purchased. All were purified before use and exhibited physical properties in agreement with literature values. Δ^9-Octalin was prepared[24] and purified[25] by procedures in the literature. Tetraethylethylene was prepared by a modified Eastwood procedure.[26] Physical properties agreed with literature values, and proton NMR indicated no spurious signals.

The di-*tert*-butyl ester of 2-bromomalonic acid was prepared from the nonbrominated ester. This, in turn, was prepared from the acid by the method of Raha.[27] The bromination was carried out by the procedure developed by Hori et al.[28] The yield was 60%. The following physical properties were observed: bp 62 °C (1 Torr); $n^{21}{}_D$ 1.4437; ^{1}H NMR (CDCl$_3$) δ 1.45 (s, 18 H), 4.6 (s, 1 H); ^{13}C NMR (CDCl$_3$) δ 163.32 (s), 83.54 (s), 45.43 (s), 27.44 (s); IR (KBr) 1756 cm^{-1} (C=O); MS, *m/e* 297, 295 (M$^+$), 241, 239 (M$^+$ - C$_4$H$_8$).

Determination of Selectivities. A standard competitive kinetic approach was used.[29] Stock solutions of a tetraalkylethylene, 1-octene, radical precursor, internal GLC standard, AIBN (radical chain initiator), and benzene (solvent) were prepared in approximate relative molar ratios of 1:1:4:1:0.1:13. The solution was divided among several reaction tubes. Air was removed from the samples by repeated freeze–thaw cycles. Tubes were sealed while samples were under a nitrogen atmosphere at reduced pressure. One tube was reserved as a starting mixture sample and the remainder were put in a 70.0 ± 0.1 °C constant-temperature bath for times varying from 4 to 90 h. Relative rates of disappearance of the two competing alkenes were determined by GLC evaluation of relative concentrations. All GLC analyses were carried out on a Varian 200 chromatograph. A 15 ft × $^1/_4$ in. packed column of 5% SE-30 on Cromosorb-W was used throughout this study. The reaction times employed corresponded to 4–90% disappearance of each alkene in any given run.

Acknowledgment. One of us (A.J.A.) wishes to express gratitude to the Oregon State University Undergraduate Honors Program for providing financial support.

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Preparations and Reactions of Symmetrical Dimethylenebiphenyl Dianions; Conformations of [0.*n*]-*o*-Cyclophanes. A Simple NMR Method for Determining Twist Angles in Biphenyls[†]

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With *n*-butyllithium/potassium *tert*-butoxide, a proton is removed from each methyl group of the symmetrical dimethylbiphenyls to give dianions in good yield. The reactions of these dianions with alkyl halides, dialkyl sulfates, trimethylchlorosilane, trimethylchlorogermane, α,ω-dihalides, and oxidizing agents were found to provide the best routes to many symmetrically substituted biphenyls, including [0.*n*]- and [0.*n*.0.*n*]cyclophanes. NMR and molecular mechanical studies of some of these cyclophanes gave information on their preferred conformations. An NMR method for determining the angle of twist in biphenyls from the chemical shifts of the ortho hydrogens is developed.

Preparation and Reactions of Dianions from the Dimethylbiphenyls. Dianions formed from the xylenes by the removal of a proton from each methyl group are useful intermediates for the preparation of symmetrically substituted benzenes, [*n*]cyclophanes, and [*n*.*n*]cyclophanes.[3] We now report that analogous preparations of dianions **1** from the symmetrical dimethylbiphenyls **2a** followed by reactions with similar electrophiles and oxidizing agents provide in most cases the best routes to biphenyl derivatives **2b–i**, [0.*n*]cyclophanes **3**, [0.*n*.0.*n*]cyclophanes **4**, and miscellaneous cyclophanes **5–8** (Chart I). In a related study, dianion *o*-**1** with lithium and magnesium rather than potassium counterions was prepared from *o*-**2a** and reacted with Me$_2$SiCl$_2$ to give a good yield of **5**.[4]

Our yields are given in Table I. The Me$_2$SO$_4$ and Et$_2$SO$_4$ reactions indicate the yields of each of the dianions **1** to be at least 84%.[5] Monoalkylated products **9** can arise either from undermetalation or from the dianion **1** obtaining a proton and an alkyl group rather than the desired two alkyl groups. The yield dropped considerably with the secondary halide *i*-PrBr, with electron transfer possibly becoming the predominant mechanism. With *t*-BuI, dialkylation (presumably entirely by electron transfer) rose to a respectable 44% in the para case, but, due to severe steric interactions, no di- or even monoalkylation product was detected in the ortho case. Instead, oxidation to

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[†] Dedicated to George H. Büchi on his 65th birthday.

[1] University of Arizona.

[2] Carnegie-Mellon University.

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[5] These dianions have calculated resonance energies per atom (REPA's) of 0.068, 0.067, and 0.070, respectively (kindly provided by B. A. Hess and L. J. Schaad), which suggest that they should be readily preparable; see Bates et al. (Bates, R. B.; Hess, B. A.; Ogle, C. A.; Schaad, L. J. *J. Am. Chem. Soc.* **1981**, *103*, 5052) for REPA's for many other delocalized dianions.

0022-3263/89/1954-0311$01.50/0

Table I. Yields (%, in parentheses) of Products from Dimethylbiphenyls 2a via Dianions 1

electrophile	from *o*-**2a**	from *m*-**2a**	from *p*-**2a**
Me_2SO_4	*o*-**2a** (5); *o*-**2b** (86); *o*-**9b** (8)	*m*-**2b** (84); *m*-**9b** (16)	*p*-**2b** (79); *p*-**9b** (21)
Et_2SO_4			*p*-**2c** (86); *p*-**9c** (14)
i-PrBr	*o*-**2a** (6); *o*-**2d** (50); *o*-**3** (n = 2) (20); *o*-**9d** (8)		*p*-**2d** (18); *p*-**9d** (22)
t-BuI	*o*-**3** (n = 2) (67)		*p*-**2e** (44); *p*-**9e** (15); p-**11e** (n = 2) (20)
Me_3SiCl	*o*-**2f** (44)	*m*-**2f** (69); *m*-**9f** (20)	*p*-**2f** (71); *p*-**9f** (25)
Me_3GeBr	*o*-**2g** (39); **12** (3)		*p*-**2g** (77); *p*-**9g** (17)
allyl chloride			*p*-**2h** (79); *p*-**9h** (19)
n-$C_5H_{11}Br$	*o*-**2i** (35)		
I_2		*m*-**4** ($n = n'$ = 2) (19); *m*-**11a** (n = 2) (40); **14** (17)	**16**
$ClCH_2Cl$	*o*-**2a** (18); *o*-**3** (n = 2) (2); *o*-**3** (n = 3) (29); *o*-**10** (29)		*p*-**10** (31); *p*-**11a** (n = 3) (14); **15** (13)
$Cl(CH_2)_2Cl$	*o*-**3** (n = 4) (4)		
$Br(CH_2)_2Br$	*o*-**3** (n = 2) (68)	*m*-**4** ($n = n'$ = 2) (39)	**16**
$Br(CH_2)_3Br$	*o*-**3** (n = 5) (31)		*p*-**4** (n = 2, n' = 5) (2); *p*-**4** ($n = n'$ = 5) (6); *p*-**9h** (24)
$Br(CH_2)_4Br$	*o*-**2a** (8); *o*-**3** (n=2) (1); *o*-**3** (n=6) (41)		
$Br(CH_2)_5Br$	*o*-**3** (n = 2) (1); *o*-**3** (n = 7) (26)		
$Br(CH_2)_7Br$		*m*-**3** (n = 9) (7)	
$Br(CH_2)_8Br$		*m*-**3** (n = 10) (38); *m*-**4** (n = 10) (20)	
$Br(CH_2)_{10}Br$			*p*-**3** (n = 12) (0.3); *p*-**4** ($n = n'$ = 12) (20)
$Br(CH_2)_{12}Br$			*p*-**3** (n = 14) (14); *p*-**4** ($n = n'$ = 14) (20)
$Br(CH_2)_{14}Br$			*p*-**3** (n = 16) (5); *p*-**4** ($n = n'$ = 16 (22)
Me_2SiCl_2	*o*-**2a** (19); *o*-**3** (n = 2) (2); **5** (55)		
m-C_6H_4-$(CH_2Br)_2$	*o*-**3** (n = 2) (32); **6** (8); **13** (4)		
p-C_6H_4-$(CH_2Cl)_2$		**7** (4); **8** (6)	

Chart I

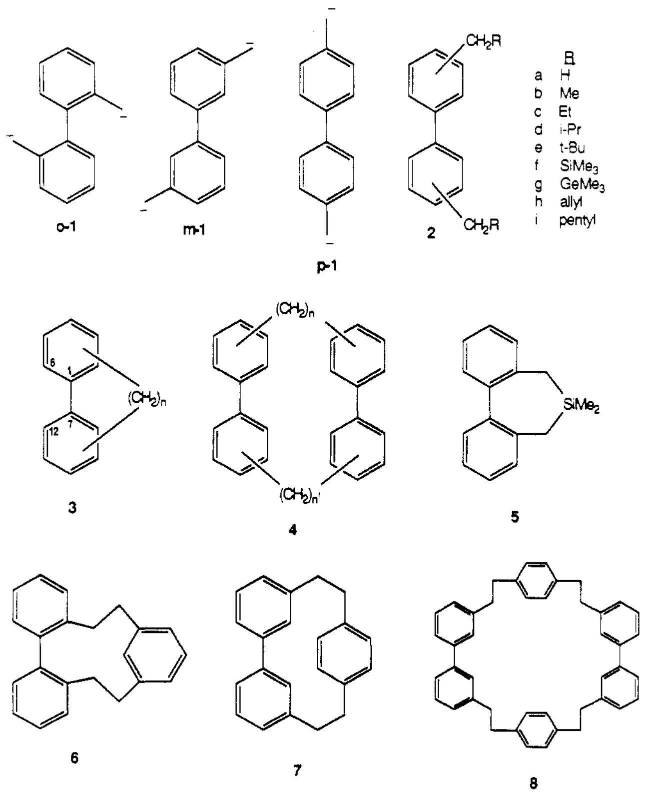
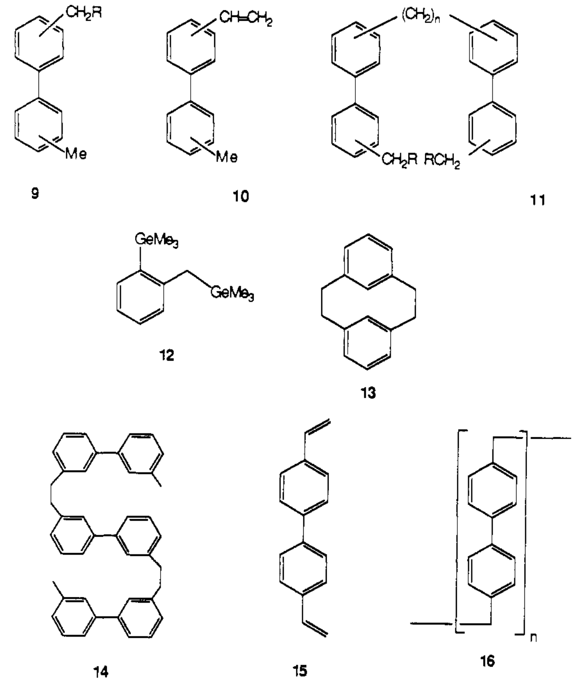


Chart II



9,10-dihydrophenanthrene (*o*-**3**, n = 2) occurred in essentially the same good yield as when this product was purposely sought by using $Br(CH_2)_2Br$. The reactions with Me_3SiCl and Me_3GeBr proceeded well, even in the ortho case; the longer bonds to the heavier atoms reduce the steric hindrance.

The oxidizing agents I_2 and $Br(CH_2)_2Br$ gave largely *mono*meric oxidation product (*o*-**3**, n = 2) in the ortho case, *di*meric product (*m*-**4**, $n = n'$ = 2) in the meta case, and *poly*mer (**16**) in the para case (Chart II).

Dianions **1** were reacted with α,ω-dibromo- and -dichloroalkanes $X(CH_2)_mX$ with m = 1–14. Dichlorides were used in the cases where m = 1, 2 to minimize oxidation. *o*-**2a** gave the desired products *o*-**3** (n = 3–7) in 26–41% yield except for *o*-**3** (n = 4), which was formed in only 4% yield. *m*-**2a** was reacted with 1,7-dibromoheptane and 1,8-dibromooctane to give cyclic monomers *m*-**3** (n = 9, 10) and cyclic dimers *m*-**4** ($n = n'$ = 9, 10) in the yields shown. With the appropriate dibromides, *p*-**2a** gave cyclic dimers *p*-**4** ($n = n'$ = 5, 12, 14, 16) (the last three in 20–22% yields), and, in the last two cases, significant amounts of cyclic monomers *p*-**3** (n = 14, 16). Thus the yields of highly strained cyclophanes (fortunately preparable by ring-contraction and other methods[6]) are vanishingly small by

Table II. Chemical Shifts (δ), Coupling Constants (*J*, in hertz followed in parentheses by chemical shifts calculated for the most stable conformation), Calculated Torsion Angles (C6–C1–C7–C12, in degrees), and Calculated Strain Energies for *o*-3 (*n* = 1–7) and *o*-2i

	o-3, *n* =							
	1[13]	2	3	4	5[c]	6	7	*o*-2i
				δ				
HC6	7.84	7.72	7.25–7.38	7.25–7.29	7.13	7.02	7.09	7.09
α	3.87	2.84	2.50	2.72	2.65	2.53	2.78	2.36
α′				2.08–2.25	2.09	2.53	2.53	2.29
β			2.19	1.52	1.54	1.68	1.41	1.41
β′				2.08–2.25	1.75	1.43	1.51	
γ					1.37	0.73	1.11	1.14
γ′						1.18	1.11	
δ,δ′							0.96	1.14
				J				
αβ			7.0^a (6)	0.0 (0)	3.8 (3)	9.0^b (8)	8.5 (11)	7.9^a
αβ′				8.6 (9)	7.0 (7)	3.5^b (3)	4.6 (3)	
α′β				^{d} (13)	10.4 (9)	9.0^b (8)	4.7 (3)	7.9^a
α′β′				0.0 (0)	3.4 (3)	3.5^b (3)	7.8 (5)	
βγ					5.0^a (5)	2.4 (1)	6.6^b (6)	7.4^a
βγ′						4.2 (5)		
β′γ					7.2^a (5)	13.4 (12)	6.6^b (6)	
β′γ′						0.9 (1)		
γδ							6.6^a (6)	
				Torsion Angle, Degrees				
	0.0	28.0	49.7	66.6	78.1/94.2	97.7	104.0	70–110
				Strain Energy, kcal/mol				
		23.0	25.1	24.9	30.1/30.2	27.6	35.3	19.4

[a] *Apparent J*, with averaging of *J*'s due to symmetry. [b] *Apparent J*, with averaging of *J*'s due to coincidence of δ's. [c] Calculated *J*'s are averages for the two minimum energy conformers. [d] Indeterminate.

these methods. However, these are the methods of choice for most of the relatively unstrained examples (e.g., *p*-**3** (*n* = 14) was prepared earlier by a much more laborious procedure involving about 20 steps[7]).

In reactions involving other dihalides, *o*-**2a** with Me_2SiCl_2 gave a 55% yield of the desired cyclic monomer **5**,[4] and with *m*-$C_6H_4(CH_2Br)_2$, it gave the desired mixed cyclophane **6**[8] in 8% yield along with substantial amounts of the symmetrical cyclophane monomer *o*-**3** (*n* = 2) and dimer **13**.[3] *m*-**2a** with *p*-$C_6H_4(CH_2Cl)_2$ gave mixed cyclophane **7**[9] in 4% yield and larger mixed cyclophane **8** in 6% yield.

Some unexpected products obtained in these reactions deserve mention. The reactions of anions *o*- and *p*-**1** with CH_2Cl_2 gave large amounts of styrene derivatives *o*- and *p*-**10** and **15** by as yet undefined elimination reactions. Less surprising were products of type **11** and **14**, in which cyclophane formation has been thwarted either by the undesired protonation of an intermediate anion or by failure to make the *di*anion in the first place. Lastly, germane **12** obtained in the reaction of *o*-**2a** with Me_3GeBr undoubtedly arose from a small amount of *o*-chlorotoluene present in the dimethylbiphenyl.

Conformations of [0.*n*]-*o*-Cyclophanes. Many of the cyclophanes **3** and **4** have ^1H NMR parameters that provide information on their conformational preferences. We have previously reported on the conformations of *p*-**3** (*n* = 14)[10] and *m*-**4** (*n* = *n*′ = 2)[11] in solution and in the crystal and now discuss the solution conformations of *o*-**3** (*n* = 2–7), as studied by NMR and molecular mechanics calculations. This series is useful in that its members have lowest energy conformations with twist angles of the biphenyl system which cover the possible range of 0–90°. The lower members of this series, *o*-**3** (*n* = 1–4), which cover the range to 60°, were used by Paquette et al.[12] in a study of conjugation in twisted systems.

The NMR parameters for *o*-**3** (*n* = 2–7) (Table II) that provide the most information about the favored conformations are the chemical shifts of the methylene protons, the vicinal coupling constants between these protons, and the chemical shifts of the aryl protons ortho to the other aromatic ring. Since the protons within the α-methylenes absorb differently for the cases where the ring has more than seven members, rotation about the central bond in the biphenyl system must be slow on the NMR time scale in these cases. In all cases of odd-numbered rings, the protons of the *central* methylene in the chain are equivalent to one another either directly by symmetry or because low energy barriers exist between conformations in which they are equivalent. In the 10- and 11-membered ring compounds, the γ and δ protons absorb upfield from the limiting value of δ 1.25 for methylene groups in $CDCl_3$, indicating that they lie over a benzene ring.

Figure 1 depicts the lowest energy conformation we have been able to find for each member of this series using MMPMI[15] calculations, as well as for a conformation for *o*-**3** (*n* = 5) calculated to be only 0.1 kcal/mol higher than the most stable one, and for the most stable conformation

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[15] MMPMI is a molecular mechanics program based on MM2, but taking π overlap into account with MMP1 π subroutines (Serena Software, Bloomington, IN 47402-3076).

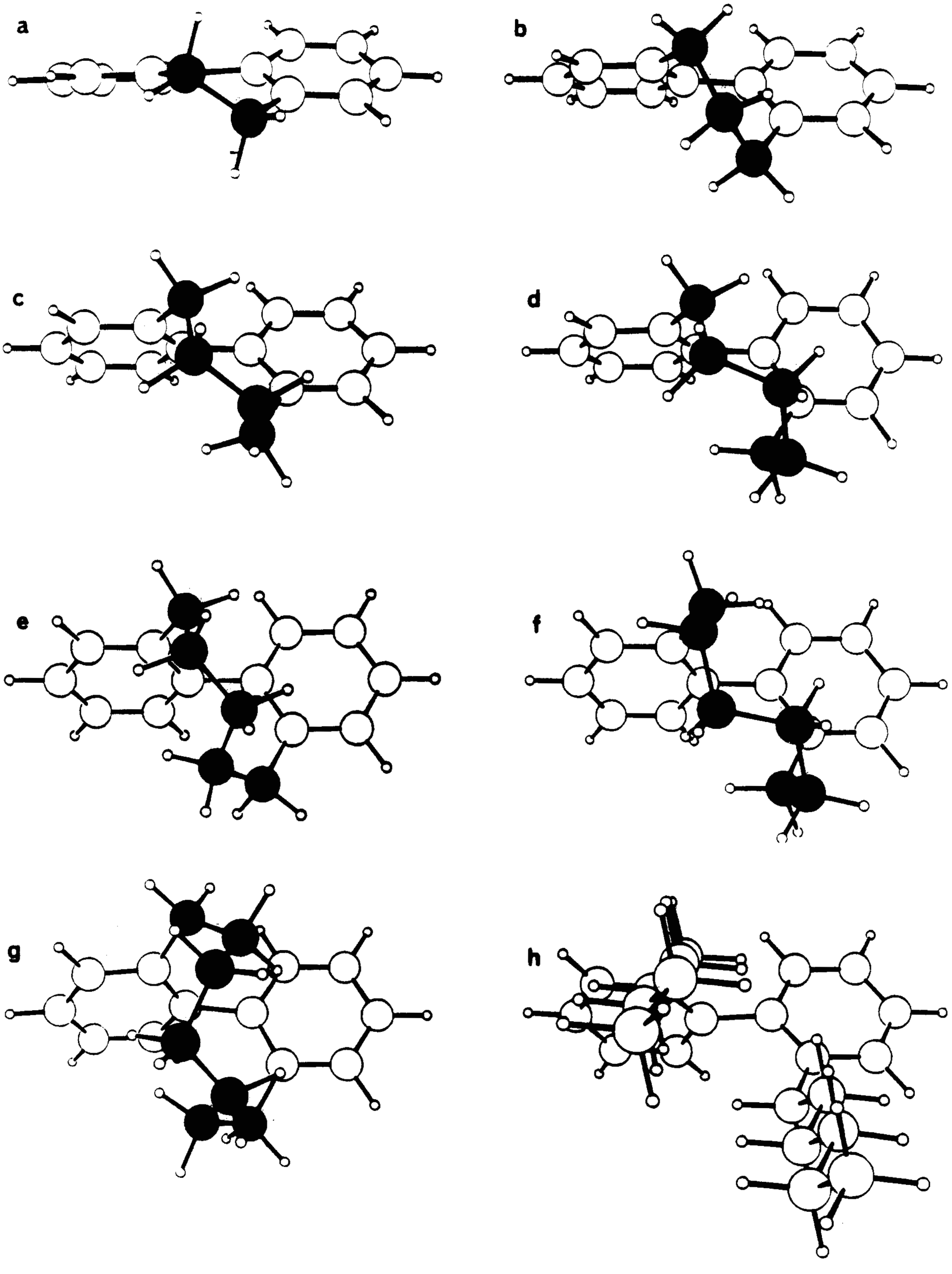

Figure 1. ORTEP[14] views of the lowest energy conformations calculated for cyclophanes *o*-**3** (n = 2–7) (a–d,f,g, respectively; e is the *second* lowest minimum found for n = 5) and model compound *o*-**2i** (h).

found for model compound *o*-**2i**. The corresponding calculated strain energies and biphenyl twist angles (C6–C1–C7–C12 was used) are given in Table II; in the case of *o*-**3** (n = 5), the assumption was made that equal amounts of the lowest and second lowest minimum energy forms are present, and the average values of the two forms were used. In the other cyclic cases, the lowest energy conformations are evidently sufficiently better than other conformations (>2.2 kcal/mol than the second best local minimum that we could find) in that their NMR parameters are quite well approximated by assuming that they consist largely of these and symmetry-equivalent confor-

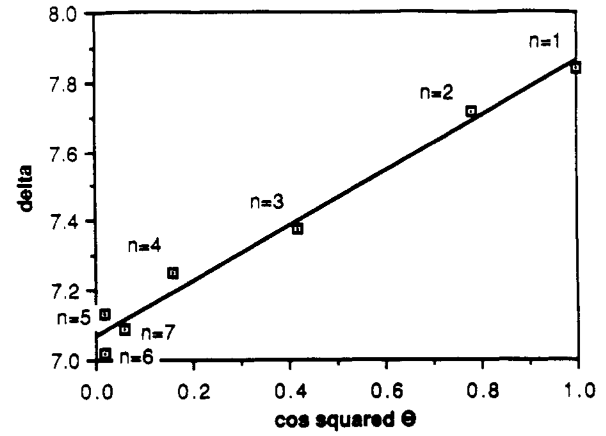

Figure 2. $\cos^2 \theta$ vs δ for *o*-**3** (n = 1–7).

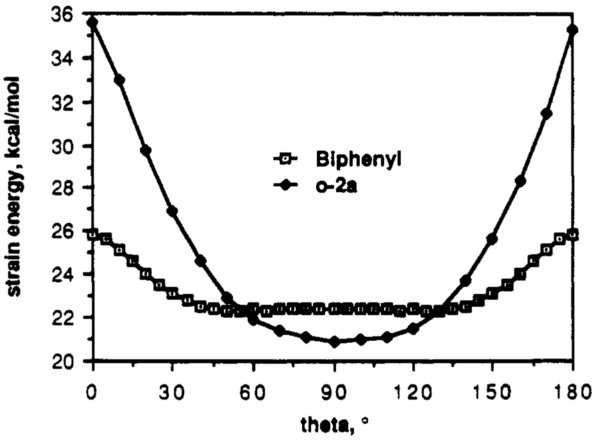

Figure 3. Rotation barriers in biphenyls.

mations (compare in Table II the observed coupling constants with the values in parentheses calculated from the Karplus curve). The cases where n = 2, 3, 4, and 6 each have a 2-fold axis in the most stable conformation. The cases in which n = 5 (nine-membered ring) and n = 7 (11-membered ring) do not have as stable conformations, as indicated by the higher strain energies (>30 kcal/mol) of their best conformations.

o-**2i** is included in Table II as a model for a cyclophane of type *o*-**3** with an infinitely large ring. Its calculated lowest energy conformation, which is depicted, does not completely fit the observed NMR parameters, no doubt due to contributions from conformations of only slightly higher energy (two other local minimum energy conformations differing only in rotation about the aryl–alkyl and aryl–aryl bonds were calculated to be only 0.8 and 1.5 kcal/mol less stable, and there must also be significant contribution from conformations in which the side chains bend since the γ–ζ protons all absorb ~0.1 ppm upfield from their limiting values, i.e., δ 1.25 for methylenes and δ 0.88 for methyls). That the largest ring we have made, the 11-membered one, still has a conformation far from that of acyclic model *o*-**2i** is clear from the large differences in their α-proton NMR shifts (Table II).

It can be seen in Figure 1 and Table II that the twist angles of cyclophanes *o*-**3** (n = 1–7) vary from 0° at n = 1 to 104° at n = 7. The twist angles of 28° in the calculated minimum energy conformation for *o*-**3** (n = 2), 50° for *o*-**3** (n = 3), and 66° for *o*-**3** (n = 4) agree reasonably well with values from previous studies of these substances; Paquette[12] favored values of 16°, 49°, and 59°, respectively, for these three compounds; others[16,17] have favored larger values for the former more in keeping with our value. Of our additions to the series (n = 5–7), the case where n = 5 is complicated by the presence of two local minima near the minimum energy value, as noted above. The case where n = 6 seems especially clearcut, as the unusual coupling constants observed for this substance are well-rationalized by using the lowest energy conformer only. Where n = 7, the conformer described fits quite well, but the number of local minimum conformations is quite large, and it is more likely in this case than in the others that there are other local minima which we have not found which contribute significantly to the observed NMR parameters. Thus *o*-**3** (n = 6) is a good model for biphenyls with a twist angle of about 98°, whereas *o*-**3** (n = 5 and n = 7) are reasonable models for biphenyls with twist angles of about 85° and 104°, respectively.

A Simple NMR Method for Determining the Twist Angle in Biphenyls. Figure 2 shows that a good linear correlation exists (correlation coefficient 0.99) between the chemical shift (δ) of the ortho hydrogen in the biphenyl system of *o*-**3** (n = 1–7) and the square of the cosine of the twist angle θ calculated for the most stable conformation using MMPMI. The equation of the least-squares line is $\delta = 7.068 + 0.796 \cos^2 \theta$. This equation should prove useful for estimating twist angles in other biphenyls, bearing in mind that substituent effects, available for some common substituents,[18] also affect the chemical shifts of aromatic hydrogens.

Non-cyclophane derivatives *o*-**2a,b,d,i** provide examples of the use of this equation without the complication of substituent effects: Their observed ortho proton absorptions of δ 7.09–7.10 from the equation yield calculated twist angles of 78–80°; these are reasonable in view of the curve of energy as a function of twist angle calculated for *o*-**2a** (Figure 3; θ = 0° refers to syn), which is fairly flat over the 70–90° range.

Application of the equation to biphenyls with meta and para rather than ortho substituents (e.g., *m*- and *p*-**2a,b**) and to biphenyl itself can be done by using correction factors for the effects of various ring substituents on aromatic hydrogen shifts, derived by comparing the shifts of monosubstituted benzenes with that of benzene.[18] *m*- and *p*-**2a,b**, with no ortho substituents, should be similar in twist angle to biphenyl itself; after substituent corrections, application of the equation to these four compounds leads to twist angles of 40–45°, and to biphenyl itself (whose ortho hydrogens absorb at 7.59) to an angle of 40°. Previous experimental evidence indicates that in solution the twist angle of biphenyl itself is about 45°,[12] and most calculations[19] suggest that the perpendicular form is higher than a minimum-energy form (twist angle ~45°) by 1–2 kcal/mol. It should be noted that while the rotation barriers calculated by using MMPMI for rotation through the high-energy planar forms of biphenyl and 2,2′-dimethylbiphenyl (*o*-**2a**) of 3 and 15 kcal/mol, respectively (Figure 3), fit well with experiments and with previous calculations,[19-21] the MMPMI curve for biphenyl does not show a sufficiently high energy for the perpendicular form relative to a form twisted about 45°. Supporting evidence

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that the ~45° form really is a minimum in solution comes from the application of the equation above (based on the series *o*-**3** (n = 1–7) to biphenyl itself and to *m*- and *p*-**2a**,**b**.

As a further example of the use of the equation, the biphenyl systems in the 40- to 48-membered rings of *p*-**4** ($n = n'$ = 12, 14, 16) have the same calculated twist angle (44–45°) as the corresponding non-cyclophanes, whereas the biphenyl systems in 20- to 24-membered ring cyclophanes *p*-**3** (n = 12, 14, 16) are calculated to be more nearly coplanar (calculated twist angles 38–40°; cf. 39° calculated by using MMPMI for the minimum-energy conformation of *p*-**3** (n = 14)[10]).

Experimental Section

^{1}H NMR spectra were run at 250 MHz on a Bruker WM-250 or at 600 MHz at Carnegie-Mellon. For other general procedures, see ref 3.

Symmetrical Dimethylenebiphenyl Dianions 1. Via syringe, 8.0 mL of 1.55 M *n*-BuLi (12.4 mmol) in hexane was added to a stirred mixture of 1.4 g (12.5 mmol) of KO-*t*-Bu, 1.0 mL (5.5 mmol) of 2,2′- (*o*-**2a**),[22] 3,3′- (*m*-**2a**),[23] or 4,4′-dimethylbiphenyl (*p*-**2a**),[23] and 125 mL of pentane under argon. After 45 min (2 h in the ortho case) of continued stirring, the dianion salt (*o*-**1**, dark orange-red; *m*-**1**, dark reddish purple; *p*-**1**, darker reddish purple) was collected on a Schlenk filter and washed with 100 mL of pentane. The residue was blown dry with argon and suspended in precooled THF (60 mL) at 0 °C for reactions.

Reactions of Dianions 1 with Electrophiles. A few reactions were done by direct addition of 2 equiv of electrophile to a stirred THF suspension of the dianion **1**. Almost all of the reactions with *mono*functional electrophiles involved inverse addition, i.e., the addition of the dianion suspension to 2 equiv of electrophile in 200 mL of THF with stirring. Reactions with *di*halides were done by simultaneous addition of the stirring dianion suspension in 200 mL of pentane and 1 equiv of dihalide in 50 mL of THF to 200 mL of stirring THF at 0 °C over about 40 min. After addition, the reaction mixtures were stirred while being warmed to 25 °C, the THF was removed in vacuo, and 200 mL of methylene chloride and 50 mL of water were added. Both phases were filtered through Celite, which was then washed with 50 mL of methylene chloride. The organic phases were combined, washed with 5 × 200 mL of water, dried over $MgSO_4$, and evaporated. Yields were determined by adding known amounts of a standard such as dioxane and measuring areas of pertinent NMR signals. Products were usually separated by LC on silica gel. *o*-**2b**,[22] *o*-**2f**,[4] *m*-**2b**,[23] *p*-**2b**,[22] *p*-**2c**,[24] *p*-**2f**,[25] *o*-**3** (n = 2–4),[12,20] *o*-**3** (n = 5, 6),[26] *m*-**3** (n = 9, 10),[27] *p*-**3** (n = 12, 14, 16),[10,28] *m*-**4** ($n = n'$ = 2),[11] **5**,[4] **6**,[7], **7**,[8] **13**,[3] and **15**[29] are known compounds. Many of the new compounds were minor byproducts that were not completely separated from the reaction mixtures and thus were not analyzed for elements. Satisfactory C and H analyses were obtained for *p*-**2d**,**e**,**g**, *p*-**4** ($n = n'$ = 12, 14), and *p*-**11a** (n = 2). Melting points (if solid) and ^{1}H NMR parameters are given below for all of the new compounds.

***o*-2d**: ^{1}H NMR δ $H_3 = 7.25$, $H_4 = 7.28$, $H_5 = 7.19$, $H_6 = 7.09$, $H_\alpha = 2.25$, $H_{\alpha'} = 2.17$, $H_\beta = 1.69$, $H_\gamma = 0.78$, $H_{\gamma'} = 0.66$; $J_{3,4} = 6.2$, $J_{3,5} = 2.7$, $J_{4,5} = 6.5$, $J_{4,6} = 0.8$, $J_{5,6} = 7.2$, $J_{\alpha,\alpha'} = 13.6$, $J_{\alpha,\beta} = 7.2$, $J_{\beta,\gamma} = 6.6$ Hz.

***o*-2g**: ^{1}H NMR δ $H_3 = 7.11$, $H_4 = 7.24$, $H_5 = 7.14$, $H_6 = 7.09$, $H_\alpha = 2.16$, $H_{\alpha'} = 2.15$, $H_\gamma = -0.01$; $J_{3,4} = 7.2$, $J_{3,5} = 1.6$, $J_{4,5} = 7.3$, $J_{4,6} = 1.8$, $J_{5,6} = 7.4$, $J_{\alpha,\alpha'} = 12.3$ Hz.

***o*-2i**: ^{1}H NMR in Table II except δ $H_3 = H_4 = 7.28$, $H_5 = 7.19$, $H_\epsilon = 1.18$, $H_\zeta = 0.81$; $J_{4,6} = 0.9$, $J_{5,6} = 7.4$, $J_{\epsilon,\zeta} = 7.1$ Hz.

***m*-2f**: ^{1}H NMR δ $H_2 = 7.21$, $H_4 = 6.97$, $H_5 = 7.28$, $H_6 = 7.29$, $H_\alpha = 2.15$, $H_\gamma = 0.03$.

***p*-2d**: mp 47–48 °C; ^{1}H NMR δ $H_2 = 7.50$, $H_3 = 7.20$, $H_\alpha = 2.50$, $H_\beta = 1.89$, $H_\gamma = 0.93$; $J_{2,3} = 8.1$, $J_{\alpha,\beta} = 7.2$, $J_{\beta,\gamma} = 6.6$ Hz.

***p*-2e**: mp 131–133 °C; ^{1}H NMR δ $H_2 = 7.50$, $H_3 = 7.18$, $H_\alpha = 2.52$, $H_\gamma = 0.93$; $J_{2,3} = 8.2$ Hz.

***p*-2g**: mp 76–78 °C; ^{1}H NMR δ $H_2 = 7.47$, $H_3 = 7.06$, $H_\alpha = 2.25$, $H_\gamma = 0.15$; $J_{2,3} = 8.2$ Hz.

***p*-2h**: ^{1}H NMR δ $H_2 = 7.51$, $H_3 = 7.26$, $H_\alpha = 2.75$, $H_\beta = 2.40$, $H_\gamma = 5.89$, $H_\delta = 5.00$, $H_{\delta'} = 5.07$; $J_{2,3} = 8.1$, $J_{\alpha,\beta} = 7.8$, $J_{\beta,\gamma} = 6.6$, $J_{\beta,\delta} = 1.2$, $J_{\gamma,\delta} = 17.0$, $J_{\gamma,\delta'} = 10.4$, $J_{\gamma,\gamma'} = 2.0$ Hz.

***o*-3 (*n* = 7)**: ^{1}H NMR in Table II except δ $H_3 = 7.28$, $H_4 = 7.27$, $H_5 = 7.19$; $J_{5,6} = 8.0$ Hz.

***m*-3 (*n* = 9)**: ^{1}H NMR δ $H_2 = 7.36$, $H_4 = 7.11$, $H_5 = 7.30$, $H_6 = 7.37$, $H_\alpha = 2.80$, $H_\beta = 1.78$, $H_{\gamma-\epsilon} = 1.34$; $J_{2,4} = J_{2,6} = 1.8$, $J_{4,5} = J_{5,6} = 7.5$, $J_{4,6} = 1.0$, $J_{\alpha,\beta} = 5.8$, $J_{\beta,\gamma} = 6.6$ Hz.

***m*-3 (*n* = 10)**: ^{1}H NMR δ $H_2 = 7.53$, $H_4 = 7.12$, $H_5 = 7.34$, $H_6 = 7.47$, $H_\alpha = 2.79$, $H_\beta = 1.76$, $H_\gamma = 1.34$, $H_\delta = H_\epsilon = 1.40$; $J_{2,4} = J_{2,6} = 1.7$, $J_{4,5} = J_{5,6} = 7.6$, $J_{4,6} = 1.3$, $J_{\alpha,\beta} = 6.1$, $J_{\beta,\gamma} = 6.7$ Hz.

***p*-3 (*n* = 16)**: ^{1}H NMR δ $H_2 = 7.53$, $H_3 = 7.23$, $H_\alpha = 2.67$, $H_\beta = 1.65$, $H_{\gamma-\theta} = 0.76–1.40$; $J_{2,3} = 8.0$, $J_{\alpha,\beta} = 6.7$ Hz.

***m*-4 (*n* = 9)**: ^{1}H NMR δ $H_2 = 7.35$, $H_4 = 7.11$, $H_5 = 7.29$, $H_6 = 7.36$, $H_\alpha = 2.64$, $H_\beta = 1.66$, $H_{\gamma-\epsilon} = 1.34$; $J_{2,4} = J_{2,6} = 1.8$, $J_{4,5} = J_{5,6} = J_{\alpha,\beta} = 7.5$, $J_{4,6} = 1.0$, $J_{\beta,\gamma} = 6.7$ Hz.

***m*-4 (*n* = 10)**: ^{1}H NMR δ $H_2 = 7.37$, $H_4 = 7.11$, $H_5 = 7.30$, $H_6 = 7.35$, $H_\alpha = 2.65$, $H_\beta = 1.67$, $H_{\gamma-\epsilon} = 1.35$; $J_{2,4} = J_{2,6} = 1.8$, $J_{4,5} = 7.5$, $J_{4,6} = 1.1$, $J_{5,6} = 7.3$, $J_{\alpha,\beta} = 7.2$, $J_{\beta,\gamma} = 6.6$ Hz.

***p*-4 (*n* = 2, *n′* = 5)**: ^{1}H NMR δ $H_2 = 6.94$, $H_3 = 6.69$, $H_{2'} = 6.89$, $H_{3'} = 7.07$, $H_\alpha = 3.02$, $H_{\alpha'} = 2.56$, $H_{\beta'} = 1.70$, $H_{\gamma'} = 1.45$; $J_{2,3} = J_{2',3'} = 8.2$, $J_{\alpha',\beta'} = 6.2$, $J_{\beta',\gamma'} = 7.0$ Hz.

***p*-4 (*n* = *n′* = 5)**: ^{1}H NMR δ $H_2 = 7.49$, $H_3 = 7.23$, $H_\alpha = 2.65$, $H_\beta = 1.70$, $H_\gamma = 1.44$; $J_{2,3} = 8.2$, $J_{\alpha,\beta} = 7.6$, $J_{\beta,\gamma} = 6.9$ Hz.

***p*-4 (*n* = *n′* = 12)**: mp 132–135 °C; ^{1}H NMR δ $H_2 = 7.47$, $H_3 = 7.21$, $H_\alpha = 2.63$, $H_\beta = 1.63$, $H_{\gamma-\zeta} = 1.24$; $J_{2,3} = 8.1$, $J_{\alpha,\beta} = 7.3$ Hz.

***p*-4 (*n* = *n′* = 14)**: mp 132–135 °C; ^{1}H NMR δ $H_2 = 7.48$, $H_3 = 7.22$, $H_\alpha = 2.63$, $H_\beta = 1.63$, $H_\gamma = 1.31$, $H_\delta = 1.29$, $H_{\epsilon-\eta} = 1.24$; $J_{2,3} = 8.2$, $J_{\alpha,\beta} = 7.3$ Hz.

***p*-4 (*n* = *n′* = 16)**: mp 131–135 °C; ^{1}H NMR δ $H_2 = 7.48$, $H_3 = 7.23$, $H_\alpha = 2.63$, $H_\beta = 1.63$, $H_\gamma = 1.34$, $H_\delta = 1.32$, $H_{\epsilon-\theta} = 1.25$; $J_{2,3} = 8.1$, $J_{\alpha,\beta} = 7.6$ Hz.

8: ^{1}H NMR δ $H_2 = 6.85$, $H_4 = 7.14$, $H_5 = 7.31$, $H_6 = 7.36$, $H_7 = 7.10$, $H_\alpha = H_{\alpha'} = 2.83–2.90$; $J_{2,4} = J_{2,6} = J_{4,6} = 1.7$, $J_{4,5} = J_{5,6} = 7.5$ Hz.

***p*-9h**: ^{1}H NMR δ $H_2 = 7.50$, $H_3 = 7.25$, $H_{2'} = 7.48$, $H_{3'} = 7.23$, $H_\alpha = 2.75$, $H_\beta = 2.40$, $H_\gamma = 5.89$, $H_\delta = 5.07$, $H_{\delta'} = 5.00$, $H_{\alpha'} = 2.39$; $J_{2,3} = 8.1$, $J_{2',3'} = J_{\alpha,\beta} = 7.9$, $J_{\beta,\gamma} = 6.6$, $J_{\beta,\delta} = 1.3$, $J_{\gamma,\delta} = 17.1$, $J_{\gamma,\delta'} = 10.2$, $J_{\delta,\delta'} = 1.9$ Hz.

***o*-10**: ^{1}H NMR δ $H_3 = 7.66$, $H_{4-6,3'-6'} = 7.08–7.40$, $H_\alpha = 6.40$, $H_\beta = 5.66$, $H_{\beta'} = 5.08$, $H_{\alpha'} = 2.05$; $J_{3,4} = 7.3$, $J_{3,5} = 2.0$, $J_{\alpha,\beta} = 17.5$, $J_{\alpha,\beta'} = 11.0$, $J_{\beta,\beta'} = 1.2$ Hz.

***p*-10**: ^{1}H NMR δ $H_2 = 7.54$, $H_3 = 7.25$, $H_{2'} = 7.49$, $H_{3'} = 7.24$, $H_\alpha = 6.75$, $H_\beta = 5.77$, $H_{\beta'} = 5.25$, $H_{\alpha'} = 2.37$; $J_{2,3} = J_{2',3'} = 8.4$, $J_{\alpha,\beta} = 17.6$, $J_{\alpha,\beta'} = 10.8$, $J_{\beta,\beta'} = 0.8$ Hz.

***m*-11a (*n* = 2)**: ^{1}H NMR δ $H_{Ar} = 7.12–7.43$, $H_\alpha = 3.03$, $H_{\alpha'} = 2.40$.

***p*-11e (*n* = 2)**: mp 188–192 °C; ^{1}H NMR δ $H_2 = 7.53$, $H_3 = 7.27$, $H_{2'} = 7.50$, $H_{3'} = 7.19$, $H_\alpha = 2.99$, $H_{\alpha'} = 2.53$, $H_{\gamma'} = 0.94$; $J_{2,3} = J_{2',3'} = 8.1$ Hz.

***p*-11a (*n* = 3)**: ^{1}H NMR δ $H_2 = 7.46$, $H_3 = 7.24$, $H_{2'} = 7.49$, $H_{3'} = 7.22$, $H_\alpha = 2.71$, $H_\beta = 2.01$, $H_{\alpha'} = 2.38$; $J_{2,3} = J_{2',3'} = 8.4$, $J_{\alpha,\beta} = 6.4$ Hz.

12: ^{1}H NMR δ $H_{Ar} = 7.01–7.19$, $H_\alpha = 1.77$, $H_{\alpha'} = 1.57$, $H_\gamma = 0.03$, $H_{\beta'} = -0.05, -0.06, -0.08$; $J_{\alpha,\alpha'} = 14.7$ Hz.

14: ^{1}H NMR δ $H_{Ar} = 7.13–7.30$, $H_\alpha = 3.01$, $H_{\alpha'} = 2.39$.

Acknowledgment. We thank the NSF for financial support (CHE-8306125 and -8600957) and Profs. B. A. Hess and L. J. Schaad for calculating REPA's for dianions **1**.

Registry No. *o*-**1**, 84980-69-8; *m*-**1**, 84980-68-7; *p*-**1**, 55976-86-8; *o*-**2a**, 605-39-0; *m*-**2a**, 612-75-9; *p*-**2a**, 613-33-2; *o*-**2b**, 13049-35-9;

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m-**2b**, 13049-38-2; *p*-**2b**, 13049-40-6; *p*-**2c**, 14584-23-7; *o*-**2d**, 117712-96-6; *p*-**2d**, 117712-97-7; *p*-**2e**, 108292-13-3; *o*-**2f**, 57754-02-6; *m*-**2f**, 117712-98-8; *p*-**2f**, 61342-05-0; *o*-**2g**, 117712-99-9; *p*-**2g**, 117713-00-5; *p*-**2h**, 117713-01-6; *o*-**2i**, 117713-02-7; *o*-3 (*n*=2), 776-35-2; *o*-**3** (*n*=3), 1015-80-1; *o*-**3** (*n*=4), 1082-12-8; *o*-**3** (*n*=5), 4444-45-5; *o*-**3** (*n*=6), 76692-01-8; *o*-**3** (*n*=7), 117713-05-0; *m*-**3** (*n* = 9), 117713-03-8; *m*-**3** (*n* = 10), 51739-47-0; *p*-**3** (*n* = 12), 2013-42-5; *p*-**3** (*n*=14), 2013-43-6; *p*-**3** (*n*=16), 117713-04-9; *m*-**4** (*n*=9), 117713-06-1; *m*-**4** (*n*=10), 117713-07-2; *m*-**4** (*n*=*n*′=2), 24656-54-0; *p*-**4** (*n*=2,*n*′=5), 117713-08-3; *p*-**4** (*n*=*n*′=5), 117713-09-4; *p*-**4** (*n*=*n*′=12), 117713-10-7; *p*-**4** (*n*=*n*′=14), 117713-11-8; *p*-**4** (*n*=*n*′=16), 117713-12-9; **5**, 90732-77-7; **6**, 117773-79-2; **7**, 61983-95-7; **8**, 117713-13-0; *o*-**9b**, 76708-83-3; *m*-**9b**, 7435-49-6; *p*-**9b**, 76708-90-2; *p*-**9c**, 117713-15-2; *o*-**9d**, 117713-20-9; *p*-**9d**, 117713-16-3; *p*-**9e**, 117713-17-4; *m*-**9f**, 117713-26-5; *p*-**9f**, 117713-18-5; *p*-**9g**, 117713-19-6; *p*-**9h**, 117713-14-1; *o*-**10**, 117713-21-0; *p*-**10**, 4040-29-3; *p*-**11a** (*n*=2), 43012-23-3; *p*-**11a** (*n*=3), 117713-24-3; *p*-**11e** (*n*=2), 117713-23-2; **12**, 113419-98-0; **13**, 2319-97-3; **14**, 117713-25-4; **15**, 4433-13-0; **16**, 31693-66-0; Me_2SO_4, 77-78-1; Et_2SO_4, 64-67-5; *i*-PrBr, 75-26-3; *t*-BuI, 558-17-8; Me_3SiCl, 75-77-4; Me_3GeBr, 1066-37-1; $H_2C{=}CHCH_2Cl$, 107-05-1; $C_5H_{11}Br$, 110-53-2; I_2, 7553-56-2; Cl_2CH_2, 75-09-2; $Cl(CH_2)_2Cl$, 107-06-2; $Br(CH_2)_2Br$, 106-93-4; $Br(CH_2)_3Br$, 109-64-8; $Br(CH_2)_4Br$, 110-52-1; $Br(CH_2)_5Br$, 111-24-0; $Br(CH_2)_7Br$, 4549-31-9; $Br(CH_2)_8Br$, 4549-32-0; $Br(CH_2)_{10}Br$, 4101-68-2; $Br(CH_2)_{12}Br$, 3344-70-5; $Br(CH_2)_{14}Br$, 37688-96-3; Me_2SiCl_2, 75-78-5; *m*-$C_6H_4(CH_2Br)_2$, 626-15-3; *p*-$C_6H_4(CH_2Cl)_2$, 623-25-6.

Supplementary Material Available: Calculated atomic coordinates of the low-energy conformations of *o*-**3** (*n* = 2–7) and *o*-**2i** depicted in Figure 1 (8 pages). Ordering information is given on any current masthead page.

Effect of Substituent on Reactions Remote from Silicon:[1] Regioselective α-Alkylation of α-Silylallyl Carbanions

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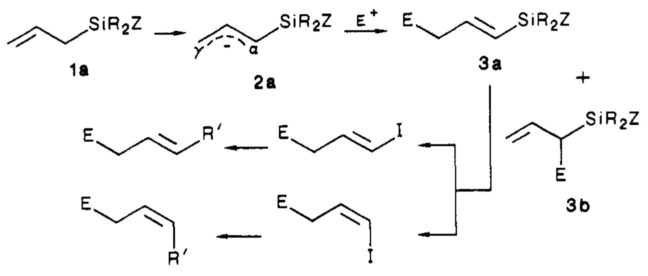
α-Silylallyl carbanions having metal-ion complexing substituents on silicon react with alkyl halides to give α-substituted allylsilanes regioselectively. The extent of α-selection depends significantly on the nature of the ligand and solvent. The synthetic utility of these systems is demonstrated by application in the synthesis of α-(*E*)-bisabolene.

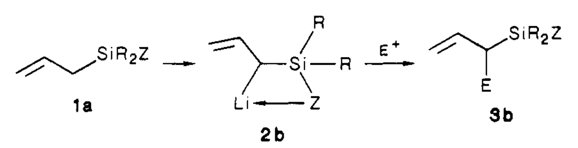
While organosilicon compounds have been used extensively in organic synthesis,[2] the substituents on silicon are typically alkyl or aryl groups. Substituent effects have been recognized and exploited to control reactions occurring at silicon. One good example is the use of a *tert*-butyl substituent to confer reasonable hydrolytic stability in *tert*-butyldimethylsilyl as a hydroxy protecting group.[3] On the other hand, the effect of silyl substituents on reactions occurring not at, or *remote* from, silicon is less known.[1]

An interesting area for the study of substituent effects is on the regiochemical control in substitution reactions of silylallyl anions.[4,5] Corriu has shown that the α-trimethylsilylallyl anion (**2a**, R, Z = CH_3) can be generated from allyltrimethylsilane (**1a**, R, Z = CH_3) and reacted with electrophiles.[6] The regioselectivity of the reaction depended on the nature of the electrophile. Carbonyl electrophiles gave regioselectively the γ-adducts[6] and, if complexed with a Lewis acid, the reaction gave the α-adducts.[7] More complicated were reactions with alkyl halides. Mixtures of α- and γ-alkylated products were obtained.[8] Our laboratory has demonstrated that by replacing the methyl groups on silicon by sterically larger groups (Et, Pr, or Ph), alkylation of the α-silylallyl anion gave higher γ-regioselection.[8] This observation has served as the basis of a useful method to prepare regio- and stereoselectively (*E*)-vinylsilanes and, after appropriate transformations, disubstituted alkenes (Scheme I).[9]

Scheme I



Scheme II



Z = lithium chelating group

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