J. Am. Chem. Soc. 1983, 105, 4481-4483

removal of methanol under reduced pressure and extraction with ether, the residual aqueous solution was chromatographed on a Sephadex LH-20 column with distilled water as solvent. Fractions that gave LNA (**1**) upon treatment with 0.5 M $H_2SO_4$ (100 °C, 1 h) or 1 M NaOH (room temperature, 1 h) were combined and purified further by successive treatments on a Waters Sep-pak $C_{18}$ cartridge (10% acetonitrile in water), cellulose, and Sephadex LH-20 column (water) to give 2 mg of a noncrystalline compound that we name prelunularic acid (preLNA, **2**).

The IR spectrum (film, $cm^{-1}$) of preLNA shows the presence of the following functional groups: hydroxyl (3300), aromatic ring (1600, 1514, 830), carboxylate (1573, 1402), and enone (1610). Since separation and purification processes were carried out in water, the nature of the countercation is not clear. Brief treatment of etheral solution of **2** in free acid form with diazomethane afforded a methyl ester ($\nu_{max}$ 1735 $cm^{-1}$, 3 H singlet at 3.78 ppm). The high-resolution mass spectrum of the methyl ester showed $M^+$ at 290.1133 (11.2%, $C_{16}H_{18}O_5$), together with prominent peaks at 272.1076 (23.8%, $C_{16}H_{16}O_4$, $M^+ - H_2O$), 258.0195 (35.7%, $C_{15}H_{14}O_4$), and 107.0503 (100%, $C_7H_7O$). Absorption maximum of preLNA in water are as follows: at pH 7, 257 nm ($\epsilon$ 10 400) and 220 ($\epsilon$ 10 100) and at pH 2, 280 nm (sh), 240 ($\epsilon$ 9600), and 222 ($\epsilon$ 12 000). Its UV spectrum at pH 12 showed time-dependent changes with a clear set of isosbestic points at 247, 284, and 307 nm, and the final curve after 160 min was identical with that of LNA (**1**) at the same pH, i.e., $\lambda_{max}$ 238 nm ($\epsilon$ 17 800) and 293 ($\epsilon$ 5200). This indicates the direct conversion of preLNA (**2**) to LNA (**1**) under basic conditions.

The $^1H$ NMR spectrum of preLNA (**2**, 360 MHz, $D_2O$) showed peaks at 2.4–2.8 (8 H, m), 4.26 (1 H, br s, CH(O–)), 6.86, and 7.21 ppm (each 2 H, d, $J$ = 8.6 Hz, four protons on para-substituted benzene). First-order analysis of the multiplet at 2.4–2.8 ppm indicated the presence of a $CH_2CH(O–)CH_2$ moiety: 2.46 (dd, $J$ = 10.5, 19.5 Hz, $4_{ax}$-H), 2.50 (dd, $J$ = 8.0, 21.0 Hz, $6_{ax}$-H), 2.70 (dd, $J$ = 5.0, 21.0 Hz, $6_{eq}$-H), 2.74 ppm (dd, $J$ = 5.0, 19.5 Hz, $4_{eq}$-H). These spectroscopic properties together with its direct conversion to LNA (**1**) led to structure **2** for preLNA.

Absolute configuration of the hydroxyl group at C-5 was determined as *S* by CD measurements of a derivative of preLNA (**2**). Reduction of **2** with sodium borohydride and subsequent treatment with diazomethane yielded two epimeric diol methyl esters, **3** and **4**, in a 4:1 ratio. The $^1H$ NMR spectrum of **3** and **4** showed the relative configurations of two hydroxyl groups at C-3 and C-5 as eq–eq and ax–eq, respectively.[8] Diol ester **4** was converted to the corresponding bis(*p*-(dimethylamino)benzoate) (reflux 24 h with $Me_2N-C_6H_4COCl$ in THF/$Et_3N$; EI MS, *m/z* 600 ($M^+$); $\lambda_{max}$ (MeOH) 314 nm), which showed typical exciton-split CD Cotton effects at 321 nm, $\Delta\epsilon = +46.3$, and 295 nm, $\Delta\epsilon = -14.8$.[9] The long axes of the two benzoate chromophores thus constitute a right-handed screwness, and this defines the absolute configurations at C-3 and C-5 as *R* and *S*, respectively (as shown in **4**).[10]

Hydrangenol **5**, a $C_{15}$ stilbenoid isolated from Hydrangea species, has been postulated as the direct precursor of LNA (**1**) on the basis of the highly efficient bioconversion of labeled **5** to **1** in *L. cruciata*.[3] However, hydrangenol **5** has never been detected in liverworts,[3,4] and its absence was attributed to the small pool size of this compound.[3] In contrast, the newly isolated preLNA (**2**) is a reasonable cyclization product of *p*-coumaryl $\beta$-triketo acid and is a more plausible immediate precursor of LNA (**1**) than hydrangenol **5**. Formation and accumulation of preLNA is not limited to the cells of *M. polymorpha* cultured under specific conditions as has been demonstrated by its presence in the intact plant of the same liverwort.

PreLNA (**2**) is also of interest since it is the first example of an intermediate possessing "prearomatic" structure in the phenylpropanoid–polymalonate pathway.[11] Further studies on this new biosynthetic intermediate will contribute in clarifying the genesis of the aromatic ring of polymalonate origin.

**Supplementary Material Available:** Repeatedly scanned UV spectra of prelunularic acid **2** in water at pH 12 and UV and CD spectra of bis(*p*-(dimethylamino)benzoate) of the diol methyl ester **4** (2 pages). Ordering information is given on any current masthead page.

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[8] Partial $^1H$ NMR of **3** (360 MHz, MeOH-$d_4$): 1.71 (ddd, $J$ = 7.9, 10.0, 12.5 Hz, $4_{ax}$-H), 2.19 (dddd, $J$ = 1.6, 3.0, 5.9, 12.5 Hz, $4_{eq}$-H), 2.24 (ddd, $J$ = 2.4, 7.6, 17.6 Hz, $6_{ax}$-H), 2.40 (br ddt, $J$ = 1.3, 1.6, 4.9, 17.6 Hz, $6_{eq}$-H), 3.89 (dddd, $J$ = 3.0, 4.9, 7.6, 10.0 Hz, 5-H), 4.64 ppm (br t, $J$ = 1.3, 2.4, 5.9, 7.9 Hz, 3-H). Partial $^1H$ NMR of **4**: 1.62 (ddd, $J$ = 4.4, 11.2, 12.7 Hz, $4_{ax}$-H), 2.05 (ddt, $J$ = 1.3, 3.4, 12.7 Hz, $4_{eq}$-H), 2.07 (br dd, $J$ = 0.6, 9.1, 18.0 Hz, $6_{ax}$-H), 2.56 (br dd, $J$ = 1.2, 1.3, 5.2, 18.0 Hz, $6_{eq}$-H), 4.07 (dddd, $J$ = 3.4, 5.2, 9.1, 11.2 Hz, 5-H), 4.78 ppm (br t, $J$ = 0.6, 1.2, 3.4, 4.4 Hz, 3-H).

[9] In view of the minute quantity of the dibenzoate, the $\Delta\epsilon$ value was estimated from the UV absorbance by taking $\epsilon$ 31 600 as the standard value for a monobenzoate, see: Harada, N.; Suzuki, H.; Uda, H.; Nakanishi, K. *J. Am. Chem. Soc.* **1971**, *93*, 5577–5579.

[10] The chirality between the two benzoate transition moments are the same and independent of the ring conformation, except for an unlikely skewed boat conformation in which the two benzoate groups are axial. The $^1H$ NMR spectrum of bis(*p*-(dimethylamino)benzoate) of the diol **4** measured for confirmation showed signals at 6.19 (tripletlike s, $W_{1/2}$ = 7 Hz, $3_{eq}$-H) and 5.36 ppm (br peak, $W_{1/2}$ = 22 Hz, $5_{ax}$-H), indicating that the same conformation of cyclohexane ring in the diol **4** was retained in its dibenzoate.

[11] Cf.: Weiss, U.; Edwards, J. M. "The Biosynthesis of Aromatic Compounds"; Wiley-Interscience: New York, 1980; pp 326–381.

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# Adsorption of Bifunctional Organic Disulfides on Gold Surfaces

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The preparation and structural characterization of supported monolayer assemblies of oriented organic molecules are of great interest in a variety of interface studies. Examples involve lubrication,[1] electrochemistry,[2,3] electronic and vibrational spectroscopy,[4,5] photochemical mechanisms,[4,6] electrical conduction,[4,7] catalysis,[8] and biological membranes.[9] In this communication we report a useful technique for preparing supported, oriented monolayers of polyfunctional organic molecules with a variety of molecular structures, particularly with a wide range of choice for the functional group located at the ambient interface. This technique employs solution adsorption of disulfides on zerovalent gold substrates (useful because of their inertness toward corrosion or oxidation) and involves spontaneous[10] organization of the films, in contrast to the well-known Langmuir–Blodgett deposition,[11]

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[1] For examples see: Adamson, A. W. "Physical Chemistry of Surfaces", 3rd ed.; Wiley: New York, 1976; Chapter 10.

[2] Murray, R. W. *Acc. Chem. Res.* **1980**, *13*, 135–141.

[3] Soriaga, M. P.; Hubbard, A. T. *J. Am. Chem. Soc.* **1982**, *104*, 3937–3945 and references therein. Hubbard, A. T. *Acc. Chem. Res.* **1980**, *13*, 177–184.

[4] Kuhn, H.; Mobius, D. In "Techniques of Organic Chemistry"; Weissberger, A., Rossiter, B. W., Eds.; Wiley: New York, 1972; Vol. 1, Chapter 7.

[5] Knoll, W.; Philpott, M. R.; Golden, W. G. *J. Chem. Phys.* **1982**, *77*, 219–225. Rabolt, J. F.; Santo, R.; Swalen, J. D. *Appl. Spectrosc.* **1980**, *34*, 517–521.

[6] Whitten, D. G. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 440–450.

[7] Polymeropoulos, E. E.; Sagiv, J. *J. Chem. Phys.* **1978**, *69*, 1836–1847. Sugi, M.; Fukui, T.; Lizima, S. *Phys. Rev. B* **1978**, *18*, 725–732. Furtlehner, J. P.; Messier, J. *Thin Solid Films* **1980**, *68*, 233–239.

[8] Richard, M. A.; Deutsch, J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1979**, *100*, 6613–6625.

[9] Waldbillig, R. C.; Robertson, J. D.; McIntosh, T. J. *Biochim. Phiophys. Acta* **1976**, *448*, 1–14. McIntosh, T. J.; Waldbilling, R. C.; Robertson, J. D. *Ibid.* **1976**, *448*, 15–28. Kornberg, R. D.; McConnell, H. M. *Biochemistry* **1971**, *10*, 1111–1118.

[10] Evidence for spontaneous organization of supported organic monolayers has been demonstrated recently for a variety of molecules on Pt surfaces in a series of significant studies by Hubbard et al.[3] and for fatty acids and alcohols on oxide surfaces.[12]

[11] For leading references, see: Gaines, G. L. "Insoluble Monolayers at Liquid-Gas Interfaces"; Interscience: New York, 1966.

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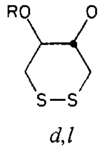
Table I. Solution Adsorption of Organic Disulfides on Evaporated Gold Films at Room Temperature

| <br>*d,l*<br>R = | thickness of film by ellipsometry,[a-c] Å | estimated max vert extension of adsorbed molecules with attachment at the S–S group,[f] Å | contact angle of water, deg[i] |
|---|---|---|---|
| $CF_3(CF_2)_6CO$ (1a) | 10.5 ± 1.0[d] | 15.5, 11[g] | 104 ± 1 |
| $CH_3(CH_2)_{14}CO$ (1b) | 20.5 ± 1.0[e] | 25 | 96 ± 1 |
| $O_2NC_6H_4CO$ (1c) | 9.5 ± 2.5 | 12.5 | 52 ± 2 |
| $CH_3CO$ (1d) | 7.0 ± 2.5 | 8 | 47 ± 1 |
| $CF_3CO$ (1e) | 4.0 ± 0.5 | 9 | 57 ± 1 |
| H (1f) | 5.0 ± 0.5 | 6 | 34 ± 1 |
| $(HO_2C(CH_2)_2S)_2$ (**2**) | 4.0 ± 0.5 | 6[h] | 13 ± 2 |
| $(CH_3(CH_2)_{15}S)_2$ (**3**) | 21.5 ± 1.0 | 22[h] | 99 ± 1 |

[a] Determined at 6328 and 4420 Å with good agreement at both wavelengths. Measurements were made on a Ruldoph 423 null ellipsometer. The majority of the data were taken at 6328 Å. Film thicknesses were calculated from the differences in the measurements between untreated and treated gold substrates. Untreated substrates allowed to stand for periods of up to ~30 min gave stable readings that could be interpreted in terms of ~1 Å of contaminants adsorbing. Methanol washes consistently gave back the original control readings within an equivalent film thickness (of refractive index ~1.5) of ±~0.5 Å. [b] Thicknesses with error limits are the averages of two-four different samples. The others represent only one sample. Spot to spot variations on any one sample were less than the sample to sample errors. [c] Film thicknesses calculated for an index of refraction (*n*) of 1.50 unless otherwise noted. This value is an estimate on the basis of typical values for similar organic molecules. [d] Calculated for *n* = 1.333 with *n* extrapolated from solution data measured in a refractometer. Using a value of 1.50 would give films calculated to be ~2.5 Å thinner. [e] Calculated for *n* = 1.48. Using a value of *n* = 1.50 would give films calculated to be ~0.5 Å thinner. [f] Measured from space-filling models with the axis connecting to the two sulfur groups assumed to be one edge and the distance measured along an axis perpendicular to the S-S axis. [g] The most strain-free conformation does not have fully extended, parallel fluorinated side chains; rather, the chains are spread at an angle of ~120° to each other. This conformation has a S-(molecule end) distance of 12.5 Å measured from a point between the sulfur atoms to the maximum extension of the molecule along the axis of rotation between the two fluorinated side chains. [h] The chain extensions for the acyclic disulfides are those determined for a single sulfur and its chain groups. [i] Average of six measurements of static drops at ambient temperature. For a discussion of contact angles, see: Adamson, A. W. "Physical Chemistry of Surfaces"; Wiley-Interscience: New York, 1976; pp 333-363.

an arduous procedure that severely restricts the types of bifunctional molecules used to those containing only one polar group. Further, we demonstrate that structural characterization of these monolayers can be done conveniently by reflectance infrared spectroscopy. Our findings also point out a sparsely studied and interesting property of gold surfaces.[13]

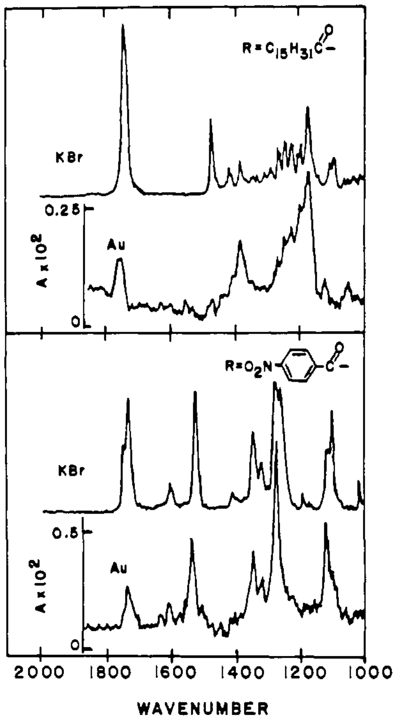


**Figure 1.** Infrared spectra of the $C_{15}H_{31}CO$ and *p*-nitrobenzoate derivatives of the diol **1f** in KBr pellets and absorbed on gold surfaces. The units of intensity in the monolayer spectra are absorbances (Å) defined as –log (sample reflectivity/unreacted gold surface reflectivity).

Table I lists a representative series of organic disulfides that have been absorbed on freshly evaporated gold substrates.[20] The table shows measured film thicknesses, maximum chain extensions determined from molecular models, and measured contact angles of water. The film thickness in Table I are quite close but slightly smaller than the estimated values that would be obtained for an arrangement of molecules having *bulk* packing densities and full vertical chain extensions away from the substrate surface. This interpertation of closest packing of disulfide monolayers is further supported by an independent radioisotopic labeling study using a tritiated isomer of **1e** (methyl $^3H$) that shows that site densities of ~4.4 × $10^{14}$ molecules $cm^{-2}$ are obtained.[21] In addition, the observation of variations of wetting angles in a manner consistent with the polarity of the nondisulfide functional groups gives additional strong evidence for adsorption of the disulfide moiety at the gold surface (in analogy with previous studies of Pt[3]).

Figure 1 shows respective comparisons of the bulk transmission (KBr pellet) and monolayer reflectance infrared[22] spectra of **1b** and **1c**. The appearance of the series of sharp bands in the 1200-1350-$cm^{-1}$ region of the spectra of **1b** is ascribed to the twisting and wagging modes of the alkyl chain $CH_2$ groups and indicates that the chains are at full extension with a planar zigzag conformation.[23] Both monolayer spectra show that the ester C=O mode (~1703 $cm^{-1}$) has a weakened intensity relative to the CO-O mode in the monolayer spectrum. We interpret this as indicating that the carbonyl group is in a conformation nearly

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(12) (a) Boerio, F. J.; Chen, S. L. *J. Colloid Interface Sci.* **1980**, *73*, 176-185. (b) Sagiv, J. *J. Am. Chem. Soc.* **1980**, *102*, 92-98.

(13) Gold is recognized to be one of the least active metals in chemisorption as evidenced by its inertness toward molecular oxygen.[14-16] Most studies with organic molecules have focused on reversible physisorption.[14,16,17] Carbon monoxide, strongly chemisorbed on many transition metals, interacts only weakly with gold.[14,16,18] An earlier infrared study reported dissociation of acetic acid on evaporated gold, suggesting some surface chemistry exists although its nature was not understood.[19]

(14) Trapnell, B. M. W. *Proc. Roy. Soc. Lodon, Ser. A* **1953**, *A218*, 566-577.

(15) (a) Chrader, M. E. *Surf. Sci.* **1978**, *78*, L227-232. (b) Schrader, M. E. J. *Colloid Interface Sci.*, **1977**, *59*, 456-460. (c) Ford, R. R.; Pritchard, A. J. *Chem. Commun.* **1968**, 326-363.

(16) Chesters, M. A.; Somorjai, G. A. *Surf. Sci.* **1975**, *52*, 21-28.

(17) Lee, W. Y.; Slutsky, L. J. *Surf. Sci.* **1976**, *54*, 169-178.

(18) Kottke, M. L.; Greenler, R. G.; Tompkins, H. G. *Surf. Sci.* **1972**, *32*, 231-243.

(19) Tompkins, H. G.; Allara, D. L. *J. Colloid Interface Sci.* **1974**, *49*, 410-421.

(20) These substrates were covered for a minute or so with dilute solutions of the disulfides ($10^{-3}$-$10^{-1}$ M) in a variety of solvents (typical solvents included methylene chloride, hexane, ethanol, and acetone), removed from solution, and thoroughly rinsed with fresh solvent. A zerovalent gold surface is necessary for adsorption: plasma oxidation to form gold oxide surfaces results in no detectable adsorption.

(21) This value is approximately twice that predicted with a space-filling model as would be expected from scanning electron microscope analyses of the real sample surface area (~1.5-2 times the geometrical area).

(22) Monolayer spectra were obtained by reflection at an 86° angle of incidence by using a modified Digilab 15-B Fourier transform spectrometer (see: Allara, D. L. In "Vibrational Spectroscopies For Absorbed Species"; Bell, A. T., Hair, M., Eds.; American Chemical Society: Washington, DC, 1980; ACS Symp. Ser. 137 Chapter 3.

(23) Snyder, R. G. *J. Mol. Spectrosc.* **1960**, *4*, 411-434.

parallel to the surface. We have quantified this approach for **1c** using a theoretical treatment previously described.[24] The differences between the calculated isotropic and experimental monolayer spectra are interpreted in terms of a model structure having a tilt of the aromatic-$NO_2$ axis of 57° from the surface normal with the ring plane perpendicular to the surface plane and is consistent with the wetting angle and ellipsometry data.

While the absorption of disulfides on many transition metals is well-known, there are important differences that distinguish their closest-packed adsorption on Au. First, "clean", zerovalent gold surfaces are easy to prepare by vacuum evaporation. Second, these surfaces only slowly become contaminated under laboratory ambient conditions and do not form oxides. This feature is particularly significant as we have observed that adsorption of **2** on evaporated Ag shows evidence, by IR, of bonding at both the disulfide and carboxylate ends of the molecule (the latter presumably at oxide sites). Related to this point is the observation[25] that both C-S and S-S bond cleavage occurs in disulfide adsorption on silver. It is expected that other clean transition-metal surfaces will also cleave the C-S bond. Our data give no evidence for such cleavages on Au. At present, the bonding involved in disulfide adsorption on gold is unknown. It can be speculated that S-S dissociative chemisorption occurs similar to the case of silver,[25] but no definitive evidence exists.[26]

We conclude that gold surfaces can be easily functionalized by disulfide adsorption. We will report in greater detail about the preparation and characterization of these monolayers and on their application in model interface studies in subsequent publications.

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(24) Allara, D. L.; Swalen, J. D. *J. Phys. Chem.* **1982**, *86*, 2700-2704.

(25) Sandroff, C. J.; Hershbach, D. R. *J. Phys.* Chem. **1982**, *86*, 3277-3279.

(26) X-ray photoelectron emission measurements and surface-enhanced Raman scattering have not shown definitive evidence of a dissociated S-S bond or formation of an Au-S bond.

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## Approach to Stereochemically Defined Cycloheptadiene Derivatives Using Organoiron Chemistry[1]

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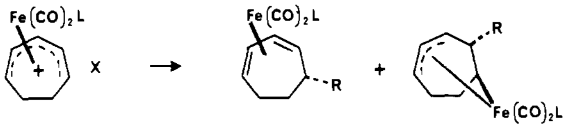
The attachment of a transition-metal moiety to an olefinic ligand offers a unique means of attaining stereospecificity during a variety of chemical transformations and C-C bond-forming processes.[2,3] The cycloheptadienylmetal system is ideally suited for 1,3-stereocontrol, but inspection of the literature reveals that the reactivity of cycloheptadienyl-$Fe(CO)_3$ complexes, e.g., **1a**, bears little resemblance to that of the well-behaved six-membered ring counterparts. In general, addition of nucleophiles to **1a** results in a mixture of products of type **2a** and **3a**, often in poor yield.[4] Since these complexes offer a unique means of synthesizing cycloheptadiene derivatives, we decided to investigate the possibility of controlling the reactivity of the cycloheptadienyliron system, with gratifying results.

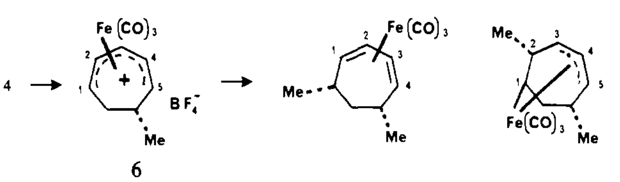


**1**a, L = CO; X = $BF_4^-$
b, L = $Ph_3P$, X = $PF_6^-$
c, L = $(PhO)_3P$, X = $PF_6^-$

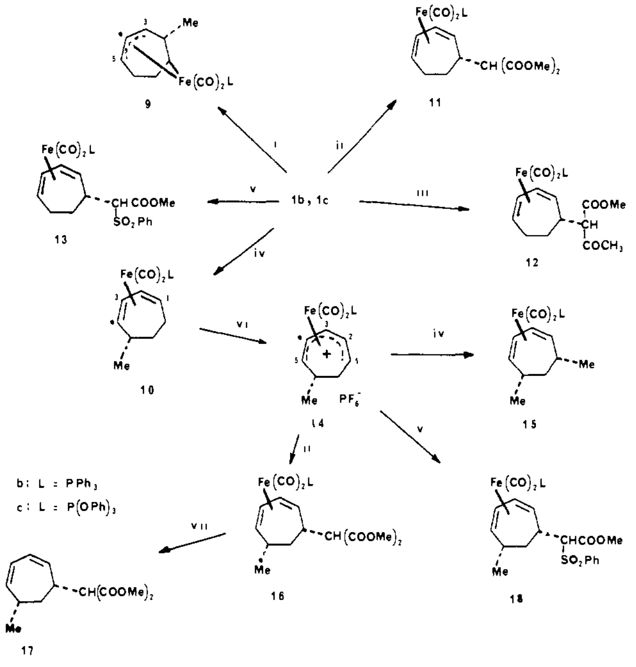
**2a**, L = CO
b, L = $PPh_3$; R = H
**4**, L = CO; R = Me

**3a**, L = CO
b, L = $PPh_3$; R = H

Scheme I



Scheme II[a]



[a] Reagents: (i) MeLi, $CH_2Cl_2$, -78 °C; (ii) $NaCH(CO_2Me)_2$, THF, 20 °C; (iii) $NaCH(CO_2Me)COCH_3$, THF, 20 °C; (iv) $Me_2CuLi$, $Et_2O$, 0 °C; (v) $NaCH(SO_2Ph)CO_2Me$, THF, 20 °C; (vi) $Ph_3C^+PF_6^-$, $CH_2Cl_2$; (vii) $Me_3NO$, $CH_3CONMe_2$, 55 °C, 36 h.

We commence by describing some preliminary, less successful experiments performed on the tricarbonyliron complex **1a**, which will be seen to contrast with the triphenylphosphine and triphenylphosphite derivatives **1b** and **1c**.[5] Treatment of **1a** with methyllithium ($CH_2Cl_2$, -78 °C)[6] *or* lithium dimethylcuprate

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(1) Organoiron Complexes in Organic Synthesis. Part 30. Part 29: Pearson, A. J.; Richards, I. C. *Tetrahedron Lett.*, in press.

(2) See, for example: Pearson, A. J. "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Vol. 8, Chapter 58. Jaouen, G. "Transition Metal Organometallics in Organic Synthesis"; Alper, H., Ed.; Academic Press: New York, 1978; Vol. 2, Chapter 2.

(3) Pearson, A. J.; Ong, C. W. *J. Org. Chem.* **1982**, *47*, 3780.

(4) Aumann, R. *J. Organomet. Chem.* **1973**, *47*, C28. Edwards, R.; Howell, J. A. S.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1974**, 2105. Burton, R.; Green, M. L. H.; Abel, E. W.; Wilkinson, G. *Chem. Ind.* (*London*) **1958**, 1952. Burton, R.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1961**, 594. Dauben, H. J.; Bertelli, D. J. *J. Am. Chem. Soc.* **1961**, *83*, 497. Hashmi, M. A.; Munro, J. D.; Pauson, P. L.; Williamson, J. M. *J. Chem. Soc. A.* **1967**, 240. Evans, J.; Howe, D. V.; Johnson, B. F. G.; Lewis, J. *J. Organomet. Chem.* **1973**, *61*, C48. Brown, D. A.; Chawla, S. K.; Glass, W. K. *Inorg. Chim. Acta* **1976**, *19*, L 31. Kane-Maguire, L. A. P.; Odiaka, T. I.; Williams, P. A. *J. Chem. Soc., Dalton Trans.* **1981**, 200. Hackett, P.; Johnson, B. F. G.; Lewis, J.; Jaouen, G. *Ibid.* **1982**, 1247.

(5) Preparation of **1b** and **1c** was as follows: Cycloheptadiene-$Fe(CO)_3$ was obtained in 88% yield from the reaction of cycloheptadiene and $Fe(CO)_5$ in $Bu_2O$ (reflux under $N_2$ 42h). This was converted to the desired complexes. **1b**: Treatment of cycloheptadiene-$Fe(CO)_3$ with $Ph_3P$ (1.2 equiv) in $Bu_2O$ (reflux, 24 h) to give crystalline cycloheptadiene-$Fe(CO)_2PPh_3$ (46% yield). Treatment of this product with $Ph_3C^+PF_6^-$ (1.2 equiv, $CH_2Cl_2$, 20 °C, 2 h) followed by precipitation with wet ether gave **1b** (91%). **1c**: Treatment of cycloheptadiene-$Fe(CO)_3$ with $P(OPh)_3$ (1.1 equiv, $Bu_2O$, Ar balloon, reflux 17 h) gave cycloheptadiene-$Fe(CO)_2P(OPh)_3$ as an oil that could not be separated from small amounts of residual $P(OPh)_3$. Reaction of the crude complex with $Ph_3C^+PF_6^-$ (1.2 equiv, $CH_2Cl_2$, 20 °C, 45 min) gave **1c** (80% *overall* from cycloheptadiene-$Fe(CO)_3$).

0002-7863/83/1505-4483$01.50/0