port of this research and to the National Science Foundation for its contribution to the purchase of a Bruker 360-MHz NMR spectrometer.

Registry No. 4, 66267-06-9; 5, 60968-15-2; benzenebutanoic acid, 1821-12-1; benzenepropanoic acid, 501-52-0; 2-naphthalenebutanoic acid, 782-28-5; 2-naphthalenepropanoic acid, 21658-35-5; 1-naphthalenebutanoic acid, 781-74-8; α-methyl-1-naphthalenebutanoic acid, 7498-80-8; 3-phenanthrenebutanoic acid, 13728-56-8; 2-phenanthrenebutanoic acid, 77520-30-0; 8,9,10,11-tetrahydro-8-benz[*a*]anthraceneacetic acid, 6299-45-2; 1-pyrenebutanoic acid, 3443-45-6; 1-tetralone, 529-34-0; 1-indanone, 83-33-0; 2,3-dihydro-4(1*H*)-phenanthrenone, 778-48-3; 2,3-dihydro-1*H*-benzinden-1-one, 6342-87-6; 3,4-dihydro-1-(2*H*)-phenanthrenone, 573-22-8; 3,4-dihydro-2-methyl-1(2*H*)-phenanthrenone, 3580-60-7; 10,11-dihydrobenz[*a*]anthracen-8-(9*H*)-one, 5472-20-8; 2a,3,4,5-tetrahydrobenz[*j*]aceanthrylen-1-(2*H*)-one, 87883-45-2; 9,10-dihydrobenzo[*a*]pyren-7(8*H*)-one, 3331-46-2; benzenebutanoyl chloride, 18496-54-3; benzenepropanoyl chloride, 645-45-4; 2-naphthalenebutanoyl chloride, 87883-46-3; 2-naphthalenepropanoyl chloride, 27673-99-0; 1-naphthalenebutanoyl chloride, 87883-47-4; α-methyl-1-naphthalenebutanoyl chloride, 87883-48-5; 3-phenanthrenebutanoyl chloride, 87883-49-6; 2-phenanthrenebutanoyl chloride, 87883-50-9; 8,9,10,11-tetrahydro-8-benz[*a*]anthraceneacetyl chloride, 87901-08-4; 1-pyrenebutanoyl chloride, 63549-37-1; trifluoromethanesulfonic acid, 1493-13-6.

Reaction of *n*-, *sec*-, and *tert*-Butyllithium with Dimethoxyethane (DME): A Correction

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Two recent communications report on kinetic and spectral evidence for the formation of a complex between metalating agent and substrate prior to deprotonation.[1,2] The second account[2] describes results obtained in the attempted metalation of formamidines with *t*-BuLi in dimethoxyethane (DME). The lack of D incorporation in these experiments was rationalized on the basis of a rather *stable complex* between substrate, metalating agent, and the bidentate solvent (DME). Furthermore, upon addition of benzaldehyde, benzyl alcohol and benzyl benzoate were isolated, the products of an apparent Cannizzarro reaction. We have evidence that the interpretation of these results[2] with DME is incorrect.

Dimethoxyethane has only rarely been used as a solvent in metalation reactions. Our own previous negative experience with this solvent and the peculiar results of the recent report[2] called for a more careful investigation of the stability of DME toward alkyllithiums. In several experiments we have shown that DME has a very limited stability toward butyllithium. With *t*-BuLi in particular, DME is readily deprotonated and undergoes β-elimination characteristic of several 1,2-diheterosubstituted ethanes. Thus, in contrast to the behavior of tetramethylethylenediamine (TMEDA), DME does not form a stable complex with *t*-BuLi. As illustrated in Scheme I, it is assumed that after coordination with one of the two oxygen atoms, a proton in the β-position is abstracted in a fast reaction (higher acidity than in TMEDA) followed by β-elimination and formation of methyl vinyl ether and lithium methoxide. By reproducing the reported[2] conditions (*t*-BuLi/pentane, 0.5 M solution in DME,[3] –20 °C/20 min), the expected white precipitate was indeed formed. Titration (1 M *sec*-BuOH/xylene) using either phenanthroline, as reported,[2] or the more reliable 2,2′-biquinoline[4] as an indicator gave no evidence of any remaining *t*-BuLi. When the addition of *t*-BuLi was carried out at –70 °C, followed by a 20-min reaction time at –20 °C, a clear yellow solution developed initially followed by the white precipitate. Titration with the two indicators showed less than 8% and 9%, respectively, of *t*-BuLi to be present under these conditions. After 20 min at –70 °C, 45% (phenanthroline) and 28% (2,2′-biquinoline) of *t*-BuLi was still detectable by titration with the two indicators. A control experiment under identical conditions (–70 °C, 20 min) using freshly distilled benzaldehyde as substrate, rather than a titration, led to a mixture consisting of 60% unreacted benzaldehyde, 25% *tert*-butylphenylcarbinol, and several unidentified impurities. This result is in good agreement with the titration value (28%) obtained by using the 2,2′-biquinoline indicator.

Scheme I

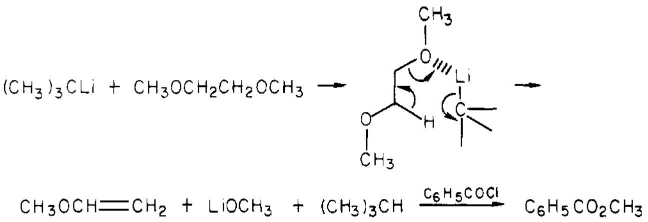

Table I

	$t_{1/2}$, min	
	–20 °C	–70 °C
DME/*n*-BuLi[a]	111 ± 5	
DME/*sec*-BuLi[b]	~2 ± 1	120 ± 5
DME/*t*-BuLi[c]	<<2	11 ± 2

[a] *n*-BuLi, 2.6 M/hexane, Alfa Products; 0.5 M solution in DME (12 mMol). [b] *sec*-BuLi, 1.4 M/hexane, Alfa Products; 0.25 M solution in DME (14 mMol). [c] *t*-BuLi, 2.3 M/pentane, Alfa Products; 0.5 M solution in DME (11.5 mMol).

Chemical proof for the formation of lithium methoxide was obtained by treatment of the white precipitate (formed after 20 min/–20 °C) with an equimolar amount of benzoyl chloride. After a reaction time of 20 min at –20 °C, the mixture was quenched (–20 °C) with NaH_2PO_4 buffer. After workup, the product mixture (92% recovery) consisted of methyl benzoate (84%) and unreacted benzoyl chloride (Scheme I). The approximate half-lives of *n*-BuLi, *sec*-BuLi, and *t*-BuLi in DME were determined by using the 2,2′-biquinoline titration technique and are listed in Table I. The reactivity of the various butyllithiums with DME thus decreases in the order of *t*-BuLi > *sec*-BuLi ≫ *n*-BuLi.

In summary, our results indicate that DME has a rather limited stability toward butyllithiums and is cleaved extremely rapidly by *t*-BuLi. Furthermore, the reported

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[1] Al-Aseer, M.; Beak, P.; Hay, D.; Kempf, D. J.; Mills, S.; Smith, S. G. *J. Am. Chem. Soc.* **1983**, *105*, 2080.

[2] Meyers, A. I.; Rieker, W. F.; Fuentes, L. M. *J. Am. Chem. Soc.* **1983**, *105*, 2082.

[3] Dimethoxyethane (DME): Baker, analyzed reagent, less than 0.1% H_2O.

[4] 2,2′-Biquinoline produces a sharper and clearer color change. Cf.: Gschwend, H. W.; Rodriguez, H. R. *Org. React.* (*N.Y.*) **26**, 1 (1979). Watson, S. C.; Eastham, J. F. *J. Organomet. Chem.* **1967**, *9*, 165.

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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 $\mathrm{Ph_3P{=}CHR}$ (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 $\mathrm{Ph_3P{=}CHR}$ (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 $\mathrm{Ph_3P{=}CHR}$ to $\mathrm{Ph_2(R'CH_2)P{=}CHR}$ (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 $\mathrm{NaNH_3}$/liquid $\mathrm{NH_3}$[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 $\mathrm{Ph_3P{=}CHCH_3}$ 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 $\mathrm{Ph_3P{=}CHR}$ reactions, it is the *Z selectivity* that is decreased.

We have shown that the lithium ion effect in reactions of $\mathrm{Ph_3P{=}CHCH_3}$ is due to competition between the normal salt-free process and a $\mathrm{Li^+}$-catalyzed ylide–aldehyde reaction of unknown mechanism and unknown but lower *Z* selectivity.[6] The $\mathrm{Li^+}$ effect on $\mathrm{Ph_3P{=}CHCH_3}$ + aliphatic aldehydes is *not* due to equilibration of the initially formed oxaphosphetane.[6] In an attempt to probe the $\mathrm{Li^+}$ effect in Table I, we have examined the reaction of $\mathrm{Ph_2(CH_3)P{=}CHC(CH_3){=}CH_2}$ 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 + $\mathrm{Ph_3P{=}CHCH_3}$ + LiBr, although crossover has not previously been demonstrated for aliphatic aldehydes under typical Wittig conditions.[3b,6,7,11]

Analogous experiments using *salt-free* $\mathrm{Ph_2(CH_3)P{=}CHC(CH_3){=}CH_2}$ 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 $\mathrm{Li^+}$-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

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[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 $\mathrm{NaNH_2}$ 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 $\mathrm{CH_2{=}C(CH_3){=}CHR''}$ vs. $\mathrm{CH_2{=}C(CH_3){=}CHC_6H_3Cl_2}$ 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 + $\mathrm{Ph_3P}$ 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.

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