ments. The fact that radical anions might have a concentration-dependent structure justifies the search for information under the above-mentioned conditions. It is felt that this information is more realistic and directly applicable by the organic chemist who deals with the chemistry of radical anions. Although solutions of radical anions may contain a plethora of species which differ in the degree of association, the magnetic state, the ion-pair situation, etc., our results, in certain instances, reveal that the situation is astonishingly simple. For example, the abrupt break in the $\Delta\nu$ vs. C curve in Figure 4 hardly suggests the existence of more than one thermodynamically distinct species, under those conditions.

Experimental Section

A Varian A60A NMR spectrometer was used for the solvent shift measurements. Details of the method have been given elsewhere.[7] In certain instances a Varian FT-80 spectrometer was employed (see the preceding discussion). The great stability of this instrument makes the use of external markers unnecessary. In order to obtain a lock, C_6D_6 was sealed in thin-walled capillaries. Under these conditions the THF proton bands exhibited resonances centered at 502.4 ± 0.3 and 355.6 ± 0.3 Hz from the "zero" of the instrument. The indicated values were obtained from a set of seven NMR tube–capillary pairs. Paramagnetic solvent shifts were measured relative to the THF bands in the absence of any paramagnetic solute, namely, by subtracting the resonance frequency of the α-proton band of THF, in the paramagnetic solution, from 502.5 Hz and the resonance frequency of the β THF band from 355.5 Hz. In the cases where a double internal reference was used, i.e., THF and cyclohexane, the solvent shifts were referred to the relevant resonance bands in 80:20 (v/v) THF–cyclohexane, in the absence of any solute. The centers of these bands were 500.3 (α-proton band of THF), 353.3 (β protons of THF), and 327.2 Hz (cyclohexane) downfield from the "zero" of the instrument. Bulk paramagnetism was measured with a Gouy balance. The Raman spectra were recorded on a Jobin-Yvon Ramanor Model HG-2S spectrometer. The exciting radiation was provided by a Spectra Physics Model 165-03 argon laser. The aromatic hydrocarbons were commercial products of 99% purity or better, and they were used without further purification. Tetrahydrofuran was purified as described previously.[6] Diethyl ether and triethylamine were distilled from lithium aluminum hydride under argon shortly before use. Solutions of radical anions were prepared by stirring strictly equivalent amounts of the hydrocarbon and the metal in THF for 16–24 h under an atmosphere of pure argon and using a glass-coated stirring bar. Solutions of the radical anions were standardized as previously described.[7] Aromatic hydrocarbon dianions were prepared in 0.5–1.0 M solutions in THF by following the method for preparing the radical anions. Double titrations of dianion solutions were carried out by using ethylene bromide.[3]

Carbonation of "Lithium Phenanthrene Dianion". Phenanthrene (1.78 g, 10 mmol), lithium chips (0.140 g), and THF (18 mL), were stirred under argon for 18 h at room temperature. The reaction mixture was diluted with 10 mL of anhydrous THF and carbonated. From the carbonation mixture was isolated an acid fraction which weighed 1.5 g and was a glassy solid. The NMR spectrum of this material exhibited the following resonances in parts per million downfield from Me_4Si: 1.17, (br s), 3.23 (br s), 3.63 (br s), 4.25 (br s), 5.10 (sharp s). The number of aliphatic plus olefinic protons was nearly equal to the number of aromatic ones. The neutral fraction from the carbonation mixture (0.70 g) exhibited resonances in the aliphatic region the NMR spectrum, namely: 0.88 (diffuse t), 1.23 (br s), 2.70 (br s), 3.35 (diffuse t).

Carbonation of Potassium Naphthalene Radical Anion in THF–Et_3N. A solution of potassium naphthalene radical anion prepared from 2.6 g (ca. 20 mmol) of naphthalene, 0.79 g (ca. 20 mol) of potassium, and 20 mL of THF was diluted with 20 mL of anhydrous triethylamine and carbonated. From the carbonation mixture by a conventional workup was isolated 2.0 g of an acid. This acid exhibited an NMR spectrum identical with that obtained by carbonation of $K^+C_{10}H_8^-\cdot$ in pure THF, namely: 4.33 (unsym d), 6.22 (unsym br d), 6.95–7.45 (unsym br m).

Acknowledgment. We thank Dr. G. C. Papavassiliou for recording the laser Raman spectra. We are indebted to a referee for suggesting an alternative interpretation of the "individuality" of molar paramagnetic solvent shifts.

Registry No. THF, 109-99-9; biphenyl radical anion·Li^+, 34467-57-7; *p*-terphenyl radical anion·Li^+, 34509-62-1; *p*-terphenyl radical anion·Na^+, 34525-85-4; naphthalene radical anion·Li^+, 7308-67-0; naphthalene radical anion·Na^+, 3481-12-7; naphthalene radical anion·K^+, 4216-48-2; 2-*tert*-butylnaphthalene radical anion·Li^+, 83816-80-2; 2,6-di-*tert*-butylnaphthalene radical anion·Li^+, 73049-04-4; phenanthrene radical anion·Li^+, 34509-57-4; phenanthrene radical anion·Na^+, 14252-59-6; phenanthrene radical anion·K^+, 41887-04-1; anthracene radical anion·Li^+, 34509-60-9; anthracene radical anion·Na^+, 12261-48-2; anthracene radical anion·K^+, 34475-54-2; pyrene radical anion·Li^+, 10349-29-8; pyrene radical anion·Na^+, 34510-87-7; pyrene radical anion·K^+, 34510-72-0; chrysene radical anion·Li^+, 13090-88-5; chrysene radical anion·Na^+, 42900-91-4; chrysene radical anion·K^+, 34469-93-7; *cis*-stilbene radical anion·Li^+, 83816-81-3; *trans*-stilbene radical anion·Li^+, 83816-82-4; *trans*-stilbene radical anion·Na^+, 62913-93-3; chrysene dianion·$2K^+$, 83831-03-2; chrysene dianion·$2Na^+$, 83831-05-4; chrysene dianion·$2Li^+$, 83831-06-5; pyrene dianion·$2Li^+$, 60740-03-6; phenanthrene dianion·$2Li^+$, 54667-02-6; *p*-terphenyl dianion·$2Li^+$, 83831-08-7; anthracene dianion·$2K^+$, 39399-93-4; anthracene dianion·$2Na^+$, 11065-56-8; anthracene dianion·$2Li^+$, 39399-94-5.

β-Lactam Synthesis Using Organoiron Intermediates. Preparation of 3-Carbomethoxycarbapenam

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Received June 11, 1982

Claisen rearrangement of the vinyl allyl ether derived from methyl pyruvate diallyl ketal provides a convenient route to methyl 2-oxo-5-hexenoate (**3**). Exchange complexation with η-$C_5H_5Fe(CO)_2$(isobutylene)PF_6 in methylene chloride gives the olefin complex **4**, and this is transformed to the pyrroline complex **5** on exposure to ammonia. Reduction of this substance with sodium borohydride yields a mixture of stereoisomeric pyrrolidine complexes **6**-c,t. This is converted to a mixture of stereoisomeric chelate complexes **10** and thence by oxidation with silver oxide or air to the stereoisomeric 3-carbomethoxycarbapenams **11a,b**.

Current interest in fused ring β-lactams, especially those of the carbapenem[1] class, led us to examine methods for the synthesis of the parent saturated ring system using organoiron intermediates based on the η-$C_5H_5Fe(CO)_2$

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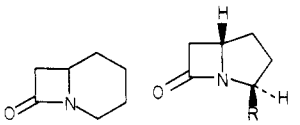
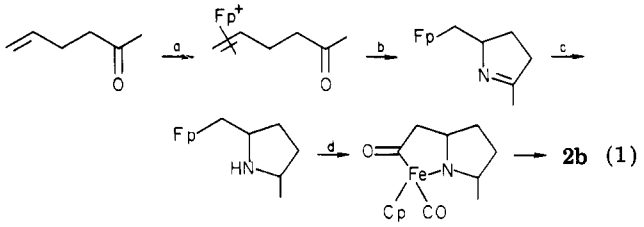
functionality. We had earlier reported the use of this chemistry for the construction of the fused ring β-lactams **1**[2] and **2a,b**.[2,3]



1 **2a**, R = H; **b**, R = Me

The sequence used in the synthesis of **2b** serves to illustrate the facility with which the basic ring skeleton may be assembled and the unique regenerative properties of the η^5-$C_5H_5Fe(CO)_2$ group, which allows for its successive use, first in activating an olefin for nucleophilic addition and then in carbonylation and ring closure (eq 1).

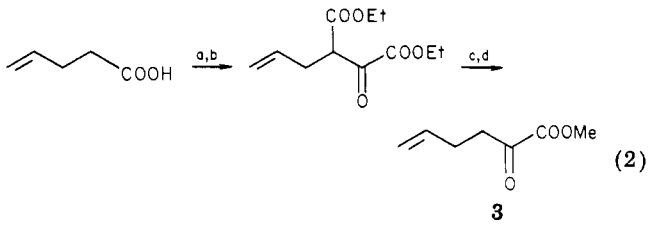


2b (1)

Fp = η-$C_5H_5Fe(CO)_2$. (a) Fp$^+$  BF_4^-, CH_2Cl_2, Δ; (b) NH_3, CH_2Cl_2, 25 °C; (c) $NaBH_4$, EtOH, 25 °C; (d) CH_3CN, 65 °C. (e) Ag_2O, THF, 25 °C.

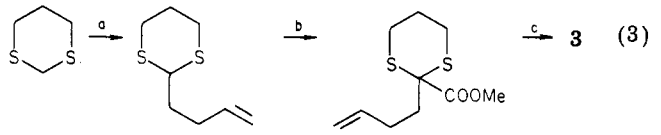
The present paper extends this methodology to the synthesis of 3-carbomethoxycarbapenam. The synthesis of the corresponding benzyl and *tert*-butyl esters employing a more classical sequence has recently been reported.[4]

The requisite starting material, methyl 2-oxo-5-hexenoate (**3**), was initially prepared by condensation of diethyl oxalate with ethyl 4-pentenoate,[5] followed by hydrolysis and decarboxylation (eq 2), but this sequence proved la-



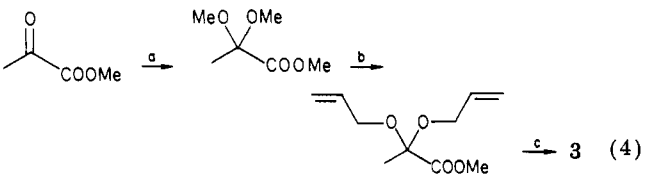
3 (2)

(a) EtOH, PhH, TsOH; (b) NaOEt, EtOCOCOOEt; (c) HCl, H_2O, Δ; (d) MeOH, PhH, TsOH.



(3)

(a) *n*-BuLi, $CH_2CHCH_2CH_2Br$, 0 °C; (b) *n*-BuLi, ClCOOMe, −78 °C. (c) $AgNO_3$, *N*-chlorosuccinimide, CH_3CN-H_2O

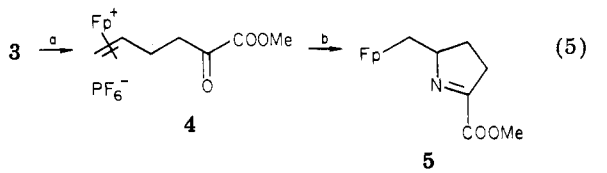


(4)

(a) $HC(OMe)_3$, MeOH, TsOH, 25 °C; (b) CH_2CHCH_2OH, TsOH, PhH, 68 °C; (c) 170 °C.

borious. An alternative sequence involving alkylation of 1,3-dithiane with 4-bromo-1-butene followed by acylation with methyl chloroformate was therefore examined[6] (eq 3). Although the disubstituted dithiane could readily be prepared in moderate yield, oxidative hydrolysis[7] gave only low yields of **3**, especially when carried out on a gram scale. The Claisen rearrangment sequence (eq 4) proved finally to be the method of choice. Although the Claisen rearrangement has found extensive use in the allylation of aldehydes, ketones, and carboxylic acid derivatives,[8] it does not appear to have been applied to vinyl ethers derived from pyruvic esters.[9] In practice, transketalization of methyl pyruvate dimethyl ketal with allyl alcohol, followed by heating to 170 °C, allowed the preparation of **3** to be carried out on a large scale and in good yield.

Exchange complexation[10] of **3** with Fp(isobutylene)BF_4 proceeded readily in refluxing methylene chloride, but the product proved difficult to crystallize. However, when the exchange was carried out by using the Fp(isobutylene)PF_6 complex, the product salt **4** (eq 5) was readily isolated as



(5)

4 **5**

(a) Fp(isobutylene)PF_6, CH_2Cl_2, 40 °C; (b) NH_3, CH_2Cl_2, −25 to +25 °C

a yellow crystalline solid in good yield. Although contaminated with a small amount of $((CO)_3CpFe)^+PF_6^-$, the crude product can nevertheless be used directly for conversion to the pyrroline complex **5**.

Attempted catalytic reduction of **5** with platinum or palladium oxide, 10% palladium on carbon black, or Rainey nickel led to Fe–C bond cleavage. Reduction with sodium borohydride in methanol at 0 °C gave a 2:1 mixture of the *cis*- and *trans*-1,3-disubstituted pyrrolidine complexes **6**-c and **6**-t (85%), when care was taken during workup of the reaction mixture to maintain the aqueous methanol solutions at a pH greater than 7.[11] However, when the reaction mixture was quenched with aqueous HCl, and the pH adjusted to 7, an additional product, which proved to be the piperidine complex **7**, was formed

(1) Saltzmann, T. N.; Ratcliffe, R. W.; Chistensen, B. G.; Bouffard, F. A. *J. Am. Chem. Soc.* **1980**, *102*, 6161 and references therein. Bouffard, F. A.; Johnson, D. B. R.; Christensen, B. G. *J. Org. Chem.* **1980**, *45*, 1130. Johnson, D. B. R.; Schmitt, S. S.; Christensen, B. G. *Ibid.* **1980**, *45*, 1125, 1142.

(2) Wong, P. K.; Madhavarao, M.; Marten, D. F.; Rosenblum, M. *J. Am. Chem. Soc.* **1977**, *99*, 2823.

(3) Berryhill, S. R.; Rosenblum, M. *J. Org. Chem.* **1980**, *45*, 1984.

(4) Schmitt, S. M.; Johnson, D. B. R.; Christensen, B. G. *J. Org. Chem.* **1980**, *45*, 1135.

(5) Lindstead, R. P.; Rydon, H. N. *J. Chem. Soc.* **1933**, 580.

(6) Corey, E. J.; Seebach, D. *Angew Chem., Int. Ed. Engl.* **1965**, *4*, 1075. Corey, E. J.; Seebach, D. *J. Org. Chem.* **1975**, *40*, 231.

(7) Corey, E. J.; Erickson, B. W. *J. Org. Chem.* **1971**, *36*, 3553.

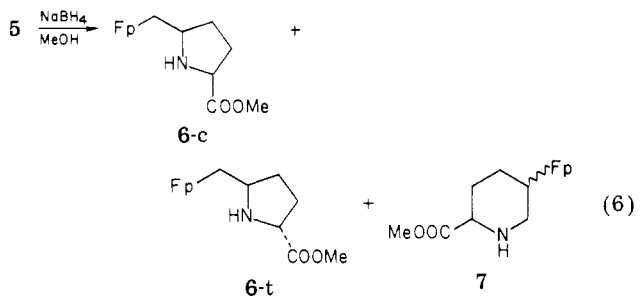
(8) Ziegler, F. E. *Acc. Chem. Res.* **1977**, *10*, 227. Rhoads, S. J.; Raulins, N. R. *Org. React.* **1975**, *22*, 1. Bennett, G. B. *Synthesis* **1977**, 589.

(9) The Claisen rearrangement of allyl vinyl ethers derived from diosphenols has recently been reported. Dauben, W. G.; Ponaras, A. A.; Chollet, A. *J. Org. Chem.* **1980**, *45*, 4413. Ponaras, A. A. *Tetrahedron Lett.* **1980**, *21*, 4803.

(10) Cutler, A.; Ehntholt, D.; Lennon, P.; Nicholas, K.; Marten, D. F.; Madhavarao, M.; Raghu, S.; Rosan, A.; Rosenblum, M. *J. Am. Chem. Soc.* **1975**, *97*, 3149.

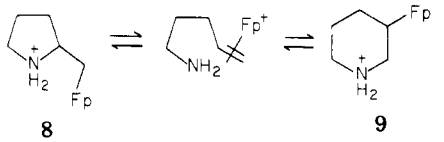
(11) A further examination of the mixture of products derived from sodium borohydride reduction of the related 2-methylpyrroline complex (eq 1)[3] shows that it too is a mixture of pyrrolidine and piperidine complexes when the reaction is quenched under acidic conditions. When the reaction solution is kept basic during the workup, only the *trans*-1,3-disubstituted pyrrolidine complex is obtained in 70% yield.

with 6-c and 6-t (eq 6; (ratio of 6-c,t/7 of 1:1).



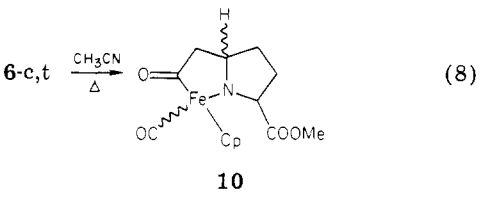
(6)

It seems likely that the isomerization of **6** to **7** takes place through protonation and reversion to the olefin complex, followed by regioisomeric ring closure. A very similar and facile isomerization of the pyrrolidinium salt **8** to the piperidinium salt **9** has previously been observed by us[12] (eq 7).



(7)

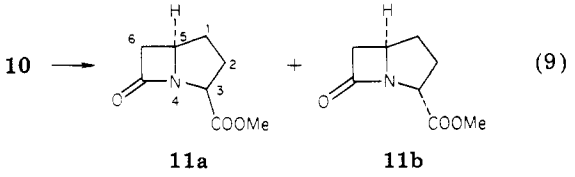
On being heated in acetonitrile solution, the pyrrolidine complexes **6-c,t** are converted to a mixture of diastereomeric chelates **10** (eq 8; 57%), as evidenced by the presence



(8)

of three cyclopentadienyl proton signals in the NMR spectrum of the product. Two of these must be stereoisomeric at C-3 and C-5, while the third is related to one of these but with opposite configuration at the chiral iron center.

Oxidation of the mixture of chelates with freshly prepared silver oxide in THF suspension gave the β-lactam in 32% yield as a 2:1 mixture of stereoisomers **11a** and **11b**.[13] By contrast, oxidation of **10** with either Fe^{III}(bipyridyl)$_3$$(PF_6)_3$ or cupric triflate failed to yield lactam. However, air oxidation of solutions of **10**, the most advantageous solvent being THF, gave a yield of lactams **11a,b** (eq 9) only slightly inferior to that obtained with silver oxide.



(9)

It seems likely that the lactams **11a,b** are formed by stereoselective conversion of each of the isomeric chelates rather than by preferential conversion of one of these to **11a**, followed by partial isomerization of this to the thermodynamically more stable isomer **11b**.[4] Evidence for this is provided by the following observations. When chelation of pyrrolidine complexes **6-c,t** is carried out in the presence of DBU, a single chelate is formed in low yield. Similar treatment of the mixture of chelates **10** with DBU gave the same substance.[14] When this complex is oxidized with silver oxide, the β-lactam **11b** is obtained in 48% yield, as the sole product.

Further application of this chemistry for the synthesis of carbapenam and carbapenem systems is being pursued.

Experimental Section

All reactions and subsequent maniupulations involving organoiron complexes were carried out in flame-dried glassware under a dry nitrogen atmosphere. Ether and THF were routinely dried by distillation in a nitrogen atmosphere from sodium benzophenone ketyl. All other solvents were stored over molecular sieves and deoxygenated by bubbling nitrogen through with a dispersion tube for 5 min. The alumina used for chromatography was Camag alumina, made up to Brockmann activity III unless otherwise noted.

Infrared spectra were recorded on a Perkin-Elmer spectrophotometer, Model 567. Proton NMR spectra were obtained with a Perkin-Elmer R-32 (NSF GU-3852) or Bruker WH-90 spectrometer (NSF GU-3852, GP-37156). Carbon-13 NMR spectra were determined at 22.63 MHz on the latter instrument. Mass spectra were obtained on an AEI MS-12 direct-inlet spectrometer (NSF GP 3644). Microanalyses were performed by Galbraith Laboratories, Knoxville, TN.

(A) Claisen Rearrangement Sequence. Methyl pyruvate dimethyl ketal[15] (21 g, 0.14 mol), allyl alcohol (75 g, 1.29 mol), and *p*-toluenesulfonic acid (0.5 g, 2.3 mmol) were placed in a flash fitted with a distilling column and were heated at 120 °C. The fraction distilling between 85 and 95 °C was removed over a period of 3 h. An additional 50 g of allyl alcohol (0.86 mol) was then added and the distillation was continued until an NMR spectrum of the pot mixture indicated no remaining dimethyl ketal. Benzene (50 mL) was then added, and the reaction mixture was concentrated in vacuo. The residue was then heated in an oil bath at 160–180 °C, collecting the distillate boiling in the range of 85–115 °C. When the head temperature had dropped below 90 °C, the pot was allowed to cool to room temperature, and 100 mL of ether was added. The organic solution was washed several times with 15 mL of saturated Na_2CO_3 solution and then with water to neutrality. After the mixture was dried over $MgSO_4$, the solvent was removed, leaving 20 g of a mixture of methyl and allyl 2-oxo-5-hexenoates. This was stirred at room temperature with 75 mL of methanol and 0.4 g of *p*-toluenesulfonic acid. After 72 h, the solvent was removed in vacuo. Ether (100 mL) was then added to the residue, which was thens washed with saturated Na_2CO_3 and then water to neutrality. The solution was then dried over $MgSO_4$, the solvent was removed, and the residue was distilled at 61–62 °C (3 mm) to give 14 g (71%) of product **3** as a colorless oil: IR (CH_2Cl_2) 1730, 1745, 1640 cm^{-1}; NMR ($CDCl_3$) δ 5.85 (ddt, 1, J = 6.3, 9.9, 17.1 Hz, CH=), 5.05 (m, 2, CH_2=), 3.87 (s, 3, OCH_3), 2.97 (t, 2, J = 7 Hz, (CH_2CO), 2.38 (m, 2, CH_2). Anal. Calcd for $C_7H_{10}O_3$: C, 59.14; H, 7.09. Found: C, 58.94; H, 6.78.

(B) Dithiane Sequence. A solution of 1,3-dithiane (5.08 g, 42 mmol) in 100 mL of THF was cooled to −35 °C and treated with *n*-butyllithium (44 mmol) in hexane. After 2 h, the solution was warmed to 0 °C and treated with 4-bromo-1-butene (6.38 g, 47.2 mmol). The resulting solution was stirred for 6 h at 0 °C and then cooled to −30 °C, and an additional 44 mmol of *n*-butyllithium was added. After 1.5 h, the yellow solution was cooled to −78 °C, and methyl chloroformate (12.36 g, 131 mmol) was added dropwise over 5 min. The reaction solution was maintained at −78 °C for 4 h, warmed to room temperature, and quenched with 300 mL of water. This solution was neutralized (pH 5) with 1 N HCl and extracted with ether (3 × 100 mL). The combined ether extracts were washed with 5% NaOH and then with water

(12) Madhavarao, M. Thesis, Brandeis University, 1977.

(13) Assignments are made by comparison of the NMR spectrum of the product with those of the related stereoisomeric benzyl and *tert*-butyl esters.[4]

(14) It is not clear if prototopic isomerization or selective destruction of two of the three isomeric chelates is involved in this reaction, but the latter seems more probable, since, when the reaction is followed by NMR spectrometry, a progressive decrease in the cyclopentadienyl proton resonance for all three chelates is observed. After 45 h only the low-field resonance at δ 4.46, characteristic of one of these, remains.

(15) Auwers, K. *Ber. Dtsch. Chem. Ges.* **1911**, *44*, 3514.

and dried over K_2CO_3. Removal of solvent and distillation of the residue gave the product: 4.45 g (48%); bp 122–123 °C (0.2 mm); colorless oil; NMR ($CDCl_3$) δ 5.80 (m, 1, CH=), 5.05 (m, 2, CH_2), 3.80 (s, 3, OCH_3), 3.25 (m, 2, SCH cis to ester), 2.65 (dt, 2, J = 4, 15 Hz, SCH trans to ester), 2.15 (m, 6, CH_2).

The above 2,2-disubstituted dithiane (3.1 g, 14 mmol) dissolved in 15 mL of acetonitrile was added to a mixture of 10.2 g (60 mmol) of silver nitrate and 7.23 g (54 mmol) of *N*-chlorosuccinimide in 125 mL of 80% aqueous acetonitrile. A white precipitate formed immediately. The mixture was stirred for 10 min and then treated successively with 15 mL of saturated Na_2SO_3, 15 mL of saturated Na_2CO_3, and 15 mL of brine. Hexane–Methylene chloride (1:1) was added, and the mixture was filtered through Celite and finally dried over $MgSO_4$. Kugelrohr distillation in vacuo gave 0.5 g (25%) of the pyruvic ester **3**.

(C) Oxalic Ester Sequence. Allylacetic acid[5] (9.0 g, 90 mmol) was esterified (ethanol, benzene, toluenesulfonic acid) to give 10.0 g (86%) of ethyl 4-pentenoate: NMR ($CDCl_3$) δ 5.80 (m, 1, CH=), 5.05 (m, 2, CH_2=), 4.15 (q, 2, J = 8 Hz OCH_2), 2.4 (m, 4, CH_2), 1.25 (t, 3, J = 8 Hz, CH_3). Sodium ethoxide in ether was prepared from 3.8 g (81 mmol) of ethanol and 1.8 g (80 mmol) of sodium sand in 35 mL of ether. A mixture of diethyl oxalate (11.6 g, 79 mmol) and ethyl 4-pentenoate (10 g, 78 mmol) was added dropwise over a period of 2 h. The solvent was removed, and the residue was treated with 15 mL of 33% aqueous acetic acid and then extracted with ether. The combined ether extracts were washed with saturated Na_2CO_3 solution and then with water to neutrality. After the mixture was dried over $MgSO_4$, the solvent was removed, and the residue was distilled to give 8.66 g (49%) of product: bp 98–100 °C (0.09 mm); NMR ($CDCl_3$) δ 5.80 (m, 1, CH=), 5.12 (m, 2, CH_2=), 4.28 (m, 5, OCH_2, COCHCO), 2.68 (t, 2, J = 7 Hz, CH_2), 1.30 (m, 6, CH_3).

The above product (5.63 g, 25 mmol) was added to 26 mL of 2 N HCl solution and heated at reflux for 4 h. The solution was cooled and extracted continuously with ether for 4 h, and the ether solution was extracted with saturated NaCl solution and then dried over $MgSO_4$. Removal of the solvent and distillation of the residue gave 1.07 g (33%) of 2-oxo-5-hexenoic acid: bp 27–28 °C (0.07 mm); IR (CH_2Cl_2) 1680, 1725 cm^{-1}; NMR ($CDCl_3$) δ 8.65 (s, 1, COOH), 5.85 (m, 1, CH=), 5.10 (m, 2, CH_2=), 3.05 (t, 2, J = 7 Hz, CH_2CO), 2.40 (m, 2, CH_2).

Preparation of Fp(η^2-methyl 2-oxo-5-hexenoate)PF_6 (4). Fp(η^2-isobutene)PF_6 (9.00 g, 23.8 mmol) and methyl 2-oxo-5-hexenoate (6.73 g, 46.5 mmol) were dissolved in 195 mL of methylene chloride, and the solution was heated to reflux for 17.5 h. The solution was cooled to 0 °C, and 100 mL of ether was added slowly. The crystalline product was collected in a Schlenk tube, washed throughly with ether, and then recrystallized from acetone–ether at 0 °C to give 8.88 g (74%) of yellow crystalline salt **4**: IR (CH_3CN) 2075, 2040, 1751, 1733 cm^{-1}; NMR (CD_3NO_2) δ 5.72 (s, 5, Cp), 5.08 (m, 1, CH=), 4.01 (d, 1, J = 9 Hz, CH_2=), 3.87 (s, 3, OCH_3), 3.62 (d, 1, J = 13.5 Hz, CH_2=), 3.22 (t, 2, J = 8 Hz, CH_2CO), 2.82 (m, 1, CH_2), 1.78 (m, 1, CH_2). Anal. Calcd for $C_{14}H_{15}O_5FePF_6$: C, 36.23; H, 3.26. Found: C, 36.03; H, 3.23.

Preparation of Pyrroline Complex 5. A solution of ammonia in methylene chloride was prepared by passing ammonia through 175 mL of methylene chloride, cooled to −25 °C, for 10 min. A solution of the salt **4** (8.41 g, 16.7 mmol) in 20 mL of acetonitrile was added by cannula over a period of 5 min to the stirring NH_3 solution. The reaction was continued for 10 min at −25 °C, the cold bath was removed, and the solution was allowed to come to room temperature over a period of 35 min. An additional 100 mL of methylene chloride was added and then 100 mL of water. The separated organic layer was washed with water (6 × 50 mL) and saturated aqueous $NaHCO_3$ (1 × 50 mL) and dried over K_2CO_3. Filtration through Celite in vacuo followed by removal of solvent left 5.08 g (96%) of product **5** as a red oil, which crystallized after standing in the freezer overnight; mp 40–43 °C; IR (CH_2Cl_2) 2000, 1940, 1735, 1620 cm^{-1}; NMR ($CDCl_3$) 4.85 (s, 5, Cp), 4.15 (br m, 1, CHN=), 3.85 (s, 3, OCH_3), 2.82 (m, 2, CH_2C=), 2.21 (m, 1, CH_2C=N), 2.12 (dd, 1, J = 5, 10 Hz, $FeCH_2$), 1.62 (m, 1, CH_2C=N), 1.18 (dd, 1, J = 9, 10 Hz, $FeCH_2$). Anal. Calcd for $C_{14}H_{15}NO_4Fe$: C, 53.02; H, 4.77. Found: C, 53.04; H, 4.80.

Reduction of Pyrroline Complex. Preparation of 6-c,t. A solution of complex **5** (2.6 g, 8.29 mmol) in 65 mL of methanol, cooled to 0 °C, was treated with $NaBH_4$ (128 mg, 4.6 mmol) in three portions over a period of 40 min. After 1 h, 20 mL of water was added, and the solution was stirred for an additional 25 min. The solution was concentrated in vacuo and then extracted with methylene chloride (2 × 50 mL). The combined extracts were washed with water and saturated $NaHCO_3$ and dried over K_2CO_3. Removal of solvent left a red oil (2.24 g, 85%), which was used without further purification: IR (CH_2Cl_2) 1997, 1937, 1730 cm^{-1}; NMR ($CDCl_3$) 4.81 (s, 5, Cp), 3.87 (m, 1, $CHCO_2$), 3.74 (s, 3, OCH_3), 3.20 (m, 1, NH), 2.5–1.2 (m, 7, $FpCH_2$, CH, CH_2); NMR (benzene-d_6) δ 4.29, 4.25 (2 s, 5, 2 Cp (2:1), 3.89 (br m, 1, $CHCO_2$), 3.42 (s, 3, OCH_3), 3.28 (m, 1, NH) 2.5–1.2 (br m, 7, $FpCH_2$, CH, CH_2); ^{13}C NMR δ 217.5, 217.3 (2 s, Fe–CO), 176.8, 176.0 (2 s, COOR), 85.4 (d, Cp), 67.0, 65.5 (2 d, C-2), 58.6, 59.6 (2 d, C-5), 52.3, 52.2 (OCH_3), 35.1, 34.5 (ring CH_2) 30.1, 31.2 (ring CH_2), 7.3, 6.2 ($FpCH_2$).

Chelation of the Mixture of Pyrrolidine Complexes. Preparation of 10. A solution of the mixture of pyrrolidine complexes (387 mg, 1.21 mmol) in 17 mL of CH_3CN was heated at 65 °C for 20 h. Solvent was removed in vacuo, and the residue was chromatographed on 35 g of activity IV neutral alumina. Fp dimer (25 mg) was eluted with 30% ether–petroleum ether, while the chelate mixture **10** was eluted with 5% acetone–ether and was obtained as a brick red solid: 220 mg, (57%); IR (CH_2Cl_2) 1980, 1730, 1608 cm^{-1}; NMR ($CDCl_3$) 4.92 (br m, 1, NH) 4.47, 4.41, 4.39 (3 s, 5, Cp (2:1:1)), 3.92 (br m, 1, CHCOOR), 3.88, 3.84 (2 s, 3, OCH_3 (1:1)), 3.55 (br m, 0.5, CHN), 3.20 (br m, 0.5, CHN), 2.7–1.5 (br m, 6, CH_2). Anal. Calcd for $C_{14}H_{17}NO_4Fe$: C, 52.69; H, 5.37; N, 4.39. Found: C, 52.17; H, 5.38; N, 4.39.

Reduction of Pyrroline Complex 5 to a Mixture of Pyrrolidine and Piperidine Complexes 6-c,t and 7. A solution of the pyrroline complex **5** (2.45 g, 7.78 mmol) in 60 mL of methanol was cooled to 0 °C and treated with 157 mg of $NaBH_4$ (4.15 mmol) in two portions over a period of 20 min. After 30 min, 10 mL of water was added, and the pH of the solution was adjusted to 7 with 1 N HCl. The solution was concentrated in vacuo and then extracted with methylene chloride (2 × 40 mL). The combined extracts were washed with saturated Na_2CO_3 and dried over K_2CO_3. Removal of solvent left 2.39 g (90%) of the product as a red oil: IR 1998, 1938, 1730 cm^{-1}; NMR ($CDCl_3$) 4.80, 4.75 (2 s, 5 Cp, 1:1 **6-c,t/7**), 3.75, 3.72 (2 s, 3, OCH_3), 3.6–1.3 (br m, 9, CH, CH_2; ^{13}C NMR ($CDCl_3$) peaks assigned to **7** δ 173.9 (s, COOR), 59.1 (d, CHCOOR) 51.8 (q, OCH_3), 40.3 (t, CH_2), 35.4 (CH_2), 23.6 (d, FpCH).

Oxidation of the Chelate Mixture 10. A solution of the chelate mixture (0.574 g, 1.80 mmol) in 45 mL of THF was stirred at room temperature and treated with 1.42 g (6.13 mmol) of Ag_2O[16] in seven equal portions over a period of 8.5 h. The reaction was complete at the end of 23 h as judged by the disappearance of the metal carbonyl absorption at 1905 cm^{-1}. Ether (60 mL) was added to the reaction mixture, and this was filtered through Celite. Removal of solvent left 184 mg of a dark red oil. Preparative thin-layer chromatography on silica gel (1000 μm, 20% EtOAc/$CHCl_3$) yielded the desired product (R_f 0.5) as an amber oil: 98 mg (32%); IR (CH_2Cl_2) 1772, 1742 cm^{-1}; NMR ($CDCl_3$) for **11a** δ 3.08 (m, 1, H-6), 2.75 (dd, 1, J = 2, 16 Hz, H-6); for **11b** δ 4.45 (t, 1, J = 7 Hz, H-3), 4.0–3.7 (m, 1, H-5), 3.16 (dd, 1, J = 5, 16 Hz, H-6), 2.65 (dd, 1, J = 2, 16 Hz, H-6), 2.6–2.1 (m, 4, H-1, H-2); ^{13}C NMR ($CDCl_3$) δ 29.2, 30.5 (C-2), 34.8, 35.9 (C-1), 40.8, 42.0 (C-6), 51.7, 52.5 (C-5), 52.6 (OCH_3), 58.5, 59.1 (C-3), 172.4, 175.5 (CON, COOR).

An analytical sample was prepared by recrystallization from hexane ether; mp 30.5–31.0 °C. Anal. Calcd for $C_8H_{11}NO_3$: C, 56.79; H, 6.56; N, 8.28. Found: C, 57.02; H, 6.67; N, 7.99.

Air Oxidation of the Chelate Mixture. A 0.07 M solution of the chelate mixture in the solvent shown was prepared. Air was bubbled through the solution for 1 min then allowed to stir open to the air until all the chelate had been consumed, as evidensed by loss of the metal carbonyl absorption at 1908 cm^{-1} typical of this substance. The solution was then diluted by addition of 50 mL of ether to precipitate insoluble material and then filtered through Celite. The solvent was removed in vacuo, and the product was isolated by preparative thin-layer chroma-

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Table I

chelate, mg	solvent	time, h	product amt, mg	product % yield
114	CHCN	3.5	8	13
170	C_6H_6	1	12	13
220	CH_2Cl_2	3.5		0
113	THF	8.5	17	28

tography (silica gel, 1000 μm, 20% EtOAc/$CHCl_3$, R_f 0.5; see Table I).

Reaction of BDU with Chelate 10. A solution of chelate **10** (0.237 g, 0.74 mmol) in 10 mL of CH_3CN was treated with DBU (107 mg, 0.70 mmol) and heated at 67 °C for 45 h. Concentration of the solution left a dark red oil which was chromatographed on 40 g neutral activity IV alumina. Ether elution yielded the product as a red solid: 77 mg (0.24 mmol, 32%); IR (CH_2Cl_2) 1908 (M–CO), 1608 (M–acyl), 1730 cm^{-1} (ester); NMR ($CDCl_3$) δ 4.95 (br m, 1 H, NH), 4.46 (s, 5 H, Cp), 3.95 (br m, 1 H, CH–CO_2), 3.84 (s, 3 H, OCH_3), 3.18 (br m, 1 H, N–CH), 2.5–1.8 (br m, 6 H, CH_2).

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Registry No. **4**, 84027-50-9; **5**, 84027-51-0; **6-c**, 84027-52-1; **6-t**, 84049-22-9; **7**, 84027-53-2; **10**, 84027-54-3; **11a**, 84011-99-4; **11b**, 84012-00-0; Fp(η^2-isobutene)PF_6, 84027-56-5; methyl pyruvate dimethyl ketal, 10076-48-9; allyl alcohol, 107-18-6; methyl 2-oxo-5-hexenoate, 84012-01-1; allyl 2-oxo-5-hexenoate, 84012-02-2; 1,3-dithiane, 505-23-7; 4-bromo-1-butene, 5162-44-7; methyl chloroformate, 79-22-1; methyl 2-(3-buten-1-yl)-1,3-dithiane-2-carboxylate, 84012-03-3; allylacetic acid, 591-80-0; ethyl 4-pentenoate, 1968-40-7; diethyl oxalate, 95-92-1; 2-oxo-5-hexenoic acid, 80003-58-3; diethyl 2-allyl-3-oxobutanedioate, 56716-05-3; ammonia, 7664-41-7.

Interaction of 3,4-Dinitro-1-methylpyrrole with Secondary Amines: Alternative Formation of Pyrrolines or Cine Substitution Products

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The course of the reaction of 1-methyl-3,4-dinitropyrrole with piperidine or morpholine in acetonitrile depends upon the reaction conditions. At refluxing temperature the main products are the cine substitution products, whereas at room temperature 2-pyrrolines are formed. Base-promoted decomposition of the latter yields products of formal direct denitration, whereas in the presence of Me_3NH^+ ion cine substitution products are obtained.

In connection with our studies concerning the reactions of nitro pyrroles with nucleophiles,[1] we recently reported that a cine substitution reaction occurs when 1-methyl-3,4-dinitropyrrole (**1**, Chart I) reacts with piperidine in refluxing acetonitrile to yield 1-methyl-4-nitro-2-piperidinopyrrole (**2a**) as the main product. A minor amount of a ring-opening product, 2,3-dinitro-1,4-dipiperidinobuta-1,3-diene (**3a**), was also obtained.

We have now found that the course of the reaction of **1** with secondary aliphatic amines may be sensibly affected by the initial reactant ratio and by the temperature.

The reactions of **1** with piperidine and the less nucleophilic morpholine in acetonitrile, either at room temperature or at reflux temperature, are here described, together with some reactions involving one of the possible primary reaction products.

Results

(A) Reaction of 1 with Piperidine. At Room Temperature with a Tenfold Excess of Piperidine. Under these conditions pyrroline **4a** is the only product. It was characterized by ^1H NMR and CI mass spectroscopy, which showed an intense $(M + 1)^+$ peak. Pyrroline **4a**, like other related compounds such as 4,5-bis(dialkylamino)-4,5-dihydroimidazoles,[2] shows a very weak molecular peak in EI mass spectroscopy. A nitro enamine structure, similar to that of pyrroline **4c**, as formed from **1** and MeO^-,[3] is supported by the UV spectrum of **4a**. The low coupling constant between protons at positions 4 and 5 suggests a trans structure, similar to that of **4c** and 1-substituted *trans*-4,5-dimorpholino-4,5-dihydroimidazoles.[2] The stereochemical course of the formation of pyrrolines is similar to that of the formation of 2,5-dimethyl-*trans*-2,3-bis(dialkylamino)-4-nitro-2,3-dihydrothiophenes (**5**), whose structures were established by X-ray crystallography.[4] Both courses indeed lead to compounds bearing two trans amino groups at position α and β. Although this stereoselective behavior may be due to thermodynamic control, trans isomers being generally more stable, the formation of the trans isomer could also occur under kinetic control. As shown in Scheme I, nucleophilic attack at the α position could be followed by protonation of the adjacent β position, intramolecular nucleophilic displacement of the β nitro group by the neighboring α R_2N group, and the eventual attack of another R_2NH molecule at the ensuing bicyclic cation.[18] Nitro groups have been indeed shown to be good leaving groups in aliphatic substitution and elimination reactions.[5,6]

The reaction of pyrroline formation is not so straightforward as suggested by the formation of one product only. At least one other product is formed together with **4a** at the beginning of the reaction but eventually disappears, as shown by ^1H NMR and TLC measurements. The disappearance of the signal of **1** at δ 7.5 is accompanied by the appearance of the signals of pyrroline **4a** at δ 7.9

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