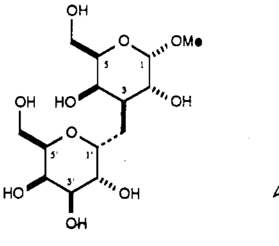
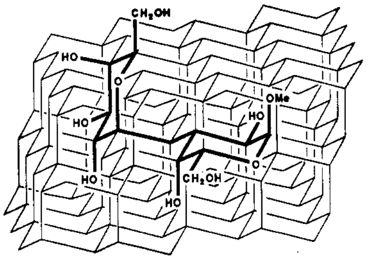
ferred conformation of **5** and **6** can also be analyzed in the same manner.[6] The conformational behavior of **5**–**8** seems to agree well with that of the corresponding parent disaccharides.[9]

It is noteworthy that the conformation preference around the C-glycosidic bond is so overwhelming that a structural deviation from the ideal staggered conformer to avoid the steric interactions takes place in rotating primarily the nonglycosidic C4–Cα bond rather than the glycosidic C1′–Cα bond. The recognition of this phenomenon allows to predict the conformational behavior of di-C-saccharides and higher C-saccharides and their parent substances. For example, the carbon analogue **9** of 3-*O*-α-D-galactopyranosyl-*D*-galactopyranose, a structural unit of human blood group determinants,[10] possesses one unique conformer **9A**, which meets with all the criteria to exist predominantly in one conformer. Indeed, we have recently succeeded in the synthesis of **9** and demonstrated that the NMR data confirm this prediction.[11]



9



9A

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Registry No. **1**, 110316-61-5; **2**, 110352-41-5; **3**, 110352-42-6; **4**, 110352-43-7; **5**, 107032-98-4; **6**, 106929-15-1; **7**, 106974-31-6; **8**, 106974-29-2; i, 110316-62-6; ii, 110316-63-7; iii, 110352-44-8; iv, 110316-64-8; v, 110316-65-9.

Supplementary Material Available: The complete tables listing chemical shifts and spin–spin coupling constants, the synthesis of monodeuteriated substances, and the conformational analysis of **3**–**6** based on a diamond lattice (4 pages). Ordering information is given on any current masthead page.

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[8] We observed small temperature effects; for instance, $J_{4,\alpha(pro\text{-}R)}$ and $J_{4,\alpha(pro\text{-}S)}$ of **5** were 3.7 and 4.7 Hz at 40 °C, 3.5 and 4.7 Hz at 25 °C, 3.1 and 4.9 Hz at 0 °C, 2.9 and 5.1 Hz at −20 °C, and 2.8 and 5.2 Hz at −40 °C. We are currently engaged in NOE experiments to gain more information.

[9] For the conformational analysis of cellobiose and maltose in solution, for example, see: (a) Shashkov, A. S.; Lipkind, G. M.; Kochetkov, N. K. *Carbohydr. Res.* **1986**, *147*, 175 and references cited therein. (b) Nardin, R.; Saint-Germain, J.; Vincendon, M.; Taravel, F.; Vignon, M. *Nouv. J. Chim.* **1984**, *8*, 305 and references cited therein. (c) Lemieux, R. U.; Bock, K.; Delbaere, L. T. J.; Koto, S.; Rao, V. S. *Can. J. Chem.* **1980**, *58*, 631 and references cited therein. (d) St. Jacques, M.; Sundararajan, P. R.; Taylor, K. J.; Marchessault, R. H. *J. Am. Chem. Soc.* **1976**, *98*, 4386 and references cited therein.

[10] There are a number of excellent review articles on this subject. For example, see: Lemieux, R. U. *Chem. Soc. Rev.* **1978**, *7*, 423. *Frontiers of Chemistry*; Laidler, K. J. Ed.; Pergamon: New York; 1982; p 1 and references cited therein.

[11] The spin–spin coupling constants observed for **9** are $J_{1',\alpha(pro\text{-}S)}$ = 12.1 Hz, $J_{1',\alpha(pro\text{-}R)}$ = 3.1 Hz, $J_{3,\alpha(pro\text{-}S)}$ = 3.3 Hz, $J_{3,\alpha(pro\text{-}R)}$ = 11.1 Hz, and $J_{\alpha,\alpha}$ = 14.3 Hz: Goekjian, P. G.; Kang, H.-Y.; Kishi, Y., unpublished results.

Reaction of the Dianion of ($\eta^6{:}\eta^6$-Biphenyl)bis(tricarbonylchromium)with Electrophiles. A Highly Regioselective Route from Biphenyl to 2-Alkylbiphenyls and 5-Alkyl-5-phenyl-1,3-cyclohexadienes

Summary: The dianion formed by reduction of ($\eta^6{:}\eta^6$-biphenyl)[$Cr(CO)_3$]$_2$ reacts with electrophiles such as H_2O, D_2O and methyl or primary alkyl halides in a highly stereoselective and regioselective manner to form an intermediate with one ring coordinated to a $Cr(CO)_3$ group as a η^5-cyclohexadienyl anion, substituted in the 1-position by the electrophile, and the other ring η^6 coordinated to the second $Cr(CO)_3$ group. Appropiate workup of the alkylated intermediates yields either 2-alkylbiphenyls or (5-alkyl-η^6-5-phenyl-1,3-cyclohexadiene)chromium tricarbonyls in essentially quantitative yields.

Sir: Two-electron reduction of conjugated arenes complexed by two $Cr(CO)_3$ groups produces stable dianions.[1,2] ($\eta^6{:}\eta^6$-Biphenyl)[$Cr(CO)_3$]$_2$ (**1**, Scheme I) has been reduced chemically to generate a dianion which is sufficiently stable to isolate and store in an argon drybox.[2] ^{13}C and ^{1}H NMR spectrometric data of the dilithium salt of the dianion are consistent with a ($\eta^5{:}\eta^5$-biphenyl)[$Cr(CO)_3$]$_2$ structure (**2** in Scheme I).[3,4] In this paper we wish to report the intermediates and products of the reaction of ($\eta^5{:}\eta^5$-biphenyl)[$Cr(CO)_3$]$_2$ dianion (**2**) with H_2O, D_2O, and methyl or 1-alkyl iodides and bromides.

In a typical reaction, **2** is placed in dry, argon-saturated THF or DMF-d_7.[5] One equivalent of the electrophile (E in Scheme I) is injected into the reaction vessel and stirred at ambient temperature. D_2O or H_2O causes a nearly instantaneous color change from the dark brown of the dianion to a yellow orange solution. Alkyl halides react more slowly to give similar color changes over the course of several minutes. NMR data for products obtained from the reaction of **2** with the electrophiles listed are consistent with structure **3** in which one ring is a $Cr(CO)_3$-coordinated η^5-cyclohexadienyl anion substituted by the electrophile in the 1-position and the other arene ring is neutral and η^6 coordinated to the other $Cr(CO)_3$ group. ^{13}C and ^{1}H NMR data of some of the products formed by reaction of **2** with electrophiles are shown in Tables I and II, respectively. NMR shift assignments are made by comparison with isoelectronic (η^5-cyclohexadienyl)metal-carbonyl complexes for which ^{13}C NMR[2,6–10] and ^{1}H NMR [2,6,7,11–15]

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[1] Milligan, S. N.; Rieke, R. D. *Organometallics* **1983**, *2*, 171.

[2] Rieke, R. D.; Milligan, S. N.; Schulte, L. D. *Organometallics* **1987**, *6*, 699 and references therein. Note: The isolated ($\eta^5{:}\eta^5$-biphenyl)[$Cr(CO)_3$]$_2$ dianion (**2**) has been found to be pyrophoric.

[3] Deviation of saturated carbon 1 from the plane formed by carbons 2–6 is well known for a variety of η^5-cyclohexadienyl rings.[7,13] The angle of deformation is on the order of 38° to 45° in complexes for which X-ray data is available. A MO explanation of the deformation has been presented in a theoretical discussion of η^5-cyclohexadienyl rings.[7] The angle of deformation in **2**, with its unsaturated carbon 1, is unknown at present.

[4] Hoffmann, R.; Hofmann, P. *J. Am. Chem. Soc.* **1976**, *98*, 598.

[5] The ($\eta^5{:}\eta^5$-biphenyl)[$Cr(CO)_3$]$_2$ dianion (**2**) is not sufficiently soluble in THF for optimum NMR examinations. DMF-d_7 was found to be an excellent solvent for NMR work. THF was used for the reactions for which yield data is described.

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[10] Pearson, A. J. *J. Chem. Soc., Perkin Trans. 1* **1977**, 2069.

[11] Semmelhack, M. F.; Hall, H. T.; Farina, R.; Yoshifuji, M.; Clark, G.; Bargar, T.; Hirotsu, J.; Clardy, J. *J. Am. Chem. Soc.* **1979**, *101*, 3535 and references therein.

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Table I. ^{13}C NMR Shifts (ppm) and $^{1}J_{CH}$ Coupling Constants (Hz) Obtained for 1, 2, and 3a–d,f,g[a]

compd	CO	CO′	C1	C2	C3	C4	C1′	C2′	C3′	C4′
1	233.4 (s)	233.4 (s)	106.2 (s)	94.5 (d, 174)	93.3 (d, 174)	94.8 (d, 177)	106.2 (s)	94.5 (d, 174)	93.3 (d, 174)	94.8 (d, 177)
2	243.0 (s)	243.0 (s)	102.2 (s)	67.2 (d, 158)	98.0 (d, 159)	69.6 (d, 168)	102.2 (s)	67.2 (d, 158)	98.0 (d, 159)	69.6 (d, 168)
3a	242.1 (s)	234.8 (s)	41.7 (d, 135)	51.1 (d, 160)	*b*	75.9 (d, 169)	122.8 (s)	*b*	*b*	92.9 (d, 164)
3b	242.1 (s)	234.8 (s)	41.3 (t, 20)[c]	51.1 (d, 160)	*b*	75.9 (d, 169)	122.8 (s)	*b*	*b*	92.9 (d, 164)
3c	241.4 (s)	235.6 (s)	40.7 (s)	57.2 (d, 163)	*d*	75.9 (d, 173)	125.2 (s)	*d*	*d*	96.5 (d, 176)
6d	241.0 (s)	235.3 (s)	44.3 (s)	56.4 (d, 162)	*e*	76.0 (d, 172)	124.3 (s)	*e*	*e*	97.4 (d, 176)
3f	241.2	235.5	44.0	56.5	*f*	76.1	124.9	*f*	*f*	97.5
3g	241.2	235.6	43.9	56.1	*g*	76.4	124.2	*g*	*g*	97.9

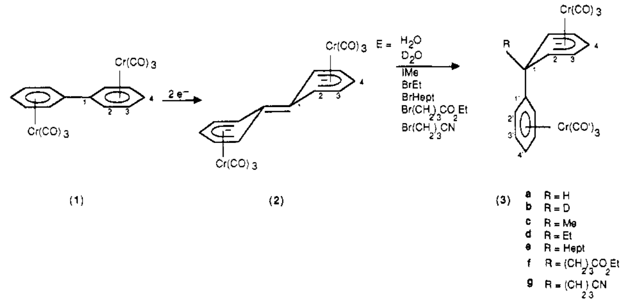
[a] All spectra were obtained in and referenced to DMF-d_7 (30.10 ppm) by using a Varian XL-200 or XL-300 NMR spectrometer. Samples **2** and **3a–d,f,g** showed signals for residual THF at 67.7 and 25.8 ppm. [b] Three signals for **3a** and **3b** are not unambiguously assigned at present. The signals are observed at 95.9 (d, 170 Hz), 95.8 (d, 171 Hz), and 93.3 ppm (d, 168 Hz) and correspond to C3, C2′, and C3′. [c] Coupling constant reported is for $^{1}J_{CD}$, which is observed in both decoupled and gated decoupled spectra. The size of the deuteriated carbon signal was much smaller than the others. [d] Three signals for **3c** are not unambiguously assigned at present. The signals observed at 98.4 (d, 172 Hz), 96.1 (d, 162 Hz), and 92.1 (d, 175 Hz) correspond to C3, C2′, and C3′. The signal for the methyl group is tentatively assigned to a peak observed at 34.9 ppm which is partially obscured by solvent. [e] Three signals for **3d** are not unambiguously assigned at present. The signals observed at 99.2 (d, 171 Hz), 96.3 (d, 161 Hz), and 91.0 (d, 168 Hz) correspond to C3, C2′, and C3′. The ethyl group is also visible in **3d** at 40.1 (t, 126 Hz) and 8.2 ppm (q, 125 Hz). [f] Three signals for **3f** are not unambiguously assigned at present. The signals observed at 99.1, 96.4, and 91.1 ppm correspond to C3, C2′, and C3′. Signals for the alkyl chain are observed at 173.4, 60.8, 47.8, 35.0 (in DMF signal), 19.5, and 14.3 ppm. [g] Three signals for **3g** are not unambiguously assigned at present. The signals observed at 99.4, 96.5, and 91.2 ppm correspond to C3, C2′, and C3′. Signals for the alkyl chain are observed at 120.7, 47.2, 20.2, and 17.1 ppm.

Table II. ^{1}H NMR Shifts (ppm) and $^{1}J_{HH}$ Splitting Patterns and Integration and Coupling Constants (Hz) for 1, 2, and 3a–d,f,g[a]

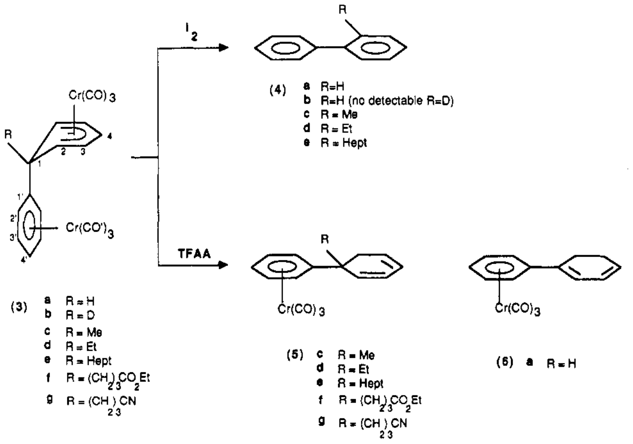
compd	H1	H2	H3	H4	H2′	H3′	H4′
1		6.27 (d, 4 H, 7.1)	5.91 (t, 4 H, 6.3)	5.81 (t, 2 H, 6.2)	6.27 (d, 4 H, 7.1)	5.91 (t, 4 H, 6.3)	5.81 (t, 2 H, 6.2)
2		2.88 (d, 4 H, 7.0)	4.29 (dd, 4 H, 7.0 and 5.5)	4.67 (t, 2 H, 5.2)	2.88 (d, 4 H, 7.0)	4.29 (dd, 4 H, 7.0 and 5.5)	4.67 (t, 2 H, 5.2)
3a	3.30 (t, 1 H, 5.7)	2.70 (t, 2 H, 6.3)	4.58 (t, 2 H, 6.3)	4.98 (dt, 1 H, 5.4)	5.27 (d, 2 H, 5.7)	5.57 (t, 2 H, 6.4)	5.40 (t, 1 H, 6.3)
3b		2.69 (d, 2 H, 6.1)	4.59 (t, 2 H, 6.3)	4.99 (t, 1 H, 5.6)	5.31 (d, 2 H, 7.1)	5.56 (t, 2 H, 6.4)	5.41 (t, 1 H, 6.7)
3c[b]		2.29 (d, 2 H, 6.2)	4.55 (t, 2 H, 6.1)	5.09 (t, 1 H, 5.2)	6.28 (d, 2 H, 5.9)	5.60 (t, 2 H, 5.9)	5.78 (t, 1 H, 6.0)
3d[c]		2.26 (d, 2 H, 6.9)	4.56 (t, 2 H, 5.9)	5.00 (t, 1 H, 5.2)	6.21 (d, 2 H, 6.3)	5.51 (t, 2 H, 6.3)	5.82 (t, 1 H, 5.9)
3f[d]		2.27 (d, 2 H, 6.3)	4.57 (t, 2 H, 5.3)	5.01 (t, 1 H, 5.4)	6.25 (d, 2 H, 6.2)	5.54 (t, 2 H, 6.0)	5.85 (t, 1 H, 5.4)
3g[e]		*e*	4.60 (t, 2 H, 5.5)	5.05 (t, 1 H, 4.4)	6.28 (d, 5.8)	5.57 (t, 2 H, 5.5)	5.90 (t, 1 H, 5.8)

[a] All spectra were obtained in DMF-d_7 and referenced to DMF-d_7 at 2.74 ppm by using a Varian XL-200 or XL-300 NMR spectrometer. Samples **2** and **3a–d,f,g** showed signals for residual THF at 3.61 and 1.76 ppm. The signals for H3 in compounds **3a–d,f,g** are probably not true triplets but doublets of doublets which are not resolved. [b] A signal was observed for the methyl group at 0.71 ppm (s, 3 H). [c] Signals were observed for the ethyl group at 1.13 (q, 2 H, $^{3}J_{HH}$ = 7.5 Hz) and 0.76 ppm (t, 3 H, $^{3}J_{HH}$ = 7.4 Hz). Signals for the methylene protons were observed at 2.11 (t, 2 H, 6.5 Hz), 1.7 (m, overlapping with large THF peak), and 1.1 ppm (m, overlapping with methyl of ester function. [e] Signals were observed for the alkyl substituent at 2.4–2.2 (m, overlapping signals for H_2 and one of the methylenes), 1.3 (m, overlapping with large THF peak), and 1.3–1.1 ppm (m, 2 H).

Scheme I



Scheme II



data have been reported.

The carbon–electrophile bond formation is both highly regioselective and stereoselective for each of the electrophiles reported, as only one isomer is observed in the ^{13}C and ^{1}H NMR. The regioselective attack of the arene ring at the 1-position was somewhat unexpected based on simple electronic considerations. Nucleophilic and electrophilic substitution patterns of (η^6-arene)Cr(CO)$_3$ complexes have been correlated with the coefficient of the LUMO and HOMO, respectively, of the arene ligand,[16] as well as conformational preferences of the Cr(CO)$_3$ group.[17,18] Hückel calculations for the biphenyl dianion HOMO shows position 4 to have the largest coefficient.[19] Electrophilic aromatic substitution of biphenyl usually occurs in the

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(19) Values of coefficients are given by: Coulson, C. A.; Streitwieser, A. *Dictionary of Electron Calculations*; W. H. Freeman and Company: San Francisco, 1965; p 91. Values listed for the HOMO of the biphenyl dianion are: 1 = –0.35, 2 = –0.30, 3 = +0.14, 4 = +0.40.

4-position for the electronic reasons above, and for steric advantages.[20]

A close examination of the ^{1}H NMR coupling constant for the protons on positions 1 and 2 for **3a** ($^3J_{HH}$ = 5.7 Hz) reveals strong evidence that the new proton (or deuterium in **3b**) is endo substituted on the η^5-cyclohexadienyl ring with respect to the coordinating $Cr(CO)_3$ group. Endo protons in η^5-cyclohexadienyl complexes have a larger $^3J_{HH}$ coupling (5–6 Hz) with vicinal protons than do exo protons (<2 Hz) in several cases of unambiguous structure assignment.[6,10–14,21] The stereospecificity of the alkylated analogues **3c–g** has not been determined as exo or endo; however, the reaction is highly stereoselective as only one stereoisomer is observed.

Oxidative decomposition of the alkyl-substituted products **3c–e** with I_2 results in the exclusive formation of 2-alkylbiphenyls from the dianion in essentially quantitative yields (See Scheme II).[22,23] Interestingly, similar decomposition of deuterium-substituted **3b** does not result in any measurable amount of deuterium incorporation in the biphenyl product, indicating that the endo deuterium is lost as the complex is oxidized and the ring aromatizes. Many examples of the loss of the endo proton under the oxidative conditions employed here are known for (η^5-cyclohexadienyl)$Cr(CO)_3$ anions formed by exo attack of nucleophiles.[11] As **3c,d,g** are oxidized, a rearrangement must take place in which either the alkyl substitutent or the arene ring undergoes, in effect, a 1,2-shift. The mechanism by which this rearrangement occurs is currently under study.

Protonation of **3c–g** with 1 equiv of trifluoroacetic acid generates the diene species **5c–g** shown in Scheme II, with loss of a $Cr(CO)_3$ group. The protonation occurs with complete regiospecificity and without attack upon the second $Cr(CO)_3$ group. Others have used TFAA to protonate (η^5-cyclohexadienyl)$Cr(CO)_3$ anions formed by exo attack of nucleophiles with varying degrees of regiospecificity.[11,24] The $Cr(CO)_3$ group which remains may be easily cleaved by exposure to air and sunlight to generate the free 5-alkyl-5-phenyl-1,3-cyclohexadiene in quantitative yields from the dianion. The formation of the quaternary center and subsequent reaction with TFAA to form the diene is of potential synthetic value. An excess of TFAA is needed to protonate **3a**, presumably because of the residual hydroxide ion from the initial protonation. NMR evidence suggests that the product formed from protonation of **3a** is the conjugated diene **6**, presumably by rearrangement from the unconjugated species **5** with R = H. The conjugated diene **6** is prone to rearomatize to biphenyl with air exposure. The ^{13}C NMR spectra of **5c–g** is interesting as six distinct aromatic carbon resonances are observed in each case instead of the usual four. Protonation of **3c–g** to form **5c–g** has made the quaternary center at carbon 1 chiral.[25]

In summary, this work provides a facile route for the highly regioselective introduction of an alkyl group to form a quaternary center at the 1-position of biphenyl. Oxidative workup of the reaction with I_2 produces 2-alkylbiphenyls in quantitative yields from the starting dianion. Acidic workup of the alkylated intermediates with trifluoroacetic acid generates 5-alkyl-5-phenyl-1,3-cyclohexadienes. These dienes may retain the $Cr(CO)_3$ group coordinated to the phenyl substituent intact for possible further reaction or it may be easily removed depending upon reaction conditions. Remote nitrile or ester functionality does not interfer with the reaction conditions and may be useful in future work to promote ring cyclizations by deprotonation and attack upon the intact (η^6-arene)-$Cr(CO)_3$ ring. Work on these and related compounds continues in our laboratories.

Acknowledgment. We thank the National Science Foundation for the support of this research (Grant CHE-8318335). We thank Dr. Don Nagel of the Eppley Cancer Research Institute for use of the Varian XL-300 NMR spectrometer.

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[20] Dabrowski, R.; Witkiewicz, Z.; Kenig, K. *Mol. Cryst. Liq. Cryst.* **1980**, 251. The HOMO of the biphenyl neutral has the same coefficients as listed in reference 19 with sign changes.

[21] The larger coupling has been attributed by one author[14] to differences in the dihedral angle of the exo and endo protons, relative to the vicinal protons, caused by the deformation of the ring from planarity discussed previously (ref 4).

[22] Yields over 95% have been observed via GC analysis, based on the (η^6:η^6-biphenyl)$[Cr(CO)_3]_2$ dianion (**2**).

[23] Satisfactory ^{1}H NMR and ^{13}C NMR data have been obtained for all products from the dianion. Mass spectral data have been obtained for all products following loss of $Cr(CO)_3$ groups, and several of the (5-alkyl-η^6-5-phenyl-1,3-cyclohexadiene)chromium tricarbonyls. A sample of 2-heptylbiphenyl was independently synthesized for direct comparison. 2-Methylbiphenyl was compared with commercially available 3-methylbiphenyl and 4-methylbiphenyl.

[24] Semmelhack, M. F.; Hall, H. T. *J. Am. Chem. Soc.* **1974**, *96*, 7092.

[25] The protons of a methylene group near a chiral center have long been known to be chemical shift inequivalent as they cannot be interchanged by rapid rotaton of a symmetry operation. A similar argument explains the inequivalence of the ortho and meta carbons of the coordinated arene ring. The rotamers are not interchangable by rotation about the 1-1′ bond or any allowed symmetry operation until the $Cr(CO)_3$ group is removed.

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Sharply Contrasting Behaviors of [*o*- and *p*-(*N*,*N*-Dimethylamino)phenyl]phosphonium Salts in Alkaline Decomposition Reactions

Summary: Benzyl[2-(*N*,*N*-dimethylamino)phenyl]diphenylphosphonium bromide (**3**) undergoes alkaline cleavage in 1:1 dioxane–water [to give *N*,*N*-dimethylaniline (96.5%), benzene (3.5%), and benzyldiphenylphosphine oxide (**5**, 96%)] 1.1 × 10^3 times more rapidly (at 37.7 °C) than benzyl[4-(*N*,*N*-dimethylamino)phenyl]diphenylphosphonium bromide [which gives toluene (100%) as the hydrocarbon product].

Sir: In a recent paper,[1] we have reported that benzylidine [2-(*N*,*N*-dimethylamino)phenyl]diphenylphosphorane (**1**) exhibits a strikingly different behavior in the Wittig reaction with benzaldehyde in ether solution at −78 °C in the presence of lithium ion than does benzylidene [4-(*N*,*N*-dimethylamino)phenyl]diphenylphosphorane (**2**). In order to examine further the influence of this apparent through-space N_{2p}–P(IV) interaction in the ortho isomer,[2] we have now examined the alkaline cleavage reactions of

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[1] Cairns, S. M.; McEwen, W. E. *Tetrahedron Lett.* **1986**, *27*, 1541.

[2] We have previously used the designation "N_{2p}–P_{3d} overlap" for such effects, but with the proviso that this is a convenient abbreviation rather than a statement of theory.[19] Now, however, it is time to change the abbreviation to "N_{2p}–P(IV)" since there are numerous theoretical treatments extant which indicate that d orbital involvement may be a minor component or even completely unnecessary in the description of either phosphorus "hypervalency" or a transition-state interaction.[14]