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Convenient and Improved Synthesis of Tricarbonyl(1,2-dihydropyridine)iron Complex

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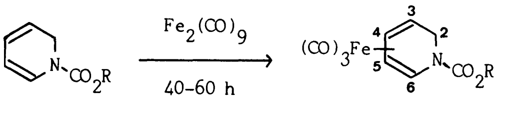
Synopsis. (*N*-Alkoxycarbonyl-1,2-dihydropyridine)-tricarbonylirons are conveniently prepared in good yields by photo-irradiation in the presence of excess pentacarbonyliron without any solvent. ^{13}C NMR spectra of the complexes are also described.

Alhough chemistry and synthetic utility of tricarbonyl(1,3-cyclohexadiene)iron complexs have been extensively studied for past several years,[1,2] there have been few investigations on the *N*-heterocyclic analogues.[3] Alper first reported the synthesis of (*N*-alkoxycarbonyl-1,2-dihydropyridine)tricarbonyliron complexes by reaction of *N*-alkoxycarbonyl-1,2-dihydropyridines (**1**) with enneacarbonyldiiron.[3a] However, the yields were relatively low [42 and 34% for *N*-methoxycarbonyl- and *N*-ethoxycarbonyl-1,2-dihydropyridines (**2a** and **2b**), respectively] and, in addition, the reaction time was exceedingly long (40—60 h).



1a R=Me
1b R=Et

2a R=Me (Y=42%)
2b R=Et (Y=34%)

Scheme 1.

In connection with our recent study on synthesis and reaction of 1,2-dihydropyridines,[4,5] we are interested in the tricarbonyliron complex, because 1,2-dihydropyrodines have turned out to be valuable synthetic intermediates for alkaloids and other *N*-heterocycles[4] and therefore tricarbonyl(1,2-dihydropyridine)iron complexes may find inherent utility in these fields.

Results and Discussion

At first, we tried to prepare **2a** according to Alper's procedure. However, 50% conversion of the reaction could be achieved after 65 h and the yield was 23% (46% based on the conversion) in our hands. It is highly desirable to develop more convenient and improved procedure to prepare **2**. Then, we have tried photochemical reaction of **1** with pentacarbonyliron, since in some cases photochemical reactions of simple 1,3-dienes with pentacarbonyliron have been used for the preparation of tricarbonyl(1,3-diene)iron complexes.[6] Thus, we have found that photo-irradiation of **1** in the presence of cxcess pentacarbonyliron *without any solvent* affords **2** in good yield within reasonably short reaction time. The results are summarized in Table 1.

There are a few points which should be noted here. First, the reaction time is significantly diminished in comparison with the Alper's method which requires 40—60 h. Second, the yields are higher than those of the Alpers'. Third, as the amount of pentacarbonyliron increases, the yield becomes higher. Thus, **2a** could be obtained in up to 80% yield by 18 h irradiation in the prseence of 5 fold excess of pentacarbonyliron. The reaction was clean and 90—95% of unreacted pentacarbonyliron was recovered.

TABLE 1. PHOTOCHEMICAL REACTION OF **1** WITH PENTACARBONYLIRON

$$\mathbf{1} \xrightarrow[Fe(CO)_5]{h\nu} \mathbf{2}$$

R	**1** (mmol)	$Fe(CO)_5$ (mmol)	Time/h	Yield/%
Me	10	20	28	45
Me	10	30	16	75
Me	20	100	18	80
Et	10	30	18	55

The tricarbonyl(1,2-dihydropyridine)iron complex (**2a**) thus obtained gave the correct elemental analysis and was identical with the authentic sample prepared according to the Alper's procedure in spectroscopic comparison. However, we have observed 59—59.5° for the melting point of **2a**, whereas Alper described 42—44° for it. In order to obtain further evidence for the structure of **2a**, we have measured ^{13}C NMR spectrum of **2a**, which has not been reported yet. Only one absorption due to the terminal carhonyls appears at 210.6 ppm, indicating that the three carbonyls are equivalent to each other. Three signals due to the ester carbonyl, the methyl, and the methylene carbons appear in the ordinary regions (154.0, 52.8, and 44.9 ppm, respectively). On the other hand, four signals due to the olefinic carbons are considerably shifted to the up-fieldds (83.4, 75.6, 73.0, and 56.7 ppm, respectively), as is expected by the complexation with iron carbonyl.[7] The ^{13}C NMR of **2b** also showed the similar absorptions to that of **2a**, except for the ethyl carbons instead of the methyl carbon. These ^{13}C NMR spectra clearly indicate that the tricarbonyliron moiety is coordinated to the double bonds of the dihydropyridine but not to its nitrogen atom.[6]

Since enneacarbonyldiiron is prepared from pentacarbonyliron by photo-irradiation, the present procedure provides more convenient and efficient method for synthesis of tricarbonyl(1,2-dihydropyridine)iron complex than the reported one.[3a]

Experimental

All the temperature were uncorrected. The IR spectra were obtained on a Shimadzu IR-27 spectrometer. The MS spectra were taken by using a Hitachi RMS-4 mass spectrometer. The ^{1}H NMR spectra were obtained on a Varine EM-360 or EM-390 spectrometer and the ^{13}C NMR spectra were obtained on a Varian CFT-20 spectrometer, TMS being chosen as the internal standard.

N-Methoxycarbonyl- and N-Ethoxycarbonyl-1,2-dihydropyridines (1a and **1b***).* The 1,2-dihydropyridine derivatives were prepared by the reported method.[8]

*Tricarbonyl(*N*-methoxycarbonyl-1,2-dihydropyridine)iron (**2a**).* A mixture of **1a** (2.78 g, 20.0 mmol) and pentacarbonyliron (19.60 g, 100 mmol) in a Pyrex tube fitted with a small rubber balloon was irradiated with stirring by means of 220 W medium pressure mercury lamp at room temperature for 18 h. The excess pentacarbonyliron was removed under reduced pressure and recovered in a Dry Ice–acetone trap (14.00 g, 89%). The residue was chromatographed on silica gel. Elution by hexane followed by benzene gave **2a** (4.47 g, 80%), which crystallized on standing in a refrigerator. **2a**: mp 59.0—59.5°C. MS *m/z* (rel intensity): 279 (M^+, 1), 251 (M^+-28, 10), 223 (M^+-56, 11), 195 (M^+-84, 18), 79 (100). IR (CCl_4): 2040, 1945, 1715 cm^{-1}. ^1H NMR $\delta(CDCl_3)$: 5.33—5.67 (2H, m, H-4 and H-5), 4.90 (1H, br s, H-6), 3.68 (3H, s, $-OCH_3$), 3.10—3.43 (2H, m, H-2 and H-3), 2.93 (1H, d. d, $J=15$ and 3 Hz, H-2). ^{13}C NMR $\delta(CDCl_3)$: 210.6 (s, C=O), 154.0 (s, $-CO_2-$), 83.4 (d, C-6), 75.0 (d, C-4 or C-5), 73.0 (d, C-4 or C-5), 56.7 (d, C-3), 52.8 (q, $-OCH_3$), 44.9 (t, C-2).

*Tricarbonyl(*N*-ethoxycarbonyl-1, 2-dihydropyridine)iron (**2b**).* A mixure of **1b** (1.53 g, 10.0 mmol) and pentacarbonyliron (5.88 g, 30.0 mmol) was irradiated in the similar manner to the above for 18 h. The excess pentacarbonyliron was removed under reduced pressure and recovered in a Dry Ice–acetone trap (3.72 g, 95%). The residue was chromatographed on silica gel. Elution by hexane followed by benzene gave **2b** (1.61 g, 55%): MS *m/z* (rel intensity): 293 (M^+, 1), 265 (M^+-28, 2), 237 (M^+-56, 2), 209 (M^+-84, 3), 80 (100). IR (neat): 2030, 1970, 1715 cm^{-1}. ^1H NMR $\delta(CDCl_3)$: 5.33—5.68 (2H, m, H-4 and H-5), 4.90 (1H, br s, H-6), 4.15 (2H, q, $J=7$ Hz, $-OCH_2-$), 3.13—3.46 (2H, m, H-2 and H-3), 2.93 (1H, d. d, $J=15$ and 3 Hz, H-2), 1.27 (3H, t, $J=7$ Hz, $-CH_3$). ^{13}C NMR $\delta(CDCl_3)$: 210.5 (s, CO), 153.6 (s, $-CO_2-$), 83.2 (d, C-6), 75.7 (d, C-4 or C-5), 72.9 (d, C-4 or C-5), 61.8 (t, $-OCH_2-$), 56.8 (d, C-3), 44.8 (t, C-2), 14.6 (q, $-CH_3$).

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