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

A close examination of the ^1H 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.

(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^5-biphenyl)$[Cr(CO)_3]_2$ dianion (**2**).

(23) Satisfactory ^1H 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

(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]

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benzyl[2-(*N*,*N*-dimethylamino)phenyl]diphenylphosphonium bromide (**3**) and benzyl[4-(*N*,*N*-dimethylamino)phenyl]diphenylphosphonium bromide (**4**), the precursors of **1** and **2**, respectively.

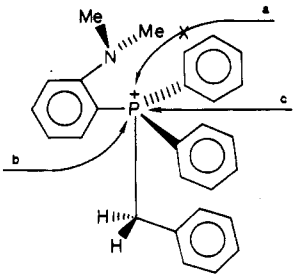
The phosphonium bromide **3** was found to undergo alkaline cleavage (KOH) at 37.70 ± 0.05 °C in 1:1 1,4-dioxane–water containing 0.400 M potassium bromide in a third-order reaction (relative rate = 4.76).[3,4] The products of the reaction were determined to be $PhNMe_2$ (96.5%), PhH (3.5%), and benzyldiphenylphosphine oxide (**5**, 96%). The phosphonium bromide **4** was subjected to alkaline cleavage under the same conditions (relative rate = 0.0043) to give toluene (100%) as the sole hydrocarbon product. No benzene or *N*,*N*-dimethylaniline could be detected.

Equally spectacular divergencies were found in the alkaline cleavage reactions of benzylbis[2-(*N*,*N*-dimethylamino)phenyl]phenylphosphonium bromide (**6**) and benzylbis[4-(*N*,*N*-dimethylamino)phenyl]phenylphosphonium bromide (**7**). Reaction of **6** under the standard conditions (relative rate = 0.11) gave $PhNMe_2$ (94.2%) and PhH (1.05%), with no toluene being detected. Reaction of **7** (relative rate = 0.00070) gave toluene (100%) as the only hydrocarbon product; no $PhNMe_2$ or PhH could be detected.

The mechanism of alkaline decomposition of ordinary acyclic quaternary phosphonium salts is well understood[5] and need not be given in detail here. It is sufficient to state that, with an uncomplicated, noncyclic quaternary phosphonium cation, hydroxide ion first adds reversibly to the tetrahedral phosphorus to form a trigonal bipyramidal intermediate in which the hydroxyl and the most apicophilic group originally bonded to phosphorus (benzyl > aryl > alkyl)[6] occupy apical positions. Without the necessity for a Berry pseudorotation,[7] the conjugate base of the phosphorane expels the apical group as a carbanion (which is protonated as it is being formed[8]), with concomitant formation of a phosphine oxide. Since neither **3** nor **6** gives any toluene at all, there is obviously some special effect operative in the alkaline cleavage of these compounds.

It is our belief that a reasonably strong N_{2p}–P(IV) through-space interaction exists in the cations of **3** and **6** (as shown previously for benzyl(2-methoxyphenyl)diphenylphosphonium bromide by X-ray diffraction[9]), as depicted in Scheme I for the cation of **3**. Attack by hydroxide ion does not occur by path a because the dimethylamino group is strongly attracted to the positive

Scheme I



phosphorus atom and shields the face of the phosphorus tetrahedron opposite to the benzyl group. Since Eaborn's concept of electrophilic participation by a solvent molecule can apply well to the departure of *N*,*N*-dimethylaniline,[10,11] path c for attack of hydroxide ion is favored over path b.

Rationalization of the relative rates of alkaline decomposition of compounds **3**–**6** depends on many factors. When benzyltriarylphosphonium salts are treated with sodium hydroxide solution and an incipient benzyl anion is the departing group, the presence of electron-donating substituents on the stationary aryl groups causes a decrease in rate; ρ values of +4.62,[12] +3.64,[13] and +3.19[3] have been found for systems of this and closely related types. This is in qualitative accord with the fact that the relative rate for reaction of **7** (0.000 70) is smaller than that for reaction of **4** (0.0043).

Eaborn and co-workers[10,15] have provided evidence that departure of an aryl anion from an ate complex is quite facile in a polar, protic solvent, the effect increasing with the ability of the protic solvent to form a hydrogen bond with the incipient aryl anion in the transition state of the departure step. Thus, when steric effects (which may arise from a rigidity of the substrate attributable to an N_{2p}–P-(IV) interaction) inhibit attack by the hydroxide ion at the face of the essentially tetrahedral phosphonium cation opposite to the most apicophilic group (benzyl > aryl),[6] the relative rate of attack by pathway c shown in Scheme I can be enhanced by operation of the Eaborn effect. This offers at least a partial rationalization for the fact that the relative rates of alkaline decompositions of **3** and **6** are greater than those of **4** and **7**, respectively. Also, in order to have departure of an incipient benzyl anion from the ate complexes formed initially from **3** and **6**, respectively, a Berry pseudorotation[7] would be necessary to bring the benzyl group into an apical position, from which departure of a group ordinarily occurs in a trigonal bipyramidal unstable intermediate,[16] and this would decrease the rate of this process relative to that which actually occurs.

A subsequent full paper will also take cognizance of the changes in charge distribution owing to the overlap effect,[14] the equilibrium thermodynamics of the first step of the alkaline decomposition,[17] special solvent effects,[18] the detailed role of a second 2-(*N*,*N*-dimethylamino)phenyl

(3) The relative rates are in comparison with a value of 1.00 for the alkaline cleavage of benzyltriphenylphosphonium bromide under the same conditions to give toluene and triphenylphosphine oxide (10^3k = 730.3 ± 5.00 L^2 mol^{-2} s^{-1}). For reactions carried out at 10.1 °C, another pertinent series of relative rates is $Ph_3PCH_2Ph^+,Br^-$ (1.00), 2-MeOPh)-$Ph_2PCH_2Ph^+,Br^-$ (0.0269), (2-MeOPh)$_2$PhPCH_2Ph^+,Br^- (0.00036), (2-MeOPh)$_3PCH_2Ph^+,Br^-$ (<0.0003), and (4-MeOPh)$Ph_2PCH_2Ph^+,Br^-$ (0.139): Keldsen, G. L.; McEwen, W. E. *J. Am. Chem. Soc.* **1978**, *100*, 7312.

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group in the alkaline decomposition of 6;[19] a consideration of VSEPR effects in the reagents, transition states, and products,[1] and the principle of microscopic reversibility as applied to these systems.[20]

The kinetics measurements and product ratio determinations were carried out essentially as described previously,[13] allowance being made for the presence of the basic dimethylamino groups. The amount of *N,N*-dimethylaniline formed was determined by both potentiometric titration of the acidified solution by standardized aqueous sodium hydroxide and by VPC analysis. The amount of benzene formed was determined by VPC analysis. The presence (or absence) of toluene was also determined by VPC analysis. Benzyldiphenylphosphine oxide (**5**), mp 191–192 °C, was collected by filtration and its physical and spectral properties compared with those of an authentic sample.[21]

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Asymmetric Addition of (*E*)- and (*Z*)-Crotyl-*trans*-2,5-dimethylborolanes to Aldehydes

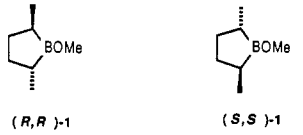
Summary: Reactions of homochiral (*E*)- and (*Z*)-crotyl-*trans*-2,5-dimethylborolanes with aldehydes proceed to provide homoallylic alcohols with excellent diastereo- and enantioselectivity.

Sir: The stereoselective construction of the 3-hydroxy-2-methylcarbonyl structural units,[1] often embedded in natural products of propionate origin such as macrolides,[2] continues to attract attention. While the aldol methodology[1] is considered the most direct approach toward this synthetic objective, asymmetric crotylboration[3,4] has emerged as an effective and practical alternative. In this connection it is timely to record herein the titled reagents derived from *B*-methoxy-(*R,R*)- and *B*-methoxy-(*S,S*)-2,5-dimethylborolanes [(*R,R*)-**1**, (*S,S*)-**1**].[1a,5] The new reagents equal or surpass the enantioselectivities of the boron reagents thus far recorded in the literature.[3,4] Diastereoselectivities observed in the reactions with chiral aldehydes conform to the rule of double asymmetric synthesis.[6]

Table I. Reaction of Cortylborolanes (*E*)-(*R,R*)-2 and (*Z*)-(*R,R*)-2 with Representative Achiral Aldehydes

entry	crotylborane	aldehyde	yield,[a] %	anti/syn[b] ratio	major product	% ee[c]
1	(*E*)-**2**		81	93/7	**4a**[d]	96
2	(*E*)-**2**		76	96/4	**4b**[e]	97
3	(*E*)-**2**		72	96/4	**4c**[e]	95
4	(*Z*)-**2**		73	7/93	**6a**[d]	86
5	(*Z*)-**2**		70	4/96	**6b**[f]	93
6	(*Z*)-**2**		75[g]	5/95	**6c**[h]	97

[a] Combined yield for syn and anti products. Unless otherwise noted yields were based on the amount of borolane reagent used and calculated by capillary GC analysis (5% phenylmethylsilicone, 0.20 mm × 12 m) of the alcohols using an internal standard. [b] Determined by capillary GC analysis (see footnote *a*). [c] Determined by HPLC analysis (Chemcosorb Si60 3 μm 4.6 × 250 mm) of bis[(*R*)-MTPA] esters of the corresponding 1,3-diols obtained from ozonolysis of **4** and **6** followed by reductive workup. Values are corrected for the purity of (*R,R*)-**1** (97.9% ee). [d] Bis-[(*R*)-MTPA] esters of the corresponding 1,3-diols (see footnote *c*) from the products were compared with authentic samples obtained from the crotyl derivatives of (−)-Ipc_2BH, see ref 4a. [e] The absolute configuration of the products was determined by the comparison of bis[(*R*)-MTPA] derivatives of the corresponding 1,3-diols (see footnote *c*) with those of authentic diols provided from our previous work. See ref 1a. [f] $[\alpha]^{25}_D$ −7.54° (*c* 0.83, $CHCl_3$) for the corresponding 1,3-diol (lit. $[\alpha]^{25}_D$ +10.29° (*c* 0.91, $CHCl_3$) for the antipode. Masamune, S.; Choy, W.; Kerdesky, F. A. J.; Imperiali, B. *J. Am. Chem. Soc.* **1981**, *103*, 1566). [g] Yield was based on the amount of the aldehyde used. [h] The absolute configuration was assumed and in accordance with predicted ^1H NMR and HPLC behavior of the bis[(*R*)-MTPA] derivaive of the corresponding 1,3-diol. See: Dale, J. A.; Mosher, H. S. *J. Am. Chem. Soc.* **1973**, *95*, 512.



(*R,R*)-**1** (*S,S*)-**1**

Reaction of (*E*)- and (*Z*)-Crotyl-(*R,R*)-2,5-dimethylborolanes [(*E*)-(*R,R*)-2 and (*Z*)-(*R,R*)-2] with Aldehydes. The preparation of the crotylborolanes (*E*)-(*R,R*)-**2** and (*Z*)-(*R,R*)-**2** adopted the Schlosser procedure[7] modified by Brown[4a,b] as shown in Scheme I.[8] Thus,

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(8) Full experimental procedure and spectral data are available in the supplementary material.

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