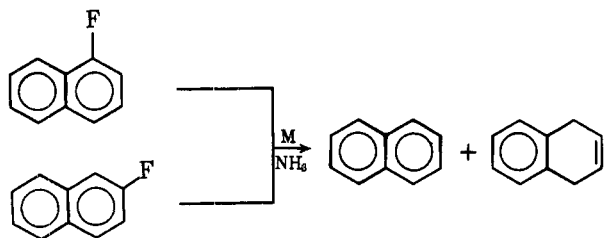


corresponding hydrocarbons often results in significant localization of the charge in the intermediate radical anions or dianions.⁹ However, both 1- and 2-fluoronaphthalene afforded only naphthalene and its reduction products.



Experimental Section

General. Reductions were carried out by adding sodium or lithium metal to the fluoroaromatic compound in liquid ammonia with anhydrous ether as a cosolvent. In the case of polynuclear and biphenyl derivatives, solid ammonium chloride or water was used to quench the reaction whereas absolute alcohol was used with monobenzenoid compounds.

In cases where fluorine was lost (*p*-fluorobenzoic acid, 4-fluorobiphenyl, 4,4'-difluorobiphenyl, *p*-fluorotoluene, *p*-fluoroanisole, 1-fluoronaphthalene, and 2-fluoronaphthalene), the reduction products are identical with those resulting from reduction of the corresponding nonfluorinated derivatives, and these compounds have previously been characterized (i.e., 1,4-dihydrobenzoic acid, 1,4-dihydrobiphenyl, 2,5-dihydrotoluene, 2,5-dihydroanisole, and 1,4-dihydronaphthalene).⁵ The absence of fluorinated reduction products in these cases was determined by GLC and/or NMR analysis. In addition, we have previously described the experimental procedure for the preparation of 3-fluoro-1,4-dihydrobenzoic acid.¹⁰

3,3'-Difluoro-1,4-dihydrobiphenyl. Sodium metal (10.4 mg-atoms) was added to 3,3'-difluorobiphenyl (5.2 mmol, 1 g) in 60 mL of anhydrous ether and 100 mL of anhydrous ammonia at -78°C . After 20 min, solid ammonium chloride was added and the crude product isolated by ether extraction. The resultant oil was distilled, bp 135°C (5 mm), to give 0.5 g (50%) of pure material: NMR (CDCl_3) δ 7.2 (m, 1 H), 6.9 (m, 3), 5.7 (m, 2, H_5 and H_6), 5.2 (d, 1, H_2), 4.1 (m, 1, H_1), 2.9 (d, 2, H_4).

Anal. Calcd for $\text{C}_{12}\text{H}_{10}\text{F}_2$: C, 74.99; H, 5.24; F, 19.77. Found: C, 74.75; H, 5.32; F, 19.70.

3-Fluorotrimethylsilylbenzene. A slight excess of *n*-butyllithium (1.1 equiv, 2 M in hexane) was added to 3-fluorobromobenzene (3 g, 17 mmol) in anhydrous ether at -78°C . After stirring for 1 h, chlorotrimethylsilane (1 equiv, 1.8 g) was added and the solution was allowed to warm to room temperature (1.5 h). Water was then added followed by ether extraction resulting in an oil which was distilled, bp 60°C (5 mm), to give pure material (1.2 g, 40%): NMR (CDCl_3) δ 7.3 (m, 4 H), 0.25 (s, 9).

Anal. Calcd for $\text{C}_9\text{H}_{13}\text{FSi}$: C, 64.26; H, 7.79; F, 11.30. Found: C, 63.95; H, 8.02; F, 11.55.

3-Fluoro-1,4-dihydrotrimethylsilylbenzene. Lithium wire (0.13 g, 18 mg-atoms) was added to 3-fluorotrimethylsilylbenzene (1.2 g, 7.2 mmol) in 60 mL of anhydrous ammonia containing 5 mL of absolute ethanol. After the blue color had disappeared, saturated ammonium chloride was added and the product was isolated by ether extraction. Distillation gave a colorless oil, bp 37°C (5 mm), 0.5 g (40%): NMR (CDCl_3) δ 5.7 (m, 3 H), 2.8 (m, 2), 2.2 (m, 1), 0.05 (s, 9).

Anal. Calcd for $\text{C}_9\text{H}_{15}\text{FSi}$: C, 63.53; H, 8.88; F, 10.59. Found: C, 64.17; H, 9.05; F, 10.22.

3-Fluoro-1,4-dihydrobiphenyl. 3-Fluorobiphenyl¹¹ was reduced in the same manner as described above for 3,3'-difluorobiphenyl, to afford 3-fluoro-1,4-dihydrobiphenyl as the major reduction product together with minor products which could not be characterized. An analytical sample was trapped from the gas chromatograph. Structural assignment was based on the appearance of a vinyl proton shifted to higher field and exhibiting large (18 Hz) coupling from the adjacent ^{19}F . NMR (CDCl_3) δ 7.2 (m, 5 H), 5.7 (m, 2), 5.27 (d of m, 1), 4.2 (m, 1), 2.8 (d, 2).

Anal. Calcd for $\text{C}_{12}\text{H}_{11}\text{F}$: C, 82.73; H, 6.36; F, 10.90. Found: C, 82.68; H, 6.49; F, 10.75.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

Registry No.—Ammonia, 7664-41-7; 3,3'-difluoro-1,4-dihydrobiphenyl, 62476-43-1; 3,3'-difluorobiphenyl, 396-64-5; 3-fluorotrimethylsilylbenzene, 7217-41-6; 3-fluorobromobenzene, 1073-06-9; chlorotrimethylsilane, 75-77-4; 3-fluoro-1,4-dihydrotrimethylsilylbenzene, 62476-44-2; 3-fluorobiphenyl, 2367-22-8; 3-fluoro-1,4-dihydrobiphenyl, 62476-45-3.

References and Notes

- (1) (a) A. J. Birch and G. Subba Rao, *Adv. Org. Chem.*, **8**, 33 (1972); (b) M. Smith, "Reduction", R. L. Augustine, Ed., Marcel Dekker, New York, N.Y., 1968, p 144; (c) H. Smith, "Chemistry in Nonaqueous Ionizing Solvents", Vol. 1, G. Jander, H. Spandau, and C. C. Addison, Ed., Interscience, New York, N.Y., 1963, Part 2, p 196.
- (2) See also R. A. Rossi and J. F. Bunnett, *J. Am. Chem. Soc.*, **96**, 112 (1974), and references cited therein.
- (3) B. J. Wakefield, "The Chemistry of Organolithium Compounds", Pergamon Press, Oxford, 1974, p 51.
- (4) With some aryl halides, benzyne intermediates have been observed.^{1,2} Both the product analysis and the observed substituent effects in the systems under current study negate the possibility of such intermediates.
- (5) R. G. Harvey, *Synthesis*, 161 (1970), and references cited therein.
- (6) Depending on the amount of metal used (2 equiv is consumed in the loss of fluoride), the hydrogenolyzed benzene nuclei can be subsequently reduced to non-fluorine-containing cyclohexadienes. Chlorine is lost even from the meta position.
- (7) Electrochemical generation of radical anions in the isomeric fluorobenzonitrile have also illustrated unique behavior with the meta isomer: K. J. Hauser, D. E. Bartak, and M. D. Hawley, *J. Am. Chem. Soc.*, **95**, 6033 (1973).
- (8) A. Streitwieser, Jr., and F. Mares, *J. Am. Chem. Soc.*, **90**, 2444 (1968).
- (9) A. Streitwieser, Jr., and S. Suzuki, *Tetrahedron*, **16**, 153 (1961).
- (10) P. W. Rabideau, J. W. Paschal, and L. E. Patterson, *J. Am. Chem. Soc.*, **97**, 5700 (1975).
- (11) Prepared by the reaction of 3-fluorobenzene diazonium chloride with sodium hydroxide and benzene.

Steric Effects in Photochemical Intramolecular $[\pi 2 + \pi 2]$ Ring Closure Reaction of Polycyclic Diolefins Leading to Strained Cage Molecules. Empirical Force Field Calculations

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The effect of ground state conformation on photochemical reactivity has rarely been studied¹ except in the solid state reactions.² The $[\pi 2 + \pi 2]$ cycloaddition, one of the most well-studied photochemical processes,³ of polycyclic dienes leading to strained cage molecules provides an ideal material to probe the possible role of steric requirements. A variety of examples have already been accumulated wherein the steric environments with respect to the reacting double bonds differ considerably. In accordance with expected steric control, recorded yields of such reactions range between zero and quantitative (Table I). We are interested, from a rather practical standpoint, in studying how steric factors in the ground state influence the appalling difference in the yields.

Photochemical yields are also affected by other factors such as nearby substituents and side reactions including cycloreversions.⁴ In order to reduce complications arising from these secondary factors to a minimum, we primarily limit our attention to sensitized irradiation of diolefins having no substituent. Diolefins carrying electron-deficient substituents not directly attached to the double bond are considered only for comparison purposes, while those carrying the substituents directly attached to the double bond are not considered except for a homologous series. The effects of side reactions will be discussed when the yield of expected product is poor.

Table I. Calculated Distance r and Orientation θ between Two Double Bonds in Polycyclic Diolefins and Strain Increase Accompanying Photochemical Ring Closure

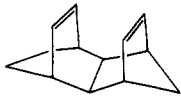
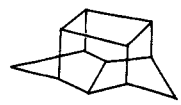
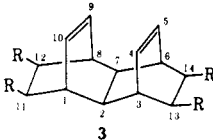
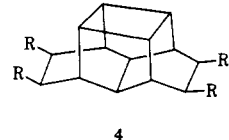
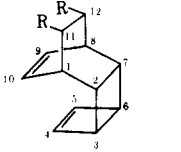
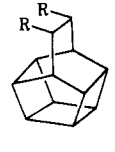
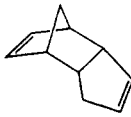
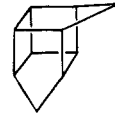
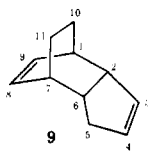
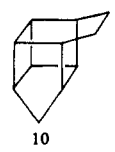
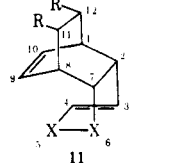
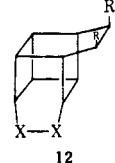
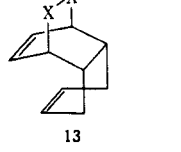
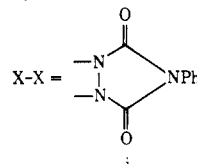
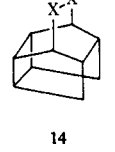
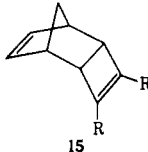
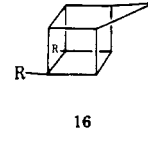
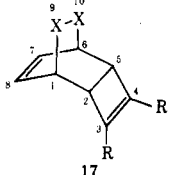
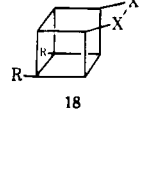
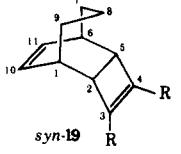
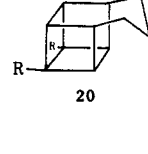
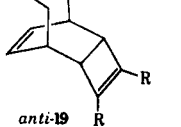
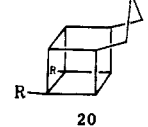
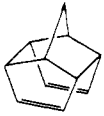
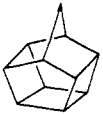
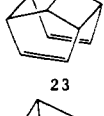
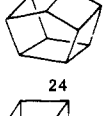
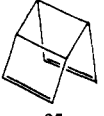
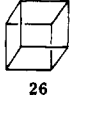
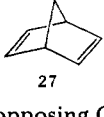
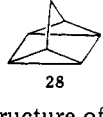
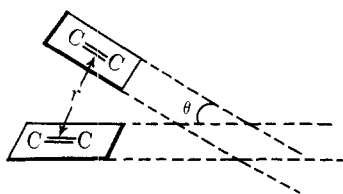
r , Å ^a	θ , deg ^b	Starting diene	Yield, %	Product	Δ_{strain} , kcal/mol ^c
2.94	0		100 ^d		14.29 ^e
2.80 ^f 3.05 ^g	0 ^f 12.4 ^g		85 ^h		29.92 ⁱ 26.31 ^j
3.05 ^f 3.07 ^g	0 11.5 ^g		80, ^h 75 ^k		18.78 ⁱ 18.26 ^j
3.08	28.9		61, ^l 31 ^m		52.28
3.04 ^f 3.04 ^g	21.6 ^f 21.6 ^g		15 ⁿ		52.17 ⁱ 54.45 ^j
3.62 ^f 3.01 ^g	33.2 ^f 40.0 ^g		Trace, ^o 63 ^p		51.61 ⁱ 52.01 ^j
2.93 ^f 2.95 ^g	0 ^f 11.3 ^g		80, ^{q,r} 83 ^q X-X = 		35.09 ⁱ 34.95 ^j
2.87	0		—, ^t 80–85 ^{u,v}		65.13 ^{e,w}
2.86 ^f	0 ^f		5, ^u 20–25, ^x 58–62 ^y		72.64 ^{e,i}
2.92 ^f	0 ^f		0 ^u		78.14 ⁱ
2.92 ^f	0 ^f		0 ^u		77.05 ⁱ

Table I
(Continued)

r , Å ^a	θ , deg ^b	Starting diene	Yield, %	Product	Δ_{strain} , kcal/mol ^c
2.77	0		50 ^z		70.72
2.86	0		0 ^{aa}		110.87 ^e
3.05	0		0 ^{bb}		71.88 ^e
2.4 ^{cc}	0 ^{cc}		95 ^{dd}		66.4 ^{ee} 53.1 ^s

^a Distance between midpoints of opposing CC double bonds in minimum energy structure of the starting diene. ^b Dihedral angle between two planes containing four unsaturated carbon atoms in the minimum energy structure. ^c (Calculated strain energy of product) - (calculated strain energy of starting diene), according to Allinger 1971-1972 force field, 25°C, gas phase. The values refer to unsubstituted structures (R = H). See Tables II and III and ref 8a for individual strain energy values. ^d Reference 11. ^e For calculated strain of the product, see Table XII of ref 8a. ^f Eclipsed conformation. ^g Twisted conformation. ^h R, R = (CO)₂O, (CN)₂; ref 12. ⁱ Based on eclipsed starting diolefin conformation. ^j Based on twisted starting diolefin conformation. ^k R, R = CH₃O, CNCO, CH₃; ref 13. ^l G. O. Schenck and R. Steinmetz, *Chem. Ber.*, **96**, 520 (1963); J. Blum, C. Zlotogorski, and A. Zoran, *Tetrahedron Lett.*, 1117 (1975). ^m Refers to corresponding 5-exo alcohol: W. L. Dilling and C. E. Reineke, *Org. Photochem. Synth.*, **1**, 85 (1971). ⁿ E. Osawa, Y. Fujikura, K. Aigami, Y. Inamoto, N. Takaishi, P. Grubmüller, and P. v. R. Schleyer, manuscript in preparation. ^o R = H; X = CH₂; ref 17. ^p R, R = (CO)₂O, (CN)₂; X-X = CH=CH; ref 12. ^q Reference 19. ^r X-X = *trans*-CH(CO₂Et)-CH(CO₂Et). ^s Based on strain energies (norbornadiene 25.6, quadricyclane 78.7 kcal/mol) derived from combustion analysis: H. K. Hall, Jr., C. D. Smith, and J. H. Baldt, *J. Am. Chem. Soc.*, **95**, 3197 (1973). ^t R = H, yield not reported, ref 20. ^u R = OSi(CH₃)₃; X = CH₂; ref 14. ^v The ring closure reaction with an oxa analogue proceeds in 15-35% yield: W. Eberback and M. Perroud-Argüelles, *Chem. Ber.*, **105**, 3078 (1972). ^w Calculated heat of formation of homocubane reported in Table XII of ref 8a should read 99.03 kcal/mol. ^x R = COOCH₃; X = CH₂; W. G. Dauben, C. H. Schallhorn, and D. L. Whalen, *J. Am. Chem. Soc.*, **93**, 1446 (1971); R = H; X-X = benzo: L. A. Paquette, M. J. Kukla, and J. C. Stowell, *ibid.*, **94**, 4920 (1972); R = H; X-X = cyclobuteno: L. A. Paquette and M. J. Kukla, *J. Chem. Soc., Chem. Commun.*, 409 (1973). ^y R, R = (CO)₂O; X = CH₂; S. Masamune, H. Cuts, and M. G. Hogben, *Tetrahedron Lett.*, 1017 (1966); H. G. Cuts, E. N. Cain, H. Westberg, and S. Masamune, *Org. Photochem. Synth.*, **1**, 83 (1971); L. A. Paquette and J. C. Stowell, *J. Am. Chem. Soc.*, **93**, 2459 (1971). ^z Reference 24. ^{aa} Reference 25. ^{bb} References 26, 28. ^{cc} Reference 5, based on electron diffraction analysis: Y. Morino, K. Kuchitsu, and A. Yokozeki, *Bull. Chem. Soc. Jpn.*, **40**, 1552 (1967). ^{dd} Reference 31. ^{ee} Based on strain energies derived from heats of hydrogenation data. Schleyer's strain energy values [P. v. R. Schleyer, J. E. Williams, and K. R. Blanchard, *J. Am. Chem. Soc.*, **92**, 2377 (1970)] are to be corrected using a revised heat of formation of norbornane (Table IV). Revised enthalpies and strain energies (kcal/mol) are 55.7 and 30.7 for norbornadiene, and 79.6 and 97.1 for quadricyclane. Allinger and Sprague (ref 7b) give a slightly higher value (31.59 kcal/mol) for the strain of norbornadiene.

Steric factors considered include the midpoint distance r and the orientation θ between opposing double bonds, the



strain increase, Δ_{strain} , in the product relative to the starting diene.⁵ These quantities can be estimated most readily and accurately by molecular mechanics calculations⁶ based on Allinger 1971-1972 force field,⁷ and summarized in Table I. The strain increase (Δ_{strain}) was obtained as the difference in strain energies of starting diolefin (Table II) and product (Table III). Table III includes corresponding energies obtained by using the Engler force field⁸ for comparison. For those starting diolefins containing bicyclo[2.2.2]octane and bicyclo[3.2.2]nonane skeletons (3, 5, 9, 11, and 13), twist as well as eclipse conformations are considered in view of the flexible nature of these systems.^{9,10}

The criteria considered here appear to contribute more or less to the reactivity of diolefins listed in Table I. Most of the calculated distances r between opposing double bonds are in the vicinity of 3 Å, considerably shorter than the limiting distance of about 4 Å beyond which neither intra- nor intermolecular [π 2 + π 2] cycloadditions take place in solid state photochemical reactions.^{2,5} Thus, the observed high yield of 2¹¹ can be best explained by a remarkably small strain increase accompanying the ring closure, rather than the obvious close and parallel orientation of the double bonds in 1. Close, parallel orientations of double bonds in 15, 17, and 21 lead to poorer yields in the ring closure, indicating that the orientation factor does not always dominate. High-yield reactions 3 \rightarrow 4¹² and 5 \rightarrow 6^{12,13} are also accompanied by only moderate Δ_{strain} values, although these examples are assisted by the electron-deficient substituents.

There appears to be essentially no difference between two reactions (7 \rightarrow 8 and 9 \rightarrow 10) as far as the three criteria, r , θ , and Δ_{strain} , are concerned. The poor yield of 10 should then be attributed to the lower reactivity of the bicyclo[2.2.2]octene type double bond of 9 relative to the norbornene type double bond of 7, as suggested by Miller and Dolce.¹⁴ The reactivity

Table II. Calculated Heats of Formation and Strain Energies of Polycyclic Diolefins and Monoolefins Based on Allinger 1971-1972 Force Field^a (kcal/mol, 25 °C, Gas)

Registry no.	Diolefin		ΔH_f°	
			ΔH_f°	Strain
1076-13-7	<i>endo,endo</i> -Tetracyclo[4.2.1.1 ^{3,6} .0 ^{2,7}]dodeca-4,9-diene (1) ^b		59.74	49.15
62415-10-5	<i>endo,endo</i> -Tetracyclo[6.2.2.2 ^{3,6} .0 ^{2,7}]tetradeca-4,9-diene (3, R = H) ^c	Eclipse	25.72	25.51
		Twist ^{d,e}	29.03	28.82
62415-15-0	<i>endo,endo</i> -Tetracyclo[6.2.2.0 ^{2,7} .0 ^{3,6}]dodeca-4,9-diene (5, R = H) ^c	Eclipse	88.61	78.02
		Twist ^{d,f}	89.13	78.54
1755-01-7	<i>endo</i> -Tricyclo[5.2.1.0 ^{2,6}]deca-3,8-diene (dicyclopentadiene, 7)		42.48	27.58
54483-01-1	<i>endo</i> -Tricyclo[5.2.2.0 ^{2,6}]undeca-3,8-diene (9) ^g	Eclipse	31.20	21.49
		Twist ^{d,h}	28.92	19.21
62415-13-8	<i>endo</i> -Tricyclo[6.2.2.0 ^{2,7}]dodeca-3,9-diene (dicyclohexadiene, 11, R = H; X = CH ₂) ⁱ	Eclipse	22.78	18.26
		Twist ^{d,j}	22.38	17.86
62447-34-1	<i>endo</i> -Tricyclo[6.2.2.0 ^{2,7}]dodeca-4,9-diene (13, X = CH ₂) ^k	Eclipse	23.41	18.89
		Twist ^{d,l}	23.55	19.03
15564-45-1	<i>endo</i> -Tricyclo[4.2.1.0 ^{2,5}]nona-3,7-diene (15, R = H) ^m		76.42	56.33
55054-12-1	<i>endo</i> -Tricyclo[4.2.2.0 ^{2,5}]deca-3,7-diene (17, R = H; X = CH ₂) ⁿ	Eclipse	61.65	46.75
		Twist ^{d,o}	61.73	46.83
62415-17-2	<i>syn,endo</i> -Tricyclo[4.3.2.0 ^{2,5}]undeca-3,10-diene (<i>syn</i> - 19, R = H) ^m	Eclipse	54.52	44.81
	<i>anti,endo</i> -Tricyclo[4.3.2.0 ^{2,5}]undeca-3,10-diene (<i>anti</i> - 19, R = H) ^m	Twist ^{d,p}	57.69	47.98
		Eclipse	55.61	45.90
		Twist ^{d,q}	55.55	45.84
30114-57-9	Tetracyclo[6.3.0 ^{4,11} .0 ^{5,9}]undeca-2,6-diene (homohyprophene, 21) ^r		49.97	34.19
34324-40-8	Tetracyclo[5.3.0.0 ^{2,6} .0 ^{3,10}]deca-4,8-diene (hyprophene, 23) ^s		89.43	68.46
20380-30-7	<i>syn</i> -Tricyclo[4.2.0.0 ^{2,5}]octa-3,7-diene (25) ^{t,u}		120.30	95.02

^a Reference 7. ^b P. Buck, D. Thompson, and S. Winstein, *Chem. Ind. (London)*, 405 (1960); R. B. Turner, A. D. Jarrett, P. Goebel, and B. J. Mallon, *J. Am. Chem. Soc.*, **95**, 790 (1973); J. K. Stille and D. R. Witherell, *ibid.*, **86**, 2188 (1964). ^c See ref 12 for derivatives. ^d See footnote 10. ^e Twist angles: C₁C₁₀C₉C₈, 2.5°; C₁C₁₃C₁₄C₈, 8.6°; C₁C₂C₇C₈, 11.5°. ^f Twist angles: C₁C₂C₇C₈, 8.5°; C₁C₁₁C₁₂C₈, 6.0°; C₁C₁₀C₉C₈, 2.1°; C₃C₂C₇C₆, 6.5°; C₃C₄C₅C₆, 1.1°. ^g N. Takaishi, Y. Inamoto, K. Aigami, K. Tsuchihashi, and H. Ikeda, *Synth. Commun.*, **4**, 225 (1974). ^h Twist angles: C₁C₂C₆C₇, 9.6°; C₁C₉C₈C₇, 4.0°; C₁C₁₀C₁₁C₇, 8.9°. ⁱ Reference 17. ^j Twist angles: C₁C₂C₇C₈, 19.6°; C₁C₁₀C₉C₈, 5.3°; C₁C₁₁C₁₂C₈, 13.6°. ^k See ref 19 for derivatives. ^l Twist angles: C₁C₂C₇C₈, -10.9°; C₁C₁₀C₉C₈, -3.1°; C₁C₁₁C₁₂C₈, -7.8°. ^m See ref 14 for a derivative. ⁿ See ref 14 and references cited in footnotes x and y of Table I for derivatives. ^o Twist angles: C₁C₂C₅C₆, 1.4°; C₁C₉C₁₀C₆, 1.9°; C₁C₈C₇C₆, 0.7°. ^p Twist angles: C₁C₂C₅C₆, 0.7°; C₁C₁₀C₁₁C₆, 0.8°. ^q Twist angles: C₁C₂C₅C₆, 2.0°; C₁C₁₀C₁₁C₆, 0.5°. ^r Reference 24 and G. R. Underwood and B. Ramamoorthy, *Tetrahedron Lett.*, 4125 (1970). ^s Reference 25 and L. A. Paquette, R. F. Davis, and D. R. James, *Tetrahedron Lett.*, 1615 (1974). ^t Reference 27 and M. Avram, I. D. Dinulescu, E. E. Marica, G. Mateescu, E. Slim, and C. D. Nenitzescu, *Chem. Ber.*, **97**, 382 (1964). ^u Reference 28 for a permethyl derivative.

Table III. Calculated Heats of Formation and Strain Energies of Cage Hydrocarbons (kcal/mol, 25 °C, Gas)

Registry no.	Compd	ΔH_f°		Strain	
		E ^a	A ^b	E ^a	A ^b
62415-11-6	Hexacyclo[6.4.2.0 ^{2,7} .0 ^{3,11} .0 ^{6,10} .0 ^{9,12}]tetradecane (4, R = H) ^c	11.04	13.12	53.16	55.43
62415-16-1	Hexacyclo[6.4.0.0 ^{2,7} .0 ^{3,6} .0 ^{4,12} .0 ^{5,9}]dodecane (1,1'-bishomopentaprismane, 6, R = H) ^c	58.96	64.87	90.82	96.80
6707-86-4	Pentacyclo[5.3.0.0 ^{2,5} .0 ^{3,9} .0 ^{4,8}]decane (1,3-bishomocubane, 8) ^d	48.33	52.24	75.87	79.86
62415-12-7	Pentacyclo[5.4.0.0 ^{2,5} .0 ^{3,11} .0 ^{4,8}]undecane (1,3-ethanomethanocubane, 10) ^e	40.99	43.82	73.66	76.63
62415-14-9	Pentacyclo[6.4.0.0 ^{2,5} .0 ^{3,12} .0 ^{4,9}]dodecane (1,3-bisethanocubane, 12, R = H; X = CH ₂) ^{d,f}	31.65	38.87	69.45	69.87
4421-33-4	Pentacyclo[6.4.0.0 ^{2,7} .0 ^{3,11} .0 ^{6,10}]dodecane (14, X = CH ₂) ^g	15.11	15.98	52.91	53.98
61304-39-0	Pentacyclo[5.4.0.0 ^{2,10} .0 ^{6,9} .0 ^{8,11}]undecane (20, R = H)	85.34	90.14	118.01	122.95
25107-14-6	Hexacyclo[6.2.1.0 ^{2,7} .0 ^{3,6} .0 ^{4,10} .0 ^{5,9}]undecane (homopentaprismane, 22) ^h	69.64	78.17	96.37	104.91

^a Engler force field, ref 8. ^b Allinger 1971-1972 force field, ref 7. ^c See ref 12 for derivatives. ^d Computational results for this molecule preliminarily reported in E. Ōsawa, P. v. R. Schleyer, L. W. K. Chang, and V. V. Kane, *Tetrahedron Lett.*, 4189 (1974). ^e E. Ōsawa, Y. Fujikura, K. Aigami, Y. Inamoto, N. Takaishi, P. Grubmüller, and P. v. R. Schleyer, manuscript in preparation. ^f Reference 18; K. Hirao, T. Iwakuma, M. Taniguchi, E. Abe, O. Yonemitsu, T. Date, and K. Kotera, *Chem. Commun.*, 691 (1974); T. Iwakuma, H. Nakai, O. Yonemitsu, and B. Witkop, *J. Am. Chem. Soc.*, **96**, 2564 (1974); T. Iwakuma, K. Hirao, and O. Yonemitsu, *ibid.*, **96**, 2570 (1974). ^g J. Dekker, J. J. Dekker, L. Fourie, and G. L. Wenteler, *J. S. Afr. Chem. Inst.*, **28**, 321 (1975); K. G. R. Pachler, P. L. Wessels, J. Dekker, J. J. Dekker, and T. G. Dekker, *Tetrahedron Lett.*, 3059 (1976). ^h Reference 24.

difference may be most readily understood in terms of the steric strain at these double bonds in the ground state, for which the strain energy difference between the alkene and corresponding alkane is proposed to be a good measure.^{7b} This proposal is illustrated in Table IV for the parent systems, norbornene and bicyclo[2.2.2]octene, using experimental heats of formation as the basis of calculation. About 5 kcal/mol higher strain in the norbornene double bond relative to the bicyclo[2.2.2]octene double bond, which has virtually no extra

strain compared to the ethylene double bond, is in accord with their known chemical and physical behavior.^{15,16}

The failure of dicyclohexadiene (11, R = H; X = CH₂) to effect intramolecular ring closure¹⁷ aroused some speculations.^{17,18} The relatively large distance *r* (3.6 Å) of 11 is not likely to be an obstacle in view of the known examples in solid state photochemistry.² Strain increase in the reaction 11 → 12 is comparable to the reaction 9 → 10. Therefore, from a steric standpoint, uncomfortable orientation of the double

Table IV. Alkene-Alkane Strain Energy Difference Based on Experimental Heats of Formation (kcal/mol, 25 °C, Gas)

	ΔH_f° (exptl)	Strain		Difference	
		S ^g	A ^h	S ^g	A ^h
Norbornene	20.7 ^a (21.1) ^b (15.12) ^c	23.2	23.6		
Norbornane	-12.42 ^d (-12.60) ^a	17.6	18.9	5.6	4.7
Bicyclo[2.2.2]octene	4.88 ^e	12.2 ^e	13.0		
Bicyclo[2.2.2]octane	-23.67 ^e (-23.75) ^f	11.4 ^e	13.7	0.8	-0.7

^a Based on heat of hydrogenation data: H. K. Hall, Jr., C. D. Smith, and J. H. Baldt, *J. Am. Chem. Soc.*, **95**, 3197 (1973). ^b Based on equilibration between cyclopentadiene and ethylene: R. Walsh and M. Wells, *J. Chem. Thermodyn.*, **8**, 55 (1976). ^c Combustion analysis by Hall et al. (footnote a). ^d Combustion analysis: P. v. R. Schleyer, J. E. Williams, and K. R. Blanchard, *J. Am. Chem. Soc.*, **92**, 2377 (1970). ^e Combustion analysis: S. S. Wong and E. E. Westrum, Jr., *ibid.*, **93**, 5317 (1971). ^f Combustion analysis: R. H. Boyd, S. N. Sanwal, S. Shary-Tehrany, and D. McNally, *J. Phys. Chem.*, **75**, 1264 (1971). ^g Based on Schleyer's group enthalpy increments (footnote d). ^h Based on Allinger's enthalpy increment scheme, ref 7b.

bonds (θ larger than 30°) appears responsible. The double bond isomer 13 having an ideal orientation undergoes the reaction with high yield,¹⁹ albeit this example is assisted by electron-deficient substituents and moderate strain increase. The reaction 11 → 12 also proceeds smoothly when electron-deficient substituents are present in the molecule.¹²

A homologous series of fused cyclobutene derivatives, 15, 17, and 19, provides a unique opportunity to test the effects of steric environments. Since only the first member (11, R = H) of the hydrocarbon series has been studied (without description of yield),²⁰ we first concentrate on the series of bis-(trimethylsiloxy) derivatives (R = OSiMe₃). The reaction series 15 → 16, 17 → 8, 19 → 20 shows progressive and sharp decrease in the yield of ring closure product in this order.¹⁴ Contrary to an earlier suggestion,¹⁴ calculated distances r are invariably favorable 2.9 Å within the series. High yield in the reaction 15 → 16 despite a considerably large Δ_{strain} value will be the result of the high reactivity of the norbornene type double bond.²¹ Sudden decrease in the yield of the reaction 17 → 18 is partly due to the lack of extra reactivity in the bicyclo[2.2.2]octene type double bond of 17 and partly due to an increase in Δ_{strain} by 7.5 kcal/mol. Complete inertness of 19 under irradiation must be attributed to the still higher Δ_{strain} value predicted for its ring closure reaction. The photochemical behavior of this series indicates that the maximum strain increase that can be overcome will be about 70 kcal/mol. In the presence of suitable substituents, the yield of 18 increases to a moderate range.^{22,23}

The successful ring closure of homohypostrophene (21) to homopentaprismane (22)²⁴ provides an example of hydrocarbon reaction where a Δ_{strain} value of 70 kcal/mol is tided over. This reaction is undoubtedly assisted by an ideal juxtaposition of the double bond in 21. In contrast, hypostrophene (23)²⁵ and tricyclo[4.2.0.0^{2,5}]octa-3,7-diene (25)^{26,28} are inert under any photolytic conditions and their inertness has been attributed to the mixing effect of high-lying σ orbitals with π orbitals.^{27,29} Nevertheless, we note here that an extremely large strain increase, which we predict to accompany the formation of pentaprismane (24) from 23, could well be a key factor in the failure of this reaction. On the other hand, calculated Δ_{strain} arising from the formation of cubane (26)

from 25 (72 kcal/mol) is comparable to that of homopentaprismane formation (21 → 22). Thus, the reaction (25 → 26) has a good chance to proceed on steric grounds alone, especially if activating substituents are present.³⁰

Finally, the high-yield conversion of norbornadiene (27) to quadricyclane (28)³¹ under sensitized irradiation can be understood in terms of the shortest distance r among the diolefins in Table I, not unsurmountable Δ_{strain} (less than 70 kcal/mol) and expectedly high steric strain in the double bonds of 27.

In conclusion, intramolecular [$\pi_2 + \pi_2$] photochemical ring closure reactions of polycyclic diolefins leading to strained cage products are recognized to be under the great influence of three steric criteria: r , θ , and Δ_{strain} . Although the higher limit of r could not be determined based on the available data, the limit of orientation factor θ appears to be near 35°. The maximum recorded Δ_{strain} that could be overcome among the known examples is about 70 kcal/mol. The norbornene type double bond is about 5 kcal/mol more strained than the usual double bonds and highly reactive in the cycloaddition reactions.

Rationale for the arguments presented above lies in Hammond's postulate.³² Evaluation of relative contribution of steric factors to the overall activation process remains to be explored.

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Registry No.—2, 704-02-9; 3 (R,R = (CO)₂O), 24145-84-4; 3 (R,R = (CN)₂), 62415-18-3; 5 (R,R = (CO)₂O), 24147-34-0; 5 (R,R = (CN)₂), 62415-02-5; 5 (R,R = CH₃O₂CNCO₂CH₃), 62415-03-6; 11 (R,R = (CO)₂O; X-X = CH=CH), 62415-00-3; 11 (R,R = (CN)₂; X-X = CH=CH), 62415-04-7; 12 (R = H; X-X = CH=CH), 62415-05-8; 13 (X-X = *trans*-CH(CO₂Et)CH(CO₂Et)), 41181-93-5; 13 (X-X = *i*), 41182-02-9; 14 (X-X = *trans*-CH(CO₂Et)CH(CO₂Et)), 41181-96-8; 14 (X-X = *i*), 62415-01-4; 15 (R = OSi(CH₃)₃), 39762-43-1; 16 (R = H), 452-61-9; 17 (R = OSi(CH₃)₃; X = CH₂), 39762-44-2; 17 (R = COOCH₃; X = CH₂), 62415-06-9; 17 (R = H; X-X = benzo), 27487-45-2; 17 (R = H; X-X = cyclobuteno), 62415-07-0; 17 (R,R = (CO)₂O; X = CH₂), 62415-08-1; 18 (R = H; X = CH₂), 5603-27-0; 18 (R = H; X-X = benzo), 29443-82-1; 18 (R = H; X-X = cyclobuteno), 62415-09-2; 19 (R = OSi(CH₃)₃), 39762-45-3; 24, 4572-17-2; 26, 277-10-1.

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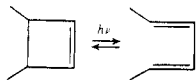
saturated counterparts,⁹ as indicated by small twist angles around the CC double bond in the energy minimum structures (Table II). For **17** and **19** having a fused cyclobutene ring as well as for *anti*-**29**, no energy minimum could be found for twist conformations, whereas twist forms of **15** and *syn*-**29** have well-defined energy minima.

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	Allinger ^{7b}	This work
Norbornene	5.72	3.58
Bicyclo[2.2.2]octene	4.30	4.60 (eclipse) 3.30 (twist)

Recalculations of enthalpies using a different energy minimization scheme (pattern search method)⁹ and taking the conformational flexibility of the bicyclo[2.2.2]octane skeleton⁹ into account give essentially the same results as shown above. Comparison between experimental (Table IV) and calculated enthalpies revealed that our calculations overestimated the enthalpy of bicyclo[2.2.2]octene and underestimated those of bicyclo[2.2.2]octane and norbornene, although the discrepancies were close to the known accuracy range of ± 2 kcal/mol.^{8a} For these reasons, we do not extend the alkene-alkane strain energy difference scheme to other systems like **7**, **9**, **15**, **17**, and **19** for which calculated enthalpy values must be used.

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 (22) The ring closure reactions of bis(trimethylsilyloxy) series **15**, **17**, and **19** occur only under direct irradiation, and not at all under sensitized conditions. In this context, the generality of conclusions obtained with this series may be limited.
 (23) The possibility of cycloreversion is ruled out based on the logic that cycloreversion should have been most prominent, if it occurs at all, in **15**



where strain release accompanying the ring opening must be the largest. The observed high yield of ring closure in **15** indicates the practically negligible extent of the cycloreversion.

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A Synthesis of Terminal Arylacetylenes—*in Situ* Generated Copper(I) Acetylide

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Terminal arylacetylenes can be prepared by several routes. Dehydrohalogenation of halogenated ethanes,²⁻⁶ amine-

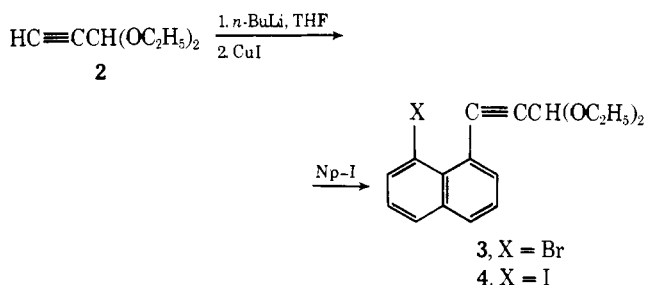
induced decomposition of 5-aryl-3-nitroso-2-oxazolidones,⁷ and pyrolysis of 4-aryl-1,2,3-selenadiazoles⁸ are methods recently reported in the literature. Alternatively, the triple bond can be preformed with a protecting group attached to one end and then coupled at the unprotected end to a suitable aromatic ring, followed by removal of the protecting group.^{9,10}

In connection with other studies, we required 1-ethynyl-8-halonaphthalenes. Because of the lability of the halogen atom in the 8 position, only the last method seemed a feasible preparative route. Curtis and co-workers⁹ have reported using the Castro reaction¹¹ to couple 1-iodonaphthalene and copper(I) 3,3-diethoxy-1-propyne (**1**). Hydrolysis and deformation of the coupled product gave 1-ethynyl-naphthalene in moderate yield.

Our attempts to employ Curtis' method using 1,8-diiodonaphthalene¹² or 1-bromo-8-iodonaphthalene¹³ gave the desired coupled product but in low yield. The lack of success of this method was apparently due to the difficulty in preparing and isolating **1**. Rather than isolate **1**, we generated and reacted **1** *in situ*. We have observed that **1** is soluble in THF and pyridine, unlike most other copper(I) acetylides.^{11d} Soluble *in situ* generated copper(I) acetylides have been reported using *N*-ethylpiperidine as base. The yields of coupled products were low, however.^{11e}

1,1-Diethoxy-2-propyne¹⁵ (**2**) was dissolved in dry tetrahydrofuran (THF) and deprotonated with *n*-butyllithium. To this solution was added cuprous iodide, and the solution was allowed to stir until the CuI had dissolved. The desired naphthyl iodide was added and the solution refluxed for 12 h. Excellent yields of the coupled product were obtained after work-up. (Scheme I).

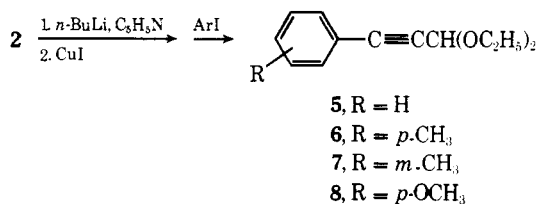
Scheme I



Cuprous trimethylsilylacetylide proved too unstable to undergo coupling under our conditions.¹⁴ Use of potassium *tert*-butoxide as the deprotonating base resulted in lower yields. 1-Bromonaphthalene and several substituted phenyl iodides failed to react when subjected to the same conditions.

A number of substituted phenyl iodides did undergo coupling with **1** when the THF was replaced with dry pyridine and the reflux time extended to 48 h. The yields of the 1,1-diethoxy-3-aryl-2-propynes were lower but still useful. To achieve maximum yields the ratio of **2** to aryl iodide was 2:1. Variation of the ratio from 1:1 to 4:1 did not give any improvement in the yield (Scheme II). Our results are summarized in Table I.

Scheme II



- 5**, R = H
6, R = *p*-CH₃
7, R = *m*-CH₃
8, R = *p*-OCH₃