final stage of synthesis are crucial, because of the presence of various water-solubilizing functionalities.

L-α-Hydroxy γ-butyrolactone (**4**),[9] readily available from L-malic acid, was converted (dihydropyran, *p*-toluenesulfonic acid, 0 °C) into a diastereomeric mixture of tetrahydropyranylated derivatives **5**[10] (95%) which were separated by chromatography[11] (Scheme I) [IR (neat) 1780 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.49 (dd, 1 H, J = 8, 9 Hz), 4.27 (m, 2 H)]. Hydrolysis of **5** [2.5% KOH–THF (1:1), room temperature, 1 h], followed by benzylation [benzyl bromide, 18-crown-6, DMF–H_2O(4:1)] afforded γ-hydroxybenzyl ester **6**[10] (84%) [IR ($CHCl_3$) 3450, 1735 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.35 (s, 5 H), 5.21 (d, 1 H, J = 12 Hz), 5.14 (d, 1 H, J = 12 Hz), 4.57 (dd, 1 H, J = 4.5, 9 Hz)]. Oxidation of **6** with pyridinium chlorochromate (PCC) in methylene chloride yielded L-malic half-aldehyde **7**[10] (72%) [IR ($CHCl_3$) 1738, 1730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.76 (t, 1 H, J = 2 Hz), 7.34 (s, 5 H), 5.19 (s, 2 H), 4.84 (t, 1 H, J = 8 Hz), 2.86 (dd, 2 H, J = 2, 8 Hz)]. Coupling of half-aldehyde **7** and the homoserine moiety **8**[12] was achieved via a reductive amination procedure[13] (sodium cyanoborohydride, MeOH, room temperature, 14 h) and afforded the desired lactone amine **9**[10] in 90% yield [IR ($CHCl_3$) 3300, 1775, 1736 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.35 (s, 5 H), 5.20 (d, 1 H, J = 12 Hz), 5.12 (d, 1 H, J = 12 Hz), 4.50 (t, 1 H, J = 7 Hz); mass spectrum, *m/e* 292 (M^+ – THP)]. Protection of **9** by using di-*tert*-butyl dicarbonate [Et_3N (0.05 equiv), CH_2Cl_2, room temperature, 14 h] gave the *tert*-butoxycarbonyl derivative **10**[10] (90%) [IR ($CHCl_3$) 1780, 1745, 1695 cm^{-1}; ^1H NMR ($CDCl_3$ at 50 °C)[14] δ 4.40 (dd, 1 H, J = 5, 8 Hz), 4.26 (dd, 1 H, J = 4, 9 Hz), 1.35 (s, 9 H)]. Successive treatment of **10** via the same sequence of reactions described above (**5** → **6**) gave rise to the dibenzyl ester **11**[10] in 63% yield [IR ($CHCl_3$) 3450, 1740, 1695 cm^{-1}; ^1H NMR ($CDCl_3$ at 50 °C)[14] δ 7.24 (s, 5 H), 7.22 (s, 5 H), 5.05 (s, 4 H)]. Azetidine-2-carboxylic acid was transformed into the trifluoroacetic acid salt of 2-benzyloxycarboxyl azetidine **13** via the following three-step sequence in 80% yield: (1) 2-(*tert*-butoxycarbonyloxyimino)-2-phenylacetonitrile (Boc-ON), Et_3N, dioxane–H_2O (1:1); (2) 2.5% KOH (1 equiv), benzyl bromide, 18-crown-6, DMF; (3) CF_3COOH, room temperature, 30 min. PCC oxidation of **11** afforded the aldehyde **12**[10] (75%) [IR($CHCl_3$) 2725, 1743, 1735, 1695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.76 (br s, 1 H)], which upon reductive amination with azetidine **13** yielded the protected 2′-deoxymugineic acid **14**[10], 59% yield [IR ($CHCl_3$) 1740, 1690 cm^{-1}; ^1H NMR ($CDCl_3$ at 50 °C)[14] δ 7.30 (s, 10 H), 7.27 (s, 5 H), 5.20 (d, 1 H, J = 12 Hz), 5.11 (s, 4 H), 5.06 (d, 1 H, J = 12 Hz), 1.35 (s, 9 H); mass spectrum, *m/e* 759 (M^+) + 1)]. All five protecting groups were removed under mild acidic conditions in two steps: (1) H_2, 5% Pd–C, EtOH–H_2O (4:1), 1 N HCl (trace); (2) CF_3COOH, room temperature, 1 h. The resultant trifluoroacetic acid salt was immediately treated with Dowex 50W-X4 ion exchange resin (H^+ form), eluted with aqueous ammonia, and chromatographed on Sephadex G-10 to afford optically pure 2′-deoxymugienic acid (**2**) as white crystals, mp 196–199 °C (lit.[4] 198.5–200.5 °C), 100% yield, $[\alpha]^{23}_{D}$ −66.6° (c 0.71) (lit.[4] −70.5°).

Synthetic **2**, which was obtained in 12% overall yield from lactone **4**, was identical in all respects (paper chromatography and IR, ^1H NMR, and ^{13}C NMR spectra) with the natural product. No racemization was encountered during the course of synthesis.[15] This study establishes both the structure and absolute configuration of 2′-deoxymugineic acid as that depicted in structure **2**. Further studies employing the synthetic specimen are in progress to clarify the mode of action of these metal chelators.

Acknowledgment. We are indebted to Professor Koji Nakanishi, Director of the Suntory Institute for Bioorganic Research, for discussions.

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[9] Collum, D. B.; McDonald, J. H., III; Still, W. C. *J. Am. Chem. Soc.* **1980**, *102*, 2118.

[10] Oily compound. Satisfactory spectroscopic data as well as elementary analytical data were obtained for this substance.

[11] The synthesis was carried out with the THP derivatives rather than other derivatives despite the fact that they gave rise to a diasteromeric mixture; this was due to the ease of diastereomeric separation and deblocking. The synthetic sequence was carried through independently for both diastereomers which were readily separated by column chromatography (SiO_2), ether–hexane (3:2); the reactivity and yields of both series were comparable. The spectral data in the text refer to those for the less polar isomer. The intermediates possessed the following physical constants. Less polar compounds in $CHCl_3$: **5**, $[\alpha]^{23}_{D}$ −172° (c 1.17); **6**, $[\alpha]^{23}_{D}$ −117° (c 1.0); **7**, $[\alpha]^{23}_{D}$ −120° (c 1.05); **9**, $[\alpha]^{23}_{D}$ −100° (c 1.85); **10**, $[\alpha]^{23}_{D}$ −74° (c 0.85); **11**, $[\alpha]^{23}_{D}$ −74° (c 0.7); **12**, $[\alpha]^{23}_{D}$ −84° (c 1.2); **14**, $[\alpha]^{23}_{D}$ −97° (c 0.5). More polar compounds in $CHCl_3$: **5**, $[\alpha]^{23}_{D}$ +118° (c 0.98); **6**, $[\alpha]^{23}_{D}$ +20° (c 0.83); **7**, $[\alpha]^{23}_{D}$ +19° (c 1.33); **9**, $[\alpha]^{23}_{D}$ +20° (c 1.25); **10**, $[\alpha]^{23}_{D}$ +19° (c 1.05); **11**, $[\alpha]^{23}_{D}$ +8° (c 0.7); **12**, $[\alpha]^{23}_{D}$ +1° (c 0.6); **14**, $[\alpha]^{23}D$ −34° (c 2.0).

[12] Obtained by treatment of L-*tert*-butoxycarbonylhomoserine lactone with trifluoroacetic acid or L-homoserine in CF_3COOH at room temperature for 48 h.

[13] Borch, R. F.; Bernstein, M. D.; Durst, H. D. *J. Am. Chem. Soc.* **1971**, *93*, 2897. Recently Nozoe et al. have used a similar sequence of reactions for the preparation of a related compound: Fushiya, S.; Sato, Y.; Nozoe, S. *Chem. Lett.* **1980**, 1215.

[14] Measurement at room temperature showed broad signals for this compound.

[15] Since each diastereoisomer **5**, **6**, and **10** (prepared by treatment with excess LDA) was cleanly separated in the high-pressure liquid chromatography (HPLC) (Waters Associates μ-Porasil column using $CHCl_3$ or $CHCl_3$–AcOEt system), the diastereomeric purity of compounds throughout the synthesis was examined to indicate homogeneous peaks. On the other hand, compounds **6**, **9**, **10**, and **11** were treated under the individual conditions described in the text to give no diastereoisomers even for longer reaction times.

Matrix Photolysis of Tetracarbonyldihydridoiron. Evidence for Oxidative Addition of Dihydrogen on Tetracarbonyliron

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Received December 29, 1980

The photolysis of transition-metal, organometallic hydrides can lead to ligand loss which may or may not be apparent from the stoichiometry of the products, metal–hydrogen bond cleavage, or dihydrogen loss in polyhydrides.[1-3] The matrix-isolation technique offers a unique method for studying these processes, because the reactive intermediates which form as the primary photoproducts can in many cases be preserved for spectroscopic study and identification. In this report, I show evidence of the loss of dihydrogen from $H_2Fe(CO)_4$ and the subsequent recombination (oxidative addition).

Oxidative addition reactions in matrices have rarely been reported. Methane oxidatively adds to metals under photolytic conditions.[4] Methane has also been shown to add to iron dimers under conditions in which it is not clear whether photolysis is required.[5] Heretofore, there have been no reports of dihydrogen oxidatively adding to a metal center at such low temperatures. That such reactions should occur with very small activation energies is not surprising, because the coordinatively unsaturated centers which undergo oxidative addition are themselves very short-lived. Processes which scavenge them must be fast in order to be significant.[6]

Figure 1 shows the matrix infrared spectrum of $H_2Fe(CO)_4$ isolated in Ar. The apparatus and techniques used to obtain matrices of unstable materials has been described previously.[2] The hydride was sublimed into a stream of argon at −127 °C and

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Figure 1. (a) Infrared spectrum of matrix isolated $H_2Fe(CO)_4$. (b) Same matrix after 5-min irradiation with a low-pressure mercury lamp. (c) Same matrix after 7-min irradiation by the Nernst glower.

deposited at 10 K to obtain the matrix which is shown in Figure 1. Three features are assigned to the carbonyl stretching vibrations of $H_2Fe(CO)_4$ at 2122, 2051, and 2043 cm^{-1}. The two most intense bands appear split, but it is unclear whether the origin of the splitting is due to site perturbations or near coincidence of fundamental vibrations. The gas-phase structure of $H_2Fe(CO)_4$ is of C_{2v} symmetry and four carbonyl stretching modes are expected.[7] The matrix spectrum agrees quite well with that reported by Farmery and Kilner if one assumes their sample is contaminated with $Fe(CO)_5$.[8] This is not unreasonable because $Fe(CO)_5$ appears as a contaminant in most of the matrices which have been prepared in these studies. The matrix which produced the spectrum of Figure 1 was unique in having very little $Fe(CO)_5$ present. Still, bands at 2024 and 2005 cm^{-1} are assignable to $Fe(CO)_5$. The production of $Fe(CO)_5$ in the decomposition of $H_2Fe(CO)_4$ was hypothesized by King et al. in a sequence of reactions which led to the water gas shift[9] and is analogous to the decomposition of $H(SiPh_3)Fe(CO)_4$.[10] The infrared spectra of $H_2Os(CO)_4$ and $H_2Ru(CO)_4$ resemble that of $H_2Fe(CO)_4$ in that three of their fundamental vibrations come very close to each other in the 2070–2040-cm^{-1} region of the spectrum.[11] The splitting which is observed in the bands of Figure 1 may very well be due to near accidental degeneracy of those modes.

The matrix was photolyzed with a low-pressure mercury lamp for 5 min, and the spectrum shown in Figure 1b was obtained while using a germanium filter on the output of the Nernst glower. New bands appear at 2009, 1995, 1974, 1949, 1936, 1927, and 1917 cm^{-1}. The two most intense bands which appear at 1994 and 1974 cm^{-1} have been assigned to $Fe(CO)_4$ by Poliakoff and Turner.[12,13] A band which they report at 1988.5 cm^{-1} appears in the matrix spectrum with anomolously low intensity. This discrepancy may be due to the differing perturbations of nearby hydrogen and carbon monoxide molecules on the spectrum of $Fe(CO)_4$. To buttress this assignment other evidence suggests that $Fe(CO)_4$ is formed. The weak absorption due to CO at 2139 cm^{-1} does not perceptibly grow as a result of photolysis as might be expected for a CO loss process as extensive as shown by the growth of the bands which are assigned to $Fe(CO)_4$. Also, the photolysis of $H_2Fe(CO)_4$ in CO matrices leads to the formation of $Fe(CO)_5$. This can be explained by assuming that the principal photoprocess is dihydrogen loss which is followed by the incorporation of CO. In figure 1b, the bands at 1936 and 1917 cm^{-1} can be assigned to $Fe(CO)_3$ and $Fe(CO)_2$ and have been reported in the photolysis of $Fe(CO)_5$.[14] The other bands in the same region of the spectrum behave in the same manner as those of $Fe(CO)_3$ and $Fe(CO)_2$ and are presumed to originate from other coordinatively unsaturated species.

When the matrix of photolyzed $H_2Fe(CO)_4$ is exposed to the radiation of the Nernet glower, many of the features which became apparent in Figure 1b become less intense, in particular, those assigned to $Fe(CO)_4$. Concomittantly, bands assigned to $H_2Fe(CO)_4$ become more intense. Figure 1c shows the spectrum of the matrix after 7 min of exposure. The reverse process does not proceed to completion. Presumably some of the H_2 is too far removed from the $Fe(CO)_4$ to be able to recombine. With additional H_2 in the matrix the process can be very nearly reversed. Thus, the dominant process which these experiments have demonstrated can be described by

$$H_2Fe(CO)_4 \underset{\text{glower photolysis}}{\overset{\text{Hg lamp photolysis}}{\rightleftharpoons}} H_2 + Fe(CO)_4$$

In a related experiment, $Fe(CO)_5$ was deposited in a matrix which contained 10 atom % hydrogen in argon. Upon photolysis with the mercury lamp, the 2051-cm^{-1} band of $H_2Fe(CO)_4$ was clearly evident and the 2043-cm^{-1} band appeared as a shoulder on features due to $Fe(CO)_5$. The initial appearance of the bands due to the hydride occurred with irradiation with the mercury lamp. This was accompanied by the photolysis of $Fe(CO)_5$ leading to $Fe(CO)_4$. The growth of the hydride bands was observed to continue when the matrix was irradiated by the Nernst glower, exactly analogous to what was observed in photolyzed matrices of $H_2Fe(CO)_4$.

In addition to the bands due to $H_2Fe(CO)_4$ growing in, other bands become more intense as well, at 2087, 2009 and 1985 cm^{-1} (Figure 1c). These bands remained throughout the annealing of the matrix, while a band at 1963 cm^{-1} exhibited only a transitory existence. The former set must belong to a coordinatively unsaturated fragment. The band at 2087 cm^{-1} lies in the same region of the spectrum as the totally symmetric mode of $Fe(CO)_4$. Hence, these bands may belong to $H_2Fe(CO)_3$.

The reaction of H_2 and $Fe(CO)_4$ which is promoted by the visible radiation of the Nernst glower is analogous to the reaction of $Fe(CO)_4$ and CO in matrices.[12,12,15] In the latter system, Davies et al. have reported that absorption at 770 nm causes $Fe(CO)_4$ to undergo isomerization which, in effect, pseudorotates the fragment in the matrix.[15] Recombination occurs when the fragment rotates until a vacant coordination site is oriented at an adjacent CO. In addition to reorienting the fragment, the photon may also serve to break specific interactions with matrix molecules, such as CH_4, Xe, or Kr.[13] By annealling a photolyzed matrix of $H_2Fe(CO)_4$ composed of 10 atom % H_2 in argon at $T > 20$ K, the bands due to $Fe(CO)_4$ were also observed to decline in intensity. However, bands due to $H_2Fe(CO)_4$ did not undergo a simple increase in intensity. Rather, the growth in intensity which correlated with the decline of those bands assigned to $Fe(CO)_4$ occurred as shoulders to the parent bands. The positions at which growth appeared were positions which gain intensity when matrices of $H_2Fe(CO)_4$ are themselves annealed. Thus, it is unclear whether growth of these shoulders was due to newly formed $H_2Fe(CO)_4$ or simply due to perturbation of the spectrum

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of $H_2Fe(CO)_4$ which is already present in the matrix. However, it is difficult to reconcile the loss of intensity in the bands assigned to $Fe(CO)_4$ without presuming that H_2 combines with $Fe(CO)_4$ by a thermal process.

These results are similar to the solution behavior of $H_2Ru(PPh_3)_3CO$ in that photolysis is presumed to lead to the formation of H_2 and $Ru(PPh_3)_3CO$.[16] The reverse process has not been demonstrated. It is intriguing to note that $Fe(CO)_4$ exhibited anomolous behavior in methane matrices.[13,14] In light of this report and recent reports of the chemistry of iron atoms, the data must be seriously reexamined in order to differentiate between CH_4 which has oxidatively added and that which has formed weak adducts.

Acknowledgment. I thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

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Direct Evidence for Exciplex Formation between a Triplet Alkanone and an Alkylbenzene

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Received January 9, 1981

Exciplexes are often postulated as intermediates in the quenching of triplet carbonyl compounds by olefinic and aromatic hydrocarbons.[1] Recently,[2] we presented new evidence for the reversible formation of a triplet exciplex of acetone and benzene on the basis of results obtained with 9,10-dibromoanthracene (DBA, at concentration $<10^{-3}$ M) as an acceptor of triplet energy.[3] Two triplet species were shown to act as energy donors, triplet acetone itself and its exciplex with benzene, the exciplex being the better donor.

When triplet cyclohexanone ($^3A^*$) is quenched by *o*-xylene (Xy) in a cyclohexane solution, the same sensitized DBA method now clearly reveals the formation of a relatively long-lived transient, $^3E^*$. Figure 1 shows a typical decay curve of the DBA fluorescence intensity, following ns pulse excitation at 305 nm, a wavelength at which both the alkanone and DBA absorb.[4] The first intensity peak, followed by fast decay, corresponds to the direct excitation and emission of DBA ($\tau_F \sim 2.4$ ns). The second peak, at $t_{max} \sim 100$ ns, reflects the buildup of the exciplex. Thus the fluorescence decay function comprises three components, of which the last two result from energy transfer to DBA.

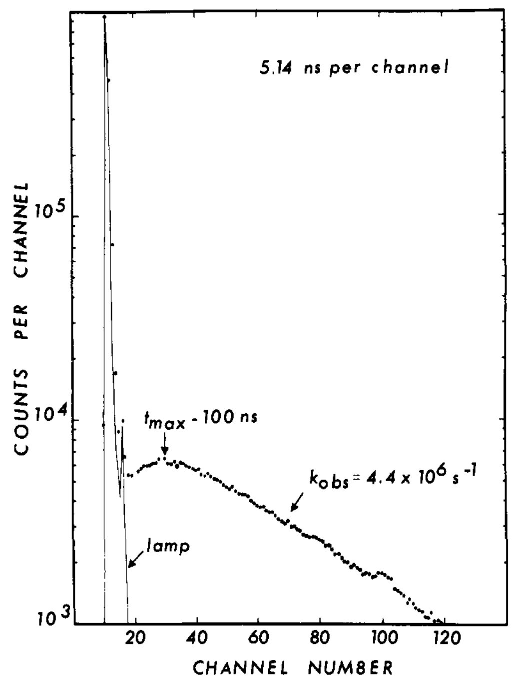


Figure 1. Fluorescence decay curve of a degassed *o*-xylene–cyclohexane (2:3 v/v) solution of DBA (1.1×10^{-4} M) and cyclohexanone (6.9×10^{-2} M) at 20 °C, with $\lambda_{exc} = 305$ nm. The full line is the lamp profile (the distortions around channels 77 and 100 in the DBA fluorescence curve are also present in the tail of the lamp curve). In the absence of cyclohexanone, the decay is strictly monoexponential ($1/\tau_F$).

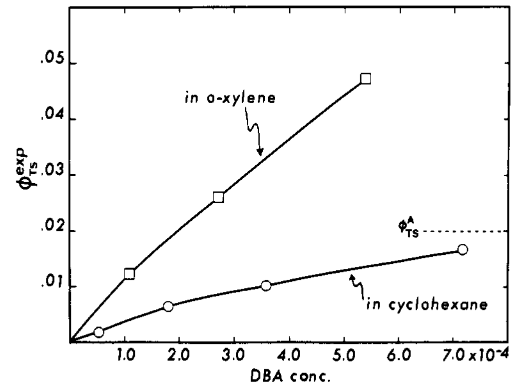
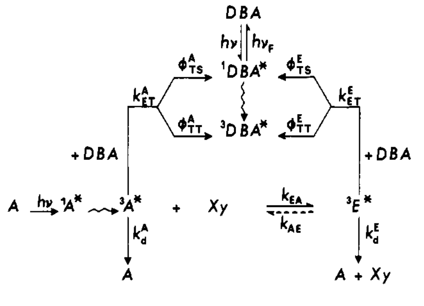


Figure 2. Efficiency of TS energy transfer as a function of DBA concentration in two solvents.

Scheme I



The main processes are presented in Scheme I, where exciplex dissociation is shown by a dashed arrow. It is in this respect that the quenching of $^3A^*$ by Xy differs most from that of triplet acetone by benzene. There, kinetic data implicated an exciplex in fast dynamic equilibrium with its components, such that triplet acetone and its benzene exciplex had the same decay rate.[2] At

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(3) In an energy-transfer process which results in the sensitized fluorescence of DBA. Although a higher triplet state of DBA (T_n, with $n \leq 2$) is probably populated before DBA (S_1), followed by $T_n \rightsquigarrow S_1$ or $T_n \rightsquigarrow T_1$, for simplicity the overall process is viewed here as a TS process. These alternatives are kinetically undistinguishable in the present work.

(4) At 20 °C in a degassed solution. The experimental method has been described.[2] Cyclohexanone (Eastman) was redistilled; *o*-xylene and cyclohexane (Burdick and Jackson "Distilled in Glass") were used without purification. The intensity decay curves were obtained by the single-photon counting method. The fluorescence was monitored at 430 nm.[2] The steady-state emission spectrum of the solution of Figure 1 is the same whether degassed or aerated; i.e., DBA fluorescence with a weak component of cyclohexanone fluorescence.

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