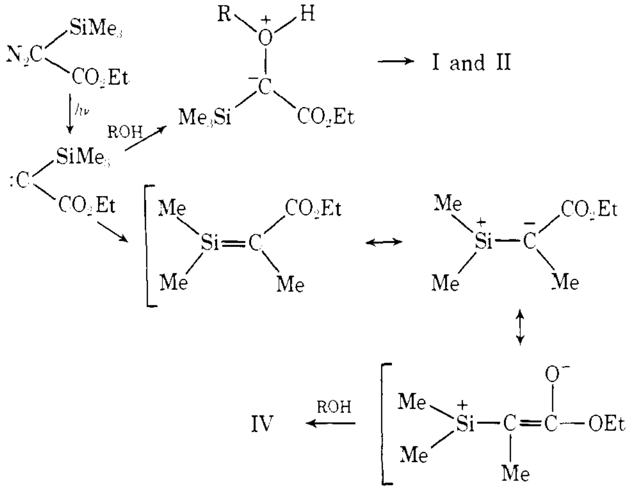
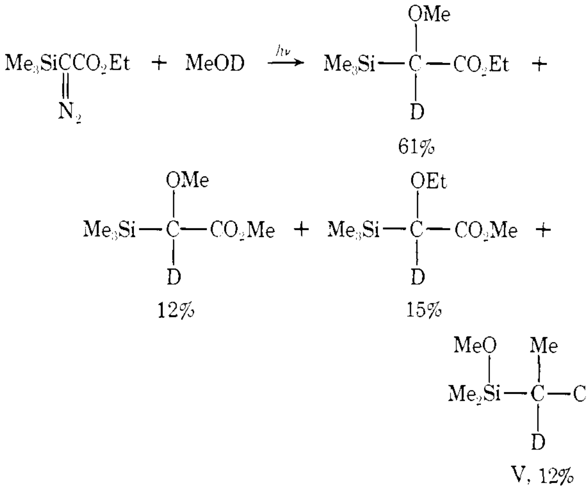
the methyl migration proceeds more rapidly. We rationalize the formation of IV from the diazo compound as shown below.[7,8]



The possibility of the intervention of a silacyclopropane intermediate *via* 1,3 insertion of the carbene[9,10] was tested. Ethyl trimethylsilyldiazoacetate in methanol-d_1 was subjected to photodecomposition. These results indicate a very low probability for a silacyclopropane intermediate; the deuterium from methanol was only found on the α carbon and not in the migrating methyl group. The structure of the methyl migration product V was deduced from its ^{1}H nmr spectrum [τ 5.95 (2 H, q, CO_2CH_2), 6.58 (3 H, s, $SiOCH_3$), 8.77 (3 H, t, CO_2CCH_3), 8.83 (3 H, br s, $SiCCH_3$), and 9.87 (6 H, s, $Si(CH_3)_2$)], and its exact parent peak (found, *m/e* 191.1023; calcd, *m/e* 191.1083). The isotopic purity of V was found to be higher than 99% from the relative peak heights.



V, 12%

Finally the evidence against the role of trimethylsilyl(carbethoxy)carbonium ion intermediate which might be formed by protonation of the diazo compound was also obtained. Ethyl trimethylsilyldiazoacetate in methanol in the presence of a catalytic amount of hydrochloric acid did not produce a methyl migration product, but did produce ethyl methoxyacetate quantitatively.[11] This reaction indicates that the carbonium ion is not implicated in the photoreaction, at least not in the formation of methyl migration product.

Further evidence against any role of trimethylsilyl(carbethoxy)carbonium ion intermediate comes from the irradiation of ethyl trimethylsilyldiazoacetate in a methanol solution of lithium bromide.[12] The photolysis did not produce the expected bromoacetate and the original product distribution was not affected by the lithium bromide.

We are currently investigating other silicon-containing diazo compounds as sources for different Si=C species as part of our study.

Acknowledgment. We thank the Shinetsu Chemical Co. for providing trimethylchlorosilane.

---

(7) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1971.

(8) M. Jones, Jr., and R. A. Moss, "Carbenes," Vol. I, Wiley, New York, N. Y., 1973.

(9) J. W. Connolly, *J. Organometal. Chem.*, **11**, 429 (1968).

(10) U. Schöllkopf, D. Hoppe, N. Rieber, and V. Jacobi, *Justus Liebigs Ann. Chem.*, **730**, 1 (1969).

(11) One-thirtieth millimole of acid decomposed 1 mmol of the diazo compound in 2 ml of methanol at room temperature, and the product was identified by comparison with an authentic sample.

(12) One millimole of lithium bromide was used for the photolysis of 1 mmol of the diazo compound in 2 ml of methanol.

Wataru Ando,* Tsuneo Hagiwara, Toshihiko Migita
Department of Chemistry, Gunma University
Kiryu, Gunma, Japan

Received June 16, 1973

A Novel One-Step Synthesis of [8]Paracyclophanes. Cycloaddition of Dispiro[2.2.2.2]deca-4,9-diene with 1,3-Butadienes

Sir:

In spite of the considerable interest in the chemistry of the lower homologs of [*m*]paracyclophanes, only a few preparation methods have been available.[1-3] We report here the cycloaddition of dispiro[2.2.2.2]deca-4,9-diene (**1**)[4] with a variety of substituted 1,3-butadienes, which provides a convenient preparation method of [8]paracyclophanes and whose reaction mechanism is of considerable interest.

In a general procedure, 200 mg (1.51 mmol) of **1** and 2 equiv of diene in 8 ml of benzene were heated at 160° for 5 hr in a sealed glass ampoule under argon. The reaction products were isolated either by preparative vpc or column chromatography on silica gel and their structures were confirmed by elemental analysis and mass, nmr, uv, and ir spectroscopies.[5] The reaction was quite general and with both 1-substituted and 1,4-disubstituted 1,3-butadienes afforded [8]paracyclophanes in 60-90% yields as shown in Table I. In nmr spectra of *trans*-[8]paracycloph-4-enes (**3**), the characteristic

---

(1) D. J. Cram and H. U. Daeniker, *J. Amer. Chem. Soc.*, **76**, 2743 (1954); D. J. Cram and M. F. Antar, *ibid.*, **80**, 3109 (1958); D. J. Cram and G. R. Knox, *ibid.*, **83**, 2204 (1961); D. J. Cram, C. S. Montgomery, and G. R. Knox, *ibid.*, **88**, 515 (1966).

(2) N. L. Allinger, L. A. Freiberg, R. B. Herman, and M. A. Miller, *ibid.*, **85**, 1171 (1963); N. L. Allinger and T. J. Walter, *ibid.*, **94**, 9267 (1972).

(3) A. D. Wolf, V. V. Kane, R. H. Levin, and M. Jones, Jr., *ibid.*, **95**, 1680 (1973).

(4) T. Tsuji, S. Nishida, and H. Tsubomura, *J. Chem. Soc., Chem. Commun.*, 284 (1972).

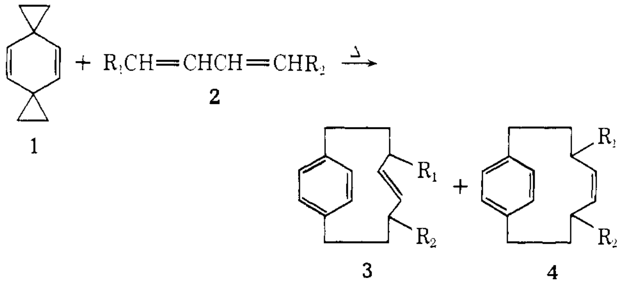
(5) For example, **3b**: *m/e* 244 (P^+); nmr (100 MHz, CCl_4, TMS) δ 0.9-2.5 (br m, 9 H), 3.02 (m, 2 H), 3.43 (s, 3 H), 3.95 (d of d, J = 8 and 15 Hz, 1 H), 4.00 (d of d, J = 9 and 15 Hz, 1 H), 6.90 (m, 4 H); uv (in EtOH) λ_{max} (ε) 222 (7300), 266 (sh, 320), 271 (400), 278 nm (360). **4b**: *m/e* 244 (P^+); nmr (100 MHz, CCl_4, TMS) δ 1.35 (m, 4 H), 2.30 (m, 5 H), 2.95 (m, 2 H), 3.43 (s, 3 H), 4.50 (d of d, J = 9 and 11 Hz, 1 H), 4.70 (d of d, J = 9.5 and 11 Hz, 1 H), 6.94 (s, 2 H), 7.00 (s, 2 H); uv (in EtOH) λ_{max} (ε) 226 (6200), 277 (370), 284 nm (330).

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

			2	3		
	R_1	R_2	geometry	Trans	Cis	4
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°.

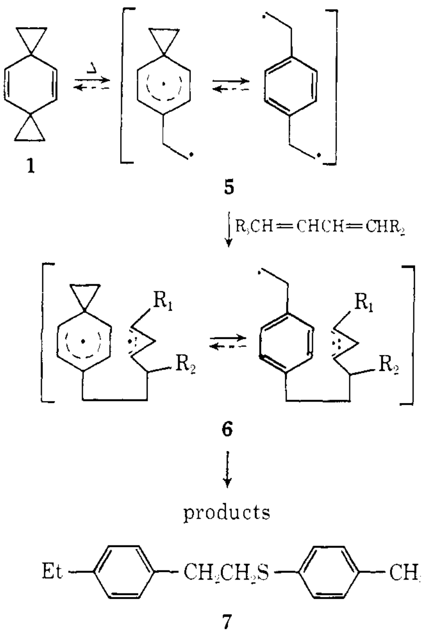
absorption bands due to the olefinic protons undoubtedly shielded by the underlying aromatic ring were observed at δ 3.7–4.3 and in those of cis isomer **4** at somewhat lower field, δ 4.3–4.7.[1] Uv spectra showed a shift of absorption bands to longer wavelengths relative to those in the open-chain 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]

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.

Scheme I



Acknowledgment. We thank the Ministry of Education for their support of this work.

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

Received May 29, 1973

---

(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

---

(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.