in the acetylation of methyl ether, ions of $m/z$ 89 from reactions 1 and 2 were unreactive toward all nucleophiles added (AcOH, $AcOCH{=}CH_2$, $Ac_2O$, $H_2O$, $CH_3OH$).

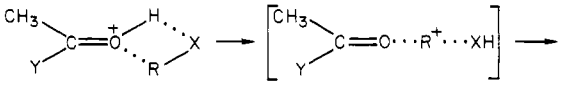
The acylation reactions described thus far can be expressed satisfactorily by the process of eq 3 where the acylium ion complex **2** is either an intermediate or a transition state. We also wish

$$RY + AcXH^+ \rightarrow [RY\cdots Ac^+\cdots XH] \rightarrow RYAc^+ + HX \quad (3)$$

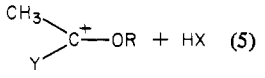
to report related reactions whereby acyl transfer occurs between the protonated parent of one acyl compound and the neutral form of another (eq 4). In the special case where AcX = AcY (eq 4a) the reaction is a self-acylation process that is mechanistically indistinguishable from reaction 3. However, when the acyl components are *different*, as in the reactions of protonated methyl acetate or thioacetate with neutral acyl derivatives, the roles of the reactants are reversed and the acyl group is transferred from the neutral to the ion rather than from the ion to the neutral (eq 4b and Table I). For example, protonated methyl acetate-$d_3$ and $Ac_2O$ gave $(CD_3CO_2CH_3)Ac^+$ ($m/z$ 120) as expected for acyl transfer from the neutral anhydride to the protonated ester. Also, sequential acyl transfers are evident in the reactions of methanol or methanethiol with acyl compounds, because the product ion of acyl transfer by reaction 3 (R = H) is the reactant ion for acyl transfer by eq 4b. These sequences are summarized in Table I. The key question is whether there is any mechanistic distinction between reactions 3 and 4. We wish to point out that reaction 4b is strikingly similar to gas-phase alkylation reactions of carbonyl compounds.[3d,11] Both reactions conform to the generalized concept of exothermic gas-phase nucleophilic displacement in which an endothermic proton transfer precedes or is concurrent with the displacement step formulated as cation transfer (eq 5, R is alkyl or acyl). Viewed in this way, any fundamental distinction between

$$AcX + AcXH^+ \rightarrow [AcX\cdots Ac^+\cdots XH] \rightarrow AcXAc^+ + HX \quad (4a)$$

$$AcYH^+ + AcX \rightarrow AcYAc^+ + HX \quad (4b)$$



R = alkyl, acyl



(5)

reactions 3–5 disappears, and there is no reason to invoke more complex acylation mechanisms of addition–elimination.

Historically, the concept of acyl transfer as a direct displacement was first described definitively by Day and Ingold[12] but has not been considered seriously since Bender demonstrated through $^{18}O$-exchange experiments that tetracovalent intermediates are involved in acid- and base-catalyzed hydrolysis reactions.[13] Yet it is fair to say that the gas-phase results described here serve to emphasize the importance of environmental conditions on the course of ionic reactions. The question arises as to whether addition–elimination acyl-transfer mechanisms are quite as general in condensed phase as now supposed. This comment is especially pertinent to enzyme-catalyzed acyl-transfer reactions, because the hydrophobic reaction environment at the active site of an enzyme[14] means that ions nearby will be poorly solvated. Lacking hydroxylic solvation, reacting ions at the enzyme surface could very well exhibit reactions and reactivities comparable to gaseous ions. In view of this, the wider applicability of the gaseous process in condensed phase is worthy of consideration.

(10) $RH^+$ are acidic fragments and product ions resulting from electron impact of the neutral reactants.

(11) (a) J. L. Beauchamp, D. Holtz, S. D. Woodgate, S. L. Patt, *J. Am. Chem. Soc.*, **94**, 2798 (1972); (b) J. M. Riveros, P. W. Tiedemann, B. C. de Melo, and J. F. Faigle, *J. Phys. Chem.*, **83**, 1488 (1979); (c) R. van Doorn and N. M. M. Nibbering, *Org. Mass. Spectrum.*, **13**, 527 (1978).

(12) J. N. E. Day and C. K. Ingold, *Trans. Faraday Soc.*, **37**, 686 (1941).

(13) M. L. Bender, *J. Am. Chem. Soc.*, **73**, 1616 (1951); *Chem. Rev.* **60**, 53 (1960); M. L. Bender and R. S. Thomas, *J. Am. Chem. Soc.*, **85**, 4189 (1961).

(14) J. Kraut, *Enzymes*, **3**, 165–183 (1971).

**Acknowledgment.** We are indebted to the National Science Foundation and the donors of the Petroleum Research Foundation, administered by the American Chemical Society, for their support of this work through Grants NSF CHE 7807993 and ACS-PRF 11585-AC4.

## Enantioselective Aldol Condensations. 2. Erythro-Selective Chiral Aldol Condensations via Boron Enolates[1]

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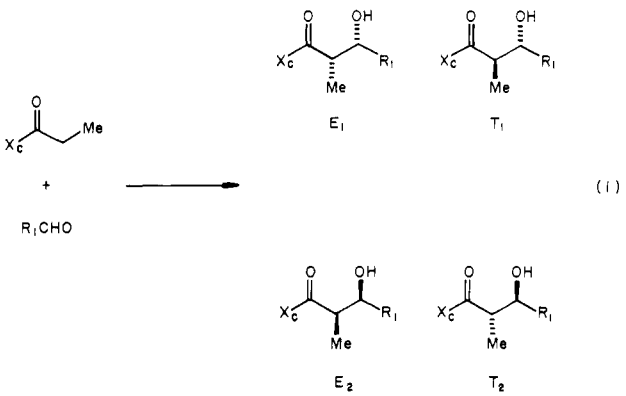
The development of chiral enolates which participate in highly stereoregulated aldol condensations has been a challenging undertaking.[2] The control of both reaction diastereoselection ($E_1 + E_2$ vs. $T_1 + T_2$) and enantioselection ($E_1$ vs. $E_2$ or $T_1$ vs. $T_2$) must be addressed in conjunction with this problem (eq 1). The



(1)

purpose of this communication is to report our observations on the utility of the chiral 2-oxazolidones **1a** and **2a** as recyclable chiral auxiliaries, $X_c$, for carboxylic acids in highly enantioselective aldol condensations via the boron enolates[2e,3,4] derived from the respective *N*-propionylimides **1b** and **2b**.

Oxazolidone **1a**, mp 71–72 °C, $[\alpha]_D$ +14.8° (*c* 7.0, $CHCl_3$), was prepared from (*S*)-valinol[5] and either phosgene or diethyl carbonate in high yield.[6] In a similar fashion, the commercially available (1*S*,2*R*)-norephedrine[7] was transformed into oxazolidone **2a**, mp 120–121 °C, $[\alpha]_D$ +163.7° (*c* 1.0, $CHCl_3$).[8] The *N*-propionyloxazolidones **1b** and **2b** were prepared in 80–90% yield by lithiation of **1a** or **1b** (*n*-BuLi, 0.3 M THF) and subsequent reaction with propionyl chloride (1.0 equiv, −78 °C). The non-

(1) Presented at the 12th International Symposium on the Chemistry of Natural Products, Tenerife, Canary Islands. Evans, D. A.; Takacs, J. M.; McGee, L. R.; Ennis, M. D.; Mathre, D. J.; Bartroli, J. *Pure Appl. Chem.* **1981**, in press.

(2) (a) Heathcock, C. H.; White, C. T. *J. Am. Chem. Soc.* **1979**, *101*, 7076–7077. (b) Heathcock, C. H.; Pirrung, M. C.; Buse, C. T.; Hagen, J. P.; Young, S. D.; Sohn, J. E. *Ibid.* **1979**, *101*, 7077–7079. (c) Masamune, S.; Ali, Sk. A.; Snitman, D. L.; Garvey, D. S. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 557–558. (d) Evans, D. A.; Taber, T. R. *Tetrahedron Lett.* **1980**, 4675–4678. (e) Evans, D. A.; Nelson, J. V.; Vogel, E.; Taber, T. R. *J. Am. Chem. Soc.*, in press. (f) Evans, D. A.; McGee, L. R. *Ibid.*, in press. (g) Mioskowski, C.; Solladie, G. *Tetrahedron* **1980**, *36*, 227–236. (h) Meyers, A. I.; Reider, P. J. *J. Am. Chem. Soc.* **1979**, *101*, 2501–2502. (i) Eichenauer, H.; Friedrich, E.; Lutz, W.; Enders, D. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 206–207.

(3) Evans, D. A.; Vogel, E.; Nelson, J. V. *J. Am. Chem. Soc.* **1979**, *101*, 6120–6123.

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(6) Newman, M. S.; Kutner, A. *J. Am. Chem. Soc.* **1951**, *73*, 4199–4204.

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Table I. Aldol Condensations of **1b** and **2b** with Representative Aldehydes (Scheme I)[9]

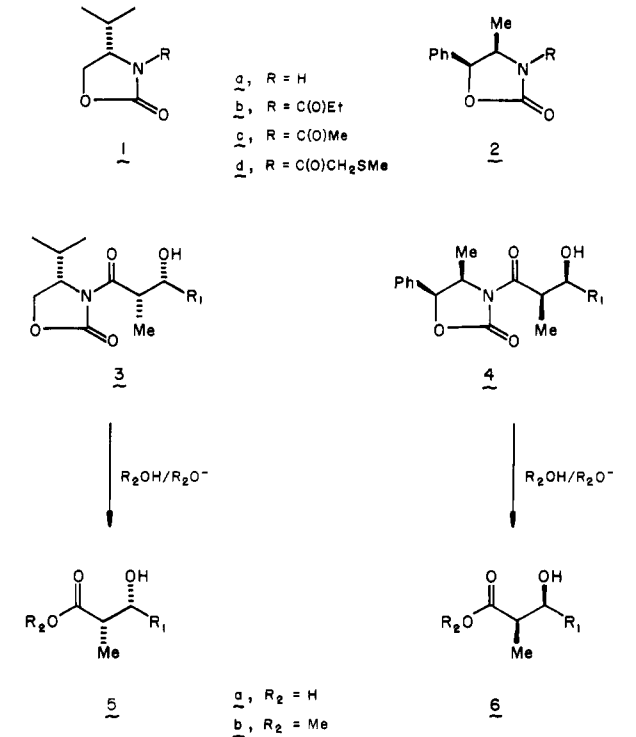
| entry | imide | $R_1CHO$ | erythro selection $E_1:E_2$[a] | aldol adduct yield, %[b] | 5b (6b) overall yield, %[c] | 5b (6b) $[\alpha]^{25}$ (c, g/mL)[d] |
|---|---|---|---|---|---|---|
| A | 1b | $Me_2CHCHO$ | 497:1 | 3, 78 | 5b, 69 | −7.9° (5.7, $CHCl_3$) |
| B | 2b | $Me_2CHCHO$ | <1:500 | 4, 91 | 6b, 78 | +7.7° (5.4, $CHCl_3$) |
| C | 1b | $n$-$C_4H_9CHO$ | 141:1 | 3, 75 | 5b, 68 | +14.9° (6.6, $CH_2Cl_2$) |
| D | 2b | $n$-$C_4H_9CHO$ | <1:500 | 4, 95 | 6b, 71 | −15.0° (5.0, $CH_2Cl_2$) |
| E | 1b | $C_6H_5CHO$ | >500:1 | 3, 88 | 5b, 81 | −23.1° (3.2, $CHCl_3$) |
| F | 2b | $C_6H_5CHO$ | <1:500 | 4, 89 | 6b, 60 | +23.2° (3.2, $CHCl_3$) |

[a] Determined by capillary gas chromatography on silylated adducts. In all cases the *threo*-aldol adducts constituted <1% of total reaction mixture. The limits of detection by this method appear to be approximately 500:1. [b] Yields reported are after recrystallization (entries A, D, E, F) or chromatography (entries B, C). [c] Values refer to overall isolated yields of **5b** (**6b**) for the aldol process, hydrolysis, and diazomethane treatment. [d] Optical purities >99% in all cases.

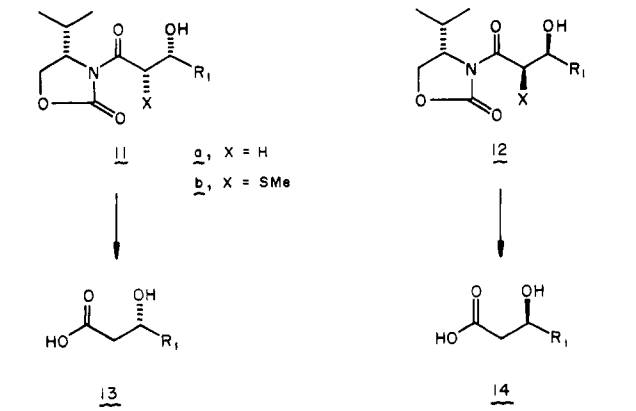
crystalline adducts **1b** and **2b**[9,10] could conveniently be purified by either molecular distillation or flash chromatography.[11]

In numerous studies carried out in this laboratory we have found that **1b** and **2b** undergo highly stereoselective enolization with either lithium amide bases [$LiN(i\text{-}C_3H_7)_2$, −78 °C, THF] or di-*n*-butylboryl trifluoromethanesulfonate (**7**)[2e,4e] to form the (*Z*)-enolates (*Z*:*E* ≥ 100).[12] The boron enolates were condensed (−78 °C) with the representative aldehydes illustrated in Table I and the diastereoisomeric aldol adducts were isolated by oxidative workup.[2e,3] The unpurified reaction mixture was silylated ($Et_2NSiMe_3$, DMAP, $CH_2Cl_2$, 25 °C) and analyzed by capillary gas chromatography.[13] The four aldol stereoisomers ($E_1$, $E_2$, $T_1$, $T_2$)[14] in all cases reported were readily resolved by this analytical method. The analogous condensations of the corresponding lithium enolates were carried out under kinetic conditions (−78 °C, 10 s).[15] In a representative condensation of the boron enolate derived from **1b** with isobutyraldehyde, the observed diastereoisomer ratios, $E_1:E_2:T_1:T_2$ were 99.4:0.2:0.2:0.2. The analogous aldol condensation with the lithium enolate afforded the product ratios 10.6:11.0:71.4:7.0. These two cases were found to be representative of the results obtained with both imides **1b** and **2b** for the two metal enolates. In all cases examined, the lithium enolate condensations were found to exhibit low levels of stereoregulation. For the boron enolate aldol reactions reported in Table I, the combined threo-adduct contaminants ($T_1 + T_2$) never exceeded 0.9%. In all instances imide **1b** afforded erythro-isomer **3** ($E_1$), while **2b** gave **4** ($E_2$) with the opposite sense of asymmetric induction (Scheme I). In most instances adducts **3** and **4** could be conveniently purified to high optical purity by a single recrystallization in 75–91% yields. The erythro-adducts **3** and **4** were found to readily hydrolyze without racemization of either center (≤1%) to the corresponding acids **5a** and **6a** upon treatment with 4.0 equiv of 2 N aqueous potassium hydroxide in methanol (0.5 M, 0 °C, 45 min). Alternatively, **3** and **4** may be directly transformed into the corresponding methyl esters **5b** and **6b** with 1.1 equiv of sodium methoxide in anhydrous methanol (0 °C, 5 min). The erythro stereochemical assignments for **5** and **6** were made by $^1H$ NMR spectroscopy, and the absolute stereochemical assignments were made in all cases by degradative removal of the hydroxyl group and correlation of the resultant α-substituted carboxylic acids.[16,17]

Scheme I




Scheme II




The illustrated aldol condensations were carried out according to the following general procedure. To a 0.2–0.5 M solution of

(7) Prepared from the Commercially available (Aldrich Chemical Co.) hydrochloride salt, $[\alpha]_D$ +33.4° (*c* 7, $H_2O$).

(8) The physical properties of the (4*S*,5*R*) enantiomer of **2a** have been reported, mp 116–117 °C, $[\alpha]_D$ −158.4 (*c* 0.44, $CHCl_3$): Fodor, G.; Stefanovsky, J. N.; Kurtev, B. J. *Monatsh. Chem.* **1967**, *98*, 1027–1040.

(9) Satisfactory spectral and analytical data were obtained on all new compounds.

(10) **1b**: $[\alpha]_D$ +96.8° (*c* 8.7, $CH_2Cl_2$); **2b**: $[\alpha]_D$ +43.8° (*c* 2.0, $CH_2Cl_2$); **1c**: $[\alpha]_D$ +98.4° (*c* 2.6, $CH_2Cl_2$); **1d**: $[\alpha]_D$ +81.9° (*c* 1.7, $CH_2Cl_2$).

(11) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–2925.

(12) The enantioselective alkylations of these systems will be reported shortly.

(13) Gas chromatographic analyses were carried out on a Hewlett-Packard instrument (Model 5880A) employing 30-m x 0.32-mm WCOT columns (Column types: Carbowax, methylsilicone SE-54).

(14) The absolute configurations of the illustrated erythro adducts conform to those illustrated in eq 1 where $X_c$ equals the chiral auxiliary employed (**1a** or **1b**). For example, **3** and **4** correspond to $E_1$ and $E_2$, respectively.

(15) Heathcock, C. H.; Buse, C. T.; Kleschick, W. A.; Pirrung, M. C.; Sohn, J. E.; Lampe, J. *J. Org. Chem.* **1980**, *45*, 1066–1081.

(16) These correlations were carried out by L. R. McGee in this laboratory and will be reported shortly.

(17) The absolute configuration of **5b** ($R_1$ = $C_6H_5$) and **6b** ($R_1$ = $C_6H_5$) have also been unequivocally determined by Professor C. H. Heathcock. Their reported rotations are $[\alpha]^{20}_D$ −19.3° (*c* 1.74, $CHCl_3$) and $[\alpha]^{20}_D$ +21.5° (*c* 1.73, $CHCl_3$), respectively. Heathcock, C. H.; White, C. T.; Morrison, J. J.; Van Derveer, D. *J. Org. Chem.*, in press.

Table II. Aldol Condensations of 1c and 1d with Representative Aldehydes (Scheme II)[a]

| imide | $R_1CHO$ | ratio 11a:12a[a] | $[\alpha]^{25}_D$ 13 | optical purity 13:14[c] |
|---|---|---|---|---|
| 1d | $Me_2CHCHO$ | 98.4:1.6 | −42.1° (1.8)[d] | 97.8:2.2 |
| 1d | $n$-$C_3H_7CHO$ | 98.9:1.1 | −27.3° (2.1)[e] | 99.4:0.6 |
| 1d | $CH_3CHO$ | 99.6:0.4 | −45.8° (1.7)[f] | >99.9:<0.1 |
| 1d | $C_6H_5CHO$ | 92.4:7.6 | −17.1° (4.1)[g] | 92.4:7.6[h] |

[a] Determined by GLC (ref 13). [b] All rotations were carried out in $CHCl_3$ except for the $C_6H_5CHO$ case. EtOH was used instead. [c] Inferred from the ratios of **11a** and **12a** after chromatographic purification. [d] Literature rotation: $[\alpha]_D$ −24.7° (c 0.98, $CHCl_3$) (ref 19a); $[\alpha]_D$ −40.3° (c 4.6, $CHCl_3$) (ref 2d). [e] Literature rotation: $[\alpha]_D$ −28° (c 2.0, $CHCl_3$) (ref 19b). [f] Value is $[\alpha]_D$ of methyl ester of **13** from methanolysis of **11a** and **12a**. Literature rotation for methyl ester of **14**: $[\alpha]_D$ +33.3° (c 1.2, $CHCl_3$) (ref 19c). [g] Literature rotation for antipode **14**: $[\alpha]_D$ +18.9° (c 5.15, EtOH) (ref 2g) $[\alpha]_D$ −18.9° (c 2.3, EtOH) (ref 19d). [h] Products **11a** and **12a**, $R_1 = C_6H_5$, are not stable on silica gel. The crude product from desulfuriztion was hydrolyzed directly to the acid.

**1b** in anhydrous $CH_2Cl_2$ under argon (0 °C) is added 1.1 equiv of boron triflate (**7**)[4e] followed by 1.2 equiv of diisopropylethylamine. After allowing 30 min for complete enolization, the reaction is cooled (−78 °C) and 1.1 equiv of freshly distilled aldehyde is added and stirred for 0.5 h at −78 °C and 1.5 h at room temperature. The boron aldol ate complex is quenched with pH 7 phosphate buffer and oxidized with 30% hydrogen peroxide–methanol (0 °C, 1 h). The aldol adduct is then isolated by ether extraction.

It appears that these reactions will be useful for more highly functionalized substrates as well. For example, the selective enolization of **8** and its subsequent condensation with benzaldehyde afforded the diastereomerically pure adduct **9** [mp 101–102 °C, $J$ (erythro) = 5.0 Hz] in 67% isolated yield. The absolute stereochemical assignment for **9** was carried out by a straightforward degradation to (2$R$)-benzylsuccinic acid (**10**), mp 162–163 °C, $[\alpha]_D$ −28.6° (c 0.9, acetone) whose optical purity was judged to be ≥98%.[18]


8 9

In view of the high levels of asymmetric induction observed in the cases cited above, it was surprising to observe that the boryl enolate derived from the $N$-acetyloxazolidone (**1c**)[10] afforded nearly 1:1 ratios of the aldol adducts **11a** and **12a** with the representative aldehydes illustrated in Table II. For example, the boron enolate derived from **1c** afforded a **11a**:**12a** ratio of 52:48 with isobutyraldehyde and 72:28 with acetaldehyde. It had been hoped that **1c** and **2c** might function as useful chiral acetate enolate equivalents.[2g] A practical solution to this objective was accomplished upon examination of the aldol condensations of oxazolidone **1d**[10] which were found to be highly stereoregular in nature. Desulfurization of the aldol adducts **11b** and **12b** to **11a** and **12a** proceeded in good yield with Raney nickel[20] (acetone, 60 °C, 20 min). Gas chromatographic analysis[13] (Table II) indicated that asymmetric induction in the range of 92–99% could be achieved. Chromatographic purification of **11a** followed by base hydrolysis, as previously described, afforded the β-hydroxy acids **13** in 80–90% yields. Since the absolute configurations of acids **13** ($R_1$ = Ph, Me, $n$-$C_3H_7$, and $i$-$C_3H_7$) have been previously established,[2g,19] it follows that the sense of asymmetric induction of both **1b** and **1d** are the same for all aldehydes examined. One important consequence of this study pertains to the *critical* role of enolate substitution in aldol asymmetric induction. In related studies we have made parallel observations that unsubstituted methyl ketone boryl enolates exhibit much lower levels of asymmetric induction than the corresponding (*Z*)-ketone enolates.[2d,2e]

Oxazolidones **1a** and **1b** appear to fulfill all of the design requirements for a generally useful chiral auxiliary for the aldol process. These systems confer high stereoselection on the enolization process, provide remarkable levels of erythro-diastereoface selection ($\Delta\Delta G^{\ddagger}$ at −78 °C ~ 3 kcal/mol), and are readily removed and recycled without attendant racemization of the substrate.

**Acknowledgment.** This research has been supported by the National Science Foundation and the National Institutes of Health.

(18) Fredga, A. *Ark. Kemi, Mineral. Geol.* **1948**, *26B* (n-11), 1–4. The reported rotation for **10** (mp 164.5 °C) is $[\alpha]_D$ −29.0° (c 3.2, acetone).

(19) (a) Büchi, G.; Crombie, L.; Godin, P. J.; Kaltenbronn, J. S.; Siddalingaiah, K. S.; Whiting, D. A. *J. Chem. Soc.* **1961**, 2843–2860. (b) Serck-Hanssen, K. *Ark. Kemi* **1956**, *10*, 135–149. (c) Lemieux, R. U.; Giguere, J. *Can. J. Chem.* **1951**, *29*, 678–690. (d) Cohen, S. G.; Weinstein, S. Y. *J. Am. Chem. Soc.* **1964**, *86*, 725–728.

(20) Billica, H. R.; Adkins, H. *Org. Synth. Coll. Vol. III* **1955**, 176–180.

## ESR Study of Iron Carbonyl Radical Anions

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The neutral carbonyl compounds of iron, $Fe(CO)_5$, $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, the related carbonylate dianions, $Fe(CO)_4^{2-}$, $Fe_2(CO)_8^{2-}$, $Fe_3(CO)_{11}^{2-}$, $Fe_4(CO)_{13}^{2-}$, and their conjugate acids, $HFe(CO)_4^-$, $HFe_2(CO)_8^-$, $HFe_3(CO)_{11}^-$, $HFe_4(CO)_{13}^-$ occupy an important position in organometallic chemistry.[1] Several of these complexes are employed as useful stoichiometric reagents or precursors to catalytically active species. They are all diamagnetic, and their very considerable chemistry has been discussed virtually exclusively in terms of even-electron mechanisms. We wish to report now our investigations on a new series of iron carbonyl species which parallel the carbonylate dianions and are related to the latter by having one less electron. The existence of these radical anions, their conjugated protonated species,[2] and other organoiron radicals[3,4] suggests an important but not yet generally recognized role for one-electron pathways in the chemistry of iron carbonyl compounds.

When dilute solutions of $Fe(CO)_5$ in rigorously dry, oxygen-free THF are stirred with excess alkali metals or alkali-metal alloys,[5] they become red brown and display ESR spectra of up to *four* paramagnetic species in variable relative concentrations. Each

(1) For a review, see *Org. Synth. Metal Carbonyls*, **1**, 1 (1968).
(2) P. J. Krusic, *J. Am. Chem. Soc.*, following paper in this issue.
(3) P. J. Krusic and J. San Filippo, Jr., submitted for publication.
(4) E. L. Muetterties, B. A. Sosinsky, and K. I. Zamaraev, *J. Am. Chem. Soc.*, **97**, 5299 (1975); N. El Murr, M. Riveccie, and P. Dixneuf, *J. Chem. Soc., Chem. Commun.*, 552 (1978).
(5) All operations and reactions were carried out in a high-quality nitrogen glove box. Solutions employed in ESR studies ranged from $1 \times 10^{-3}$ to $5 \times 10^{-3}$M. $Fe(CO)_5$ was bulb-to-bulb distilled in the dark.

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