possibilities (2) and (5) suggest that enamines may not be unreactive in some Diels–Alder reactions of "normal" electron demand; this idea is being pursued.

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Registry No. **1a**, 5675-64-9; **1b**, 32363-36-3; **1c**, 63840-06-2; **1d**, 102697-49-4; **1e**, 102697-50-7; **1f**, 22827-60-7; **1g**, 102697-51-8; **1h**, 5434-63-9; **1i**, 86367-70-6; **1j**, 13294-86-5; **1k**, 3008-09-1; **1l**, 6004-64-4; **1m**, 7673-68-9; **1n**, 92855-58-8; **1o**, 6372-65-2; **1p**, 58286-92-3; **1q**, 102697-52-9; **1r**, 102697-54-1; **1s**, 1871-17-6; **1t**, 1521-59-1; **1u**, 102697-55-2; **1v**, 21438-92-6.

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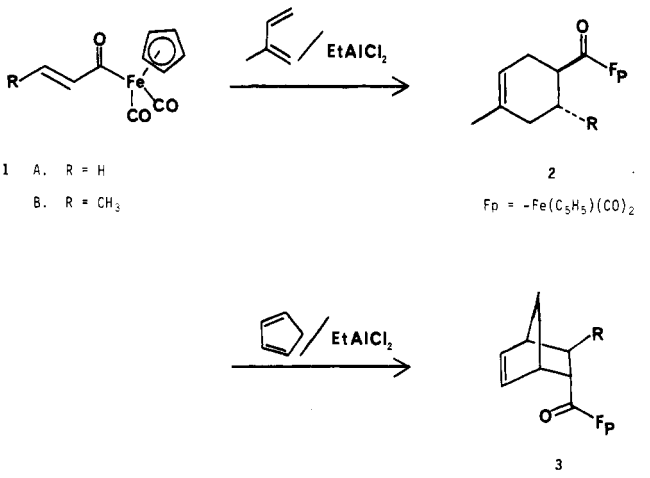
Diels–Alder Reactions of α,β-Unsaturated Acyl–Iron Complexes

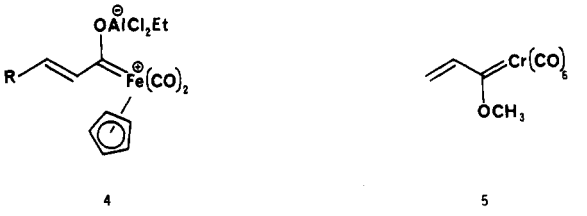
Summary: Lewis acid catalyzed Diels–Alder reactions between alkyl-substituted 1,3-butadienes and (η^1-acryloyl)(η^5-cyclopentadienyl)dicarbonyl(II) complexes have been examined and were found to proceed in excellent yields under mild conditions.

Sir: Acyl–metal complexes containing the (η^5-cyclopentadienyl)dicarbonyliron(II) unit and phosphine-substituted analogues have recently emerged as very versatile intermediates for organic synthesis,[1] being easily converted into esters and amides,[1b] rendering α-protons acidic,[1d] and undergoing facile and stereoselective decarbonylation reactions upon photolysis[2] or treatment with rhodium(I) catalysts.[3] In addition, phosphine-substituted analogues of this unit have seen exciting applications in the area of asymmetric induction.[1a] With these recent developments in mind, we were tempted to investigate the behavior of (η^1-acryloyl)(η^5-cyclopentadienyl)dicarbonyliron(II) complexes **1** (readily available by reaction of α,β-unsaturated acid chlorides with sodium [(η^5-cyclopentadienyl)dicarbonylferrate][4] in Diels–Alder reactions;[5] in this study we report the results of that investigation (Scheme I).

Compound **1b** would not react with cyclopentadiene or isoprene at 0 °C or in refluxing benzene. While the electron-withdrawing ability of the acyl(η^5-cyclopentadienyl)dicarbonyliron(II) group has not been evaluated quantitatively,[6] chemical shifts of the olefinic carbons in compound **1b** (Cα = 130.3, Cβ = 144.9) vs. those of ethyl crotonate (Cα = 123.3, Cβ = 144.0) suggest that polarization of the double bond by the acyl–metal group is considerably less than that of the carbomethoxy group. Upon addition of 1 equiv of ethylaluminum dichloride or diethylaluminum chloride, the reaction proceeds at 25 °C to give compound **3b** in excellent yields (Table I, entries 1 and 2). Ethylaluminum dichloride is the better of the two catalysts; reaction of **1b** and isoprene with diethylaluminum chloride catalyst proceeds in only 38% yield in refluxing benzene, whereas the same reaction with ethylaluminum dichloride catalyst proceeds in 81% yield at 25 °C. The reacting species in alkylaluminum-catalyzed reactions of compound **1b** is best represented by structure **4**; upon addition of ethylaluminum dichloride to compound **1b**, a species is produced having a carbon-13 signal at 306 ppm (acyl carbon)[7] which is more consistent with a Fischer–Carbene complex **4b** rather than an acyl–metal complex.[8,9] Analagous vinyl methoxycarbene complexes of chromium(0) (**5**) have been shown to be excellent dienophiles for Diels–Alder reactions.[10] Other Lewis acid catalysts, boron trifluoride etherate, titanium tetrachloride, and triethylaluminum, were not effective in promoting the desired reaction.

Scheme I. Reaction of α,β-Unsaturated Acyl–Iron Complexes with Dienes and Lewis Acids





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(6) Reactivity patterns from ref 1 suggest that the acyl–metal group behaves similarly to a carbomethoxy group.

(7) Carbene complexes of this type (heteroatom substituted) typically have chemical shifts greater than 300 ppm; for a discussion, see: Formacek, V.; Kreiter, C. G. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 141–142. In a compound related to **3b** (O–Al replaced by H), the chemical shift of the carbene carbon is 314 ppm. Kuo, G. H.; Helquist, P.; Kerber, R. C. *Organometallics* **1984**, *3*, 806–808.

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(10) (a) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1984**, *106*, 7565–7567. (b) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 6726–6727.

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Table I. Reaction of Compound 4 with Dienes

entry	R	diene	catalyst	temp, °C	endo:exo	o,p:m	yield,[a,d] %
1	CH_3	cyclopentadiene	Et_2AlCl_2	25	91:9[a]		84
2	CH_3	cyclopentadiene	$EtAlCl_2$	25	95:5[a]		87
3	CH_3	isoprene	Et_2AlCl_2	80			38
4	CH_3	isoprene	Et_2AlCl_2	25		77:23[a,b]	81
5	CH_3	*trans*-piperylene	$EtAlCl_2$	55	65:35[a]	>98% ortho[e]	72
6	CH_3	3-methyl-1,3-pentadiene	$EtAlCl_2$	55	83:17[a-c]	81:19[a,g]	73
7	H	cyclopentadiene	$EtAlCl_2$	25	>98% endo[e]		99
8	H	isoprene	$EtAlCl_2$	25		86:14[a,b,f]	95

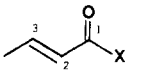
[a] Isolated yields (flash chromatography). [b] The structure of the major product was confirmed by alternate synthesis. [c] This ratio reflects the distribution in the major product only. [d] All compounds gave satisfactory spectral data and combustion analysis; stereochemistries and regiochemistries were assigned based on 200-MHz ^1H NMR data (see supplementary material). [e] The other isomer was not isolated and could not be detected in the crude ^1H NMR spectrum at 200 MHz. [f] The ratio was determined from integration of the cyclopentadienyl protons in the mixture. [g] The major product was designated as ortho relative to the terminal methyl group of the diene.

Table II. Reaction of Dienes with α,β-Unsaturated Esters

entry	diene	dienophile	endo:exo	o,p:m	ref
1	isoprene	methyl acrylate		70:30	11
2	isoprene	methyl acrylate/$AlCl_3$		95:5	14
3	isoprene	methyl crotonate		100:0	11
4	isoprene	ethyl crotonate/$EtAlCl_2$		97:3	15
5	*trans*-piperylene	methyl acrylate	57:43	88:12	16
6	*trans*-piperylene	methyl acrylate/$AlCl_3$	95:5	98:2	16
7	*trans*-piperylene	methyl crotonate	49:51	91:9	11,17
8	cyclopentadiene	methyl acrylate	78:22		11
9	cyclopentadiene	methyl acrylate/$AlCl_3$	94:6		18

In the reaction of compound 4 with dienes, the regiochemistry and stereochemistry observed were consistent with that generally observed in Diels–Alder reactions.[11] The preferred mode of addition is endo (entries 1, 2, 5, 6, 7); very high endo selectivity is observed in reactions with cyclopentadiene, while only modest endo selectivity is observed with 1-methyl-substituted butadienes (entries 5, 6). The reaction also proceeds to give ortho–para selectivity (entries 3, 4, 5, 8), and a terminal substituent controls the regioselectivity to a greater extent than an internal substituent (entry 6).[12] In general, the regioselectivities and stereoselectivities observed in the reaction of 4 with dienes are comparable with those observed for aluminum chloride catalyzed reactions of acrylates and crotonates with dienes (Table II).[13] The exception is reactions with isoprene; in this case the regioselectivity observed is substantially less than that observed in reactions with α,β-unsaturated esters and aluminum chloride. Also, crotonate esters show an increase in regioselectivity with respect to acrylates in reactions with isoprene, while the crotonyl iron complex **4b** is less regioselective than the corresponding acryloyl complex **4a**. A possible explanation for this effect can be found in Table III. Upon complexation with aluminum, the carbon-13 chemical shifts of the α- and β-olefinic carbons in **4b** become nearly indentical, whereas these difference in chemical shifts of the corresponding carbons in ethyl crotonate increases upon complexation with the Lewis acid catalyst, suggesting a decrease in polarization in the double bond upon complexation with aluminum in the iron case and thus a decrease in regioselectivity.

Table III. Carbon-13 Chemical Shifts of Crotonyl Compounds



entry	X	C1	C2	C3	ref
1	$-Fe(C_5H_5)(CO)_2$	252.3	130.3	144.9	19
2	$-Fp/EtAlCl_2$ adduct	303.8	143.8	147.8	
3	$-OC_2H_5$	166.1	123.3	144.0	20
4	$-OC_2H_5/EtAlCl_2$ adduct	174.8	120.3	159.0	

In a typical procedure, to a solution of compound **1b** (0.315 g, 1.28 mmol) in benzene (8 mL) under nitrogen at 25 °C was added a solution of ethylaluminum dichloride in hexane (1.0 M, 1.3 mL, 1.3 mmol),[21] followed by addition of cyclopentadiene (0.3 mL). The mixture was allowed to stir 2 h at 25 °C or until complete as diagnosed by TLC. The reaction mixture was cooled to 0 °C, aqueous ammonia solution (2 mL) was added, and the mixture was allowed to stir 2 min. The mixture was filtered through alumina and washed exhaustively with methylene chloride. The solvent was removed on a rotary evaporator and the residue was purified via flash chromatography on silica gel.

The Diels–Alder reaction using acyl–iron complexes is very mild, high-yielding reaction and in many cases gives very high regio- and stereoselectivity. The products of the reaction are air-stable and the acyl–iron grouping is subject to a wide variety of further manipulations which have potential applications in organic synthesis. We are presently examining further reactions of these aluminum-complexed acyl–metal complexes and their potential applications.

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Registry No. **1a**, 94486-03-0; **1b**, 102734-01-0; rp-**2a**, 102649-01-4; *m*-**2a**, 102829-69-6; *p*-**2b**, 102648-96-4; *m*-**2b**, 102648-97-5; *endo*-**3a**, 93757-27-8; *endo*-**3b**, 102648-95-3; *exo*-**3b**, 102734-02-1; **4a**-*trans*-piperlene reaction product (*o*, *endo*-isomer), 102648-98-6; **4a**-*trans*-piperylene reaction product (*o*, *exo*-isomer),

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(21) Available from Aldrich Chemical Company as a 1.0 M solution.

102734-03-2; **4a**-3-methyl-1,3-pentadiene reaction product (*o*, *endo*-isomer), 102648-99-7; **4a**-3-methyl-1,3-pentadiene reaction product (*o*, *exo*-isomer), 102734-04-3; **4a**-3-methyl-1,3-pentaidene reaction product (*m*-isomer), 102649-00-3; cyclopentadiene, 542-92-7; isoprene, 78-79-5; *trans*-piperylene, 2004-70-8; 3-methyl-1,3-pentadiene, 4549-74-0.

Supplementary Material Available: Spectroscopic data for compounds in Table I (13 pages). Ordering information is given on any current masthead page.

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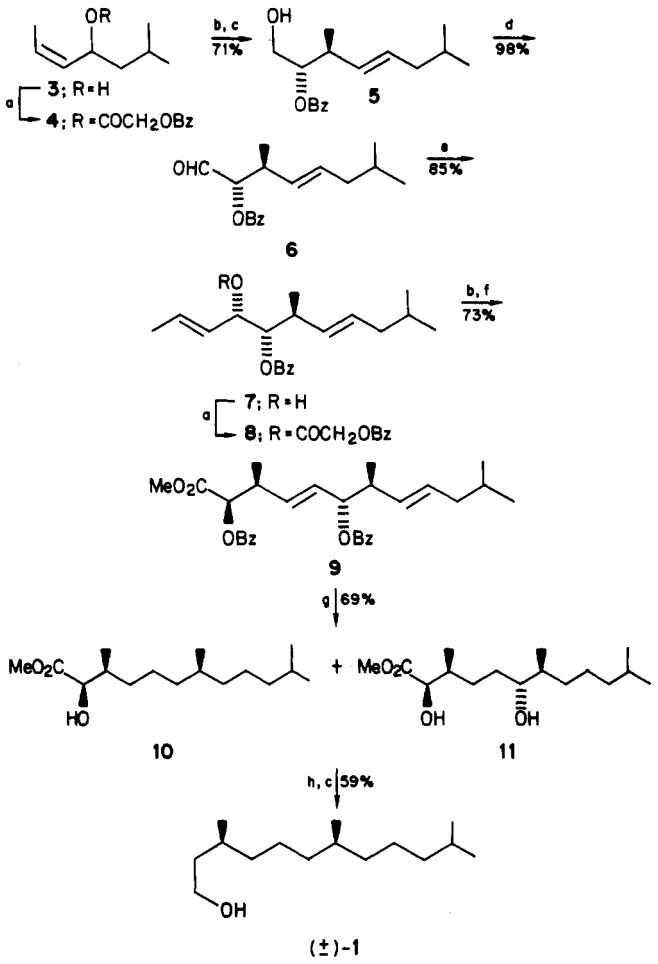
An Effective Strategy for Acyclic Synthesis via Iterative Rearrangement of Allylic Glycolates. Synthesis of a Pine Sawfly Pheromone

Summary: The stereocontrolled preparation of extended acyclic systems using the iterative enolate Claisen rearrangement of allylic glycolates is described. This strategy has been demonstrated in the stereospecific synthesis of a pine sawfly pheromone.

Sir: The development of stereoselective techniques for use in the linear elaboration of complex acyclic targets has been a focus of considerable attention in recent years.[1-4] While linear construction of extended acyclic systems offers unique synthetic advantages, this strategy places rigorous demands on the complement of reactions employed in the homologation of a nascent acyclic intermediate. Since stereochemical heterogeneity at any stage of a linear sequence will be propagated in subsequent transformations, the degree of stereocontrol required of each reaction in the sequence is high.

The Claisen and related [3,3] and [2,3] sigmatropic rearrangements occupy a prominent position among the procedures which can effectively homologate an existing acyclic intermediate with stereochemical induction at newly formed, remote chiral centers.[1,3] A powerful and potentially general strategy for acyclic synthesis is one in which the acyclic framework is developed by an iterative series consisting of sigmatropic rearrangement followed by nucleophilic homologation of the rearrangement product

Scheme I[a]



[a] Reagents: (a) $BzOCH_2COCl$, pyridine; (b) LDA, Me_3SiCl, THF, 78–0 °C; (c) $LiAlH_4$; (d) $(COCl)_2$, Me_2SO, NEt_3; (e) $((E)$-1-propenyl$)_2CuLi$, Et_2O, −78 °C, $MgBr_2{\cdot}Et_2O$; (f) aqueous NH_4Cl, CH_2N_2, Et_2O; (g) Pd–C, H_2, MeOH; (h) MsCl, pyridine.

to give a new substrate for rearrangement.[4] Practical realization of this approach has been complicated by loss of stereochemical fidelity during either the rearrangement or homologation[5] step. Recently, we and others have investigated the enolate Claisen rearrangement of allylic glycolates and demonstrated the potential of this system as an entry to functionalized acyclic intermediates.[6] The high diastereoselectivity exhibited in the rearrangement of allylic glycolates and the potential of the resulting α-alkoxy esters for further stereoselective homologation, via chelation-controlled addition of vinyl nucleophiles, suggested to us that these substrates are uniquely suited for incorporation into an iterative sigmatropic sequence.

The effectiveness of the glycolate Claisen sequence as an iterative vehicle for acyclic homologation is demon-

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