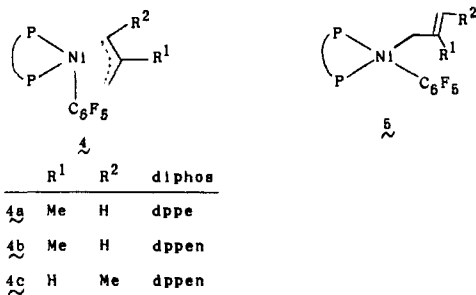


formed complexes unambiguously indicated the allyl groups to be bound to Ni solely in an η^3 -fashion. The ^1H spectra of **4c** exhibited only one resonance for the syn and anti protons of the allylic terminal, suggesting syn-anti proton exchange via a short-lived η^1 -allylnickel complex **5** rapid on the NMR time scale.^{13b} The four allylic hydrogens of **4b** also appeared as only



one resonance,^{13b} presumably attributable to both rapid syn-anti proton exchange and rapid site exchange of the two allylic termini.^{13c} The latter process is most probably associated with the well-known intramolecular rearrangement of d⁸, 5-coordinated complexes.¹⁵ The occurrence of this rearrangement in **4** manifested itself also in the coalescence of the two ^{31}P resonances of **4b** and **4c** at the higher temperatures.^{13c} This coalescence cannot be attributable to intermolecular phosphine exchange nor to occurrence of a monodentate dppen ligand, since the spin couplings between some allyl ligand hydrogens and two equivalent ^{31}P nuclei were observed in the higher temperature ^1H NMR spectra.

On raising the temperature of the solution containing **4** to above -20°C , rapid, nearly quantitative formation of the pentafluoroallylbenzenes occurred. The kinetics of this process for **4a** and **4b** were followed by ^1H NMR spectroscopy at -19 to 10°C to show clean first-order dependence of the rate on the amount of the complex, with k_1^{16} being unvaried on changing the amount of added diphosphine (1-2 equiv) and PPh_3 (0-4 equiv). Of particular note is the great difference between the activation energy (ΔH^\ddagger) for the reductive elimination from 18-electron complex **4b** ($59 \pm 4 \text{ kJ/mol}$)¹⁷ and that from 16-electron complex **1b** ($122 \pm 10 \text{ kJ/mol}$).¹⁷ The ratio of the rate constants at -10°C for **4b** versus **1b** ($9 \times 10^{-9} \text{ h}^{-1}$, extrapolated) amounts to 10^8 .

A possibility that the short-lived species **5** is responsible for the enhanced reactivity of **4** appears less likely¹⁸ for the following reasons. Provided that the relative reactivity of 16-electron η^3 -allyl and 16-electron η^1 -allyl forms described in the palladium complexes (**2** > **3**) also applies in the case of the nickel complexes **1** and **5**, the order of the reactivity is deduced to be **4** \gg **1** > **5**. The considerably low reactivity of **5** is also consistent with the slow rate of the reductive elimination of a related complex, $\text{Ni}(\text{CH}_3)(\text{C}_6\text{F}_5)(\text{dppen})$ ^{14,19} ($\Delta H^\ddagger = 98 \pm 2 \text{ kJ/mol}$), since the competitive experiments employing η^1 -allyl(methyl)metal complexes of Pt^{IV} and Au^{III} suggested²⁰ the reactivity of the η^1 -allyl

group with respect to the reductive elimination to be comparable to that of the methyl. The coupling from 18-electron η^1 -allylnickel, $\text{Ni}(\eta^1\text{-allyl})(\text{Ar})(\text{PR}_3)_3$ appears also unlikely in view of the rate from **4** being independent of the added phosphine. Efforts are under way to gain insight into structures of 18-electron η^3 -allylnickel complexes and their relevance to the low barrier exit^{6b} to the C-C coupling step.

Acknowledgment. Partial support of this work by grants from the Ministry of Education, Science and Culture is acknowledged.

Optically Active 2-Ethenyl-1,3-dioxolanones as 3-Carbon Synthons. Allylnickel Derivatives as Homoenoate Equivalents

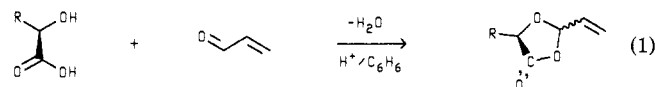
Damian J. Krysan and Peter B. Mackenzie*

Department of Chemistry, Northwestern University
Evanston, Illinois 60208

Received June 6, 1988

The development of reversed polarity synthons¹ and new methods for organic stereocontrol² are important concerns of current synthetic organic research. We report herein (1) a new, allylnickel approach to homoenoate equivalent chemistry³ and (2) the coupling of this methodology with a new enantioselective aldol equivalent reaction⁴ as part of a new approach to 3-carbon synthon stereocontrol.

As detailed elsewhere,⁵ optically active 2-ethenyl-1,3-dioxolan-4-ones are available in a single step by condensation of acrolein with optically active (*R*)- or (*S*)-2-hydroxy acids (eq 1, $\text{R} = \text{Me}, \text{Ph}, \text{c-C}_6\text{H}_{11}$).



In other work, we have shown that these compounds undergo Lewis acid⁶ and palladium⁷-catalyzed conjugate addition reactions with organic nucleophiles. We now report that the metal-centered nucleophile, bis(1,5-cyclooctadiene)nickel(0),⁸ reacts with

(1) Reviews: (a) Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 239. (b) Evans, D. A.; Andrews, G. C. *Acc. Chem. Res.* **1974**, *7*, 147.

(2) Reviews: (a) *Stereochemistry of Organic and Bioorganic Transformations. Workshop Conferences. Hoechst. Volume 17*; Bartmann, W., Sharpless, K. B., Eds.; VCH: Weinheim, 1987. (b) Posner, G. H. *Acc. Chem. Res.* **1987**, *20*(2), 72. (c) *Asymmetric Synthesis. Volume 5. Chiral Catalysis*; Morrison, J. D., Ed.; Academic Press: New York, 1985. (d) *Asymmetric Catalysis*; NATO Advanced Science Institute Series, Bosnich, B., Ed.; Martinus Nijhoff Publ.: The Netherlands, 1986. (e) ApSimon, J. W.; Collier, T. L. *Tetrahedron* **1986**, *42*(19), 5157. (f) Wynberg, H. *Top. Stereochem.* **1986**, *16*, 87. (g) Yamamoto, Y. *Acc. Chem. Res.* **1987**, *20*(7), 243. (h) *Modern Synthetic Methods. 4. Synthesis of Enantiomerically Pure Compounds*; Scheffold, R., Ed.; Springer Verlag: New York, 1986.

(3) For other approaches to homoenoate chemistry, see: (a) Yeh, M. C. P.; Knochel, P. *Tetrahedron Lett.* **1988**, *29*, 2395. (b) Kuwajima, I. *Pure Appl. Chem.* **1988**, *60*, 115. (c) Nakamura, E.; Aoki, S.; Sekiya, K.; Oshino, H.; Kuwajima, I. *J. Am. Chem. Soc.* **1987**, *109*, 8056. (d) Hoppe, D. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 932. (e) Koder, H.; Helmchen, G.; Peters, E. M.; von Schnering, H. G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 898. (f) Ahlbrecht, H.; Bonnet, G.; Enders, D.; Zimmerman, G. *Tetrahedron Lett.* **1980**, *21*, 3175. (g) Mukaiyama, T.; Hayashi, H.; Miwa, T.; Narasaka, K. *Chem. Lett.* **1982**, 1637.

(4) Reviews: (a) Braun, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 24. (b) Hoffmann, R. W. *Ibid.* **1987**, *26*, 489. (c) Heathcock, C. H. In *Asymmetric Synthesis. Volume 3*; Morrison, J. D., Ed.; Academic Press: New York, 1984; Part B, Chapter 2. (d) Evans, D. A. *Ibid.* Chapter 1.

(5) A procedure similar to that employed in the preparation of the 5,5-pentamethylene analogue by Soulier et al.^{5a} was followed. In all cases, the 2-ethenyl-1,3-dioxolanone products are isolated as 2:1 cis/trans mixtures suitable for stereoselective applications. (a) Farines, M.; Soulier, J. *Bull. Soc. Chim. Fr.* **1970**, 332. (b) Friebe, T. L.; Krysan, D. J.; Mackenzie, P. B., manuscript in preparation.

(6) Grisso, B. A.; Friebe, T. L.; Mackenzie, P. B., submitted for publication.

(7) (a) Friebe, T. L.; Krysan, D. J.; Mackenzie, P. B. 194th National Meeting of the American Chemical Society, 1987; New Orleans, LA. (b) Friebe, T. L.; Mackenzie, P. B., manuscript in preparation.

(8) Purchased from Strem Chemicals or prepared according to the following: Semmelhack, M. F. *Org. React.* **1972**, *19*, 115.

(15) (a) English, A. D.; Ittel, S. D.; Tolman, C. A.; Meakin, P.; Jesson, J. P. *J. Am. Chem. Soc.* **1977**, *99*, 117-120, and references therein. (b) DuBois, D. L.; Meek, D. W. *Inorg. Chem.* **1976**, *15*, 3076-3083. (c) Shapley, J. R.; Osborn, J. A. *Acc. Chem. Res.* **1973**, *6*, 305-312.

(16) k_1 (h^{-1}) in toluene for **4a** is 0.767 (10°C) and for **4b** 0.347 (-19°C), 0.925 (-10°C), and 4.10 (2°C).

(17) ΔS^\ddagger (J/K mol) is as follows: **4b**, -88 ± 35 (-19°C); **1b**, 3 ± 40 (101°C). The large negative value in the former case might be attributed, in part, to freezing of fluxional movements in **4** at the transition state for the C-C coupling.

(18) Participation into the rapid C-C coupling of alternative four-coordinated η^1 -allyl species having a structure considerably distorted from a regular square-planar geometry, though no precedence of this type of organonickel complexes has been known, remains to receive further experimental and theoretical scrutiny.

(19) Prepared from *trans*- $\text{Ni}(\text{CH}_3)(\text{C}_6\text{F}_5)(\text{PPh}_3)_2$ and dppen in tetrahydrofuran.¹⁴ Rate constant (h^{-1}) in benzene is 5.4 (90°C), 2.4 (82°C), and 0.78 (71°C), independent of added PPh_3 (0-5 equiv) and dppen (3 equiv). $\Delta S^\ddagger = -32 \pm 15 \text{ J/K mol}$.

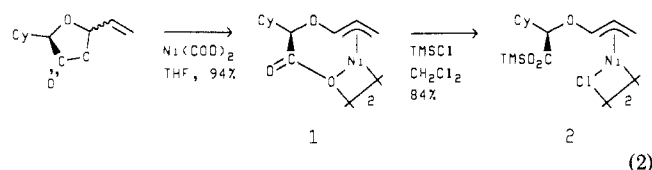
(20) (a) Brown, M. P.; Puddephatt, R. J.; Upton, C. E. E.; Lavington, S. W. *J. Chem. Soc., Dalton Trans.* **1974**, 1613-1618. (b) Ozaki, S.; Komiya, S. *Abstracts Papers 56th Annual Meeting Chem. Soc. Jpn.*, Tokyo, 1988; Abstr. no. 31VB26. We are indebted to Professor Komiya for informing us of this and related unpublished results.

Table I. Halocarbon Coupling Reactions with Compound 2

entry	halocarbon	product	yield ^a (%)
1	bromobenzene	3a	77 (96)
2	1-bromoethene	3b	79 (97)
3	(<i>E</i>)-1-bromo-2-phenylethene	3c^b	77 (96)
4	(<i>Z</i>)-1-bromo-2-phenylethene	3d^c	75 (90)
5	1-iodopropane	3e	82 (94)
6	2-iodopropane	3f	72 (93)

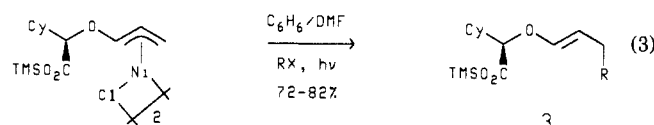
^a Isolated yield of purified product, isolated crude yield in parentheses. ^b Product >95% (*E*)-styryl derivative. ^c Product 83:17 *Z/E* mixture of styryl double bond isomers.

(5*R*)-5-cyclohexyl-2-ethenyl-1,3-dioxolan-4-one to yield the allylnickel complex **1** (eq 2), which upon in situ treatment with



chlorotrimethylsilane gives the corresponding silylated derivative **2**.⁹ ¹H NMR spectroscopy indicates that compound **2** exists in solution as a mixture of two diastereomers (8:1 ratio in C₆D₆). The major diastereomer is assigned the syn allyl stereochemistry based on the observation of a 9.6 Hz C(1)H–C(2)H allyl proton coupling constant;¹⁰ the chirality at C(1)¹¹ of the major diastereomer and the stereochemistry of the minor diastereomer have not been determined.

In the presence of light and a coordinating solvent, compound **2** undergoes efficient homoenolate coupling reactions with halocarbons to give the corresponding (*E*)-enol ethers (eq 3).¹² The



(9) Preparation of **1** and in situ conversion to **2**: (All manipulations were carried out under a nitrogen atmosphere with purified, deoxygenated solvents.) Bis(1,5-cyclooctadiene)nickel(0) (15.0 g, 0.0545 mol, 1.00 equiv) was suspended in tetrahydrofuran (210 mL) and treated with a degassed solution of (5*R*)-5-cyclohexyl-2-ethenyl-1,3-dioxolan-4-one (12.8 g, 0.0655 mol, 1.20 equiv, 2:1 cis/trans) in tetrahydrofuran (30 mL). The mixture was stirred until all of the bis(1,5-cyclooctadiene)nickel(0) had dissolved (10 min) following which time a rust-colored precipitate began to form. After 3 h, the supernatant was removed via cannula, and the remaining solid was washed with tetrahydrofuran (2 × 60 mL) and with dichloromethane (2 × 40 mL) to give compound **1** as a rust-colored microcrystalline solid. Suspension of the solid in dichloromethane (90 mL) and treatment with chlorotrimethylsilane (11.8 g, 0.109 mol, 2.00 equiv, distilled from quinoline and degassed) gave a burgundy red solution. This was stirred for 30 min after which the volatiles were removed under vacuum (0.1 Torr) to give a red oil. Crystallization from diethyl ether (50 mL) at –25 °C gave dark red crystals of **2** (two crops, 15.4 g, 77.8% overall yield from bis(1,5-cyclooctadiene)nickel(0)). Anal. (C₂₈H₅₀Cl₂Ni₂O₆Si₂) C, H, Cl.

(10) For a discussion of the relationship of allyl proton coupling constants to syn/anti stereochemistry, see: Jolly, P. W.; Wilke, G. *The Organic Chemistry of Nickel. Volume 1*; Academic Press: New York, 1974.

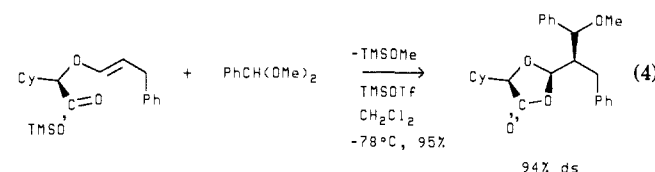
(11) (a) C(1) refers to the oxygen-substituted allyl carbon and may possess either syn-1*S* or syn-1*R* stereochemistry. Although the solution stereochemistry has not been assigned, the solid-state structure of compound **2** has been determined by X-ray crystallography.^{11b} Only one diastereomer is observed, evincing the syn-1*S* configuration. Experiments to relate the solid state and solution structures are in progress. (b) Sabat, M.; Krysan, D. J.; Mackenzie, P. B., manuscript in preparation.

(12) Typical procedure: Compound **2** (3.50 g, 0.00963 mol, 1.00 equiv) was dissolved in benzene (35 mL) and treated with dimethylformamide (7.46 mL) and 1-iodopropane (4.70 mL, 0.0482 mol, 5.00 equiv). Upon irradiation with a sunlamp (GE 275W Model RSW) for 2.5 h at 10 °C, the initially burgundy red solution became emerald green and deposited a blue-green powder. The mixture was subsequently stirred 3 h then transferred to a larger vessel via cannula and diluted with pentane (140 mL) to complete precipitation of the nickel halide. After 4 h of stirring, the supernatant was separated from the nickel halide precipitate via filtration through a filter paper tipped cannula. The near colorless filtrate was evaporated under vacuum (0.1 Torr) to give **3a** as a pale yellow oil (2.84 g, 94.4%, *E/Z* = 9:1). Vacuum distillation (bp 70–75 °C, 0.002 Torr) gave analytically pure **3e** (2.47 g, 82%). Anal. (C₁₇H₃₂O₃Si) C, H.

reactions are highly regioselective (>95%) and stereoselective (*E/Z* = 9:1 before enrichment).¹³ Treatment of the enol ether products with aqueous acid yields the corresponding aldehydes with loss of the optically active auxiliary.¹⁴

Successful reactions are observed with a broad range of halocarbons, including bromobenzene, bromoalkene, and primary and secondary iodoalkanes (Table I).¹⁵ Tertiary alkyl and allylic halides also couple; however, the yields are depressed in these cases (ca. 30% for 2-iodo-2-methylpropane and 3-chloro-1-propene). The reactions of isomerically pure (*E*)- and (*Z*)-2-bromo-1-phenylethenes (entries 3 and 4) show that the reactions proceed with high but not complete retention of bromoalkene double bond configuration. These results closely parallel those of Corey et al.¹⁶ and Hegedus et al.¹⁷ in their pioneering studies of the coupling reactions of simple allylnickel halide complexes with halocarbons.¹⁸ On the basis of this analogy, we assume a similar Ni(I)/Ni(III) radical chain mechanism¹⁹ to be operative in these reactions.

In addition to being of interest as a mild and versatile new homoenolate equivalent methodology, the allylnickel chemistry is of interest as an entry to enantioselective enol functionalization chemistry. As exemplified below, the optically active enol ether products of homoenolate coupling undergo novel aldol equivalent reactions with acetals (eq 4).²⁰



The observation of synthetically useful levels of diastereoselectivity in these reactions suggests that similarly successful reactions will also be possible with other electrophiles. We note further that the optically active dioxolanone products of these reactions are themselves potential starting materials for diastereoselective acetal carbon substitution reactions.²¹ Considered together, these reactions constitute a promising new approach to 3-carbon synthon stereocontrol.

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

Supplementary Material Available: Spectroscopic and analytical data for all new compounds (3 pages). Ordering information is given on any current masthead page.

(13) The enol ethers are subject to enrichment to higher *E/Z* ratios by fractional crystallization (e.g., for **3a**, *E/Z* > 99:1 after two crystallizations from pentane) or by fractional distillation (e.g., for **3e**, *E/Z* = 21:1 after distillation through a 10-cm Vigreux column).

(14) 1 N HCl/THF 1:1, 8 h, 25 °C, Et₂O/H₂O extraction, 95%.

(15) Satisfactory ¹H and ¹³C NMR spectra and elemental analyses have been obtained for all products. The optical purity of **3e** has been established as >95% by aldol equivalent condensation with benzaldehyde dimethyl acetal (cf. eq 4) and subsequent derivatization to (2*R*)-2-benzylhexanoic acid.²⁰

(16) Corey, E. J.; Semmelhack, M. F. *J. Am. Chem. Soc.* **1967**, *89*, 2755.

(17) (a) Hegedus, L. S.; Wagner, S. D.; Waterman, E. L.; Siirala-Hansen, K. *J. Org. Chem.* **1975**, *40*, 593. (b) Hegedus, L. S.; Stiverson, R. K. *J. Am. Chem. Soc.* **1974**, *96*, 3250.

(18) Reviews: (a) Billington, D. C. *Chem. Soc. Rev.* **1985**, *107*, 93. (b) Semmelhack, M. F. *Org. React.* **1972**, *19*, 115. (c) Hegedus, L. S. *J. Organomet. Chem. Libr.* **1976**, *1*, 329. (d) Baker, R. *Chem. Rev.* **1973**, *73*, 487.

(e) Jolly, P. W.; Wilke, G. *The Organic Chemistry of Nickel Volume 1*; Academic Press: New York, 1974.

(19) Hegedus, L. S.; Thompson, D. H. P. *J. Am. Chem. Soc.* **1985**, *107*, 5663.

(20) (a) The aldol product stereochemistry has been securely established.^{20b} (b) Losey, E. N.; Friebe, T. L.; Faunce, J. A.; Mackenzie, P. B., manuscript in preparation.

(21) Diastereoselective nucleophilic substitution of the acetal carbon of optically active 2-aryl- and 2-alkyl-5-phenyl-1,3-dioxolan-4-ones has been reported: Mashraqui, S. H.; Kellogg, R. M. *J. Org. Chem.* **1984**, *44*, 2513. Related reactions of 2-alkyl-6-methyl-1,3-dioxan-4-ones have also been reported: Seebach, D.; Imwinklerried, R.; Stucky, G. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 178. Schreiber, S. L.; Reagan, J. *Tetrahedron Lett.* **1986**, *27*, 2945.