formation of a complex between DME, *t*-BuLi, and formamidines is incorrect, as is the speculated stability thereof:[2] the white precipitate is clearly lithium methoxide. The observed[2] Cannizzarro reaction is brought about by lithium methoxide and not by a *t*-BuLi–DME complex. At −70 °C, *t*-BuLi in DME adds rather normally to benzaldehyde to give the expected carbinol. In light of these results, the scarcity of reports on DME as solvent in metalations is not surprising, and its use for these purposes is discouraged.

Registry No. *n*-BuLi, 109-72-8; *sec*-BuLi, 598-30-1; *t*-BuLi, 594-19-4; 1,2-dimethoxyethane, 110-71-4; methyl vinyl ether, 107-25-5.

Communications

An *E*-Selective 1,3-Diene Synthesis from Moderated Ylides and Aldehydes

Summary: The synthesis of *E*-1,3-dienes by the Wittig reaction of aldehydes and ylides is described.

Sir: The Wittig reaction of aldehydes with salt-free $Ph_3P{=}CHR$ (R = alkyl) is an excellent method for synthesis of *cis*-alkenes (>95% selectivity).[2] In some cases, the reaction may be diverted to *trans*-alkenes by using Schlosser's method to equilibrate the Wittig intermediate, a process that probably occurs via formation of the oxido ylide under strongly basic conditions.[3] In contrast to these examples where high *Z* or *E* selectivity can be achieved, the condensation of moderated ylides $Ph_3P{=}CHR$ (R = aryl, alkenyl) generally gives impractical *E,Z* mixtures of styrenes $PhCH{=}CHR$ or of 1,3-dienes. Several specific examples are listed in Table I, entries 1 and 2. This problem has been recognized for many years.[2,4]

We have now observed that a simple change in phosphorus substituents from $Ph_3P{=}CHR$ to $Ph_2(R'CH_2)P{=}CHR$ (R′ = alkenyl or H) dramatically increases the proportion of *E* olefin formed from *moderated ylides* (R = alkenyl) and aliphatic aldehydes. The highest *E* selectivity in the product 1,3-diene is obtained by using salt-free ylide, prepared from phosphonium salts with KO-*t*-Bu/THF or $NaNH_3$/liquid NH_3[5] (Table I, entries 3, 4, 6, 7, 10). Selectivity is significantly lower in the presence of lithium salts and is also lower when the moderated ylides are reacted with benzaldehyde rather than with aliphatic aldehydes. These examples may be compared with analogous experiments involving reactive ylides such as $Ph_3P{=}CHCH_3$ where it is also found that selectivity is substantially reduced by lithium halides and is somewhat lower with aromatic aldehyde substrates.[6,7] However, in the $Ph_3P{=}CHR$ reactions, it is the *Z selectivity* that is decreased.

We have shown that the lithium ion effect in reactions of $Ph_3P{=}CHCH_3$ is due to competition between the normal salt-free process and a Li^+-catalyzed ylide–aldehyde reaction of unknown mechanism and unknown but lower *Z* selectivity.[6] The Li^+ effect on $Ph_3P{=}CHCH_3$ + aliphatic aldehydes is *not* due to equilibration of the initially formed oxaphosphetane.[6] In an attempt to probe the Li^+ effect in Table I, we have examined the reaction of $Ph_2(CH_3)P{=}CHC(CH_3){=}CH_2$ with aldehydes in more detail. In the presence of LiBr, both benzaldehyde and cyclohexanecarboxaldehyde react at −78 °C to give an immediate precipitate of the betaine·LiBr adduct.[8] Decomposition to alkene occurs upon warming to room temperature. If 3,4-dichlorobenzaldehyde is added to the precipitate at −78 °C and the reaction mixture is warmed, extensive crossover products are formed in both the benzaldehyde and cyclohexanecarboxaldehyde experiments.[10] Similar findings are reported with PhCHO + $Ph_3P{=}CHCH_3$ + LiBr, although crossover has not previously been demonstrated for aliphatic aldehydes under typical Wittig conditions.[3b,6,7,11]

Analogous experiments using *salt-free* $Ph_2(CH_3)P{=}CHC(CH_3){=}CH_2$ do not give crossover products with either benzaldehyde or cyclohexanecarboxaldehyde at −78 °C. However, control experiments (^{31}P NMR at −60 °C; acid-quenching at −78 °C) show that the Wittig intermediate is completely decomposed to 1,3-dienes and the phosphine oxide within approximately 1 min of mixing ylide and aldehyde! This fact invalidates any conclusions from the "negative crossover" experiments because the intermediate has decomposed too rapidly.

Decomposition to alkene is retarded in the presence of LiBr due to an unfavorable oxaphosphetane–betaine·LiBr equilibrium, and there is significant adduct dissociation to starting ylide and aldehyde. We can conclude that some of the decreased *E* selectivity in the Li^+-containing experiments is due to reversal in the condensation step. However, it is not possible to say whether or not the salt-free experiments in Table I occur with kinetic control of oxaphosphetane (and therefore olefin)[12] geometry until

(1) Visiting scholar from Huazhung Normal University, People's Republic of China (1981–83).
(2) Review: Schlosser, M. *Top. Stereochem.* **1970**, *5*, 1.
(3) (a) Schlosser, M.; Christmann, K.-F.; Piskala, A. *Chem. Ber.* **1970**, *103*, 2814. (b) Anderson, R. J.; Henrick, C. A. *J. Am. Chem. Soc.* **1975**, *97*, 4327.
(4) (a) Wittig, G.; Schollkopf, U. *Chem. Ber.* **1954**, *87*, 1318. Also, selected recent examples: (b) Bestmann, H. J.; Kratzer, O. *Ibid.* **1962**, *95*, 1894. (c) Nesbitt, B. F.; Beevor, P. S.; Cole, R. A.; Lester, R.; Poppi, R. G. *Tetrahedron Lett.* **1973**, 4669. (d) Scharf, H. D.; Janus, J. *Tetrahedron* **1979**, *35*, 385. (e) Corey, E. J.; Clark, D. A.; Goto, G.; Marfat, A.; Mioskowski, C.; Samuelsson, B.; Hammarström, S. *J. Am. Chem. Soc.* **1980**, *102*, 1436.
(5) For the details of the $NaNH_2$ method, see ref 6.
(6) Vedejs, E.; Meier, G. P.; Snoble, K. A. J. *J. Am. Chem. Soc.* **1981**, *103*, 2823.
(7) Schlosser, M.; Christmann, K. F. *Liebigs Ann. Chem.* **1967**, *708*, 1.
(8) For examples of other betaine·LiX adducts, see ref 6 and 9.
(9) Schlosser, M.; Tuong, H. B.; Tarchini, C. *Chimia* **1977**, *31*, 219.
(10) Ylide solutions made from 1.1 equiv of phosphonium iodide + BuLi (1 equiv) were treated with R″CHO (R″ = phenyl and cyclohexyl) at −78 °C. The mixture of precipitated betaine·LiI adduct was then combined with 1 equiv of 3,4-dichlorobenzaldehyde, and the yields of $CH_2{=}C(CH_3){=}CHR''$ vs. $CH_2{=}C(CH_3){=}CHC_6H_3Cl_2$ were determined by PLC and NMR integration; crossover:normal product ratio = approximately 2.5:1 for R″ = phenyl and >2:1 for R″ = cyclohexyl.
(11) Crossover in high-temperature epoxide + Ph_3P reactions is considered by us not to involve typical Wittig conditions: Bissing, D. E.; Speziale, A. J. *J. Am. Chem. Soc.* **1965**, *87*, 2683.
(12) (a) Vedejs, E.; Snoble, K. A. J.; Fuchs, P. L. *J. Org. Chem.* **1973**, *38*, 1178. (b) Vedejs, E.; Fuchs, P. L. *J. Am. Chem. Soc.* **1973**, *95*, 822.

0022-3263/84/1949-0210$01.50/0

Table I. Allylic Ylides + Aldehydes R''CHO

entry	ylide	base	diene E:Z ratio[20] (% isolated),[a] R'' = phenyl[21]	cyclohexyl[23]	$PhCH_2CH_2$[24]
1	$Ph_3P{=}CHCH{=}CHCH_3$	BuLi[b]		1:1 (41)	1.1:1 (69)
2	$Ph_3P{=}CHCH{=}C(CH_3)_2$	BuLi[c]	1:1.6 (96)	1.7:1 (59)	1.2:1 (75)
3	$Ph_2[(CH_3)_2C{=}CHCH_2]P{=}CHCH{=}C(CH_3)_2$	$NaNH_2$[d]	>15:1 (93)	40:1 (99)	>15:1 (87)
4	$Ph_2[(CH_3)_2C{=}CHCH_2]P{=}CHCH{=}C(CH_3)_2$	KO-t-Bu[b]			7:1 (42)
5	$Ph_2[(CH_3)_2C{=}CHCH_2]P{=}CHCH{=}C(CH_3)_2$	BuLi[b]	5:1 (90)	18:1 (55)	4.8:1 (80)
6	$Ph_2(CH_3CH{=}CHCH_2)P{=}CHCH{=}CHCH_3$	$NaNH_2$[d]		>15:1[e] (80)	11:1[e] (63)
7	$Ph_2(CH_3CH{=}CHCH_2)P{=}CHCH{=}CHCH_3$	KO-t-Bu[b]	4:1 (50)[e]		
8	$Ph_2(CH_3CH{=}CHCH_2)P{=}CHCH{=}CHCH_3$	BuLi[b]	2:1 (76)[e]	14:1[e] (61)	5:1[e] (89)
9	$Ph_2(CH_3)P{=}CHC(CH_3){=}CH_2$	BuLi[b]	1.5:1 (57)	16:1 (44)	2.4:1 (44)
10	$Ph_2(CH_3)P{=}CHC(CH_3){=}CH_2$	KO-t-Bu[b]	2:1 (96)	26:1 (73)	6.4:1 (92)

[a] Nonoptimized yield; partial loss of volatile products is possible during standard PLC isolation. [b] THF solution. [c] Toluene solution. [d] Ylide made in liquid NH_3; Wittig reaction in THF. [e] Contaminated with a trace of Z,E and Z,Z dienes from the isomeric phosphonium salt.[14b]

conditions can be found where the oxaphosphetane can be observed and studied. We have elaborated this point to emphasize the subtle difficulties inherent in all Wittig mechanistic studies.

The trans-selective diene synthesis described in Table I should be of practical value. In the cases where an inexpensive allylic fragment is used, the starting phosphonium salt can be made simply by reacting $LiPPh_2$[12a] with 2 equiv of allylic bromide. It is also possible to selectively deprotonate the allylic position in salts such as $Ph_2CH_3P^+CH_2C(CH_3){=}CH_2$, which are easily prepared by using a two-step sequence:

$$LiPPh_2 + BrCH_2C(CH_3){=}CH_2 \longrightarrow Ph_2PCH_2C(CH_3){=}CH_2 \xrightarrow{CH_3I}$$

$$Ph_2CH_3PCH_2C(CH_3){=}CH_2 \xrightarrow{KO\text{-}t\text{-}Bu} Ph_2CH_3P{=}CHC(CH_3){=}CH_2$$

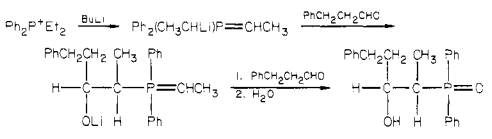
This latter method should prove convenient in cases where the allylic fragment is more complex, and where it is desirable to utilize the allylic halide efficiently. Phosphonium salt deprotonation with $NaNH_2$/liquid NH_3 generally gives the best yields, but the KO-t-Bu/THF method is more convenient. We do not recommend BuLi/THF because of the lower E selectivity and also because dialkyldiphenylphosphonium salts may deprotonate at both alkyl groups when using the stronger base.[13]

Wittig reactions of crotylphosphonium salts (entries 1, 6, 7, 8) retain the geometry of the double bond in the starting phosphonium salt. However, the P-alkylation step does cause some E,Z isomerization. Careful recrystallization of $Ph_3PC^+H_2CH{=}CHCH_3Br^-$[14a] gives a product of 40:1 E:Z geometry, while $Ph_2P^+(CH_2CH{=}CHCH_3)_2Br^-$[14b] could not be improved beyond 15:1 E:Z.

Several other systems were investigated briefly. Thus, reaction of salt-free $Ph_2CH_3P{=}CHC(CH_3){=}CH_2$ with tiglaldehyde affords 1,5-dimethylhepta-1,3,5-triene as a single geometrical isomer, presumed to be the E,E product (57%). Preliminary experiments also indicate that high E selectivity is obtained from aldehydes and benzylic diphenylalkylphosphonium ylides. Thus, salt-free $Ph_2(PhCH_2)P{=}CHPh$ reacts with crotonaldehyde to give 5-phenyl-2,4-pentadiene, 7.6:1 E,E:Z,E. However, the ylide derived from $Ph_2P^+Et_2Br^-$ with $NaNH_2$ or with BuLi reacts with mediocre 2:1 E:Z selectivity with $PhCH_2CH_2CHO$. Similar results have been reported recently by Schlosser et al. using $Et_3P{=}CHCH_3$.[15]

Accumulating evidence from Schlosser's study,[15] from Table I, and from earlier observations[16] indicates that replacing one or more P-phenyls in $Ph_3P{=}CHR$ by an alkyl group tends to favor (E)-olefin products. Since we have not yet found a suitable alkylidenealkyldiphenylphosphorane for systematic study of the Wittig intermediates, we shall postpone comments on mechanistic implications. There is at present no concensus regarding the detailed mechanism(s) of the Wittig reaction. However, the most recent rationales postulate a transition state with phosphorus having trigonal-bipyramidal geometry.[6,15,17]

(13) For example, treatment of $Ph_2P^+Et_2Br^-$ with 2 equiv of BuLi followed by $PhCH_2CH_2CHO$ results in some of the following processes in addition to the usual Wittig reaction:

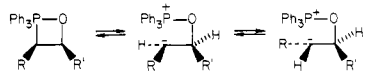


(14) (a) $Ph_3P^+CH_2CH{=}CHCH_3Br^-$, mp 239–240 °C 40:1 E:Z. (b) $Ph_2P^+(CH_2CH{=}CHCH_3)_2Br^-$, mp 158–159 °C 15:1 E:Z.

(15) Schlosser, M.; Schaub, B. *J. Am. Chem. Soc.* **1982**, *104*, 5821.

(16) Reference 4b: also: Blade-Font, A.; Vander Werf, C. A.; McEwen, W. E. *J. Am. Chem. Soc.* **1960**, *82*, 2396. Smith, D. J. H.; Trippett, S. *Chem. Commun.* **1972**, 191. James, B. G.; Pattenden, G., *J. Chem. Soc., Perkin Trans. 1* **1976**, 1476. Meyers, A. I.; Lawson, J. P.; Carver, D. R. *J. Org. Chem.* **1981**, *46*, 3119.

(17) A rationale has been advanced by Bestmann[18] and has received some support.[19] A key feature of this rationale uses the following sequence to explain stereochemical and labeling results:



More then 10 years ago, we and others[7] presented evidence in a number of related systems that oxaphosphetanes do not lose stereochemistry once formed and decompose to olefins with >99% retention.[12] Other aspects of the Bestmann rationale deserve careful consideration, but the above equilibria are clearly ruled out for R = alkyl or phenyl, whether[12] or not[7] Li^+ salts are present. Stereochemical rationales[18,19] based on Bestmann's zwitterion are not correct *unless it can be shown* that our results on oxaphosphetane stereochemistry[12] and Schlosser's results on the stereochemistry of the sequence[7]

$$Ph_3P^+CHPhCHCH_3OH\ X^- \xrightarrow{KO\text{-}t\text{-}Bu} PhCH{=}CHCH_3$$

are somehow incorrect or not applicable. Only for R' = aryl does the oxaphosphetane equilibrate.

(18) Bestmann, H. J. *Pure. Appl. Chem.* **1979**, *51*, 515; **1980**, *52*, 771; *Bull. Soc. Chim. Belg.* **1981**, *90*, 519.

(19) McEwen, W. E.; Cooney, J. V. *J. Org. Chem.* **1983**, *48*, 983. Whangbo, M.-H. *Chem. Commun.* **1979**, 1072.

(20) Stereochemical assignments are based on 200-MHz or 270-MHz NMR analysis of the olefinic region, comparison of differing E:Z mixtures, independent synthesis, or comparison to authentic spectra.[21]

(21) The benzaldehyde-derived (E,E)-dienes have been reported previously.[22] We were able to show that our (E,E)-1-phenyl-3-methyl-1,3-butadiene is identical by NMR with the compound previously reported.[22] In the case of 1-phenyl-1,3-pentadiene (i) and 1-phenyl-4-methyl-1,3-pentadiene (ii), NMR comparisons proved inconclusive due to the lower field (60 MHz) of the comparison spectra.[22] The E,E:E,Z ratio of i was determined by decoupling the overlapping CH_3 signals (ppm) and observing the relative intensities of the C_2–H and C_4–H signals. The E isomer of ii was synthesized independently from (E)-$Ph_3P{=}CHCH{=}CHPh$ (from cinnamyl bromide) + acetone.

(22) Stakem, F. G.; Heck, R. F. *J. Org. Chem.* **1980**, *45*, 3584. We thank Prof. Heck for diene comparison spectra.

This area of general agreement should serve as a starting point for future refinements.

Acknowledgment. This work was supported by the National Science Foundation (CHE-8113026).

Registry No. $PH_3P{=}CHCH{=}CHCH_3$, 41892-64-2; $Ph_3P{=}CHCH{=}C(CH_3)_2$, 31188-53-1; $Ph_2[(CH_3)_2C{=}CHCH_2]P{=}CHCH{=}C(CH_3)_2$, 27387-42-4; $Ph_2(CH_3CH{=}CHCH_2)P{=}CHCH{=}CHCH_3$, 88001-17-6; $Ph_2(CH_3)P{=}CHC(CH_3){=}CH_2$, 88001-18-7; PhCHO, 100-52-7; c-$C_6H_{11}CHO$, 2043-61-0; $PhCH_2CH_2CHO$, 104-53-0; (*E*)-$PhCH{=}CHCH{=}C(CH_3)_2$, 39491-73-1; (*Z*)-$PhCH{=}CHCH{=}C(CH_3)_2$, 39491-72-0; (*E,E*)-$PhCH{=}CHCH{=}CHCH_3$, 3909-96-4; (*E,Z*)-$PhCH{=}CHCH{=}CHCH_3$, 7642-05-9; (*E*)-$PhCH{=}CHC(CH_3){=}CH_2$, 68036-69-1; (*Z*)-$PhCH{=}CH(CH_3){=}CH_2$, 75066-88-5; (*E,E*)-c-$C_6H_{11}CH{=}CHCH{=}CHCH_3$, 88001-19-8; (*Z,E*)-c-$C_6H_{11}CH{=}CHCH{=}CHCH_3$, 88001-20-1; (*E*)-c-$C_6H_{11}CH{=}CHCH{=}C(CH_3)_2$, 88001-21-2; (*Z*)-c-$C_6H_{11}CH{=}CHCH{=}C(CH_3)_2$, 88001-22-3; (*E*)-c-$C_6H_{11}CH{=}CHC(CH_3){=}CH_2$, 88001-23-4; (*E,E*)-$PhCH_2CH_2CH{=}CHCH{=}CHCH_3$, 88015-29-6; (*Z,E*)-$PhCH_2CH_2CH{=}CHCH{=}CHCH_3$, 88001-24-5; (*E*)-$PhCH_2CH_2CH{=}CHCH{=}C(CH_3)_2$, 68099-28-5; (*Z*)-$PhCH_2CH_2CH{=}CHCH{=}C(CH_3)_2$, 83334-03-6; (*E*)-$PhCH_2CH_2CH{=}CHC(CH_3){=}CH_2$, 37904-42-0; (*Z*)-$PhCH_2CH_2CH{=}CHC(CH_3){=}CH_2$, 88001-25-6; (*E*)-$CH_3CH{=}C(CH_3)CHO$, 497-03-0; (*E,E*)-$CH_3CH{=}C(CH_3)CH{=}CHC(CH_3){=}CH_2$, 88001-26-7; $Ph_2(PhCH_2)P{=}CHPh$, 33417-25-3; $CH_3CH{=}CHCHO$, 4170-30-3; (*Z,E*)-$PhCH{=}CHCH{=}CHCH_3$, 39491-55-9; $Ph_2PEt_2{\cdot}Br$, 2999-92-0.

Supplementary Material Available: Representative procedure for synthesis of (*E,E*)-dienes and phosphonium salt precursors (2 pages). Ordering information is given on any current masthead page.

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(23) Dienes $C_6H_{11}CH_a{=}CH_bCH_c{=}C(CH_3)R$; partial 200-MHz NMR data (CCl_3, δ). R = CH_3: *E,E* isomer, H_a, 5.50 (dd, J = 8, 15 Hz), Hb, 6.18 (dd, J = 11, 15 Hz), H_c, 6.00 (d, J = 8 Hz); *Z,E* isomer, H_a, 5.17 (m), $H_b + H_c$, 6–6.2 (m). R = H: *E,E* isomer, H_a + R = H, 5.4–5.7 (m), $H_b + H_c$, 5.9–6.1 (m), allylic methine at 2.0 (m); *Z,E* isomer, H_a, 5.14 (t, J = 10 Hz), H_b or H_c, 6.34 (dd, J = 10, 11 Hz), H_b or H_c, 5.85 (t, J = 10 Hz), R = H, 5.65 (m) allylic methine, 2.42 (m). $C_6H_{11}CH_a{=}CH_bC(CH_3){=}CH_2$: *E* isomer, H_a, 5.62 (dd, J = 16, 7 Hz), H_b, 6.13 (J = 16 Hz); *Z* isomer, H_a, 5.22 (t, J = 12 Hz), H_b, 5.73 (d, J = 12 Hz).

(24) Dienes $PhCH_2CH_2CH_a{=}CH_bCH_c{=}C(CH_3)R$; partial 200-MHz NMR data ($CDCl_3$, δ). R = CH_3: *E,E* isomer, H_a, 5.57 (dt, J = 16, 8 Hz), H_b, 6.26 (dd, J = 16, 11 Hz), H_c, 5.78 (d, J = 12 Hz); *Z,E* isomer, H_a, 5.36 (dt, J = 10, 8 Hz), $H_b + H_c$, 6–6.3 (m). R = H: *E,E* isomer, H_a + R = H, 5.5–5.7 (m), $H_b + H_c$, 5.9–6.1 (m); *Z,E* isomer, Ha, 5.35 (dt, J = 10, 8 Hz), H_b or H_c, 6.3 (br t, J = ca. 10 Hz), H_b or H_c, 5.96 (t, J = 10 Hz). R = H: 5.7 (m). $PhCH_2CH_2CH_a{=}CH_bC(CH_3){=}CH_2$: *E* isomer; H_a, 5.75 (dt, J = 16, 7 Hz), H_b, 6.23 (d, J = 16 Hz); *Z* isomer; H_a, 5.49 (dt, J = 12, 8 Hz), H_b, 5.9 (d, J = 12 Hz).

Additions and Corrections

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Raymond J. Giguere, Godard von Ilsemann, and H. M. R. Hoffmann*. Homologues of Monocyclic Monoterpenes. Tetramethylated Derivatives of Carvone, Carveol, β-Terpineol, Sobrerol, and Related Compounds.

Page 4949. Scheme I. Formula **5b** should read **6**.
Page 4951. Scheme VII. Formula **6** should read **18**.
Page 4954. Last paragraph, line 26 from bottom. Formula **16** should read **18**.