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(DIHYDROPYRIDINE)IRON TRICARBONYL COMPLEXES

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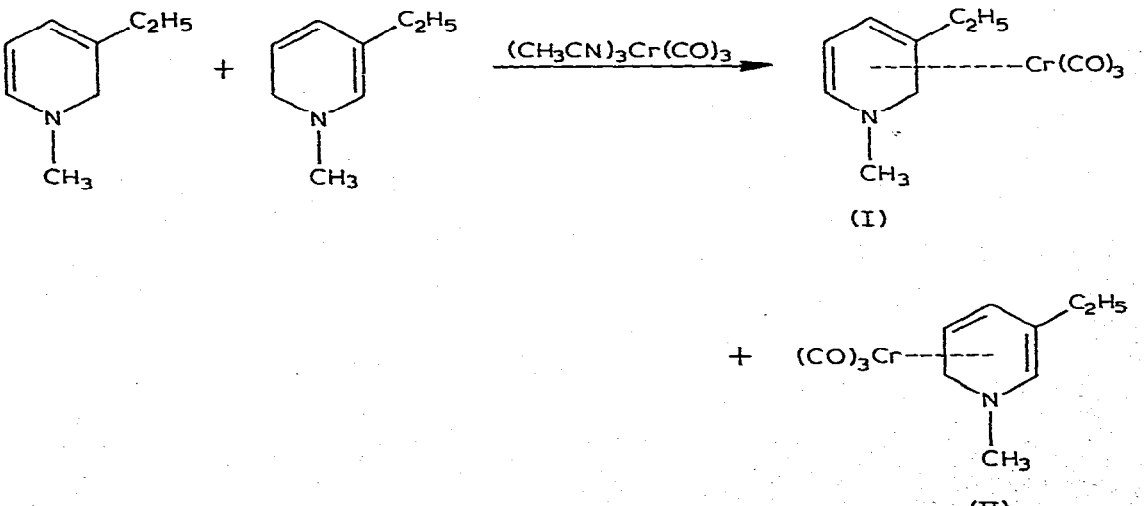
Summary

(*N*-Carboalkoxy-1,2-dihydropyridine)iron tricarbonyl complexes have been isolated by treatment of either *N*-carboalkoxy-1,2 or -1,4-dihydropyridines with diiron ennecarbonyl. The organic ligand was liberated from these complexes by use of trimethylamine oxide.

Introduction

Although 1,2- and 1,4-dihydropyridines are heterocycles of considerable biological importance (NADH, NADPH) [1], there has been surprisingly little reported in the literature regarding reactions of these heterocycles with metal carbonyls. *N*-Methyl-1,4-dihydropyridines, or the 1,2-isomers, react with chromium hexacarbonyl or tris(acetonitrile)chromium tricarbonyl, to give (1,2-dihydropyridine)chromium tricarbonyls [2,3]. Kutney and coworkers [4]

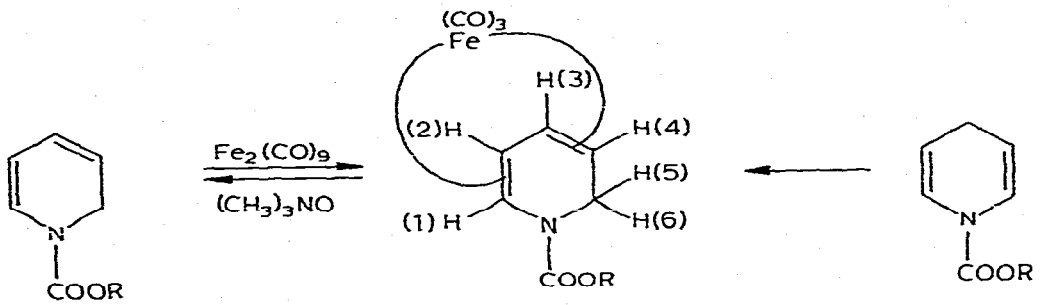


recently extended this reaction to the synthesis of (*N*-methyl-3-ethyl-1,2-dihydropyridine)chromium tricarbonyl and the 1,6-dihydro analog (I and II, respectively).

Öfele [2] claimed that *N*-methyl-1,2 and -1,4-dihydropyridines effect reduction of iron pentacarbonyl (and nickel tetracarbonyl) to give *N*-methylpyridinium salts of $Fe_4(CO)_{13}^{2-}$. We now wish to report the first iron carbonyl complexes of 1,2-dihydropyridines, obtained by treatment of 1,2- or 1,4-dihydropyridines with diiron enneacarbonyl ($Fe_2(CO)_9$). While the initial purpose of this work is to synthesize the noted complexes, it is our expectation that these complexes may find important applications in organic synthesis.

Results and discussion

N-Carbomethoxy-1,2-dihydropyridine (III, R = CH_3), obtained from pyridine by using the simple procedure developed by Fowler [5], reacts with $Fe_2(CO)_9$ in benzene at room temperature to give (*N*-carbomethoxy-1,2-di-



(III) R = CH_3 , C_2H_5 (IV) (V)

hydropyridine)iron tricarbonyl (IV, R = CH_3) in 42% yield. Terminal metal carbonyl stretching bands were observed in the infrared (IR CCl_4) at 2058vs and 1981vs cm^{-1}, in good agreement with data reported for other diene—iron tricarbonyl complexes [6]. An absorption at 1713 cm^{-1} is due to ester carbonyl stretching. The nuclear magnetic resonance (NMR) spectrum for the complex was significantly different to that of the free ligand showing: a three proton multiplet in the region of δ2.78-3.40 ppm due to H(4), H(5), and H(6); a singlet at δ3.70 ppm for the carbomethoxy group; a doublet at δ4.95 ppm due to H(1); and a multiplet at δ5.50 ppm being assigned to H(2), H(3). A molecular ion peak was observed in the mass spectrum at *m/e* 279, followed by successive loss of three carbonyls.

The same complex IV (R = CH_3), was isolated in 38% yield by treatment of the 1,4-dihydropyridine (V, R = CH_3) with $Fe_2(CO)_9$. (*N*-Carboethoxy-1,2-dihydropyridine)iron tricarbonyl (IV, R = C_2H_5) was similarly prepared in yields of 27 and 34%, from either the 1,4-dihydropyridine (V, R = C_2H_5), or the 1,2-isomer (III, R = C_2H_5), respectively. The spectral properties for the carboethoxy complex paralleled those for the carbomethoxy derivative (see Experimental).

Liberation of the diene from its complex required mild conditions, in

order to avoid oxidation of the resultant 1,2-dihydropyridine [1]. This was accomplished in good yield using trimethylamine oxide [7]. In conclusion, we have shown that (1,2-dihydropyridine)iron tricarbonyls can be readily synthesized using 1,4- or 1,2-dihydropyridines as reactants, and that, if desired, the iron tricarbonyl fragment can easily be removed from the complex. Abstraction, addition, and insertion reactions of the (1,2-dihydropyridine)iron tricarbonyls are currently being investigated.

Experimental

General

Melting points were determined on a Fisher—Johns apparatus and are uncorrected. Microanalytical determinations were carried out by Pascher Microanalytical Laboratory, Bonn, West Germany. NMR spectra were recorded on a Varian T-60 spectrometer; TMS was an internal standard. Infrared spectra were recorded on a Beckman IR-20A or Perkin—Elmer 457 spectrometer. A MS902 spectrometer was used for mass spectral determinations.

Diiron enneacarbonyl (Pressure Chemical Co.) was used as received. Solvents were dried and purified by standard techniques. All reactions were run under an atmosphere of dry nitrogen.

Dihydropyridines

N-Carbomethoxy-1,2- and -1,4-dihydropyridines were obtained from pyridine according to the methods described by Fowler [5]. *N*-Carboethoxy-1,2-dihydropyridine, a yellow oil, was prepared in 80% yield (chromatographically pure) following a procedure identical to that described for the carbomethoxy derivative [5], except for the use of ethyl chloroformate (21.7 g) instead of methyl chloroformate. (Found: C, 63.01; H, 7.22. $C_8H_{11}NO_2$ calcd.: C, 62.72; H, 7.24%.) NMR spectrum ($CDCl_3$): δ 1.28 (t, 3H, CH_3), 4.20(q, 2H, $C\underline{H}_2CH_3$), 4.32 (dd, 2H, NCH_2—), 4.90-6.00 (m, 3H, olefinic protons), 6.70 ppm (d(br), 1H, J = 7.5 Hz, NCH=). The pure 1,4-isomer (V, R = C_2H_5), was obtained in 74% yield according to the procedure detailed for V(R = CH_3), with ethyl chloroformate used in place of methyl chloroformate. (Found: C, 62.96; H, 7.48. $C_8H_{11}NO_2$ calcd.: C, 62.72; H, 7.24%.) NMR spectrum ($CDCl_3$): δ 1.27 (t, 3H, CH_3), 2.70-3.00 (m, 2H, CH_2N), 4.24 (q, 2H, $C\underline{H}_2CH_3$), 4.63-5.00 (m, 2H, NCH=C$\underline{H}$), 6.62 ppm (d, 2H, J = 8.0 Hz, NCH=).

Reaction of N-carbomethoxy-1,2- and -1,4-dihydropyridines (III or V, R = CH_3) with $Fe_2(CO)_9$

A mixture of the heterocycle (2.08 g; 15 mmol) and $Fe_2(CO)_9$ (5.46 g; 15 mmol) in dry benzene (50 ml) was stirred at room temperature for 40-60 h. The solution was filtered, and flash evaporation of the filtrate gave an oil. The latter was dissolved in hexane, and chromatographed on silica gel (activity grade II). Elution with hexane gave recovered starting material. Elution with benzene gave the diene—iron tricarbonyl complex IV(R = CH_3) as a yellow oil which slowly crystallized when kept in a freezer. The yield from III(R = CH_3), was 1.75 g (42%), and 1.58 g (38%) was obtained from V(R = CH_3). M.p.

42-44°C. (Found: C, 43.61; H, 3.17; N, 5.27. $C_{10}H_{11}FeNO_5$ calcd.: C, 43.05; H, 3.25; N, 5.02%.) IR spectrum (CCl_4): ν(C≡O) 2058vs, 1981vs; ν(C=O) 1713m cm^{-1}. NMR spectrum ($CDCl_3$): δ 2.78-3.40 (m, 3H, H(4), H(5), H(6)), 3.70 (s, 3H, CH_3), 4.95 (d, 1H, H(1)), 5.50 ppm (m, 2H, H(2), H(3)). Mass spectrum (*m/e*) 279, 251, 223, 195, 139, 84, 56.

Reaction of N-carboethoxy-1,2- and 1,4-dihydropyridines (III or V, R = C_2H_5) with $Fe_2(CO)_9$

A solution of the 1,2- or 1,4-dihydropyridines (2.30 g; 15 mmol) and $Fe_2(CO)_9$ (5.46 g; 15 mmol) in dry benzene (50 ml) was stirred at room temperature for 52-78 h. Work-up as described for IV(R = CH_3), gave (*N*-carboethoxy-1,2-dihydropyridine)iron tricarbonyl (IV, R = C_2H_5) as a yellow oil. Yield: 27% from III(R = C_2H_5); 34% from V(R = C_2H_5). (Found: C, 44.79; H, 3.83; N, 4.82. $C_{11}H_{11}FeNO_5$ calcd.: C, 45.08; H, 3.78; N, 4.77%.) IR spectrum (CCl_4): ν(C≡O) 2058vs, 1980vs; ν(C=O) 1711 cm^{-1}. NMR spectrum ($CDCl_3$): δ 1.26 (t, 3H, CH_3), 2.65-3.50 (m, 3H, H(4), H(5), H(6)), 4.27(q, 2H, CH_2CH_3), 5.00(d, 1H, H(1)), 5.55 ppm (m, 2H, H(2), H(3)). Mass spectrum (*m/e*) 293, 265, 237, 209, 153, 84, 56.

Decomplexation of (1,2-dihydropyridine)iron tricarbonyls (IV, R = CH_3, C_2H_5)

An acetone solution (50-100 ml) of the complex (0.5-1.0 g) and trimethylamine-*N*-oxide (10-15 mol excess) were stirred at 40°C for two days. The solution was cooled and poured into water (300 ml). The mixture was extracted with ether, and the ether extract was washed well with water, dried ($MgSO_4$), and concentrated in vacuo to afford the free 1,2-dihydropyridine. The yield was 61% for III (R = CH_3), and 54% for III(R = C_2H_5).

Acknowledgments

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