Table IV

| substituent | polar contribution | resonance contribution | net | obsd[a] |
|---|---|---|---|---|
| $CH_2SCH_3$ | 0.66 | −1.68 | −1.02 | −1.51 |
| $CH_2OCH_3$ | 0.52 | −0.84 | −0.32 | −0.86[b] |
| $CH_2N(CH_3)_2$ | 0.24 | −1.26 | −1.02 | −1.19 |
| $CH_2Br$ | 1.18 | −0.63 | +0.55 | +0.70 |
| $CH_2Cl$ | 1.23 | −0.63 | +0.60 | +0.33 |
| $CH_2CN$ | 1.47 | −1.89 | −0.42 | −0.43 |
| $CH_3$[c] | −0.19 | −2.73 | −2.92 | −3.05 |

[a] Measured for dilute solutions (5–10% w/v) in $CDCl_3$ containing internal benzene. [b] Measured for $OCH_2CH_3$. [c] $\sigma_I(CH_3) = -0.04$; $\sigma_R°(CH_3) = -0.13$ (private communication, professor R. W. Taft).

$$SCS = 2.85\sigma_I + 0.37\sigma_R°(C\text{-}7; DCCl_3) \quad (3)$$

In Table II, an assembly of $\sigma_I$ values from the present work, and literature reports, is presented.

In Table III, a similar compilation of available $\sigma_R°$ values together with those based on the C-6, C-7, and C-10 chemical shift data is presented. The best $\sigma_I$ values in Table II were employed in the C-10 SCS equation to calculate $\sigma_R°$ values. The agreement between the $\sigma_R°$ values based on different techniques is impressive.

With the availability now of $\sigma_I$ and $\sigma_R°$ values in which high confidence can reside, it is possible to calculate the polar and resonance contributions to the C-4 SCS in a series of benzyl derivatives ($C_6H_5CH_2X$) and then the calculated SCS by using the appropriate DSP equation (eq 4).[11] The calculated and experimental SCS can then be compared (Table IV).

$$SCS = 4.73\sigma_I + 20.98\sigma_R°(para; DCCl_3) \quad (4)$$

It is clear (Table IV) that for all groups the resonance effect is comparable to or greater than the polar contribution. It should be further noted that the calculated net effect is in good agreement with the observed. This analysis negates Shapiro's conclusion[2] that resonance contributions for these groups is unimportant (with respect to the polar effect).

The question naturally arises as to why the resonance contribution of all the $CH_2X$ groups is less than that for $CH_3$ (Table IV). This could be associated with a reduction in C–H hyperconjugation resulting from a localizing of the $\pi$-type orbitals of the $CH_2X$ group due to the electronegativity of X.[12] However, the present data do not allow dismissal of the idea of C–X hyperconjugative electron withdrawal. Indeed, there is strong evidence from several approaches that this is a significant, if not substantial, contributing interaction.[1,3,13] Comparison of the $\sigma_R°$ values of $CH_2CN$ (−0.10) and $CH_2Cl$ (−0.03) is of interest considering that $\sigma_I(Cl) < \sigma_I(CN)$, although the halogen electronegativity is greater. We associate this result with the special nature of the C≡N grouping, with polarization of the cyanomethyl substituent thus $-CH_2^{\delta\delta-}—C^{\delta+}\equiv N^{\delta-}$.[14] It is gratifying to note the good agreement (in absolute terms) of our $\sigma_R°(CH_2X)$ values with those (of largely undetermined sign) based on the IR technique.[15] The signs of $\sigma_R°$ are established by our work.

## Experimental Section

**Compounds.** The substituted 2-methylnaphthalenes were prepared by standard routes from 2-methylnaphthalene. The 2-bromomethyl- or 2-chloromethylnaphthalenes served as the immediate precursors of the other members of the series. The 6-fluoro and 7-fluoro analogues of the parent series were obtained by the same sequences from the 6-fluoro- or 7-fluoro-2-methylnaphthalenes. These latter compounds were obtained in high yield by the cyclization route recently reported.[10] All compounds exhibited appropriate $^1H$ and $^{13}C$ spectra and had other physical properties in agreement with literature values.

**Spectra.** Proton decoupled $^{13}C$ spectra were obtained at 67.89 MHz in the FT mode for dilute solutions (5% w/v) in $CDCl_3$, and referenced to internal $Me_4Si$. The $^{19}F$ NMR spectra were obtained at 84.66 MHz on a Bruker WH-90 Fourier transform NMR spectrometer operating under proton decoupled conditions using benzene solutions containing 5% wt/wt of the substituted fluoronaphthalene and 2% wt/wt of 2-fluoronaphthalene.

**Acknowledgment.** The authors are grateful to the Australian Research Grants Committee for funding parts of this research and for providing access to the National NMR Center, Canberra (Director: Dr. Alan Jones). We also wish to thank Monash University for the use of their NMR facilities.

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(16) The weak apparent dependence on $\sigma_I$ is understandable within the framework of a bond polarizability model. Simple vectorial summation of electric field components acting along the three C–C bonds about C-10 is zero.

# 1,8-Bishomocubane[1]

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Recently, we required substantial amounts of 1,8-bishomocubane (**1**)[1] in connection with our continuing studies of the chemistry of highly strained ring systems. Two synthetic routes have previously been described in the literature.[2,3] Both syntheses start with the reasonably expensive cyclooctatetraene and both involve steps which occur in low yield. We wish to report here an alternate route to 1,8-bishomocubane which utilizes benzoquinone (**2**) and 1,3-cyclohexadiene (**3**) as starting materials (Scheme I).

As shown above, *p*-benzoquinone (**2**) was readily converted into 2,5-dibromobenzoquinone (**4**) according to the literature procedure.[4] Diels–Alder addition of **4** to 1,3-cyclohexadiene (**3**) in refluxing benzene gave 2,5-dibromotricyclo[6.2.2.0$^{2,7}$]-dodeca-4,9-diene-3,6-dione (**5**) in 81% yield.[5] Irradiation of **5** for 20 min in Pyrex with a 450 W Hanovia high-pressure

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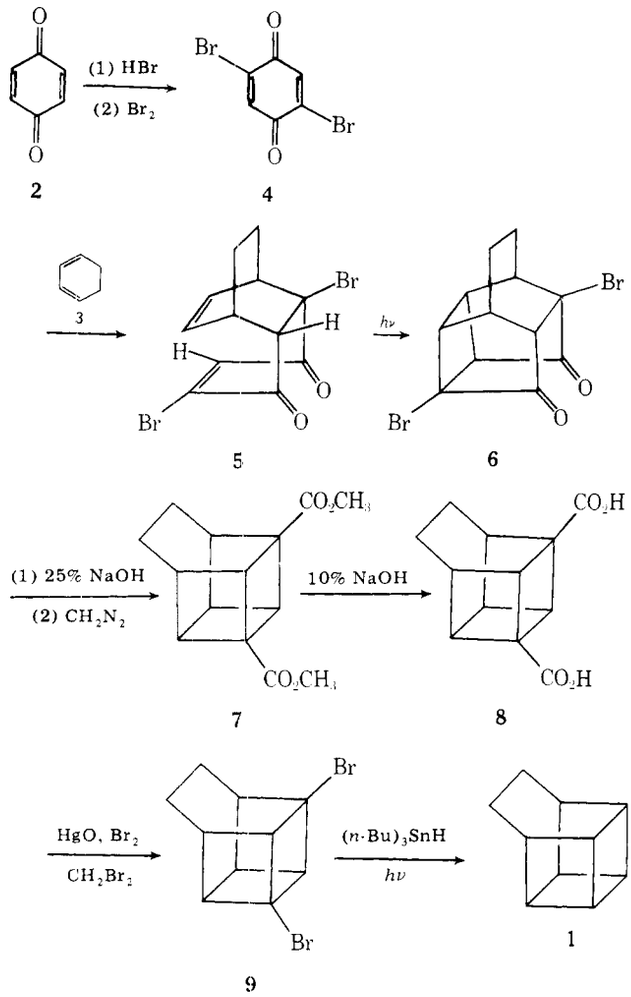
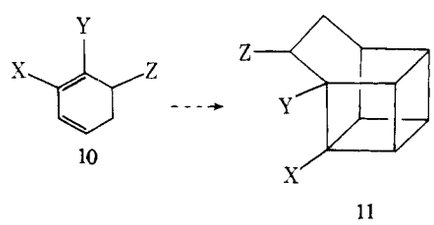
Scheme I



mercury lamp gave an 81% yield of 1,6-dibromopentacyclo[6.4.0.0$^{3,6}$.0$^{4,12}$.0$^{5,9}$]dodeca-2,7-dione (**6**). A pseudo-Favorskii rearrangement of **6** to **8** was achieved by 2 h reflux of **6** in 25% aqueous sodium hydroxide.[6] In order to purify **8**, it was converted into the dimethyl ester, **7**, which was purified and then saponified to regenerate **8** in 67% overall yield from **6**. Decarboxylation of **8** in a modified Hunsdiecker reaction[7] gave a 41% yield of 4,6-dibromopentacyclo[4.4.0.0$^{2,5}$.0$^{3,8}$.0$^{4,7}$]decane (**9**). Reductive debromination of **9** with tri-*n*-butyltin hydride and azobis(isobutyronitrile) (under irradiation)[7] gave a 63% yield of the desired 1,8-bishomocubane (**1**). This material, which was obtained in 11% overall yield from **3**, was identical in all respects to known material.[2,3]

In addition to providing a relatively simple and inexpensive route to **1**, the synthesis described provides a model for the synthesis of substituted 1,8-bishomocubane which would be difficult to prepare by currently available routes. In principle, substituted cyclohexadienes of general formula **10** should



serve as reasonable precursors of 1,8-bishomocubanes of general formula **11**. Using this approach, it should be possible to selectively prepare 1-, 2-, or 9-substituted versions of **1**.

## Experimental Section[8]

**2,5-Dibromobenzoquinone (4).** Benzoquinone (**2**) was converted into **4** according to the literature procedure.[4]

**2,5-Dibromotricyclo[6.2.2.0$^{2,7}$]dodeca-4,9-diene-3,6-dione (5).** A mixture of 2,5-dibromobenzoquinone (5.00 g, 18.8 mmol) and 1,3-cyclohexadiene (3.20 g, 40.0 mmol) in 10 mL of benzene was refluxed for 3 h. The solvent and the excess diene were evaporated to give a yellow solid, which was recrystallized from petroleum ether (60–70 °C) to give 5.28 g (81%) of **5**: mp 116–119 °C; IR (KBr) 3020, 2930, 1690, 1670, 1600, 1250, 1235, 905, 770, 715 cm$^{-1}$; $^1$H-NMR ($CDCl_3$) $\delta$ 7.39 (s, 1 H), 6.19–6.31 (m, 2 H), 3.10–3.70 (m, 3 H), 1.20–2.60 (complex m, 4 H).

Anal. Calcd for $C_{12}H_{10}Br_2O_2$: C, 41.65; H, 2.91. Found: C, 41.74; H, 2.99.

**1,6-Dibromopentacyclo[6.4.0.0$^{3,6}$.0$^{4,12}$.0$^{5,9}$]dodeca-2,7-dione (6).** A solution of **5** (5.00 g, 14.5 mmol) in 150 mL of benzene was irradiated through a Pyrex filter by means of a 450-W high-pressure Hanovia mercury lamp for 20 min. The solution was concentrated to ca. 30 mL by evaporation, and the slightly dark precipitate was collected by filtration and recrystallized from benzene to give 4.07 g (81%) of slightly dark crystals: mp 206–208 °C; IR (KBr) 2905, 1780 cm$^{-1}$; $^1$H-NMR ($CDCl_3$) $\delta$ 3.41 (broad s, 3 H), 3.00–3.14 (m, 1 H), 1.60–2.50 (complex m, 6 H).

Anal. Calcd for $C_{12}H_{10}Br_2O_2$: C, 41.65; H, 2.91. Found: C, 41.31; H, 3.05.

**Dimethyl Pentacyclo[4.4.0.0$^{2,5}$.0$^{3,8}$.0$^{4,7}$]deca-4,6-dicarboxylate (7).** A solution of **6** (2.50 g, 6.8 mmol) in 25 mL of 25% aqueous sodium hydroxide was refluxed (110 °C) for 2 h. After the reaction mixture had cooled, it was acidified by careful addition of concentrated hydrochloric acid below 5 °C. The white precipitate was collected by filtration, washed with a small amount of water, and dried to give 1.53 g of a solid. This solid was treated with excess diazomethane in ether until all of the solid dissolved. The excess diazomethane was destroyed by the addition of acetic acid and the ether solution was washed with aqueous sodium bicarbonate and brine and dried over anhydrous magnesium sulfate. After filtration, the solvent was evaporated to give 1.41 g of a yellow oil, which gradually solidified. Purification by column chromatography on silica gel (10% ether–hexane) gave 1.23 g (72%) of white crystals: mp 54–56 °C; IR (KBr) 2850, 1730, 1445, 1350, 1220, 1110 cm$^{-1}$; $^1$H-NMR ($CDCl_3$) $\delta$ 3.73 (s, 3 H), 3.70 (s, 3 H), 3.50–2.85 (complex m, 6 H), 1.54 (broad s, 4 H).

Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.57; H, 6.51.

**Pentacyclo[4.4.0.0$^{2,5}$.0$^{3,8}$.0$^{4,7}$]deca-4,6-dicarboxylic Acid (8).** A mixture of **7** (820 mg, 3.31 mmol) and 20 mL of 10% aqueous sodium hydroxide was refluxed for 1 h with stirring. After being cooled, the solution was washed once with ether and the aqueous solution was acidified by careful addition of 15% aqueous hydrochloric acid in an ice-water bath. The white precipitate was collected by filtration and dried to give 679 mg (93%) of **8**: mp 176–178 °C; IR (KBr) 3500–2300 (broad absorption), 1715, 1430, 1300, 1240 cm$^{-1}$; $^1$H-NMR ($Me_2SO$-$d_6$) $\delta$ 3.60–2.71 (complex m, 6 H), 1.42 (broad s, 4 H); exact mass calcd for $C_{12}H_{12}O_4$ *m/e* 220.073, found 220.075.

Anal. Calcd for $C_{12}H_{12}O_4$: C, 65.44; H, 5.49. Found: C, 64.78; H, 5.41.

**4,6-Dibromopentacyclo[4.4.0.0$^{2,5}$.0$^{3,8}$.0$^{4,7}$]decane (9).** To a mixture of **8** (0.66 g, 3.0 mmol) and red mercury oxide (1.44 g, 6.64 mmol) in 30 mL of dibromomethane was added a solution of bromine (1.20 g, 0.4 mL, 7.50 mmol) in 10 mL of dibromomethane dropwise with stirring at 85–90 °C. The reaction mixture was stirred at 85–90 °C for 2.5 h and cooled to room temperature. The precipitate was removed by filtration and the solvent was evaporated. The residue was extracted twice with hot hexane (100 mL) and the hot hexane solution was passed through a short basic alumina column. The solvent was evaporated to give a colorless oil, which was distilled by molecular still (25-mm pressure, 125–130 °C bath temperature) to give 0.35 g (41%) of **9**: IR (neat) 2850, 1225, 1185, 1055, 1040, 860, 825, 680 cm$^{-1}$; $^1$H-NMR ($CDCl_3$) $\delta$ 3.95–4.15 (m, 1 H), 2.82–3.84 (complex m, 5 H), 1.55 (m, 4 H).

Anal. Calcd for $C_{10}H_{10}Br_2$: C, 41.41; H, 3.48. Found: C, 41.66; H, 3.51.

**Pentacyclo[4.4.0.0$^{2,5}$.0$^{3,8}$.0$^{4,7}$]decane (1).** A mixture of **9** (0.433 g, 1.5 mmol), tri-*n*-butyltin hydride (1.04 g, 3.5 mmol), and azobis(isobutyronitrile) (20 mg) was put into a Pyrex tube under argon. The tube was placed ca. 30 cm from a light source and irradiated by means of a high-pressure mercury lamp for 4 h. The hydrocarbon (**1**) was removed under vacuum (0.1 mm) and collected in a cold trap at −78 °C to give 126 mg of **1** (63%) in almost pure form. An analytical sample was obtained by sublimation. The melting point and $^1$H-NMR spectrum were the same as the reported ones: mp 102.5–104.5 °C (lit.[2,3]

mp 102–104 °C); $^1$H-NMR ($CCl_4$) δ 2.92–3.35 (complex m, 6 H), 2.70 (broad s, 2 H), 1.43 (t, 4 H, $J$ = 1.3 Hz).

**Acknowledgment.** We are indebted to the National Science Foundation for a grant which supported this investigation.

**Registry No.**—**1**, 5603-27-0; **2**, 106-51-4; **3**, 592-57-4; **4**, 1633-14-3; **5**, 67745-70-4; **6**, 67745-71-5; **7**, 67745-72-6; **8**, 67745-73-7; **9**, 67745-74-8.

## References and Notes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(6) For an analogous pseudo-Favorskii rearrangement in the generation of a highly-strained ring system, see P. E. Eaton and T. W. Cole, Jr., *J. Am. Chem. Soc.*, **86**, 3157 (1964). See also ref 5.
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(8) Melting points and boiling points are uncorrected. Elemental analyses were performed by the Scandinavian Microanalytical Laboratories, Herlev, Denmark.


# Carbon-13 Nuclear Magnetic Resonance Spectra of Allenic Phosphonyl Compounds and the Related 1,2-Oxaphosphol-3-enes

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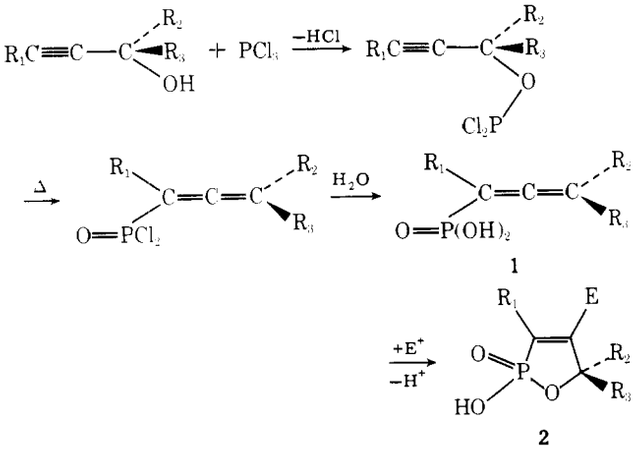
For several years we have been studying the reaction of propargyl alcohols with phosphorus trihalides under conditions which incorporate phosphorus in the products.[1-8] Of particular interest has been the reaction sequence shown in Scheme I, which leads to allenic phosphonic acids (**1**) and thence to 1,2-oxaphosphol-3-enes (**2**). Thus, a variety of allenic phosphonyl compounds have been prepared,[1,2,4] as well as oxaphospholenes with E = H,[1,2,4] Br,[5] HgX,[5] and OH (→ 4-keto-1,2-oxaphospholenes).[8] Moreover, the methyl esters of **1** and **2** are readily prepared from the free acid with diazomethane.[7]

The proton[1,2,4,5,8] and phosphorus[1,2,4] NMR spectra of these compounds have proven quite interesting, especially with

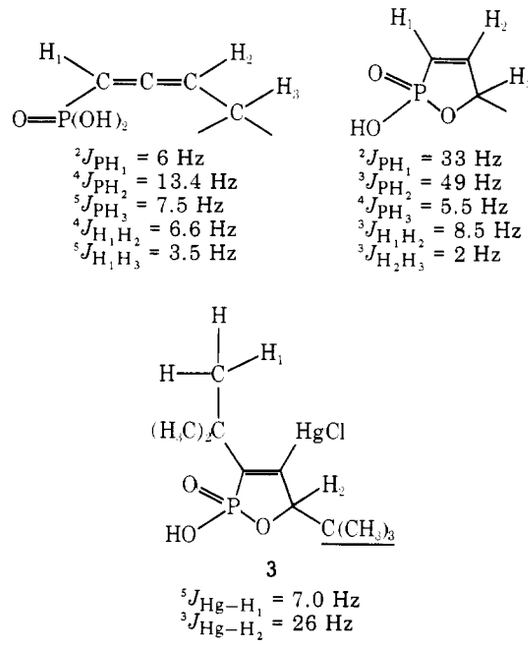
Scheme I



**1**

**2**

Chart I[9b]



**3**

respect to long-range heteronuclear coupling. Typical values[4] are shown with the structures in Chart I.[9a,b] Chloromercuri derivative **3** was especially noteworthy because it showed long-range $^{199}$Hg couplings to protons five bonds away and an apparent effect on the rotation of the underlined *tert*-butyl group.[5] As a complement to these earlier studies, we now report the $^{13}$C spectral data for some of these unique compounds. These results provide useful model data for chemical shifts and $^{13}$C–$^{31}$P coupling constants in a wide variety of organophosphorus compounds.

## Results

The $^{13}$C chemical shifts and $^{13}$C–P coupling constants for six allenic phosphonyl compounds are listed in Table I, and data for six oxaphospholene derivatives are given in Table II.

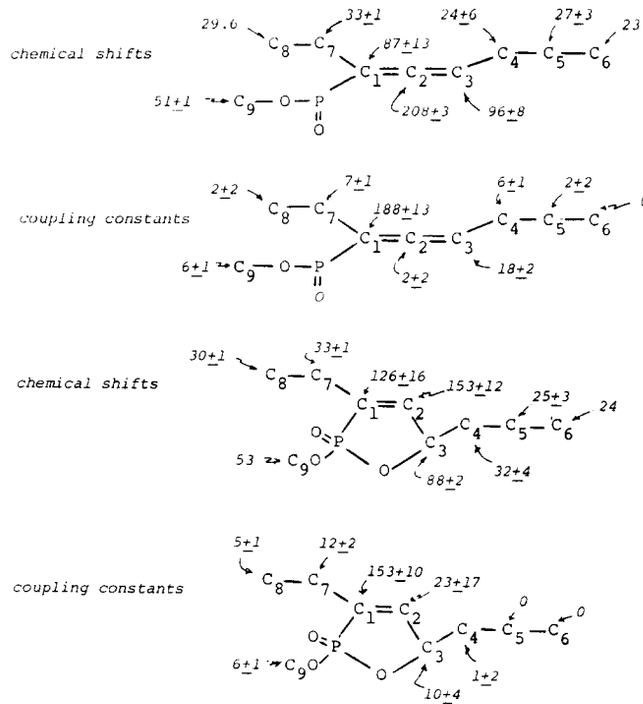



**Figure 1.** Average chemical shifts (parts per million downfield from $Me_4Si$) and coupling constants (hertz) for allenic phosphoryl derivatives and oxaphosphol-3-enes.

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