Table I. Yields of Phenylnitromethanes (2) from Phenylacetic Acids (1)

product no.	yield, %	mp (°C)[a] or bp (°C)/p (mm)	lit. mp (°C) or bp (°C)/p (mm) or mol formula[b]	IR (film)[c] ν, cm⁻¹	¹H NMR (CDCl₃/TMS)[d] δ, ppm	¹³C NMR (CDCl₃/TMS) δ, ppm	MS (70 eV)[e] m/e (%)
2a	72[f]	80–83/2.7	90–92/3[6]	1554, 1375	5.42 (s, 2 H), 7.42 (s, 5 H)	79.7, 128.8, 129.7	136 ($M-1^+$, 1.4), 91 (100)
2b	83[g]	64–65 (167.2)[b]	$C_8H_9NO_3$	1559, 1373	3.83 (s, 3 H), 5.46 (s, 2 H), 6.9–7.5 (m, 4 H)	55.4, 74.4, 110.8, 118.5, 120.6, 131.5, 131.9, 158.0	167 (M^+, 8), 131 (32), 121 (100)
2c	56,[f] 72[h]	82–85/0.15 (167.2)[b]	$C_8H_9NO_3$	1555, 1374	3.82 (s, 3 H), 5.40 (s, 2 H), 6.9–7.5 (m, 4 H)	55.1, 79.8, 115.2, 115.4, 122.0, 129.9, 130.9, 159.8	167 (M^+, 7), 151 (14), 121 (100)
2d	66,[f] 77[h]	90–95/0.15	102–103/0.5[4]	1553, 1373	3.82 (s, 3 H), 5.36 (s, 2 H), 6.93 (bd, 2 H), 7.40 (bd, 2 H)	55.1, 79.3, 114.2, 121.8, 131.3, 160.6	167 (M^+, 0.4), 166 (2.2), 121 (100)
2e	57,[f] 63[h]	91–92 (197.2)[b]	$C_9H_{11}NO_4$	1555, 1373	3.90 (s, 6 H), 5.37 (s, 2 H), 6.8–7.1 (m, 3 H)	54.4, 74.1, 109.7, 111.1, 120.7, 121.5, 147.7, 148.9	197 (M^+, 1), 151 (100)
2f	70[h]	105–107/0.15 (197.2)[b]	$C_9H_{11}NO_4$	1559, 1372	3.74–3.75 (s, 6 H combined), 5.40 (s, 2 H), 6.8–7.0 (m, 3 H)	55.5, 55.8, 74.3, 111.8, 116.0, 117.6, 119.0 152.1, 153.3	197 (M^+, 10), 151 (100), 121 (77)

[a] Uncorrected, measured on a Kofler hot-stage microscope. [b] Satisfactory microanalysis obtained: C, ±0.21; H, ±0.11; N, ±0.14. [c] Recorded on a Perkin-Elmer 1800 FT-infrared spectrophotometer. [d] Obtained on JEOL FX-90Q spectrometer. [e] Recorded on a VG 7070E spectrometer. [f] Purified by distillation. [g] Purified by recrystallization from methylene chloride–hexanes. [h] Purified by silica gel chromatography (25 g); methylene chloride.

Experimental Section

(Methoxyphenyl)nitromethanes. General Procedure. A solution of the methoxyphenylacetic acid (10.2 mmol) in THF (8 mL) was added to a magnetically stirred, chilled (0 °C) solution of LDA (23.5 mmol of *n*-butyllithium and 24.5 mmol of diisopropylamine) and HMPA (10.2 mmol) in THF (20 mL) under nitrogen. The yellow solution was stirred at room temperature for 1.5 h and then chilled to −60 °C. Addition of methyl nitrate (1.9 mL, 30.6 mmol) to the dianion solution produced a brownish yellow solution, which faded to the original yellow color. The reaction was stirred for 1 h, and then acetic acid (1.4 mL) was added. The mixture was allowed to warm to 0 °C, at which point hydrochloric acid (12 mL, 4 N) was added and evolution of carbon dioxide occurred. Water (20 mL) and ether (20 mL) were added and the layers separated. The water layer was extracted again with ether (20 mL), and the combined organic phases were successively washed with water (20 mL), aqueous bicarbonate (2 × 25 mL), hydrochloric acid (2 × 20 mL of 0.01 N), water (2 × 20 mL), and brine. The organic solution was dried ($MgSO_4$), filtered, and evaporated at reduced pressure. Final purification of the product was performed as indicated in Table I. All products were homogeneous by TLC, ¹H NMR, and ¹³C NMR.

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Registry No. **1a**, 103-82-2; **1b**, 93-25-4; **1c**, 1798-09-0; **1d**, 104-01-8; **1e**, 93-40-3; **1f**, 1758-25-4; **2a**, 622-42-4; **2b**, 33241-80-4; **2c**, 53016-47-0; **2d**, 29559-26-0; **2e**, 114131-33-8; **2f**, 79101-76-1; CH_3ONO_2, 598-58-3.

Communications

Effect of Phosphine Substitution on Nucleophilic Addition to α,β-Unsaturated Acyliron Complexes

Summary: Michael addition reactions of α,β-unsaturated acyliron complexes, where the iron atom is chiral, have been examined. Iron complexes containing various phosphine ligands were examined to determine if the steric bulk of phosphine ligands affects the diastereoselectivity in the reaction.

Sir: Chiral-at-iron acyl complexes of the type Cp(CO)(PPh₃)FeCOR have been used extensively as chiral enolate equivalents.[2] Alkylation of enolate anions derived from these complexes, and Michael addition and Diels–Alder[3] reactions with α,β-unsaturated complexes all proceed with a high degree of diastereoselectivity. It has been proposed that this selectivity arises from the ability of the triphenylphosphine ligand to lock the acyl ligand in a conformation where the acyl C=O is anti with respect to the carbonyl ligand (Figure 1, complex 4), and from the bulky triphenylphosphine ligand blocking one face of the molecule. On the basis of extended Hückel and ab initio SCF MO calculations,[4] the conformational locking of the acetyl ligand in 4 was attributed to a steric interaction between the acyl oxygen and a phenyl ring of the triphenylphosphine ligand, which was twisted out of plane. Alternatively, it has been proposed that a "metalloanomeric effect"[5] is inducing the acyl oxygen atom to go anti to the carbonyl ligand.

Reactions involving chiral-at-iron complexes of the type Cp(CO)(L)FeCOR, where L ≠ PPh_3, have not been ex-

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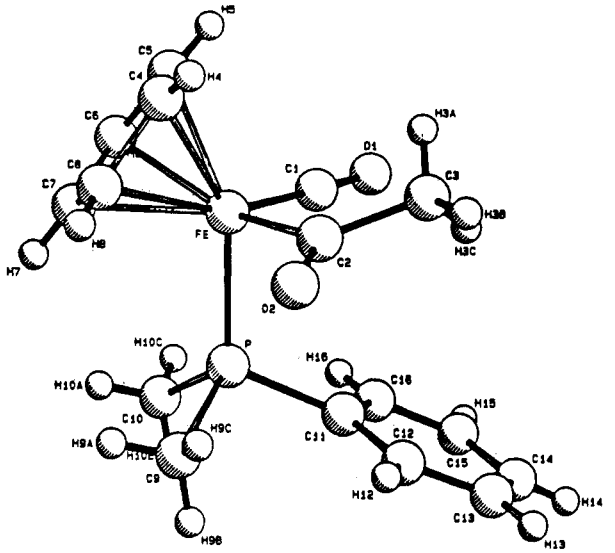
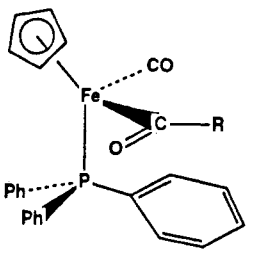


3

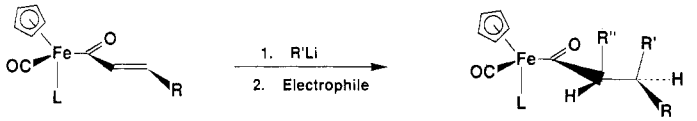


4

R = -$CH_2CHOHCH_2CH_3$

Figure 1. Crystal structures for complexes **3** and **4**.[11,12]

Table I. Diastereoselectivity in the Tandem Michael Addition–Alkylation of α,β-Unsaturated Acyliron Complexes



1. R'Li
2. Electrophile

1 A. L = PPh_3 D. L = $P(n\text{-}C_4H_9)_3$ 2

B. L = $P(p\text{-}C_6H_4CF_3)_3$ E. L = $P(OPh)_3$

C. L = $P(CH_3)_2Ph$

entry	L	R	R′	electrophile	R″	yield %	diastereoselectivity[a]
1	A	CH_3	Ph	H_2O	H	87	29:1[b]
2	B	CH_3	Ph	H_2O	H	84	39:1[c]
3	C	CH_3	Ph	H_2O	H	76	18:1[d]
4	C	CH_3	Ph	CH_3I	CH_3	72	24:1[d]
5	C	Ph	CH_3	H_2O	H	63	32:1[d]
6	D	CH_3	Ph	H_2O	H	71	11:1[d]
7	D	Ph	CH_3	H_2O	H	15	22:1[d]
7	D	Ph	CH_3	H_2O	H	49	3:1[d,e]
8	E	CH_3	Ph	H_2O	H	0	

[a] All reactions were conducted at −78 °C and allowed to proceed to completion as judged by TLC analysis. [b] Spectral data agree with that presented in ref 2a. [c] The stereochemistry of the product was assigned based on analogy to the products of entry 1. [d] See supplementary material for the spectral characterization of the major product. [e] Tetramethylethylenediamine was added to the reaction mixture.

tensively investigated.[6] We have examined the addition of nucleophiles to chiral α,β-unsaturated acyliron complexes which bear several different phosphine ligands. The high diastereoselectivity that we have obtained in these reactions relates to the issue of conformational locking of the acyl ligand in phosphine-substituted acyliron complexes.

Our results are summarized in Table I. High diastereoselectivities were obtained in Michael addition reactions of organolithium reagents with crotonyl- and cinnamoyliron complexes,[7] regardless of which phosphine ligand was present at iron. The relative configuration of the two chiral centers of complex **2** was assigned by using Davies' model,[2b] where the enone portion of the acyliron complex exists in the s-cis conformation, the acyl oxygen is anti with respect to the carbonyl ligand, and the nucleophile attacks from the side opposite the phosphine ligand (the reacting conformation is depected by structure **1**). The minor isomer obtained in entry 3 is identical with the major product in entry 5 and vice versa. The same parallel exists between the major and minor products in entries 6 and 7. As expected, a high degree of stereocontrol is also obtained from reactions at the carbon α to the acyl group. The tandem Michael addition–alkylation also proceeded with a high degree of diastereoselectivity (entry 4); only two stereoisomers could be isolated from the reaction in a 24:1 ratio. The reaction did not work if phosphite ligands were substituted for phosphine ligands; only decomposition products were obtained from the reaction of phenyllithium with complex **1E**. The reaction of complexes **1C** and **1D** with

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(7) These complexes were prepared from the corresponding dicarbonyl complexes. First decarbonylation was induced via irradiation with a tungsten lamp to give the vinyl–Fp complexes. Treatment of the vinyl–Fp complexes with phosphines or phosphites in refluxing THF for 3–12 h gave the phosphine–substituted complexes.

Table II. Dihedral Angles (in deg) within Complexes 3 and 4

dihedral angle	complex 3	analogous angle in complex 4
O2-C2-Fe-C1	162.5	169
Fe-P-C11-C16	86.0	67
C2-Fe-P-C11	60.0	34

organolithium reagents was noticeably slower than analogous reactions using **1A** and **1B**, presumably due to the more electron-donating nature of alkylphosphine vs arylphosphine ligands.[8] Tetramethylethylene diamine (TMEDA) was necessary to obtain good yields of adducts in the addition of methyllithium to complex **1D**. Lower diastereoselectivities were obtained with TMEDA present, presumably due to disruption of methyllithium aggregates,[9] which would make methyllithium sterically smaller.

It is postulated that steric interaction between a phenyl ring, twisted out of plane, and the acetyl oxygen is the cause of the conformational locking of the acetyl ligand of complex **4**. As can be seen from the X-ray structure of complex **3**[10] (Figure 1), the acetyl oxygen is anti with respect to the carbonyl ligand, in spite of the absence of tilted phenyl rings (Table II; Fe-P-C11-C16 dihedral angle = 86° in complex **3**, compared to a value of 67° for the corresponding dihedral angle in complex **4**). Clearly, the stability associated with the anti conformation does not arise simply from steric interactions involving tilted phenyl rings. The phenyl ring in **3** is situated directly underneath the acetyl ligand, which presumably accounts for the high stereoselectivity observed in Michael addition reactions to complex **1C**. If steric interactions are not responsible for conformational locking of the acyl ligand, then similar conformational preferences can be expected in complex **1D** as well, where the bulky *n*-butyl groups can effectively block one face of the acyl ligand. As can be seen in entries 6 and 7, the Michael addition reaction is also highly diastereoselective with the tributylphosphine complex **1D**.

In summary, the reaction of organolithium reagents with α,β-unsaturated acyliron complexes of the type $Cp(CO)(PR_3)FeCOCH{=}CHR'$, is highly diastereoselective. This high diastereoselectivity can be obtained regardless which phosphine ligand is present at iron; a triphenylphosphine ligand is not required to obtain high diastereoselectivity. Contrary to earlier suggestions, conformational preferences of the acyl group in these complexes is clearly due to more than steric interactions between the acyl oxygen and the aryl groups of a triphenylphosphine ligand. We are further investigating the reasons for this conformational locking and its potential for further use in organic synthesis.

Acknowledgment. We thank the donors of Petroleum Research Fund, administered by the American Chemical Society, the State of Maryland, and the General Research Board of the University of Maryland for financial support of this work. Support by the NSF (CHE-84-02155) for purchase of the diffractometer system is gratefully acknowledged.

Registry No. **1** (L = CO, R = CH_3), 74087-37-9; **1** (L = CO, R = Ph), 72028-88-7; **1A** (R = CH_3), 96645-44-2; **1B** (R = CH_3), 114466-65-8; **1C** (R = CH_3), 114466-66-9; **1C** (R = Ph), 114466-67-0; **1D** (R = CH_3), 114466-68-1; **1D** (R = Ph), 114466-69-2; **1E** (R = CH_3), 114490-27-6; **2A** (R = CH_3, R′ = Ph, R″ = H), 41529-61-7; **2B** (R = CH_3, R′ = Ph, R″ = H), 114466-70-5; **2C** (R = CH_3, R′ = Ph, R″ = H), 114466-71-6; **2C** (R = CH_3, R′ = Ph, R″ = CH_3), 114466-72-7; **2C** (R = Ph, R′ = CH_3, R″ = H), 114529-74-7; **2D** (R = CH_3, R′ = Ph, R″ = H), 114466-73-8; **2D** (R = Ph, R′ = CH_3, R″ = H), 114529-75-8; **3**, 32993-87-6; **4**, 114529-76-9; PPh_3, 603-35-0; $P(C_6H_4CF_3)_3$, 13406-29-6; $P(CH_3)_2Ph$, 672-66-2; $P(n\text{-}C_4H_9)_3$, 998-40-3; $P(OPh)_3$, 101-02-0.

Supplementary Material Available: Spectral characterization for the products in Table I and X-ray data (atomic coordinates, temperature factors, bond lengths and angles) for complex **3** (6 pages); structure factors for complex **3** (19 pages). Ordering information is given on any current masthead page.

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(10) X-ray intensity data collected from a 0.2 × 0.3 × 0.3 mm crystal sealed in a glass capillary on an Enraf Nonius CAD-4 diffractometer (Mo Kα, λ = 0.71069 Å graphite monochromator). Triclinic, $P\bar{1}$, Z = 2, a = 7.494 (2) Å, b = 8.665 (2) Å, c = 12.957 (4) Å, α = 106.85 (3)°, β = 97.96 (3)°, γ = 93.24 (2)°. 3304 total data measured to θ_{max} of 26°; 3261 unique data; 2724 data with $I > 3\sigma(I)$. Structure refinement by full-matrix least-squares with anisotropic temperatures for Fe, P, C, and O and isotopic terms for H. Final R and weighted R values of 0.034 and 0.056. Calculations were performed on a MicroVax II computer with the TEXSAN system of programs.
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Rhodium Carbenoid Induced Cycloadditions of Substituted 1-Diazo-2,5-pentanediones

Summary: Treatment of substituted 1-diazo-2,5-pentanediones with rhodium(II) acetate results in cyclization of the intermediate rhodium carbenoid to give a six-ring carbonyl ylide which readily undergoes both inter- and intramolecular dipolar cycloadditions.

Sir: The role of α-diazo carbonyl compounds in organic synthesis is well established and in recent years much effort has been devoted to the study of the effect of different transition-metal catalysts on these reactions.[1-6] We recently reported that the rhodium metal induced reaction of (enoxycarbonyl)-α-diazoacetophenones results in carbonyl ylide formation followed by intramolecular 1,3-dipolar cycloaddition across the neighboring π-bond.[7] Our initial forays into this tandem cyclization-cycloaddition chemistry involved systems in which the keto rhodium carbenoid and the remote carbonyl were attached in a

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