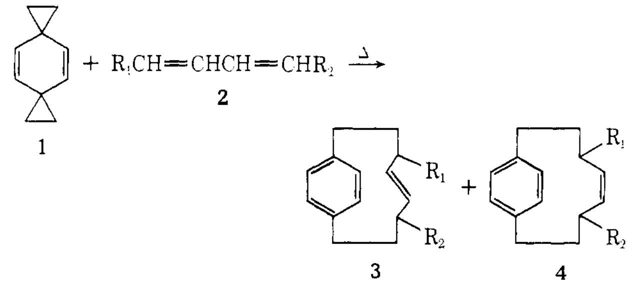
Table I. Products from the Reaction of Dispiro[2.2.2.2]deca-4,9-diene with 1,3-Butadienes[a] (% Yield)

			2	3		4
	R_1	R_2	geometry	Trans	Cis	
a	H	H		$74^{b,d}$		$10^{c,d}$
b	$COOCH_3$	H	Trans	65^{d}		5^{d}
c	CN	H	Trans	69^{d}		
			Cis	67		
d	$COOCH_3$	$COOCH_3$	Trans,trans	54^{e}	9^{f}	
			Cis,trans	39	32	
e	CN	CN	Cis,cis	58^{g}	31^{h}	
f	C_6H_5	C_6H_5	Trans,trans	30^{i}	5^{d}	

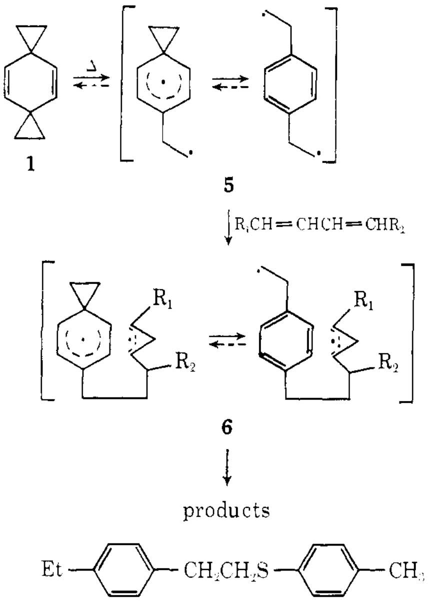
[a] The reaction condition was not optimized. [b] The nmr spectrum was in good agreement with that reported in ref 1. [c] Besides 1:1 cycloadducts, two 1:2 cycloadducts, [12]paracyclopha-4,8-diene (5%) and 7- or 8-vinyl-[10]paracycloph-4-ene (4%), were obtained. [d] Colorless oil. [e] Mp 144–145°. [f] Mp 90–90.5°. [g] Mp 155–156°. [h] Mp 134–135°. [i] Mp 110.5–111.5°.

absorption bands due to the olefinic protons undoubtedly shielded by the underlying aromatic ring were observed at δ 3.7–4.3 and in those of cis isomer **4** at somewhat lower field, δ 4.3–4.7.[1] Uv spectra showed a shift of absorption bands to longer wavelengths relative to those in the open-chain compound and the disappearance of fine structure, which were characteristic features observed in the uv spectrum of strained [*m*]paracyclophane.[1,2,6] An examination on molecular models left little doubt but that the trans isomer **3** was less strained than the cis isomer **4**. Appearance of absorption bands in the uv spectra of **4** at longer wavelengths than those in **3**, therefore, was also in accord with the assignment of structure.[5]



In the presence of 5 equiv of *p*-thiocresol, the reaction afforded no cycloadduct but *p*-diethylbenzene and the addition product **7**. Decomposition of **1** proceeded at 160° with a half-life of *ca.* 1 hr and the presence of diene appeared not to affect the decomposition rate. Thus, the reaction probably began with the homolytic cleavage of the cyclopropane bond and proceeded *via* diradical intermediates, **5** and **6**, as outlined in Scheme I. The isolation of 1:2 cycloadducts and the nonstereospecificity of the reaction, *e.g.*, *trans*-**3e** and *cis*-**3e** from *cis,trans*-**2e**, supported the above mechanism.[7] The difference in product ratios derived from the reactions with *trans,trans*-**2e** and *cis,trans*-**2e** reflected that the intermediate **6** collapsed before reaching the rotational equilibrium to the cyclophanes.[8]

Scheme I



In view of the difficulty in preparing the macrocyclic compounds, the formation of [8]paracyclophanes in high yields by way of the diradical intermediates is noteworthy. The cycloaddition of **1** with 1,3-butadienes is experimentally simple and promises to provide a route to the various interesting paracyclophane derivatives. The reaction reported here shoud be useful to explore the chemistry of paracyclophanes.

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Takashi Tsuji,* Shinya Nishida
Department of Chemistry, Faculty of Science
Hokkaido University
Kitaku, Sapporo, Japan

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(6) Uv spectra of *trans*- and *cis*-**3** closely resembled each other as did those of **4**.

(7) Under the reaction condition, the isomerizations of dienes were negligible.

(8) *Cf.* L. K. Montgomery, K. Schueller, and P. D. Bartlett, *J. Amer. Chem. Soc.*, **86**, 622 (1964).

Detection of Polytopal[1,2] Isomers in the Solution State. I. The Eight-Atom Family

Sir:

All eight-atom polyhedral boranes have a disposition of skeletal atoms that closely approximates the vertices of the D_{2d} dodecahedron.[3–6] Relatively crude molecular orbital calculations[3] for $B_8H_8^{2-}$ show that energy differentiation among the dodecahedron and alternative idealized forms such as the C_{2v} square face bicapped trigonal prism and the D_{4d} square antiprism is small with a stability order[7] of $D_{4d} > C_{2v} > D_{2d}$ and, adjusted for population analysis and solid-state parameters, of $D_{4d} > D_{2d} > C_{2v}$. We present nmr data that show structural form for $B_8H_8^{2-}$ in solution is affected by cation structure and by solvent character. For the

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(1) Polytopal[2] isomers have the same composition and connectivity relations but distinctly different geometrical skeletal frameworks, *e.g.*, the plane and the tetrahedron in the four-atom family.

(2) E. L. Muetterties, *J. Amer. Chem. Soc.*, **91**, 1636 (1969).

(3) (a) F. Klanberg, D. R. Eaton, L. J. Guggenberger, and E. L. Muetterties, *Inorg. Chem.*, **6**, 1271 (1967); (b) E. L. Muetterties and W. H. Knoth, "Polyhedral Boranes," Marcel Dekker, New York, N. Y., 1968.

(4) L. J. Guggenberger, *Inorg. Chem.*, **8**, 2771 (1969).

(5) G. S. Pawley, *Acta Crystallogr.*, **20**, 631 (1966).

(6) H. V. Hart and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **89**, 4220 (1967); *Inorg. Chem.*, **7**, 1070 (1968).

(7) These relative orderings literally should not be taken seriously because weighting of ancillary factors[3] leads to juxtaposition of order.

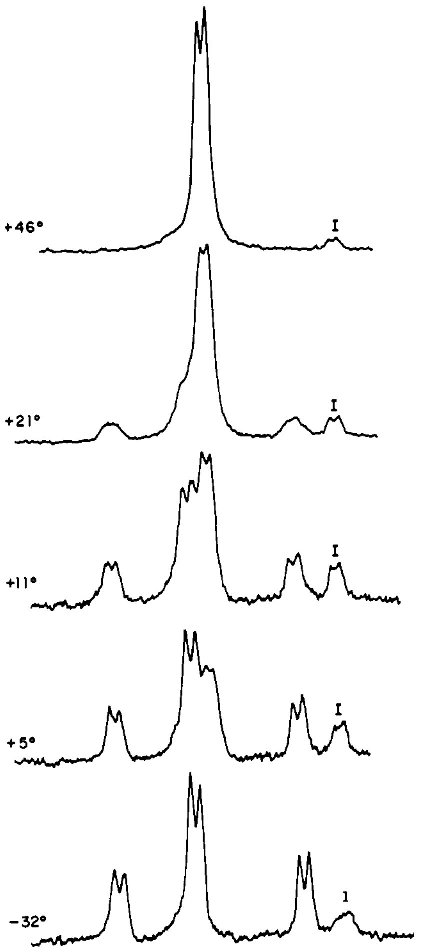

Figure 1. The temperature-dependent ^{11}B nmr spectrum for $Na_2B_8H_8 \cdot xH_2O$ in 1,2-dimethoxyethane. The smaller resonance to the right identified as "I" is due to an impurity in the polyhedral borane salt.

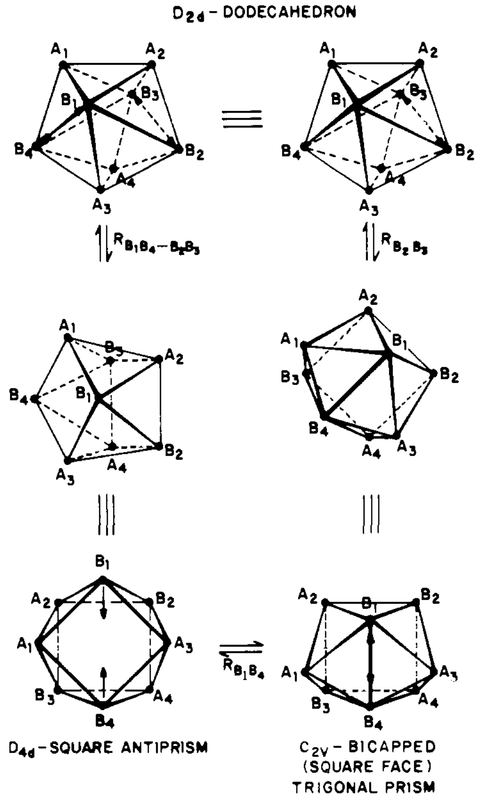

Figure 2. An idealized representation for the cyclic interrelationship for three polytopal forms in the eight-atom family. The interconversion of the dodecahedron and the square antiprism requires elongation of two of the "*b*" edges of the dodecahedron. In the rearrangement of the dodecahedron to the capped trigonal prism, elongation of only one "*b*" edge of the former is required.

$Na^+{}_2B_8H_8{}^{2-}$ salt in 1,2-dimethoxyethane, two polytopal[1,2] isomers coexist; one form is the C_{2v} isomer which is a fluxional aggregate.

The ^{11}B nmr spectrum[8] of $[(n\text{-}C_4H_9)_4N]_2B_8H_8$ in dichloromethane–toluene solution at 4° consists of three doublets (BH spin–spin coupling) of relative intensities of 2:4:2. These data are consistent only with the C_{2v} polytopal form. Above ~10° the doublets begin to broaden and in bis(2-methoxyethyl) ether the three peaks collapse into a single doublet spectrum (J_{BH} = 128 Hz) at 46°. Spectral details are consistent with those expected for a stereochemically nonrigid molecule. For $Na_2B_8H_8 \cdot xH_2O$ in 1,2-dimethoxyethane, the ^{11}B spectrum exhibits a single doublet resonance at 46°. With temperature decrease (Figure 1), the doublet intensity decreases with concomitant appearance of the 2:4:2 pattern of the C_{2v} polytopal isomer.[9] Hence, there are two different polytopal forms of $B_8H_8{}^{2-}$ in solution, both in rapid equilibrium with each other, but the rate is not comparable to the nmr time scale. At lower temperatures, *ca.* −32°, $Na_2B_8H_8$ in 1,2-dimethoxyethane is wholly, or nearly so, in the C_{2v} form. In water, $Cs_2B_8H_8$ shows only the doublet characteristic of the second polytopal form. Because the dodecahedral form *should* have a 4:4 set of doublets and because specific cation–anion or solvent–anion interactions could conceptually stabilize square faces, it is tentatively suggested that the second polytopal isomer in solution has D_{4d} square antiprismatic form.[10] The chemical shift position of this proposed D_{4d} form of $B_8H_8{}^{2-}$ then falls in line for the empirical relationship of boron coordination number with chemical shift[3] in closo boranes.

The D_{2d} dodecahedron, C_{2v} bicapped trigonal prism, and D_{4d} square antiprism are all closely interrelated by minor polyhedral edge elongations and compressions (Figure 2). It requires essentially only the stretching of one *b* edge of the dodecahedron to generate the C_{2v} bicapped trigonal prism and the stretching of *two b* edges to form the square antiprism. Simplistically then, it seems plausible that a skeletal rearrangement of the C_{2v} form could traverse the D_{2d} form more readily than could D_{4d} so that D_{4d} and C_{2v} do not rapidly interconvert on the nmr time scale (at 20–40°). A three minima potential energy surface with small differences between minima and maxima can be readily envisaged. It should be reemphasized that D_{4d} and C_{2v} do interconvert but not at rates fast with respect to the nmr experiment up to ~45°.

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(8) The ^{11}B nmr spectra were obtained at 80.5 MHz.

(9) Nmr parameters: J_{BH} = ~128 Hz; C_{2v} δ_1 −9.5, δ_2 +3.6, δ_3 +22.2 ppm; D_{4d} δ +6.8 ppm (+11°); $BF_3 \cdot O(C_2H_5)_2$ external reference.

(10) If the second form were the dodecahedral isomer, it would probably—but not unequivocally—be fluxional to conform with the observed single doublet resonance. That is, it would necessarily be in equilibrium with, or traverse, another polytopal form. In this system, there basically is the D_{4d}, D_{2d}, and C_{2v} (Figure 2) triumvirate. If one accepts the *first* thesis, then all three forms must be in fast dynamic equilibria, a situation that is patently inconsistent with the experimental data.

Additional studies of a variety of $B_8H_8^{2-}$ salts in a wide range of solvents—protic and aprotic, polar and nonpolar—are being undertaken in an attempt to identify solution-state factors that stabilize individual polytopal forms in the eight-atom family.[11]

[11] E. L. Muetterties, R. J. Wiersema, and M. F. Hawthorne, manuscript in preparation.

[12] Address correspondence to this author at the Department of Chemistry, Cornell University, Ithaca, N. Y. 14850.

E. L. Muetterties*[12]
Contribution No. 2056, Central Research Department
E. I. du Pont de Nemours and Company
Wilmington, Delaware 19898

R. J. Wiersema, M. F. Hawthorne
Department of Chemistry, University of California
Los Angeles, California 90024

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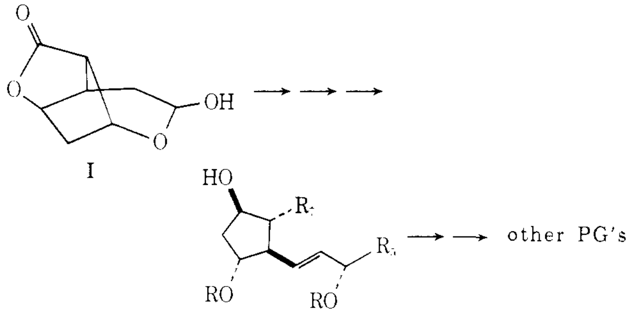
New Extensions of the Bicyclo[2.2.1]heptane Route to Prostaglandins

Sir:

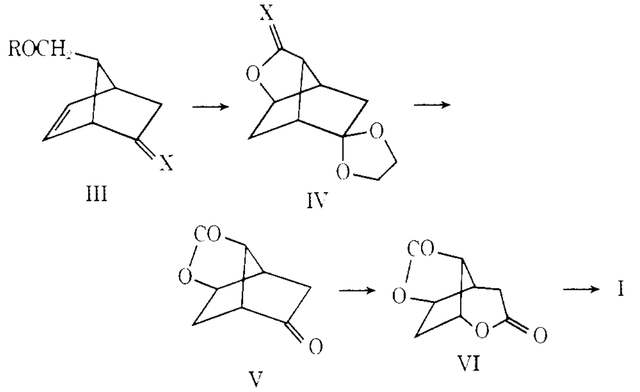
The synthetic approach to prostaglandins *via* bicyclo[2.2.1]heptane derivatives, which has previously been reported,[1] is characterized by a degree of flexibility which is unique. Not only can F_α, E, A, C, and B prostaglandins of the first, second, and third series be obtained stereoselectively and efficiently from common intermediates, but the order of synthesis can be varied (*e.g.*, F_α before E before A *or* A before E before F_α). The carboxylic side chain can be introduced before or after the 3-hydroxyoctene chain. This communication deals with the extension of the approach to allow the direct synthesis of F_β prostaglandins II specifically using the key intermediate I. Several different routes to I have been developed with the result that this substance is now very easily available. Furthermore, as a consequence of these studies, a new mode of entry into the bicyclo[2.2.1]heptane approach to prostaglandins has been uncovered.



I

II (PGF_β, R = H)

The keto 2,2,2-trichloroethyl ether (III), R = CH_2CCl_3 and X = O,[1j] was ketalized with ethylene glycol–toluenesulfonic acid in benzene to give III, R = CH_2CCl_3 and X = $O(CH_2)_2O$[2,3] (96% yield), and cleaved with zinc in methanol at 30–40° to afford (90%) the hydroxy ketal III, R = H and X = $O(CH_2)_2O$.[3] This hydroxy ketal upon treatment with mercuric acetate (1 equiv) in tetrahydrofuran (THF)–water (1:1) at 25° for 15 min followed by 0.5 *M* aqueous sodium borohydride containing NaOH yielded the ether ketal IV, X = H_2 (*ca.* 70%).[3] Oxidation of this ether with 0.03 equiv of ruthenium tetroxide in the presence of aqueous sodium periodate at 25° for 10 hr followed by treatment of the product with aqueous acid gave (*ca.* 80%) the keto lactone V,[3] mp 195–196°, infrared max 5.59 and 5.69 μ ($CHCl_3$). Baeyer–Villiger oxidation of V with 1.25 equiv of *m*-chloroperbenzoic acid in methylene chloride in the presence of powdered sodium bicarbonate yielded (75%) the dilactone VI,[3] infrared max 5.57 and 5.71 μ ($CHCl_3$). Reaction of dilactone VI with 1 equiv of diisobutylaluminum hydride in toluene or methylene chloride at −78° led to selective reduction of the δ-lactone carbonyl to afford the desired γ-lactone-δ-lactol I.



III

IV

V

VI

A parallel synthesis of I was also developed starting from the benzyl ether[2c] III, R = $CH_2C_6H_5$ and X = O, reaction of which with acetic anhydride–boron trifluoride etherate[4] gave the acetoxy ketone III, R = AcO and X = O,[3] further converted to the above-described intermediate III, R = H and X = $O(CH_2)_2O$, by acetate cleavage (K_2CO_3–methanol) and ketalization with ethylene glycol.[5]

An even simpler synthetic route to V and I has been developed starting from norbornadiene. Reaction of norbornadiene with 1 equiv of paraformaldehyde in formic acid (97%) containing a catalytic amount of sulfuric acid at 25–30° produced diformate VII,[3] bp 104° (0.3 mm), in 84% yield.[6] Oxidation of VII with

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[1] See (a) E. J. Corey, T. K. Schaaf, W. Huber, U. Koelliker, and N. M. Weinschenker, *J. Amer. Chem. Soc.*, **92**, 397 (1970); (b) E. J. Corey, R. Noyori, and T. K. Schaaf, *ibid.*, **92**, 2586 (1970); (c) E. J. Corey, S. M. Albonico, U. Koelliker, T. K. Schaaf, and R. K. Varma, *ibid.*, **93**, 1491 (1971); (d) E. J. Corey, H. Shirahama, H. Yamamoto, S. Terashima, A. Venkateswarlu, and T. K. Schaaf, *ibid.*, **93**, 1490 (1971); (e) E. J. Corey, T. Ravindranathan, and S. Terashima, *ibid.*, **93**, 4326 (1971); (f) E. J. Corey and R. K. Varma, *ibid.*, **93**, 7319 (1971); (g) E. J. Corey, K. B. Becker, and R. K. Varma, *ibid.*, **94**, 8616 (1972); (h) E. J. Corey and T. K. Schaaf, *J. Org. Chem.*, **37**, 2921 (1972); (i) E. J. Corey, *Ann. N. Y. Acad. Sci.*, **180**, 24 (1971); (j) E. J. Corey and G. Moinet, *J. Amer. Chem. Soc.*, **95**, 6831 (1973); E. J. Corey and J. Mann, *ibid.*, **95**, 6832 (1973); (k) E. J. Corey and H. E. Ensley, *J. Org. Chem.*, **38**, 3187 (1973); (l) for a review see J. S. Bindra and R. Bindra, *Progr. Drug Res.*, **17**, 410 (1973).

[2] Intermediates are racemic and liquid unless otherwise indicated.

[3] Assignment of structure supported by (a) spectroscopic data (infrared, nmr) and (b) elemental analysis.

[4] E. J. Corey and P. A. Grieco, *Tetrahedron Lett.*, 107 (1972).

[5] Jones oxidation of the alcohol III, R = H and X = O, afforded the corresponding keto acid,[3] mp 120–122°, which could also be converted to the lactone V using the sequence mercuration (mercuric acetate–aqueous THF), isolation as the chloromercurial, and reductive demercuration (zinc borohydride in dimethoxyethane). However, this process is not regioselective and produces both V and the position isomeric keto lactone.

[6] The diacetate corresponding to VII can be produced similarly from norbornadiene using acetic acid–sulfuric acid as medium. For an analogous Prins reaction with rearrangement in the bicycloheptene series, see R. Zimmerman and F. Reiners, *Naturwissenschaften*, **51**, 434 (1964).