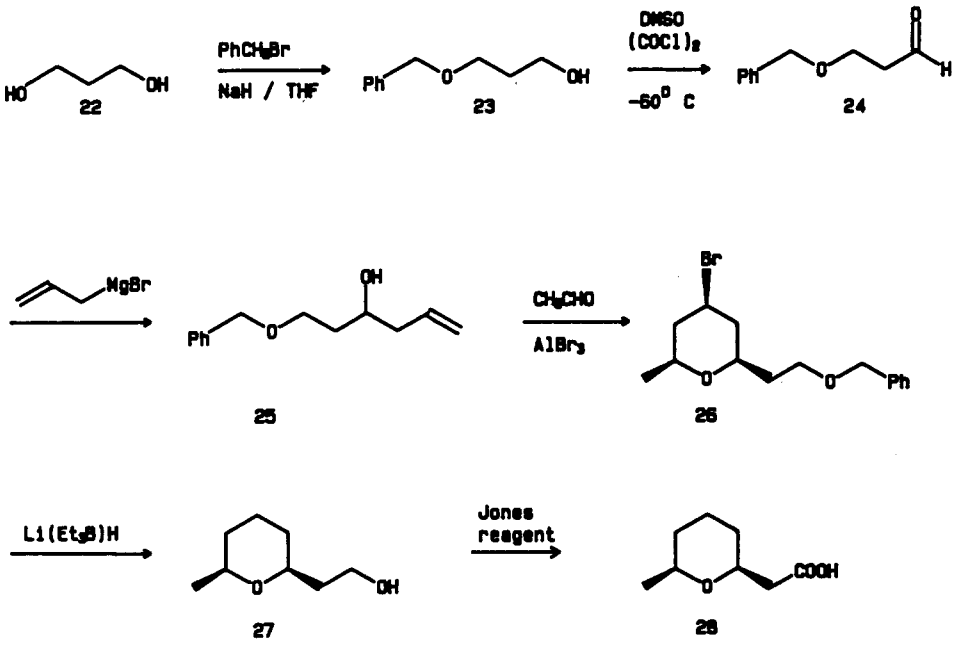
Scheme V



hydrofuran derivatives was excluded on the basis of the same ^{13}C NMR analysis.

A further advantage of this procedure over the previously reported allylsilane-based one[2] is that we can prepare larger rings starting from different unsaturated alcohols as shown in entries 7–9 of Table I which report the synthesis of oxepanes **18–20**. In the case of **18–19** we obtained a mixture of two isomers characterized by the presence of the halogen in equatorial and axial position. Nevertheless treating **19** with $Li(Et_3B)H$ debromuration occurred and 2-isopropyl-1-oxabicyclo[5.4.0]undecane **21** was formed as a single isomer.

It is noteworthy that the oxepane **20** was also obtained in the all cis configuration as the former tetrahydropyran derivatives.[11]

The high flexibility of this reaction is finally demonstrated in the synthesis of (±)-(*cis*-6-methyltetrahydropyran-2-yl)acetic acid (**28**). The synthetic way for the preparation[12] of this product is outlined in Scheme V.

Propanediol (**22**) was protected as the monobenzyl ether and oxidized to aldehyde **24** (DMSO, $(COCl)_2$, Et_3N –60 °C, 71%).

After condensation of **24** with allylmagnesium bromide, the alcohol **25** was isolated in 75% yield and cyclized with acetaldehyde and $AlBr_3$ in benzene (70% yield).

The *all-cis*-4-bromotetrahydropyran **26** was then treated with 3 equiv of $Li(Et_3B)H$ in boiling THF for 8 h to give directly the alcohol **27**, which after oxidation with Jones reagent afforded **28**, (32% overall yield for six steps). The product shows the same spectroscopic features [^1H NMR (300 MHz), ^{13}C NMR, and MS) previously reported in the literature.[5a,12a]

Acknowledgment. We are grateful to A. Degl'Innocenti (CNR, Florence) and S. Papaleo (University, Florence) for the high-field and ^{13}C NMR spectra.

Registry No. (±)-**1**, 80735-94-0; (±)-**2**, 111321-98-3; **3**, 624-97-5; **4**, 627-27-0; (±)-**5**, 111268-65-6; (±)-**6**, 54774-27-5; **7**, 78-84-2; **8**, 100-52-7; **9**, 75-07-0; (±)-**10**, 57456-98-1; **11**, 123-72-8; (±)-**12**, 111268-66-7; **13**, 111268-67-8; (±)-**14**, 111268-68-9; (±)-**15**, 111268-69-0; (±)-**16**, 111268-70-3; **17**, 111268-71-4; (±)-**18** (isomer 1), 111268-72-5; (±)-**18** (isomer 2), 111321-99-4; (±)-**19** (isomer 1), 111268-73-6; (±)-**19** (isomer 2), 111322-00-0; (±)-**20**, 111268-74-7; (±)-**21**, 111268-75-8; **22**, 504-63-2; **23**, 4799-68-2; **24**, 19790-60-4; (±)-**25**, 111322-01-1; (±)-**26**, 111268-76-9; (±)-**27**, 82280-95-3; (±)-**28**, 82335-13-5; $AlCl_3$, 7446-70-0; $AlBr_3$, 7727-15-3.

Supplementary Material Available: Spectroscopic data for compounds **12–21**, **24**, and **26–28** (5 pages). Ordering information is given on any current masthead page.

(10) (a) Gambaro, A.; Boaretto, A.; Marton, D.; Tagliavini, G. *J. Organomet. Chem.* **1983**, *254*, 293. (b) Eliel, E. L.; Hargrave, K. D.; Pietrusiewicz, K. M.; Manoharan, J. *J. Am. Chem. Soc.* **1982**, *104*, 3635.

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(12) For previous synthesis of the racemic compounds, see: (a) Semmelhack, M. F.; Bodurow, C. *J. Am. Chem. Soc.* **1984**, *106*, 1496. (b) Bates, H. A.; Deng, P. N. *J. Org. Chem.* **1983**, *48*, 4479. (c) Kim, Y.; Mundy, B. P. *J. Org. Chem.* **1982**, *47*, 3556. (d) Ley, S. W.; Lygo, B.; Molines, H.; Morton, J. A. *J. Chem. Soc., Chem. Commun.* **1982**, 1251. For synthesis of the chiral product, see: (e) Keinan, E.; Seth, K. K.; Lamed, R. *J. Am. Chem. Soc.* **1986**, *108*, 3474. (f) Seebach, D.; Pohmakotr, M. *Helv. Chim. Acta* **1979**, *62*, 843. (g) Lichtenthaler, F. W.; Klinger, F. D.; Jarglis, P. *Carbohydr. Res.* **1984**, *132*, C1.

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Novel Bicyclization Methodology via Cyclialkylation of ω-Halo-1-metallo-1-alkynes Containing Aluminum and Zinc[1]

Summary: A new bicyclization methodology involving cyclization of ω-iodo-1-alkynes via metalation–carbometalation with organometals containing Al or Zn followed by acylpalladation or cyclialkylation is described.

(1) Metal-Promoted Cyclization. 17. Part 16: Negishi, E.; Zhang, Y.; Bagheri, V. *Tetrahedron Lett.* **1987**, *28*, 5793.

0022-3263/88/1953-0913$01.50/0

Sir: Conversion of acyclic molecules into bicyclic molecules in a small number of steps may be termed *bicyclization*. One feature of bicyclization that distinguishes it from *annulation*[3] is that all or most of the skeleton-constructing atoms are incorporated in acyclic intermediates (Scheme I). The reaction of enynes with "$ZrCp_2$" followed by carbonylation[4] is an example of type I bicyclization.

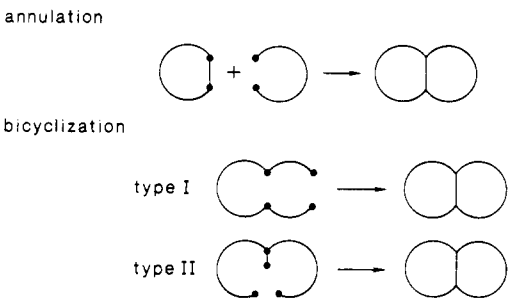
We have previously reported that allylzincation[5] of 4-bromo-1-(trimethylsilyl)-1-butyne gives 2-allyl-1-(trimethylsilyl)cyclobutene (**1**) via **2**.[6a] Unfortunately, our attempts to apply the reaction to the development of type II bicyclization sequences have met with two kinds of difficulties. Firstly, unlike acyclic alkenylsilanes, cycloalkenylsilanes are not readily converted into the corresponding halides and other functional derivatives, although Lewis acid promoted acylation has been an exception.[6b] Secondly, the presumed π-cyclization reaction[6] cannot be readily applied to the preparation of five-membered homologues.[7] The first problem has been solved by replacing the trialkylsilyl group with an Al- or Zn-containing group.[6a] However, the latter problem has persisted.

Noting our previous finding that, while π-cyclization reactions[6] are promoted by relatively nonpolar solvents,[8] e.g., CH_2Cl_2, σ-cyclization reactions[6] readily proceed in relatively polar solvents, e.g., THF, we replaced the solvents in the following reactions with THF and found that the desired cyclization proceeded in high yields (Scheme II). In less polar solvents, such as CH_2Cl_2, 1,2-dichloroethane, and even diethyl ether, no cyclization occurs, the carbometalated species being the only products obtained in high yields. Mere addition of THF without evaporation of solvents is insufficient to produce useful results. For example, omission of evaporation gave a mere 25% yield of **3** under otherwise the same conditions. The use of 5-bromo-1-pentyne in place of the iodide in the preparation of **3** led to an inferior yield of 65%.

The same procedures are applicable to the preparation of cyclohexene derivatives, such as **4** and **5**, although formation of **4** meets competition by that of **6** to the extent of 20%. The use of crotyl- and methallylzinc bromides and chlorides led to the preparation of **7–10** in the yields shown. None of the regioisomers were formed. Although the exact nature of the above-described cyclization reactions is not clear, the observed solvent effects and facile formation of cyclopentenyl derivatives disfavor the π-cyclization mechanism. *We may therefore be observing, for the first time, σ-cyclization reactions of alkenylmetals containing Al and Zn.* All previously established σ-cyclization reactions of alkenylmetals involve Li.[6]

As hoped, no difficulty was encountered in converting monocycloalkenyl iodides into bicyclic alkenes via catalytic or stoichiometric acylpalladation[9] as well as via cyclialkylation.[6] The experimental results are summarized in Table I.

Scheme I



Scheme II

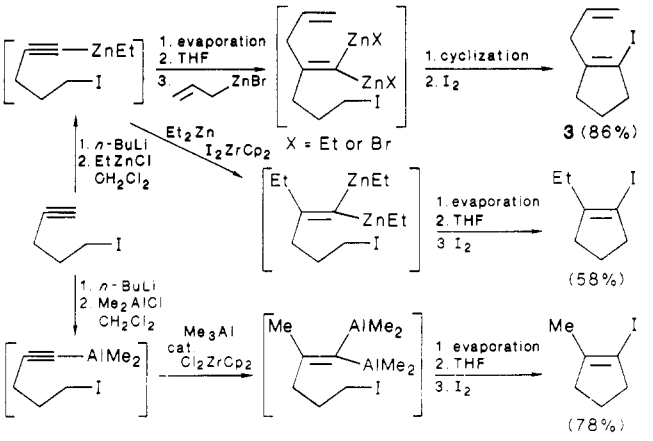
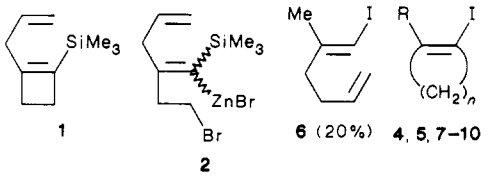


Table I. Conversion of 2-Allyl-1-iodo-1-cycloalkenes into Bicyclic Alkene Derivatives

2-allyl-1-iodo-1-cycloalkene	procedure[a]	product	product yield,[b] %
3	A	11	82
5	A	12	85
3	B	13	75
3	C	14	90
5	C	15	87
7	C	16	82
10	D	17	72

[a] A:[9] CO (40 atm), $Cl_2Pd(PPh_3)_2$ (0.05 equiv), NEt_3 (1.5 equiv), C_6H_6, CH_3CN, MeOH (4 equiv), 100 °C, 24 h. B:[5] CO (1.1 atm), $Pd(PPh_3)_4$ (1 equiv), NEt_3 (1.1 equiv), THF, 60 °C, 24 h. C:[6b] (i) *i*-Bu_3Al (1.1 equiv), Cl_2ZrCp_2 (1 equiv), $ClCH_2CH_2Cl$, 0 °C, 1 h; (ii) I_2 (4 equiv), THF, −10 to 0 °C. D: (i) $(Me_2CHMeCH)_2BH$ (1.2 equiv), THF, 0–25 °C, 2 h; (ii) I_2 (1.5 equiv), NaOMe (2.2 equiv) in MeOH; (iii) 3 N NaOH–30% H_2O_2. [b] Isolated yield based on a 2-allyl-1-iodo-1-cycloalkene.



1 2 6 (20%) 4, 5, 7–10

	R	*n*	yield, %
4	Me	4	67
5	$CH_2CH{=}CH_2$	4	75
7	$CH(Me)CH{=}CH_2$	3	77
8	$CH(Me)CH{=}CH_2$	4	64
9	$CH_2C(Me){=}CH_2$	3	80
10	$CH_2C(Me){=}CH_2$	4	82

(2) (a) John Simon Guggenheim Memorial Foundation Fellow (1987). (b) On leave from Ube Industries, Ltd., Ube, Japan. (c) Graduate Research Fellow supported by the IBM Corporation. (d) On leave from East China Institute of Technology, Nanjing, People's Republic of China.

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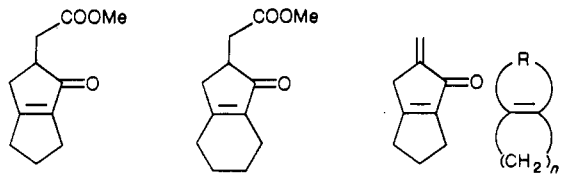
(5) Negishi, E.; Miller, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 6761.

(6) (a) Boardman, L. D.; Bagheri, V.; Sawada, H.; Negishi, E. *J. Am. Chem. Soc.* **1984**, *106*, 6105. (b) See also: Negishi, E.; Boardman, L. D.; Tour, J. M.; Sawada, H.; Rand, C. L. *J. Am. Chem. Soc.* **1983**, *105*, 6344.

(7) For example, allylzincation of 5-bromo-1-(trimethylsilyl)-1-pentyne in ether and/or THF only gives, after protonolysis, 2-(3-bromopropyl)-1-(trimethylsilyl)-1,4-pentadiene.

(8) The π-cyclization reaction of 4-bromo-1-(trimethylsilyl)-1-alkenylalanes proceeds readily in nonpolar solvents, such as hexane and CH_2Cl_2, but does not occur at all in THF.[6b]



11 (82%) 12 (85%) 13 (75%) 14–17

	R	n	yield, %
14	$(CH_2)_3$	3	90
15	$(CH_2)_3$	4	87
16	$(CH_2)_2CHMe$	3	82
17	$CH_2CHMeCH_2$	4	70

In converting 5-iodo-1-pentyne into **11** via **3**, we added *n*-BuLi (2.4 M, 12.5 mL, 30 mmol) in hexane at −90 °C to a solution of 5-iodo-1-pentyne (5.82 g, 30 mmol) in 30 mL of hexane. After the mixture was stirred at −78 °C for 1 h, EtZnCl (1.0 M, 33 mL, 33 mmol) in CH_2Cl_2, prepared from 16.5 mmol each of Et_2Zn and dry $ZnCl_2$, was added at −78 °C, and the mixture was warmed to room temperature over 1–3 h. The solvents were removed under diminished pressure at or below room temperature. To the residue were added sequentially 60 mL of THF and a solution of allylzinc bromide prepared from allyl bromide (5.44 g, 45 mmol) and Zn (2.94 g, 45 mmol) in 30 mL of THF. The reaction mixture was stirred for 12 h at room temperature, quenched at −78 °C with iodine (25.4 g, 100 mmol) in 30 mL of THF, warmed to room temperature, and treated sequentially with pentane, aqueous NH_4Cl, and $Na_2S_2O_3$. The organic phase was washed with $NaHCO_3$ and brine, dried over $MgSO_4$, concentrated, and distilled to provide 6.25 g (86%, 93% by GLC) of **3**: bp 71–74 °C (5 mm); IR (neat) 3040 (w), 1630 (w), 900 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.8–2.1 (m, 2 H), 2.1–2.5 (m, 2 H), 2.5–2.8 (m, 2 H), 2.8–3.0 (m, 2 H), 4.9–5.2 (m, 2 H), 5.5–6.0 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 23.36, 33.83, 37.68, 44.17, 91.54, 116.10, 134.12, 145.69. Anal. Calcd for $C_8H_{11}I$: C, 41.05; H, 4.74. Found: C, 41.27; H, 5.01. To a glass vial containing a magnetic bar were sequentially added **3** (0.71 g, 3.0 mmol) in 3 mL each of benzene and CH_3CN, methanol (0.38 g, 12 mmol), triethylamine (0.45 g, 4.5 mmol), and $Cl_2Pd(PPh_3)_2$ (0.11 g, 0.15 mmol). The vial was placed in an autoclave, which was then charged with carbon monoxide (40 atm) and heated to 100 °C for 24 h in a stirred oil bath. The usual workup and distillation gave 0.48 g (82%) of **11**: bp 100–105 °C (0.15 mmHg, Kugelrohr); IR (neat) 1735 (s), 1695 (s), 1633 (m), 1215 (s), 1168 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 2.2–3.1 (m with peaks at 2.40, 2.47, 2.57, 2.77, 2.81, 2.99, and 3.13, 11 H), 3.70 (s, 3 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 24.70, 27.61, 32.00, 32.66, 35.30, 48.50, 51.53, 147.65, 172.39, 185.14, 202.72; high-resolution mass spectrum calcd for $C_{11}H_{14}O_3$ 194.0943, found 194.0937.

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Registry No. **3**, 112505-80-3; **4**, 40648-08-6; **5**, 112505-81-4; **6**, 112505-82-5; **7**, 112505-83-6; **8**, 112505-84-7; **9**, 112505-85-8; **10**, 112505-86-9; **11**, 112505-87-0; **12**, 112505-88-1; **13**, 112505-89-2; **14**, 6491-93-6; **15**, 695-90-9; **16**, 112505-90-5; **17**, 112505-91-6; $CH{\equiv}C(CH_2)_3I$, 2468-55-5; EtZnCl, 2633-75-2; Me_2AlCl, 1184-58-3; Et_2Zn, 557-20-0; Me_3Al, 75-24-1; $CH_2{=}CHCH_2ZnBr$, 18925-10-5; I_2ZrCp_2, 1298-41-5; Cl_2ZrCp_2, 1291-32-3; $Cl_2Pd(PPh_3)_2$, 13965-03-2; $Pd(PPh_3)_4$, 14221-01-3; *i*-Bu_3Al, 100-99-2; $(Me_2CHMeCH)_2BH$, 1069-54-1; 1-ethyl-2-iodo-1-cyclopentene, 112505-78-9; 1-methyl-2-iodo-1-cyclopentene, 112505-79-0.

Supplementary Material Available: Spectral and analytical data for all compounds except **5**, **11**, and **15** (3 pages). Ordering information is given on any current masthead page.

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Umpolung of π-Allylpalladium Intermediates. A Chemoselective Reductive Elimination of Diols

Summary: The dicarbonates of enediols undergo reductive elimination to form conjugated dienes by using a catalytic amount of a Pd(0) complex wherein either the alkoxide liberated from the carbonate or triisopropyl phosphite serves as a stoichiometric reducing agent.

Sir: Due to the importance of carbonyl additions for C–C bond-forming reactions and the abundance of carbohydrates as starting materials, methods for deoxygenation have become powerful tools for synthesis.[1,2] Palladium-based methods for simple deoxygenation have normally required a hydride source,[3] electrolysis, or a low-valent metal reductant.[4] We wish to report that Pd(0) complexes can catalyze the reductive cleavage of enedicarbonates under very mild conditions either in the absence of any exogenous reducing agent or in the presence of a phosphite.[5] The reactions appear to involve the π-allyl-

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