ) at: 6.33(m); 6.35(sh); 6.41(sh); 6.63(m); 6.88(sh); 6.91(m); 7.07(w); 7.22(m); 7.32(m); 7.67(w); 7.90(w); 8.07, 8.20, 8.48, 8.59(w); 8.70(m); 8.85(sh); 9.24, 9.70, 10.12, 10.26, 10.80, 11.25(w); 11.58(m).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES, LOS ANGELES 24, CALIF.]

Electrophilic Substitution at Saturated Carbon. XVI. Stereochemistry of Carbanions Stabilized by Phosphine Oxide Group[1,2]

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RECEIVED OCTOBER 9, 1962

Relative base-catalyzed racemization and hydrogen–deuterium exchange rates of diphenyl-2-octylphosphine oxide in various solvents were studied. Exchange occurred with moderate retention of configuration in *tert*-butyl alcohol, very slight retention in ethylene glycol, and racemization in methanol and in dimethyl sulfoxide–methanol. The observed stereospecificity is attributed to asymmetric solvation of the intermediate carbanion, and not to intrinsic asymmetry of the carbanion itself. These results indicate that carbanion–d-orbital interactions *per se* are insufficient to confer asymmetric properties on carbanions.

Six different classes of substituent effects on carbanion stability and on stereochemical capability in open-chain systems are visualized: (1) Groups such as alkyl or hydrogen do not stabilize carbanions, and anions with only these substituents are probably rapidly inverting, sp^3 hybrids.[4] (2) Groups such as carbonyl, ester, amide, cyano or nitro attached to carbanions produce sp^2 hybrids which are ambident in character, and capable of reacting at either carbon or oxygen (nitrogen). Reactions at the more electronegative center produce substances incapable of asymmetry.[5] (3) Aryl groups produce sp^2 hybrids essentially non-ambident, but capable of giving optically active products through asymmetric solvation.[6] (4) Substituents which contain elements such as silicon, phosphorus or sulfur possess d-orbitals capable of stabilizing attached carbanions, the configuration of which in open-chain systems is unclear. With the sulfone group, the carbanions have been demonstrated to be asymmetric.[7] (5) Groups, such as quaternary ammonium, attached to carbanions stabilize the anion through inductive and electrostatic effects (ylide formation); the hybridization at carbon in ylides is not known.[4] (6) Groups such as trifluoromethyl stabilize carbanions through both inductive and "negative hyperconjugative" effects, and the geometry of such carbanions is unknown.[4] Carbanions confined in small rings must accommodate their geometry to the ring system, and have been demonstrated to be special cases.[8]

The present study is addressed to the question of whether the asymmetry-conferring properties of the sulfone group on carbanions also applies to the phosphine oxide group. The system selected for study (I) bears the greatest possible resemblance to the sulfone

(1) This work was supported by a grant from the National Science Foundation.

(2) Some of the results in this paper appeared in preliminary form: D. J. Cram, R. D. Partos, S. H. Pine and H. Jäger, *J. Am. Chem. Soc.*, **84**, 1742 (1962).

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(4) Stereochemical capabilities of such carbanions are under active study.

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