a Pd(II) species, these results suggested that Pd(0) had been regenerated, thus allowing subsequent formation of ArPdI. This experiment is summarized in the following equations:

$$\begin{array}{c} \underset{1.0}{CF_2{=}CFZnX} + \underset{0.5}{ArPdI(PPh_3)_2} \\ \downarrow \\ \underset{0.5}{CF_2{=}CFAr} + \underset{0.5}{CF_2{=}CFZnX} \\ \downarrow \text{excess ArI} \\ CF_2{=}CFAr,\ \text{all } CF_2{=}CFZnX \text{ consumed} \end{array}$$

The order of reactivity of the zinc reagents was found to be **1** ≈ **2** > **3** via competition reactions (See Table V). It is interesting to note that when **2**(*Z*) competed with **3**(*E*) for PhI, the ratio **13**/**16** (*E*/*Z* products) was 83/17. However, when these propenylzinc reagents competed for ortho-substituted iodoarenes, the average ratios were approximately 60/40. It is not obvious whether these results are due to steric or electronic effects. At any rate, an ortho substituent does not noticeably hamper the reaction.

As mentioned previously, aryl iodides with electron-withdrawing substituents were found to be more reactive than aryl iodides with electron-releasing substituents (Table IV). This behavior parallels the electronic-effect profile found for the formation of arylpalladium iodides[9] and suggests that withdrawal of electron density from the palladium enhances the reactivity of ArPdI toward the zinc reagent.

Acknowledgment. We thank the National Science Foundation and the Air Force Office of Scientific Research for financial support of this work.

Registry No. **4**, 447-14-3; **5**, 105436-16-6; **6**, 82907-00-4; **7**, 105436-18-8; **8**, 105436-20-2; **9**, 105417-07-0; **10**, 105436-15-5; **11**, 82907-01-5; **12**, 113268-53-4; **13**, 41500-48-5; **14**, 72926-84-2; **15**, 79796-49-9; **16**, 114199-15-4; **17**, 41424-70-8; **18**, 72926-85-3; **19**, 79796-48-8; $CF_2{=}CFBr$, 598-73-2; (*Z*)-$CF_3CF{=}CFI$, 102682-81-5; (*E*)-$CF_3CF{=}CFI$, 102682-82-6; iodotrifluoroethylene, 359-37-5; iodobenzene, 591-50-4; *o*-nitroiodobenzene, 609-73-4; *p*-iodoanisole, 696-62-8; *o*-isopropyliodobenzene, 19099-54-8; 2,5-dichloroiodobenzene, 29682-41-5; *o*-iodobenzotrifluoride, 444-29-1; *m*-nitroiodobenzene, 645-00-1; *p*-chloroiodobenzene, 637-87-6; *p*-diiodobenzene, 624-38-4; *p*-iodotoluene, 624-31-7.

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(9) Fitton, P.; Rick, E. A. *J. Organomet. Chem.* 1971, *28*, 287.

Aryne Cycloaddition to the Aromatic Ring of Mesitylmagnesium Bromide. An Anion-Assisted Diels-Alder Reaction?

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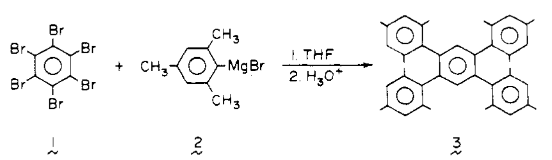
Received December 18, 1987

Hexabromobenzene and excess mesitylmagnesium bromide give, after an aqueous quench, a 20% yield of the diaryne adduct 4 (in addition to 30–55% of 1,2,4,5-tetramesitylbenzene). The aryne cycloadditions that lead to 4 occur across the 2,5-positions of the aromatic ring of the Grignard reagent. Competition experiments show that the aryl ring of mesitylmagnesium bromide is considerably more reactive as a diene than is the aryl ring of mesitylene itself.

Introduction

We describe here a reaction in which the capacity of a benzenoid ring to function as the diene in a [4 + 2] cycloaddition is enhanced through conversion to a Grignard reagent. The reaction was discovered accidentally in the following way.

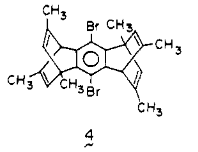
The reaction of hexabromobenzene with excess mesitylmagnesium bromide was shown recently[1] to give after aqueous quench 1,2,4,5-tetramesitylbenzene (**3**) in 30–55% yield. In scaling this reaction up, another product was isolated, whose structure and mode of formation form the basis of this paper.



1 **2** **3**

Results and Discussion

Treatment of hexabromobenzene with 8 equiv of mesitylmagnesium bromide in THF at room temperature for 12 h followed by aqueous quench gave, after workup (see Experimental Section for details), a white powder, mp 306–308 °C dec, in 20% yield, in addition to >30% of the



4

more soluble **3** (mp 258–259 °C). Structure **4** is assigned to the new product.[2] The mass spectrum of **4** showed the presence of two bromine atoms (M^+ at *m*/*e* 470, 472, and 474). The ^1H HMR spectrum showed four vinyl methyl groups (δ 1.89), two bridgehead methyls (δ 2.12), two

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(1) Harada, K.; Hart, H.; Du, C.-J. F. *J. Org. Chem.* 1985, *50*, 5524.

(2) In fact, the NMR spectrum indicated the presence of two products with nearly identical NMR spectra. We presume that the minor product (only a few percent) is the C_{2v} regioisomer of **4**.

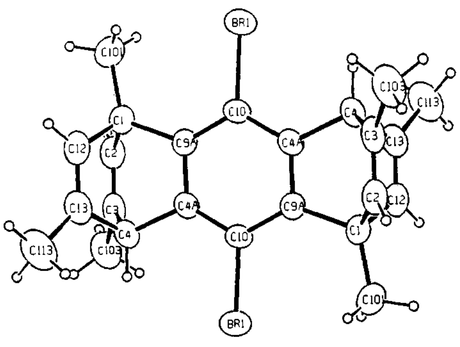


Figure 1. Single molecule of 4 showing 50% probability ellipsoids.

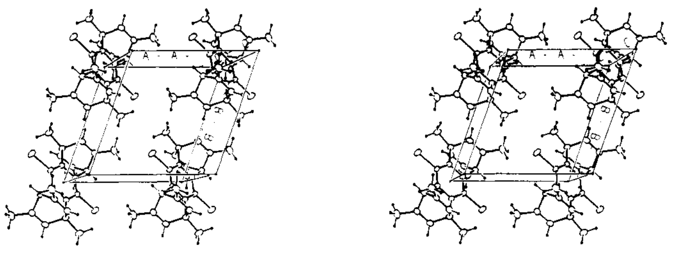
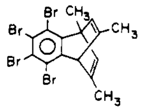


Figure 2. Stereoview of unit cell of 4 showing 20% probability ellipsoids.

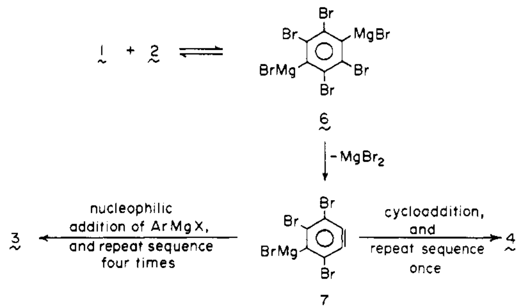
bridgehead protons (δ 4.98), and four vinyl protons (δ 6.00). These chemical shifts correspond almost exactly to those reported previously for 5,[3] the tetrabromobenzyne adduct of mesitylene (δ 1.92, 2.10, 4.90, and 6.02, respectively).



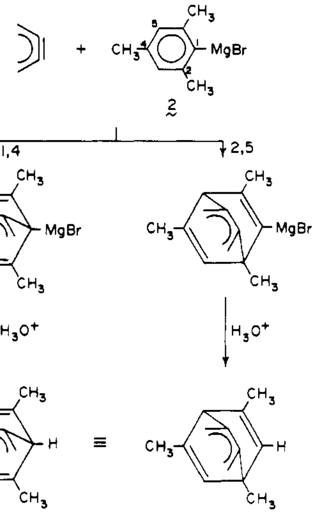
5

The ^{1}H NMR spectrum did not distinguish between structure 4 (C_{2h} symmetry) and its C_{2v} regioisomer (both bridgehead methyls on the same side of the molecule, etc.) so a single-crystal X-ray structure was determined. The results are shown in Figures 1 and 2.

Compound 4 clearly arises through aryne cycloadditions to the mesityl ring. It was demonstrated previously[1] that the first stages in the reaction of an aryl Grignard with 1 involve two metal–halogen exchanges to form the tetrabromo 1,4-di-Grignard 6. A series of aryne formation–nucleophilic addition reactions, starting with aryne 7, then leads to 3.[1] On the other hand, two sequential cycloaddition reactions to the aryl ring of 2 could lead to 4. In other words, 6 can be regarded as a synthetic equivalent of 3,6-dibromo-1,4-benzadiyne in the formation of 4.



The addition of 7 (and subsequently, a second aryne) to the mesityl ring of 2 could occur in either a 1,4 or a 2,5 sense. In either case, the product after aqueous quench, would be identical. To decide between these alternatives, the reaction was carried out with either a D_2O or a methyl iodide quench. In the former, the ^{1}H NMR spectrum of the product showed a decrease in area of the vinyl proton peak at δ 6.00 from 4 H to 2 H. In the latter, the ^{1}H NMR of the product showed a vinyl proton peak at δ 5.90 (2 H) and the vinyl methyl signals appeared as three six-proton peaks at δ 1.89, 1.81, and 1.67. These results demonstrate that the actual reaction product, the precursor of 4, is a di-Grignard reagent formed by aryne addition across the aryl ring of 2 in a 2,5 mode. We suspect that this preference represents a reflection, in the transition state, of the greater stability of the product (i.e., a vinyl Grignard reagent vis-a-vis a tertiary bridgehead Grignard reagent). We did not determine the structures of these quench products further and cannot say whether the Grignard moieties are on the same or opposite faces of the plane of the central aryl ring in 4.



Cycloadditions in which an aromatic ring functions as the diene component are of course well known, particularly for polynuclear aromatic systems (anthracenes, naphthalenes, etc.). Examples that involve benzenoid rings are more rare and in general require a particularly reactive dienophile (benzyne,[4] hexafluoro-2-butyne,[5] dicyanoacetylene,[6] etc.). In the present case, however, the cycloaddition appears to occur across the aryl ring of an aryl Grignard reagent and in effective competition with the rather facile nucleophilic addition to an aryne.

Cycloadditions to Grignard reagents are almost unprecedented. The most pertinent examples seem to be the reaction of benzyne with cyclopentadienylmagnesium bromide and substituted analogues.[7,8] The product (21–29% yield) is 7-*anti*-benzonorbornadienylmagnesium bromide, but Ford has argued[8] that the product results from cycloadditions to a σ-bonded CpMgX rather than to an aromatic cyclopentadienide ion.

Anion accelerated retro-Diels–Alder reactions are known,[9] and following the recognition by Evans[10] of the

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[3] Berry, D. J.; Wakefield, B. J. *J. Chem. Soc. C* **1969**, 2342.

[4] Tabushi, I.; Yamada, H.; Yoshida, Z.; Oda, R. *Bull Chem. Soc. Jpn.* **1977**, *50*, 285 and earlier references cited there.

[5] Krespan, C. G.; McKusick, B. C.; Cairns, T. L. *J. Am. Chem. Soc.* **1961**, *83*, 3428.

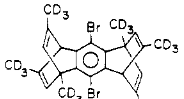
[6] Weis, C. D. *J. Org. Chem.* **1963**, *28*, 74.

[7] Wittig, G.; Knauss, E. *Chem. Ber.* **1958**, *91*, 895.

[8] Ford, W. T.; Radue, R.; Walker, J. A. *J. Chem. Soc. D* **1970**, 966. Ford, W. T. *J. Org. Chem.* **1971**, *36*, 3979. Buske, G. R.; Ford, W. T. *J. Org. Chem.* **1976**, *41*, 1995.

oxyanion accelerated Cope rearrangement in 1975, numerous examples of anion-accelerated electrocyclic reactions have been described.[9,11] Since the diene component in the reaction described here is, in a sense, substituted with a Grignard moiety, it seemed possible that the reaction (formation of 4) is an anion-assisted Diels–Alder in which the anionic substituent is directly attached to one of the diene carbon atoms (in most anion-assisted electrocyclic reactions, the negative charge is *not directly* attached to the carbon framework but is on a substituent that is connected to the framework). It seemed desirable, therefore, to test this possibility experimentally by comparing the reactivity of mesitylmagnesium bromide with that of the hydrocarbon mesitylene, toward the same arynic dienophile. This was done in the following way.

A control experiment using mesitylmagnesium bromide-d_9 with hexabromobenzene gave **4**-d_{18} whose ^{1}H NMR spectrum showed peaks for the vinyl (δ 6.00) and bridgehead (δ 4.98) protons, but only vestiges of peaks for the methyl groups (see Experimental Section for details). Mixtures of mesitylene and mesitylmagnesium bromide-d_9 in various ratios were then allowed to react with hexabromobenzene. Presumably each reagent could compete for the arynic intermediates, leading to **4** and **4**-d_{18} respectively (with some **4**-d_9, if the two cycloadditions involved reaction with 1 equiv of each mesityl-containing reagent). The appearance of *any significant* methyl signal in the ^{1}H NMR of the product would therefore detect cycloaddition to the hydrocarbon rather than to the Grignard reagent, thus providing a rather sensitive reactivity probe. This signal could be integrated against the vinyl and bridgehead proton signals (with suitable corrections; details are provided in the Experimental Section). Experiments were performed with solutions containing 5 mmol of hexabromobenzene, 40 mmol of mesitylmagnesium bromide-d_9, and varying amounts of mesitylene (0, 20, 40, 80, 200 mmol). The results indicate that the overall reactivity of the Grignard reagent is 27.6 ± 2.8 times that of the hydrocarbon. Since two successive cycloadditions are required to form bis cycloadduct 4, the reactivity ratio is probably about 5–6 in favor of the Grignard reagent, for each step.



4-d18

These experiments and calculations are not straightforward. For example, the Grignard reagent has a dual role, to initiate aryne formation through metal–halogen exchange and to serve as a diene. Also, details of timing of the various events that must occur prior to ultimate product formation are not known, nor is it known whether the selectivity is the same in the first and second cycloadditions. Nevertheless, the results show clearly that the aryl ring is substantially activated toward the dienophile through organometallic substitution. This observation may be a general phenomenon for other dienes as well, and this possibility is worth investigating in well-designed, simpler systems.

Experimental Section[12]

9,10-Dibromo-1,3,5,7,11,13-hexamethyl-1,4;5,8-diethено-1,4,5,8-tetrahydroanthracene (4). A suspension of hexabromobenzene (2.76 g, 5 mmol) in 20 mL of tetrahydrofuran (THF) was added slowly (30 min) to a solution of mesitylmagnesium bromide (prepared from 7.96 g, 40 mmol of bromomesitylene, 0.92 g, 40 mmol of magnesium in 80 mL of THF) and the mixture was stirred at room temperature for 12 h. The reaction was quenched with ice and dilute hydrochloric acid and extracted with methylene chloride. The organic layer was dried and the solvent evaporated under reduced pressure to give a mixture of solid and oil. This mixture was washed with 30–50 mL of benzene and filtered. The filtrate was saved for the isolation of 1,2,4,5-tetramesitylbenzene.[1] The white powder was essentially pure 4 (0.47 g, 20%). Small samples could be recrystallized from benzene, mp 306–308 °C dec: ^{1}H NMR δ 1.89 (d, 12 H), 2.12 (s, 6 H), 4.98 (t, 2 H), 6.00 (m, 4 H); mass spectrum, *m/e* (relative intensity) 474 (20), 472 (47), 470 (23), 312 (36), 311 (31), 297 (65), 296 (29), 282 (23), 281 (18). Anal. Calcd for $C_{24}H_{24}Br_2$: C, 61.04; H, 5.12. Found: C, 60.99; H, 5.16.

Deuterium Oxide Quench. Repetition of the above synthesis, but using D_2O for the quench, gave **4**-d_2:[13] ^{1}H NMR δ 1.89 (d, 12 H), 2.13 (s, 6 H), 4.98 (d, 2 H), 6.00 (m, 2 H); mass spectrum, *m/e* (relative intensity) 476 (64), 474 (98), 472 (53), 314 (57), 313 (52), 299 (100), 298 (44).

Methyl Iodide Quench. The procedure for 4 was repeated, but prior to aqueous quench 10 mmol of methyl iodide was added and the mixture was stirred at room temperature for 8 h and at reflux for 1 h prior to workup. There was obtained 0.45 g (18%) of 4-$(CH_3)_2$, mp 240–245 °C dec:[14,15] ^{1}H NMR δ 1.67 (s, 6 H), 1.81 (s, 6 H), 1.89 (s, 6 H), 2.12 (s, 6 H), 4.96 (d, 2 H), 5.90 (m, 2 H); mass spectrum, *m/e* (relative intensity) 502 (14), 500 (33), 498 (22), 421 (14), 419 (17), 339 (54), 325 (100), 324 (53), 310 (33), 309 (29), 295 (27), 119 (66). Anal. Calcd for $C_{26}H_{28}Br_2$: C, 62.42; H, 5.64. Found: C, 62.53; H, 5.55.

Preparation of 4-d_{18}. Mesitylene-d_9[16] was brominated[17] and converted to the Grignard reagent, after which the general procedure for 4 was followed to give **4**-d_{18} in comparable yield: ^{1}H NMR δ 4.98 (t, 2 H), 6.00 (d, 4 H); two very small, broad peaks appeared in the δ 1.84 and 2.10 regions due to incompletely deuteriated methyl groups.

Competition Experiments. The procedure for 4 was followed by using 5 mmol of hexabromobenzene, 40 mmol of mesitylmagnesium bromide-d_9, and 20, 40, 80, or 200 mmol of mesitylene. The resulting labeled 4 was isolated and the peak areas at δ 1.89, 2.12, 4.98, and 6.00 were integrated. A sample calculation follows. For the experiment with 40 mmol of mesitylene, the peak areas were 8, 4, 26, and 52, respectively. The first two peaks represent 18 protons in 4 derived from mesitylene; the area per proton is therefore $(8 + 4)/18 = 0.67$. The contribution of unlabeled adduct to the bridgehead and vinyl peaks is therefore $0.67 \times 6 = 4.0$. Thus, the area of these peaks derived from labeled adduct is $26 + 52 - 4 = 74$. The ratio of the labeled/unlabeled adducts is therefore $74/4 = 18.5$. Since 10 mmol of the Grignard reagent are consumed in metal–halogen exchange reactions and hence are unavailable for competition with mesitylene, the corrected reactivity ratio is $(18.5 \times 40)/30 = 24.7$. Reactivity ratios calculated in this way for the experiments with 20, 80, and 200 mmol of mesitylene were 26.9, 33.3, and 25.6, respectively.

X-ray Data for 4. Recrystallization of 4 from benzene gave

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[9] Oku, A.; Kakihana, T.; Hart, H. *J. Am. Chem. Soc.* **1967**, *89*, 4554. Bowman, E. S.; Hughes, G. B.; Grutzner, J. B. *J. Am. Chem. Soc.* **1976**, *98*, 8273. Neukam, W.; Grimme, W. *Tetrahedron Lett.* **1978**, 2201. Papies, O.; Grimme, W. *Tetrahedron Lett.* **1980**, *21*, 2799. Prasad, J. V. N.; Iyer, P.; Pillai, C. N. *J. Org. Chem.* **1982**, *47*, 1380. Hart, H.; Shahlai, K. *Tetrahedron Lett.* **1987**, *28*, 5437.

[10] Evans, D. A.; Golob, A. M. *J. Am. Chem. Soc.* **1975**, *97*, 4765.

[11] RajanBabu, T. V.; Eaton, D. F.; Fukunaga, T. *J. Org. Chem.* **1983**, *48*, 652. Knapp, S.; Ornaf, R. M.; Rodriques, K. E. *J. Am. Chem. Soc.* **1983**, *105*, 5494. Carpenter, B. K. *Tetrahedron* **1978**, *34*, 1877.

[12] For general procedures, see ref 1.

[13] The tetramesitylbenzene recovered from this experiment also contained two deuteriums in the central aryl ring (^{1}H NMR lacked the singlet at δ 7.05 due to these protons[1]).

[14] The product appeared to be a single isomer, probably the 1,2,3,5,6,7,11,13-octamethyl homologue of 4.

[15] The other product was 1,2,4,5-tetramesitylbenzene and *not* its dimethyl analogue; apparently the di-Grignard is too hindered to react with methyl iodide under these conditions.

[16] Chen, T.-S.; Wolinska-Mocydlarz, J.; Leitch, L. C. *J. Label. Comp.* **1970**, *6*, 285.

[17] Smith, L. I. *Organic Syntheses*; Wiley: New York, 1942; Collect. Vol. 2, p 95.

a colorless, triclinic prismatic crystal, $C_{24}H_{24}Br_2$: space group $P1$; $a = 8.728$ (2), $b = 8.958$ (2), and $c = 7.155$ (1) Å, $\alpha = 101.27$ (2), $\beta = 104.81$ (1), and $\gamma = 70.53$ (1)°; $Z = 1$; $M = 472.28$; $V = 506.2$ (2) Å^3; $\rho = 1.55$ g cm^{-3}. Preliminary examination and intensity data were measured by using Mo Kα radiation ($\lambda = 0.71073$ Å) on a Nicolet P3F diffractometer ($2\theta_{max} = 55°$), yielding 2346 unique reflections of which 1801 were used in the refinement. The structure was solved by direct methods (SHELXS-86). The final R value was 0.036.

Acknowledgment. We thank Dr. Donald R. Ward for the X-ray structure of 4 and the National Institutes of Health (GM-15997) and National Science Foundation (CHE 87-12118) for financial support.

Supplementary Material Available: Tables of atomic positional parameters, thermal parameters, bond lengths, and bond angles (7 pages). Ordering information is given on any current masthead page.

Stereoselective *E* and *Z* Olefin Formation by Wittig Olefination of Aldehydes with Allylic Phosphorus Ylides. Stereochemistry

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Received October 9, 1987

Sterically crowded allylic tributylphosphorus ylides such as β,γ-disubstituted allylic ylides react with various aldehydes to afford *E* olefins with high stereoselectivity (*E* > 92%). As the steric demand of the ylides was decreased, bulky aldehydes were required to achieve high *E* selectivity. On the other hand, predominant or exclusive formation of *Z* olefins was achieved by using allylic triphenylphosphorus ylides and tertiary aldehydes like pivaldehyde, while the combination of allylic triphenylphosphorus ylides and such large secondary aldehydes as cyclohexanecarboxaldehyde led to *E* olefin formation under the lithium salt free conditions. The distinct lithium salt effect was observed in the reaction effected with triphenylphosphorus ylides. The origin of the observed *E* or *Z* selectivity can be reasonably explained according to Vedejs' rationale on the Wittig reaction stereochemistry.

Introduction

The stereochemistry of the Wittig reaction for olefination of aldehydes with phosphorus ylides is strongly dependent on the type of ylide and exact reaction conditions.[1] Nonstabilized triphenylphosphorus ylides generally react with aldehydes to afford *Z* alkenes selectively while the corresponding trialkylphosphorus ylides give high *E* selectivity, especially under lithium salt free conditions. Stabilized ylides give predominantly *E* alkenes, regardless of the type of ligands on phosphorus. As to semistabilized ylides, marked stereoselectivity has not been observed except in two reported cases. The reaction of benzylic trialkylphosphorus ylides shows substantial *E* selectivity,[1a,2] as does the reaction of allylic diphenylalkylphosphorus ylides with bulky aldehydes.[3]

Recently, we reported that olefination of less bulky aldehydes with some allylic tributylphosphorus ylides results in high *E* stereoselectivity.[4] Thus, we began to study the scope and limitation of stereoselective *E* olefin synthesis with allylic tributylphosphorus ylides and compare such ylides with the corresponding triphenylphosphorus ylides. In these reactions, the steric effects of ylides and aldehydes turn out to have a crucial impact on the stereochemistry. In order to gain more insight into the stereochemistry, we have conducted a systematic study using structurally different allylic ylides and aldehydes. Our stereochemical results reveal a strong dependency of olefin stereoselectivity (both *E* and *Z*) on steric effects in both the allylic ylides and aldehydes as well as the selection of phosphorus ligands. Furthermore, the origin of the observed *E* or *Z* selectivity can be reasonably explained according to the Vedejs' rationale reported recently on the Wittig reaction stereochemistry.[5] Stereoselective olefination of aldehydes with allylic phosphorus ylides permits

Table I. Olefination of Aldehydes with β,γ-Substituted Allylic Phosphorus Ylide (eq 1)[a]

entry	phosphonium salt	aldehyde	product	isolated yield, %	*E*:*Z*[b]
1	**1a**	PhCHO	**2**	82 (41)[c]	*E* > 95 (*E* > 95)[c]
2	**1b**	PhCHO	**2**	63 (29)[c]	45:55 (47:53)[c]
3	**1a**	*n*-heptanal	**3**	84	92:8
4	**1b**	*n*-heptanal	**3**	60	58:42
5	**1a**	*i*-BuCHO	**4**	87	*E* > 95
6	**1b**	*i*-BuCHO	**4**	44	50:50
7	**1a**	*t*-BuCHO	**5**	67	*E* > 95
8	**1b**	*t*-BuCHO	**5**	44	15:85
9	**1a**	(*Z*)-MeCH=C(Ph)CHO	**6**	58	*E* > 95
10	**1b**	(*Z*)-MeCH=C(Ph)CHO	**6**	86	17:83
11	**1a**	c-C_6H_{11}CHO	**7**	80	*E* > 95
12	**1b**	c-C_6H_{11}CHO	**7**	45	73:27

[a] *n*-BuLi was used as base. See General Procedure in the Experimental Section. [b] Determined by GLC and ^{1}H NMR. [c] *t*-BuOK was used in place of *n*-BuLi.

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(1) For reviews, see: (a) Gosney, I.; Rowley, A. G. In *Organophosphorus Reagents in Organic Synthesis*; Cadagan, J. I. G., Ed.; Academic: New York, 1979; pp 7–205. (b) Bestmann, H. J.; Vostrowsky, O. *Top. Curr. Chem.* **1983**, *109*, 85–163. (c) Pommer, H.; Thieme, P. C. *Ibid.* **1983**, *109*, 165–188. (d) Bestmann, H. J. *Pure. Appl. Chem.* **1980**, *52*, 771–788. (e) Pommer, H. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 423–429. (f) House, H. O. *Modern Synthetic Reactions*, 2nd ed.; W. A. Benjamin, Inc.: Menlo Park, CA, 1972; pp 682–709. (g) Schlosser, M. *Top. Stereochem.* **1970**, *5*, 1–30. (h) Maercker, A. *Org. React.* (*N.Y.*) **1965**, *14*, 270–490. Also see ref 5 and 8.

(2) Bestmann, H. J.; Kratzer, O. *Chem. Ber.* **1962**, *95*, 1894–1901.

(3) Vedejs, E.; Fang, H. W. *J. Org. Chem.* **1984**, *49*, 210–212.

(4) Tamura, R.; Kato, M.; Saegusa, K.; Kakihana, M.; Oda, D. *J. Org. Chem.* **1987**, *52*, 4121–4124. In the present work, bis(dibenzylideneacetone)palladium(0) [Pd(dba)$_2$] was employed as catalyst (5 mol %) to prepare the allylic tributylphosphonium salts, which were purified by washing with ether or pentane to remove dba and unreacted PBu_3 and allylic substrate and used for further reactions.

(5) Vedejs, E.; Marth, C. F. *J. Am. Chem. Soc.* in press, and references cited therein. The authors thank Professor E. Vedejs for sending us the preprint.

0022-3263/88/1953-2723$01.50/0 © 1988 American Chemical Society