cyclizations or anion exchange followed by polymerization. Efforts to circumvent this limitation by forming the magnesium enolate with (diisopropylamino)magnesium bromide or by deprotonation *and* reduction at −78 °C were unsuccessful.

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[8] A: enolate formation with $i\text{-Pr}_2\text{NLi}$ in THF at −78 °C; LiAlH_4 added at −78 °C and solution warmed slowly to −40 °C; quench by pouring into cold dilute HCl. B: enolate formation with $i\text{-Pr}_2\text{NLi}$ in THF at −78 °C; DIBAL added at −78 °C and solution warmed slowly to −20 °C; quench by pouring into dilute acetic acid. C: enolate formation with $i\text{-Pr}_2\text{NLi}$ in benzene-hexane at −20 °C; DIBAL added at −20 °C and solution warmed slowly to 0 °C; quench by stirring in two-phase system of cold acetic acid and chloroform.

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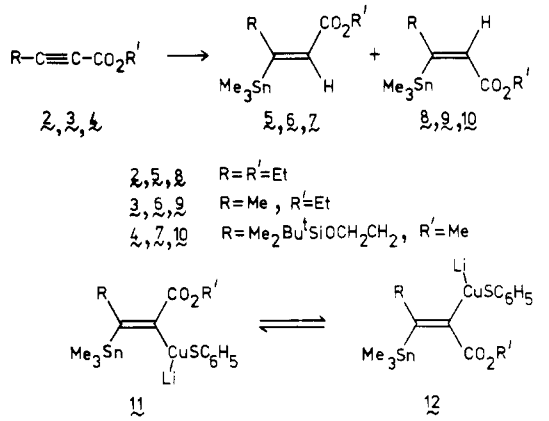
Stereoselective Conjugate Addition of Lithium (Phenylthio)(trimethylstannyl)cuprate to α,β-Acetylenic Esters. Preparation of (*E*)- and (*Z*)-4-Lithio-1,3-pentadienes and Their Reaction with Electrophiles

Summary: Depending on experimental conditions, reaction of lithium (phenylthio)(trimethylstannyl)cuprate (1) with α,β-acetylenic esters 2–4 affords, highly stereoselectively, either the (*E*)- (5–7) or the (*Z*)-β-trimethylstannyl (8–10) α,β-unsaturated esters. Two of the latter substances (6 and 9) were transformed into the geometrically isomeric 4-lithio-1,3-pentadienes (16 and 20, respectively), which react smoothly with electrophiles to afford products of general structures 21 and 22.

Sir: Recently, we reported that lithium (phenylthio)(trimethylstannyl)cuprate [$\text{C}_6\text{H}_5\text{S}(\text{Me}_3\text{Sn})\text{CuLi}$, 1][1] is an excellent reagent for transferring, in a conjugate sense, the trimethylstannyl group to α,β-unsaturated carbonyl systems.[4] This reagent was shown to be particularly effective in converting β-iodo α,β-unsaturated ketones[5] into the corresponding β-trimethylstannyl enones, which, in principle, can serve as convenient precursors of β-acylvinyl anion equivalents.[6] We report herein (a) that the cuprate reagent 1 smoothly transfers one Me_3Sn group to α,β-acetylenic esters, (b) that the course of the reaction can be controlled experimentally so as to produce, *highly stereoselectively*, either the (*E*)- or the (*Z*)-β-trimethylstannyl α,β-unsaturated esters, and (c) that the products can be converted into functionalized 4-lithio-1,3-alkadienes, species which exhibit considerable promise as reagents in organic synthesis.

Scheme I



When ethyl 2-pentynoate (2) was allowed to react with 2.5 equiv of 1 at −100 °C (THF, argon atmosphere) for 6 h and the resultant solution was treated with methanol, the two geometric isomers 5 and 8 were obtained (Scheme I) in a ratio of approximately 97:3 (81%).[7,8] The reaction could be carried out in a shorter time and with an even higher stereoselectivity by adding a THF solution of 2 *containing 1.7 equiv of methanol* to a solution (THF) of 2.0 equiv of the cuprate reagent 1 (−100 °C, 15 min; −78 °C, 3 h).[9] Under these conditions the conjugate addition product consisted of essentially pure *E* isomer 5 (79% yield, <1% 7). On the other hand, reaction of 2 with 1.2 equiv of 1 at −78 °C for 15 min and at −48 °C for 4 h, followed by protonation (methanol) and workup, afforded (76%) the two isomers 5 and 8 in a ratio of 2:98, respectively. In similar fashion, ethyl 2-butynoate (3) could be converted into either ethyl (*E*)-3-(trimethylstannyl)-2-butenoate (6) (78% yield, >99% stereoselectivity) or the corresponding *Z* isomer 9 (76% yield, 98% stereoselectivity), and methyl 5-(*tert*-butyldimethylsiloxy)-2-pentynoate (4)[10] was transformed into either of the two isomers 7 (82% yield, 96% stereoselectivity) or 10 (81% yield, 96% stereoselectivity).[11]

It is clear from the above results that the *E* isomers (5–7) are the products of kinetic control, while the *Z* isomers (8–10) are produced under thermodynamically controlled conditions. Apparently, at low temperatures (e.g., −100 °C) the "kinetic" intermediate (cf. 11) is reasonably stable and isomerizes only very slowly. At somewhat higher temperatures (e.g., −78 °C), isomerization of 11 into 12 does occur, but this transformation can be minimized by the presence of a proton source such as methanol (protonation of 11 faster than isomerization). If the reaction mixtures are allowed to warm to −48 °C in the absence of methanol, equilibration (11 $\rightleftharpoons$ 12) takes place, with the equilibrium largely favoring intermediate 12. Subsequent protonation results in the formation of the nearly pure *Z* isomers (8–10). These observations parallel to some extent those

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[1] A dark red solution of this reagent is prepared simply by addition of 1 equiv of solid (phenylthio)copper[2] to a cold (−20 °C) solution of (trimethylstannyl)lithium[3] in THF.

[2] Posner, G. H.; Brunelle, D. J.; Sinoway, L. *Synthesis* **1974**, 662.

[3] Still, W. C. *J. Am. Chem. Soc.* **1977**, *99*, 4836.

[4] Piers, E.; Morton, H. E. *J. Chem. Soc., Chem. Commun.* **1978**, 1033.

[5] Piers, E.; Nagakura, I. *Synth. Commun.* **1975**, *5*, 193.

[6] Piers, E.; Morton, H. E. *J. Org. Chem.* **1979**, *44*, 3437.

[7] The product ratios reported herein were determined by gas-liquid chromatography, employing a column ($^1/_8$ in. × 6 ft) packed with 3% OV-17 on Chromosorb W(HP) (80–100 mesh).

[8] All new compounds reported herein exhibited spectral data in full accord with assigned structures and gave satisfactory elemental analyses and/or high-resolution mass spectrometric measurements.

[9] If the reaction was allowed to proceed at −78 °C (3 h) in the absence of methanol, subsequent protonation produced a considerable amount of the *Z* isomer (5/8 ratio of ~68:32).

[10] We are very grateful to Professor L. Weiler and Dr. P. E. Sum for a sample of the tetrahydropyranyl ether of methyl 5-hydroxypentynoate, which was readily transformed into compound 4.

[11] The ^{1}H NMR spectra of the conjugate addition products fully corroborated the stereochemical assignments. For example, the vinyl methyl group of the *E* isomer 6 (methyl group cis to the CO_2Et group) gives rise to a doublet ($J \approx 2$ Hz) at δ 2.34. The corresponding signal derived from the *Z* isomer 9 (Me and CO_2Et in a trans relationship) is found, as expected, at higher field (δ 2.12, d, $J \approx 2$ Hz). Analogous differences are found in the other pairs of addition products (5, 8 and 7, 10).

Scheme II

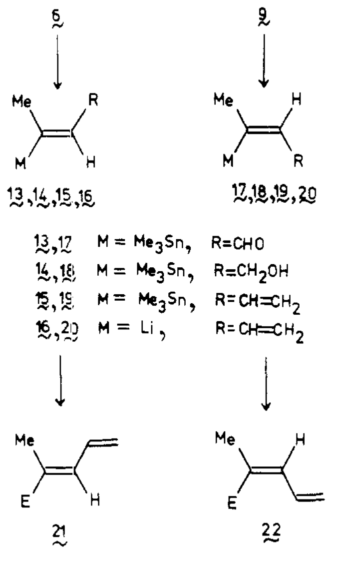

Table I. Reaction of the 4-Lithio-1,3-pentadienes 16 and 20 with Electrophiles

nucleophile	electrophile[a]	product (% yield)[b]
16	n-$C_8H_{17}Br$	21, E = n-C_8H_{17} (71)
16	RCH_2CH_2Br[c]	21, E = RCH_2CH_2[c] (69)
16	RCH_2CHO[c]	21, E = $RCH_2CH(OH)$[c] (82)
16	cyclopentanone	21, E = 1-hydroxycyclopentyl (74)
20	n-$C_8H_{17}Br$	22, E = n-C_8H_{17} (62)
20	RCH_2CHO[c]	22, E = $RCH_2CH(OH)$[c] (76)

[a] All reactions were carried out in THF solution. When the electrophile was an alkyl halide, the solution was stirred at −78 °C for 1 h, allowed to warm to room temperature over a period of 1 h, and then quenched with aqueous ammonium chloride. With carbonyl electrophiles, the solution was stirred at −78 °C for 1 h and treated at this temperature with aqueous ammonium chloride. [b] Yield of distilled, purified product. [c] R = 2-cyclopentenyl.

made for the reaction of lithium dialkylcuprates with α,β-acetylenic esters.[12,13] However, in the latter transformations, the "thermodynamically controlled" reactions did not lead to high stereoselectivity.

The possibility of employing the β-trimethylstannyl α,β-unsaturated esters **5–10** as precursors for stereochemically well-defined and isomerically pure vinyllithium[14] and related reagents appears to be very attractive. For example, reduction of the isomeric esters **6** and **9** with ~1 equiv of diisobutylaluminum hydride in pentane at −127 °C afforded the corresponding aldehydes **13** (86%) and **17** (82%), respectively.[15] Treatment of the latter substances with methylenetriphenylphosphorane in THF at room temperature gave the geometrically isomeric trimethylstannyl dienes **15** and **19** (74% and 72%, respectively). Interestingly, both of these substances underwent rapid and complete transmetalation when treated with 1.2 equiv of methyllithium in THF (−78 °C, 10 min). The resultant 4-lithio-1,3-pentadienes (**16** and **20**) reacted smoothly with a variety of electrophiles (E^+) to produce the corresponding substituted dienes (**21** and **22**, Scheme II). Some of the results we have obtained are summarized in Table I.

The potential inherent in the preliminary results described above would appear to be considerable. For example, reaction of **16** and **20** (or other lithio dienes derived from esters such as **5–10**) with electrophiles containing suitably placed dienophilic unsaturation would, presumably, produce intermediates which should undergo intramolecular Diels–Alder reactions. These possibilities, along with others, are being actively investigated.

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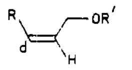
[12] Corey, E. J.; Katzenellenbogen, J. A. *J. Am. Chem. Soc.* **1969**, *91*, 1851.

[13] Siddall, J. B.; Biskup, M.; Fried, J. H. *J. Am. Chem. Soc.* **1969**, *91*, 1853.

[14] The formation of vinyllithium reagents by transmetalation of trialkylvinylstannanes with an alkyllithium is well-known. For some recent reports, along with references cited therein, see: (a) ref 6; (b) Wollenberg, R. H. *Tetrahedron Lett.* **1978**, 717; (c) Chen, S. L.; Schaub, R. E.; Grudzinskas, C. V. *J. Org. Chem.* **1978**, *43*, 3450; (d) Collins, P. W.; Jung, C. J.; Gasiecki, A.; Pappo, R. *Tetrahedron Lett.* **1978**, 3187.

[15] In each of these reductions, the aldehyde product was accompanied by a small amount (~5–7%) of the corresponding alcohol (**14** and **18**, respectively), which could be removed readily by column chromatography on silica gel. With regard to these latter substances, two items deserve explicit mention. First, both **14** and **18** could be oxidized smoothly and efficiently to the aldehydes (**13** and **17**, respectively) by treatment with barium manganate in dichloromethane.[16] Second, compounds **14** and **18**, along with the alcohols derived by reduction of **5**, **7**, **8**, **10**, and similar esters, should serve as convenient precursors of pure, geometrically isomeric vinyllithium reagents which correspond to the general d^3 synthons[17] i and ii.[18]



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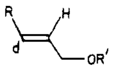

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[16] Firouzabadi, H.; Ghaderi, E. *Tetrahedron Lett.* **1978**, 839.

[17] For a stimulating review on methods of reactivity umpolung, see: Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 239.

[18] For some recent examples of reagents corresponding to similar d^3 synthons, see ref 14c and: Posner, G. H.; Ting, J.-S.; Lentz, C. M. *Tetrahedron* **1976**, *32*, 2281; Corey, E. J.; Wollenberg, R. H. *Tetrahedron Lett.* **1976**, 4705; Corey, E. J.; Bock, M. G.; Kozikowski, A. P.; Rama Rao, A. V.; Floyd, D.; Lipshutz, B. *Ibid.* **1978**, 1051.

Stereochemical Aspects of the Intramolecular Diels-Alder Reactions of Methyl Deca-2,7,9-trienoates. 1. Thermal Cyclizations

Summary: The intramolecular Diels–Alder reactions of **1**, **8**, **11**, and **12** preferentially afford *trans*-perhydroindene cycloadducts independent of dienophile stereochemistry.

Sir: The intramolecular Diels–Alder reaction has proven to be useful for the synthesis of many polycyclic compounds including natural products.[1] Despite the considerable research devoted to understanding the structural and stereochemical features of this reaction in recent years, the stereochemical aspects of the Diels–Alder reactions of trienes bearing terminal dienophile activating groups have been little studied. For these systems, it is tempting to assume that the stereochemistry of the major product can

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[1] (a) Brieger, G.; Bennett, J. N. *Chem. Rev.* **1980**, *80*, 63. (b) Oppolzer, W. *Synthesis* **1980**, 793. (c) Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 10. (d) Mehta, G. *J. Chem. Educ.* **1976**, *53*, 551. (e) Carlson, R. G. *Annu. Rep. Med. Chem.* **1974**, *9*, 270.

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