a reddish-brown solid which after recrystallization from isopropyl alcohol afforded 6.7 g (50%) of yellow plates of VI: mp 153–155°; NMR ($CDCl_3$) 3.0 (s, W = 1.0 Hz, 2 CH_3), 9.58 (d, J = 8 Hz, 1 CHO), 6.0–7.5 ppm (m, 8 H); uv (acetonitrile) λ_{max} 405 nm (ϵ 24,500); ir ($CHCl_3$) 3025, 1665, 1590 cm^{-1}.

Anal. Calcd for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.40; H, 7.44; N, 6.81.

7-(*p*-Dimethylaminophenyl)hepta-2,4,6-trienal (VII) was prepared similarly to IV from *p*-dimethylaminocinnamaldehyde. Recrystallization from ligroin (bp 90–120°) gave VII (2%) as a red powder: mp 177–179°; NMR ($CDCl_3$) 3.0 (s, W = 1.0 Hz, 2 CH_3), 5.9–7.4 (m, 10 H), 9.56 ppm (d, J = 8 Hz, 1 CHO); uv (acetonitrile) λ_{max} 425 nm (ϵ 36,260); ir ($CHCl_3$) 3020, 1665, 1560 cm^{-1}.

Anal. Calcd for $C_{15}H_{17}NO$: C, 79.26; H, 7.54; N, 6.16. Found: C, 79.17; H, 7.49; N, 6.03.

General Procedure for Synthesis of α,ω-Diphenylpolyenes (VIII → XI).[13] Into the reaction vessel were charged 7 mmol of 2,5-dimethoxybenzyl phosphonate (III), 7 mmol of the appropriate aldehyde (IV → VII), and 25 ml of 1,2-dimethoxyethane (dried over Na). To this stirred solution was added in several portions 7 mmol of NaH followed by refluxing of the mixture for 0.5–1.5 hr. The reaction mixture was then cooled to room temperature and drowned in 150 ml of cold water followed by filtration (in the case of VIII) or extraction with benzene (in the case of IX, X, and XI) of the α,ω-diphenylpolyene.

2,5-Dimethoxy-4'-dimethylaminostilbene (VIII): yield 70%; yellow hexagonal crystals (acetone), mp 120–121°; NMR ($CDCl_3$) 2.90 (s, 2 NCH_3), 3.73 (s, $-OCH_3$), 3.77 (s, $-OCH_3$), 6.6–7.5 ppm (m, 9 H); ir 705 (m), 800 (s), 840 (m), 1045 cm^{-1} (s); $E_{o\to o}$ = 70.6 ± 0.6 kcal/mol.

Anal. Calcd for $C_{18}H_{21}NO_2$: C, 76.28; H, 7.48; N, 4.94. Found: C, 76.50; H, 7.36; N, 4.84.

1-(2,5-Dimethoxyphenyl)-4-(4'-dimethylaminophenyl)buta-1,3-diene (IX): yield 52%; yellow needles (ethanol), mp 121–121.5°; NMR ($CDCl_3$) 2.93 (s, 2 NCH_3), 3.73 (s, $-OCH_3$), 3.78 (s, $-OCH_3$), 6.6–7.4 ppm (m, 11 H); ir 715 (m), 810 (m), 860 (m), 985 cm^{-1} (s); $E_{o\to o}$ = 66.0 ± 0.6 kcal/mol.

Anal. Calcd for $C_{20}H_{23}NO_2$: C, 77.62; H, 7.51; N, 4.53. Found: C, 77.80; H, 7.67; N, 4.45.

1-(2,5-Dimethoxyphenyl)-6-(4'-dimethylaminophenyl)hexa-1,3,5-triene (X): yield 40%; orange needles (isopropyl alcohol), mp 123–123.5°; NMR ($CDCl_3$) 2.90 (s, 2 NCH_3), 3.77 (s, OCH_3), 3.80 (s, OCH_3), 6.6–7.4 ppm (m 13 H); ir 800 (s), 820 (s), 995 (s), 1045 cm^{-1} (s); $E_{o\to o}$ = 61.2 ± 0.6 kcal/mol.

Anal. Calcd for $C_{22}H_{25}NO_2$: C, 78.76; H, 7.53; N, 4.18. Found: C, 79.08; H, 7.78; N, 4.08.

1-(2,5-Dimethoxyphenyl)-8-(4'-dimethylaminophenyl)octa-1,3,5,7-tetraene (XI): yield 25%; shiny copper plates (acetone), mp 146–147°; NMR ($CDCl_3$) 2.95 (s, 2 NCH_3), 3.78 (s, OCH_3), 3.80 (s, OCH_3), 6.4–7.4 ppm (m, 15 H); ir 810 (s), 1000 cm^{-1} (vs); $E_{o\to o}$ = 58.0 ± 0.6 kcal/mol.

Anal. Calcd for $C_{24}H_{27}NO_2$: C, 79.73; H, 7.54; N, 3.88. Found: C, 79.61; H, 7.72; N, 3.73.

Registry No.—**III,** 55298-76-5; **IV,** 100-10-7; **V,** 20432-35-3; **VI,** 20432-36-4; **VII,** 55298-77-6; **VIII,** 55298-78-7; **IX,** 55298-79-8; **X,** 55298-80-1; **XI,** 55298-81-2; 1-methoxybut-1-en-3-yne, 2798-73-4.

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Carbon-13 Nuclear Magnetic Resonance Spectra of 4-Phosphorinanones. Carbonyl Hydration in Oxides, Sulfides, and Quaternary Salts[1]

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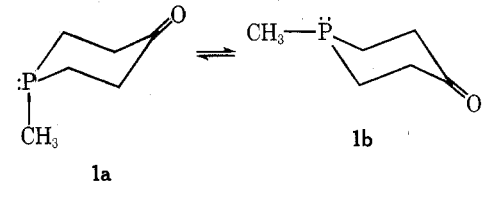
We recently reported on the ^{13}C NMR spectra of phosphorinanes[2] and their 4-hydroxy derivatives,[2,3] pointing out especially the value of the technique for gaining information on conformational aspects of this ring system. The effect of a covalence change (addition of sulfur) at the phosphorus atom was also considered.[2,4] We have extended our study to include some 4-keto derivatives of this series. On conducting ^{13}C NMR measurements on the tetracovalent species in water solution, we noted an important effect: extensive covalent hydration occurred at the carbonyl group. The present paper summarizes our observations on these compounds.

^{13}C NMR Spectra of Keto Derivatives. The ^{13}C NMR spectra of a family of *P*-methyl 4-phosphorinanone derivatives are given in Table I. In the trivalent compound **1,** assignment of the ring carbons was easily made, since their signals were separated by 12.5 ppm through the shielding effect of the phosphino group on attached carbons,[2] and the deshielding effect of carbonyl on carbons attached to it.[5] The carbonyl carbon was located in the same far-downfield position as seen for 4-methylcyclohexanone (δ 209[6]). The PCH_3 signal was in its expected high-field position. This carbon is particularly sensitive to conformational properties; the chemical shift observed is determined by the relative amounts at equilibrium of the conformer with axial (upfield) and with equatorial (downfield) methyl. Previous studies[7] on this 4-phosphorinanone have indicat-



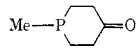
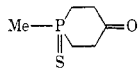
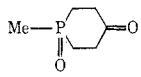
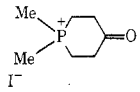
1a 1b

ed that the equilibrium lacks the very strong bias to the equatorial side that is so well known for 4-methylcyclohexanone. Indeed, there seems to be a small excess of the axial conformer, a property that has been recently confirmed for the 1-methylphosphorinane system.[8] The sterically dependent $^2J_{P-C}$ value for $C_{3,5}$ in ketophosphine 1 is quite small (<2 Hz); for the corresponding phosphorinane it is 3 Hz. Rigid models in the latter series (*cis*- and *trans*-1-methyl-4-*tert*-butyl-4-phosphorinanols) have provided[3] values for the axial methyl case of 1 Hz, and for the equatorial of 7 Hz. The small $^2J_{PC}$ value for 1 therefore is qualitatively consistent with some excess of **1a** over **1b.**

When sulfur or oxygen are added to phosphorus of **1,** it is likely that these substituents adopt the axial position in preference to methyl, as has been demonstrated for the phosphorinane compounds.[2] These atoms generally cause downfield shifts at α carbons;[2,9] this is seen in the spectrum for the sulfide (**2**) at both CH_3 and $C_{2,6}$, and in that of the oxide (**3**) at CH_3. On the other hand, quaternization of phosphines causes upfield shifts of attached carbons, and this is noted on comparing the data for the methiodide (**4**) to those for the phosphine (**1**).

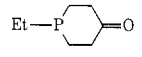
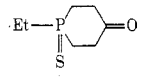
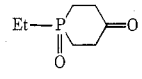
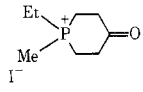
We detect a small but significant upfield shift at C_4 on converting 1-methyl-4-phosphorinanone to any of its tetra-

Table I
^{13}C NMR Spectra of 1-Methyl-4-phosphorinanone and Derivatives[a]

	Compd	Solvent	$C_{2,6}$	$C_{3,5}$	C_4	PCH_3
1		$CHCl_3$	23.8 (14)	36.3 (<2)	209 (<2)	7.9 (18)
2		$CHCl_3$	30.9 (51)	36.2 (6)	206.8 (5)	19.6 (56)
		H_2O	31.1 (52)	37.9 (8)	215.2 (7)	19.8 (55)
3		$CHCl_3$	23.3 (65)	32.8 (7)	204.9 (7)	11.5 (68)
		H_2O	26.8 (64)	37.5 (6)	214.6 (8)	15.3 (68)
4		DMSO	15.1 (51)	32.0 (6)	203.6 (11)	4.6 (52)
		H_2O	19.6 (50)	36.3 (8)	210.7 (7)	8.4 (54)

[a] Shifts were measured at ambient temperatures from the internal standards Me_4Si in $CHCl_3$, CH_3OH in H_2O, and $CHCl_3$ in DMSO. The H_2O solutions were run immediately after preparation before hydration was extensive. Values in parentheses are P–C coupling constants, in hertz.

Table II
^{13}C NMR Spectra of 1-Ethyl-4-phosphorinanone and Derivatives[a]

	Compd	Solvent	$C_{2,6}$	$C_{3,5}$	C_4	PCH_3	PCH_2	CCH_3
5		$CHCl_3$	21.9 (15)	37.1 (<2)	210.1 (<2)		17.3 (13)	9.3 (18)
6		$CHCl_3$	29.0 (50)	36.2 (4)	207.4 (5)		25.4 (53)	6.1 (4)
		H_2O	39.1 (50)	37.8 (7)	214.0 (6)		26.0 (53)	7.6[b]
7		$CHCl_3$	24.2 (60)	35.9 (5)	207.9 (7)		21.6 (70)	5.4 (5)
		H_2O	24.7 (63)	37.3 (8)	214.1 (6)		22.5 (66)	6.7 (<2)
8		DMSO	13.4 (49)	35.3 (7)	203.0 (7)	2.7 (54)	12.3 (50)	3.4 (5)
		H_2O	17.1 (49)	36.3 (7)	211.0 (6)	6.6 (53)	16.7 (50)	6.9 (5)

[a] See footnote *a*, Table I. [b] Coupling not clearly observed.

covalent derivatives **2**, **3**, or **4**. The shift is most pronounced in the salt **4** (5.4 ppm) but it is clearly present in both the sulfide (2.2 ppm) and the oxide (4.1 ppm). We have observed[2] the same upfield shift in the parent phosphorinane ring as well as in the 4-phosphorinanols, and it is therefore independent of both the hybridization of C_4 and the presence of substituents on C_4. It is also independent of the size of the substituent on phosphorus, and hence on the position of the conformational equilibrium for mobile systems in this series.[2] Furthermore, it can be determined from examination of published X-ray structural data that conversion of a phosphine to its sulfide has essentially no effect on the geometry of the ring in the vicinity of C_4. Thus, the C_3–C_4–C_5 angle in *r*-1-methyl-*c*-4-*tert*-butyl-*t*-4-phosphorinanol[10] is 111°, while that for the sulfide of the corresponding 4-methyl derivative[4] is 112°. The same values apply to the corresponding cis isomers.[11] Torsion angles about the rings are also not changed appreciably on sulfurization. We believe that the best explanation available at this time for the long-range shielding of C_4 is the operation of an electric field associated with the polar phosphorus functions. This effect has been postulated by others to explain a similar upfield shift at C_4 on S-alkylation of thianes[12] and on quaternization of piperidines.[5c] The field effect is receiving current attention in noncyclic structures as well,[13] where examples of its operation from nonionic polar groups have been presented.

In Table II are included ^{13}C NMR data for the same series of 4-phosphorinanones (**5**–**8**) but with a *P*-ethyl substituent. The features discussed for the *P*-methyl series are clearly evident in these data also. The effect of lengthening the exocyclic chain has been discussed previously,[2] and no new features are seen here.

Table III
Infrared and Ultraviolet Spectra for 1-Ethyl-4-phosphorinanone (5) and Its Oxide (6) and Sulfide (7)

Compd	$\nu_{C=O}$, cm^{-1}[a]	λ_{max}, nm (ϵ)[b]
5	1714	286 (4)
6	1717	287 (10)
7	1716	287 (14)

[a] Taken on 0.02 *M* solutions in tetrahydrofuran. [b] For the n → π^* transition, using THF solutions.

Some correlation has been noted in other systems between ^{13}C NMR shifts of the carbonyl group and the wavelength of its n → π^* transition in the ultraviolet spectrum.[14] We note no such effect in the present series of compounds; it can be seen from the data in Table III that no significant change in the uv maximum occurred when a phosphine (**5**) is converted to either the sulfide (**6**) or oxide (**7**), yet as noted changes in the ^{13}C shift do take place. Similarly, we observe no change in the carbonyl stretching frequency in the infrared spectra of these compounds (Table III), and we must assume that the electric field effect, if indeed operative in these compounds from the polar phosphorus functions, does not influence these important spectral properties of the carbonyl group.[15]

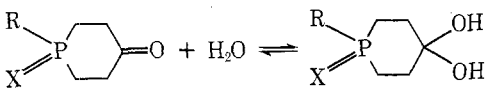
Table IV
^{13}C NMR Spectra[a] of 4,4-Phosphorinanediols in Water at 30°

Compd	$C_{2,6}$	$C_{3,5}$	C_4	PCH_3	PCH_2	CCH_3
9	26.1 (64)	35.2 (6)	95.7 (7)	14.4 (66)		
10	23.4 (64)	35.3[b]	96.0 (8)		21.9 (64)	6.5 (<2)
11	30.0 (49)	35.1 (6)	95.8 (6)	18.9 (55)		
12	27.8 (49)	34.7 (8)	95.7 (6)		25.0 (53)	7.6[b]
13	19.6 (50)	33.5 (7)	94.3 (8)	8.2 (56)		
14	17.5 (50)	33.5 (8)	94.4 (6)	5.1 (55)	15.5 (51)	6.9 (5)

[a] Shifts were determined from the signal of internal CH_3OH. Values in parentheses are C–P coupling constants, in hertz. [b] Coupling not readily measurable.

When the ^{13}C NMR spectra of the ketone oxides **3** or **7** are determined in water solution, pronounced downfield shifts relative to the signals for chloroform solutions are noted at all carbons. The same is true for salts **4** and **8** for water vs. dimethyl sulfoxide solution. For all compounds, the effect is strongest at the carbonyl carbon, where it amounts to some 7–10 ppm. These shifts are not unexpected and are clearly to be associated with the occurrence of hydrogen bonding at the carbonyl oxygen.[5b]

Hydration of the Carbonyl Group. The ^{13}C NMR spectra of freshly prepared water solutions of 4-phosphorinanone oxides **3** or **7** changed rapidly on standing, and an entirely new set of peaks appeared. This set (Table IV) lacked any signal for carbonyl carbon, but a new signal at about δ 96.0 provided the clue to the event taking place. This signal is in the characteristic region of *gem*-dioxy groups[16] and suggests that **3** and **7** are undergoing reversible covalent hydration to **9** and **10**, respectively. The ^{31}P

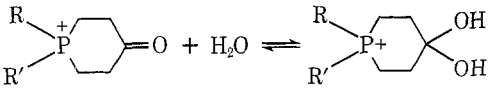


9, R = CH_3; X = O
10, R = C_2H_5; X = O
11, R = CH_3; X = S
12, R = C_2H_5; X = S

NMR signal for each compound in the equilibrium mixtures was also different; the signals were very sharp and useful for analysis of the mixtures even though they were separated by less than 1 ppm. The equilibrium compositions of Table V were obtained by this method. Signals were assigned to the keto or diol form on the basis of the similarity of peak intensities to those seen in the ^{13}C spectra.

The position of the hydration equilibrium was quite sensitive to temperature; at 70°, the ketone spectrum was in great predominance (80–90%), while at 10° only the diol spectrum was obtained.

Similar hydration effects were observed for the salts **4** and **8**, which formed **13** and **14**, respectively, and even for



13, R = R′ = CH_3
14, R = CH_3; R′ = C_2H_5

the sulfides **2** and **6** (Tables IV and V); the latter were less soluble in water, but gave readily observable signals attributable to diols **11** and **12**, respectively, in 5–10% methanol.

Contrary to the behavior of the phosphorinanes with tetracoordinate phosphorus, phosphines in this family (**1** and **5**) failed to undergo the hydration reaction to a detectable extent. They were insoluble in water, and it was necessary to test for hydration in the presence of dioxane (1:1).

Table V
^{31}P NMR Spectra and Equilibrium Compositions for the Hydration of 4-Phosphorinanones[a]

	$\delta^{31}P$[b]		Composition, %	
	Keto	Diol	Keto	Diol
3 ⇌ 9	−42.0	−41.6	35	65
7 ⇌ 10	−51.1	−51.8	47	53
4 ⇌ 13	−20.0	−17.2	40	60
8 ⇌ 14	−25.0	−21.7	42	58

[a] Spectral measurements were made on water solutions containing 5–10% of CH_3OH as ^{13}C reference. [b] Parts per million downfield from 85% H_3PO_4. Measured at 30°.

Similar hydration effects are known in other cyclic ketones with polar substituents; the methiodide of *N*-methyl-4-piperidone behaves very much like its phosphorus counterpart **4** and is extensively hydrated at room temperature,[16,17] while the free base, which is water soluble, shows about 16% hydration.[17]

It is thus seen that for both the P and the N compounds there is unusually great reactivity toward the nucleophile water in the same carbonyl groups that have the most upfield ^{13}C signals. It is possible that these effects result from similar through-space influences of the polar function on the carbonyl group; they seem less readily explained by transmission through the σ-bond structure. However, there is a change in stereochemistry about C_4 accompanying the hydration reaction and it is not known if this change has more influence on the reaction energetics for hydration of phosphorinanones with tetracoordinate phosphorus than with trivalent phosphorus. Any correlation between ^{13}C shifts and chemical reactivity for these ketones must remain speculative at this time.

Another unusual effect noted among these compounds is that oxide **3** underwent extensive proton–deuterium exchange at $C_{3,5}$ in neutral D_2O. Thus, after 24-hr exposure to D_2O at 75°, only 3% of the oxide remained undeuterated, and about 50% had achieved the d_4 stage. Such ready exchange would be more likely for the phosphine, since its basic center could promote the reaction, as has been suggested[17] to explain the rapid exchange of *N*-methyl-4-piperidone in D_2O. While the phosphine (**1**) did undergo some exchange in D_2O–dioxane (1:1), the extent was much less then that seen for the oxide. The manner in which remote phosphoryl influences the exchangeability of protons remains to be clarified.

Experimental Section

General. All manipulations of phosphines were conducted in a nitrogen atmosphere in a glove bag. Melting points are corrected.

Proton-decoupled Fourier transform ^{13}C spectra were taken with a Bruker HFX-10 system at 22.62 MHz utilizing C_6F_6 in a 3-mm coaxial capillary as external heteronuclear lock. Chemical shifts were measured from internal Me_4Si for $CHCl_3$ solutions, and from internal CH_3OH for water solutions (δ CH_3OH = 141.2; δ CS_2 = 192.5 ppm). C–P coupling constants are ±1.2 Hz. Proton-decoupled ^{31}P NMR spectra (CW mode) were obtained at 36.43 MHz again with a C_6F_6 lock; offsets relative to prerun 85% H_3PO_4 were used to determine δ values. Ir spectra were obtained with a Perkin-Elmer 621 spectrophotometer, and uv spectra with a Cary 15 spectrophotometer.

1-Methyl-4-phosphorinanone Derivatives. The parent ketone **1** was prepared as described previously.[18] Its conversion to sulfide **2** has also been reported.[2] Phosphine **1** readily gave the salt **4** with CH_3I, which was used directly for the NMR study.

Oxidation of **1** was accomplished by stirring 3.0 g (23.1 mmol) in 50 ml of benzene with 1.98 ml (23.1 mmol) of 30% H_2O_2 in an ice bath for 1 hr. Stripping of solvents left a white solid residue of **3** which was recrystallized from a mixture of methylene chloride and petroleum ether: mp 138–142°; ir ($CHCl_3$) ν 1730 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.70 (d, $^2J_{PH}$ = 13 Hz, PCH_3); NMR (D_2O, 30°) δ 2.12 and 2.25 (1:1, each d, $^2J_{PH}$ = 13.5 Hz, PCH_3 for diol and keto forms, respectively, as seen from temperature effects). The compound is extremely hygroscopic and gave only partly satisfactory analyses.

Anal. Calcd for $C_6H_{11}O_2P$: C, 49.32; H, 7.54; P, 21.21. Found: C, 48.92; H, 7.97; P, 20.87.

Oxide **3**, previously characterized as the oxime,[19] underwent exchange in D_2O at 75°. After 24 hr, a sample recovered by $CHCl_3$ extraction was found by mass spectral analysis to contain 50% d_4, 25% d_3, 12% d_2, and 7% d_1 derivative; only 3% remained undeuterated.

1-Ethyl-4-phosphorinanone Derivatives. The parent phosphine **5** has been reported previously.[20] Conversion to sulfide **6** was accomplished by a general procedure.[2] The sulfide after vacuum sublimation had mp 60–61.5°.

Anal. Calcd for $C_7H_{13}OPS$: C, 47.71; H, 7.44; P, 17.58. Found: C, 47.83; H, 7.50; P, 17.48.

Phosphine **5** was also oxidized to form compound **7**, which had previously been characterized as the oxime.[19] Quaternization of **5** with CH_3I gave salt **8** for the NMR studies.

Registry No.—**1**, 16327-48-3; **2**, 55298-82-3; **3**, 54662-09-8; **4**, 55298-83-4; **5**, 55298-84-5; **6**, 55298-85-6; **7**, 51805-19-7; **8**, 1194-42-9; **9**, 55298-86-7; **10**, 55298-87-8; **11**, 55298-88-9; **12**, 55298-89-0; **13**, 55298-90-3; **14**, 55298-91-4.

References and Notes

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Preparation of (*E,E*)- and (*Z,Z*)-1,4-Dibromo-1,4-diphenylbutadienes and Conversion to Mono- and Dilithio Derivatives

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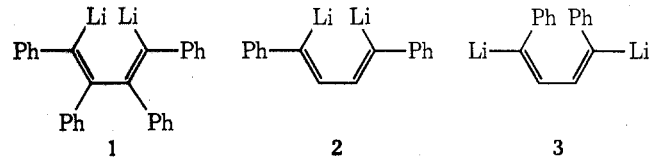
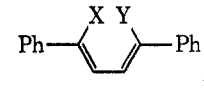
The ready availability of the dilithium reagent **1** by reduction of tolane[1,2] has resulted in its widespread use for the preparation of metallocycles (heterocyclopentadienes).[1a-c,3] The 1,4-diphenyl dilithio compound **2** should be equally and perhaps even more useful than **1**. The published synthesis[4] of the precursor dibromide **4a** is a five-step sequence, however, so that **2** and **4a** have been used infrequently.[5]



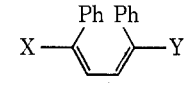
1 **2** **3**

We required dibromides **4a** and **5a**, as well as the mono- and dilithium reagents derived from them, in connection with studies on the preparation of chlorolium ions.[6] The



4

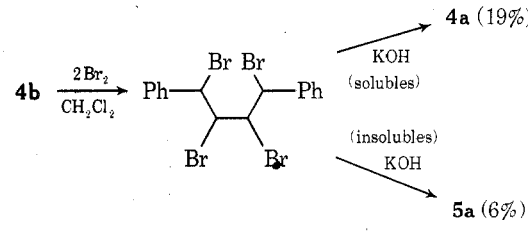
	a	b	c	d	e	f	g
X	Br	H	Cl	SCH_3	Br	Br	Br
Y	Br	H	Cl	SCH_3	H	Cl	SCH_3



5

	a	b	c
X	Br	H	Br
Y	Br	H	Li

most convenient synthesis of **4a** and **5a** would appear to be by bromination–dehydrobromination of the readily available 1,4-diphenylbutadiene.[7] We have developed procedures for the preparation of **4a** and **5a** in pure form by this route. The yields are low, but the procedures are simple, and the products are obtained in pure form by a single crystallization. The principal separation is performed at the tetrabromide stage; the precursor for **5a** is extremely insoluble and is filtered off after the bromine addition. Dehydrohalogenation (KOH–EtOH) of crystals and mother liquor gives the dibromides **5a** and **4a**, respectively.



(*E,Z*)-1,4-Dibromo-1,4-diphenyl-1,3-butadiene appeared to be formed as well (see Experimental Section), but it could not be isolated in pure form.

Stereochemical assignments were made on the basis of several arguments. The chemical shifts of the vinyl protons in **4a** and **5a** are δ 7.30 and 6.63. The pronounced upfield shift in the *E,E* isomer (**5a**) can be in part ascribed to the operation of a phenyl ring current effect. Apparently steric interactions of the ortho protons with the bromine and cis vinyl group result in the phenyl ring being turned out of the diene plane, so that the vinyl hydrogen is located in the shielding region of the phenyl ring current (see conformation **6**). An upfield shift of H_a (δ 6.64) in **7** was attributed to