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The Photochemical and Chemical Decarbonylation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ [*trans*-$C(O)CH{=}CHR$], R = CH_3 and C_6H_5

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Treatment of Na^+Fp^-, *where* Fp = $Fe(\eta^5\text{-}C_5H_5)(CO)_2$, *with either* cis- *or* trans-$ClC(O)CH{=}CHR$, *where* R = CH_3 *and* C_6H_5, *gives only the acyl complexes* trans-$FpC(O)CH{=}CHR$. *Conformational isomerism about the acyl–iron bond has been observed. Both complexes decarbonylate upon irradiation or treatment with* $Rh(PPh_3)_3Cl$ *to give the vinyl complexes* trans-$FpCH{=}CHR$.

Introduction

Previous work on the photochemical decarbonylation of $CpFe(CO)_2[C(O)R]$ systems has shown that a terminal CO is lost [1] and that alkyl migration occurs with retention at the α-carbon [2] and with inversion at iron [3]. Wilkinson's catalyst, $Rh(PPh_3)_3Cl$, chemically decarbonylates these complexes with the loss of a terminal carbonyl [1] and probably with retention at carbon [4]. In most of these systems R has been an alkyl or aryl group [5] yet it is interesting to consider complexes with R = vinyl groups. Monosubstituted vinyl groups may have either *cis* or *trans* geometry which might be subject to isomerization upon decarbonylation. The complexes *cis*- and *trans*-$Mn(CO)_5CH_2CH{=}CHCH_3$ decarbonylate in the presence of $[Ir(diphos)_2]Cl$ to give the *syn*- and *anti*-π-allyl tetracarbonyl compounds respectively, with retention of geometry [6]. Thus, the preparation of *cis*- and *trans*-complexes of the type $FpC(O)CH{=}CHR$, where Fp = $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ and R = CH_3 and C_6H_5, was undertaken to study the stereochemistry of their photochemical decarbonylation. Since the geometry of olefins is photochemically labile it seemed reasonable to study the chemical decarbonylation of these compounds using Wilkinson's catalyst.

Experimental

Synthesis of all organometallics was carried out under high purity N_2. Tetrahydrofuran was freshly distilled from sodium-benzophenone. *Trans*-cinnamic acid and phenyl propriolic acid ($C_6H_5C{\equiv}CCO_2H$) were purchased from Aldrich, *trans*-crotonoyl chloride ($CH_3CH{=}CHC(O)Cl$) from BDH, biscyclopentadienyltetracarbonyldiiron from Ventron, tetrolic acid ($CH_3C{\equiv}CCO_2H$) from Farchan, rhodium tris(triphenylphosphine) chloride and palladium-on-barium-sulfate from Strem. All chromatography was done on activated alumina, 80–200 mesh, purchased from Anachemia. All infrared spectra were taken on a Perkin-Elmer 257 spectrometer and were calibrated with polystyrene (1601 cm^{-1}). NMR spectra were done on Varian T-60 and T-60A spectrometers with an internal standard of tetramethyl silane. Elemental analyses were performed by Midwest Microanalytical, Indianapolis, Indiana. All metal complexes prepared gave molecular ion peaks in their mass spectra.

Cis-*cinnamic Acid, (*cis-$C_6H_5CH{=}CHCO_2H$*)*

Phenyl propriolic acid (2.0 g) was hydrogenated in a Parr bottle using a Lindlar catalyst (0.102 g of 5% $Pd–BaSO_4$ and 1.2 μl of freshly distilled quinoline) in 50 ml absolute ethanol [7]. A rapid and exothermic reaction occurred which was complete in 5 min. The mixture was filtered and the solvent evaporated to give a yellow liquid. Upon addition of hexane, residual starting material precipitated and was removed. The remaining solution was placed in dry ice and the solvent evaporated in a stream of N_2. White crystals were formed. Yield: 1.4 g (70%), m.p. 45–47 °C (lit 68 °C [8]). Although the melting point was lower than reported, all the spectra taken verified the purity. No isomerization occurred at room temperature over two weeks. However, storage in the cold is recommended. NMR($CDCl_3$): τ 3.37 (q, 4H, CH=CH, J(H–H) = 12 Hz), 2.15–2.67 (m, 5H, C_6H_5), –1.60 (s, 1H, CO_2H).

Cis-*crotonic Acid, (*cis-$CH_3CH{=}CHCO_2H$*)*

Tetrolic acid (3.0 g) was hydrogenated in a similar manner to give *cis*-crotonic acid, 2.6 g (87%), as a colourless liquid which was recrystallized from petroleum ether (30°–60 °C) at –78°. Care must be taken to cool the product immediately after hydrogenation to prevent isomerization. NMR($CDCl_3$): τ

7.87 (dd, 3H, CH_3, $J(CH_3–H_2)$ = 2 and 6 Hz), 3.87 (m, 4H, CH=CH, J(H–H) = 12), –3.25 (s, 1H, CO_2H).

Acid Chlorides

The acids were converted to the acid chlorides upon treatment with $SOCl_2$ in ether in the standard manner. *Cis*-cinnamoyl chloride was purified by vacuum distillation (11 °C at 6 mm). Yield: 65%. Excessive heat causes isomerization and should be avoided. NMR($CDCl_3$): τ 3.46 (q, 4H, CH=CH, J(H–H) = 12 Hz), 2.15–2.85 (m, 5H, C_6H_5). *Cis*-crotonoyl chloride was isolated by means of trap-to-trap distillation at room temperature and 0.01 mm Hg. Yield: 52%. About 15% of the *trans*-crotonoyl chloride was also present. NMR($CDCl_3$): τ 7.97 (d, 3H, CH_3, $J(CH_3–H_2)$ = 1 and 5 Hz), 3.95 (m, 4H, CH=CH, J(H–H) = 12 Hz).

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These complexes were prepared by reacting the acid chlorides with Na(η^5-C_5H_5)Fe(CO)$_2$ [5]. The *trans*-chlorides were allowed to react for 17 hr while the *cis*-chlorides were reacted for only 1 hr in an attempt to minimize isomerization of the latter. All products were isolated by column chromatography. The *trans*-acyl complexes were obtained from both the *trans* and *cis*-acid chlorides. For R = C_6H_5, the product was recrystallized from CH_2Cl_2/hexane, m.p. 90–91 °C (lit. 91–92° [5]). NMR($CDCl_3$): τ 5.12 (s, 5H, C_5H_5), 3.25 (q, 4H, CH=CH, J(H–H) = 16 Hz), 2.41–2.81 (m, 5H, C_6H_5); IR(hexane) ν(CO): 2025 (s), 2016(sh), 1968(s) cm^{-1}, ν[C(O)R]: 1643(w) cm^{-1}. *Anal.* Calcd. for $C_{16}H_{12}FeO_3$: C 62.3, H 3.90; found: C 61.7, H 4.25. For R = CH_3, the product was purified by vacuum sublimation onto a dry-ice/acetone cooled probe, and is an oil at room temperature. NMR($CDCl_3$): τ 8.30 (d, 3H, CH_3, $J(CH_3–H)$ = 6 Hz), 5.25 (s, 5H, C_5H_5), 4.00 (m, 4H, CH=CH, J(H–H) = 15 Hz); IR(hexane) ν(CO): 2027(s), 2021(sh), 1968(s) cm^{-1}, ν[C(O)R]: 1658(w) cm^{-1}. *Anal.* Calcd. for $C_{11}H_{10}FeO_3$: C 53.8, H 4.10; found: C 53.7, H 4.29.

Photochemical Decarbonylation

These were performed in acetone solvent under N_2 atmosphere using Pyrex filtered irradiation from a 100 watt Hanovia immersion type mercury-vapor lamp. The reactions were followed by monitoring the acyl peak in the infrared spectrum. Both vinyl complexes were isolated by column chromatography on alumina using toluene as eluant. The phenyl complex was recrystallized from CH_2Cl_2/hexane. Yield = 34%, m.p. 44–45 °C (lit. 46–47° [9]). NMR($CDCl_3$): τ 5.30 (s, 5H, C_5H_5), 2.96 (q, 4H, CH=CH, J(H–H) = 16 Hz), 2.65–3.00 (m, 5H, C_6H_5); IR(hexane) ν(CO): 2021(s), 1974(s) cm^{-1}. *Anal.* Calcd. for $C_{15}H_{12}FeO_2$: C 64.3, H 4.32; found: C 65.6, H 4.68. The methyl complex vacuum sublimed onto a dry-ice/acetone cooled probe and was isolated as slightly impure oil. Yield = 57%, NMR($CDCl_3$): τ 8.25 (dd, 3H, CH_3, $J(CH_3–H_2)$ = 1.5 and 6 Hz), 5.23 (s, 5H, C_5H_5), 4.15 (m, 4H, CH=CH, J(H–H) = 15 Hz); IR(hexane) ν(CO): 2015(s), 1966(s) cm^{-1}. *Anal.* Calcd. for $C_{10}H_{10}FeO_2$: C 55.2, H 4.63; found: C 47.5, H 4.40.

Chemical Decarbonylation

Stoichiometric amounts of (η^5-C_5H_5)Fe(CO)$_2$-[C(O)CH=CHR] and Rh(PPh_3)$_3$Cl were stirred at room temperature overnight in THF. The solvent was stripped and the residue chromatographed on alumina. Elution with toluene: CH_2Cl_2 (5:1) yielded the vinyl product in the first band. The second band contained the unreacted starting material. Further elution with $CH_3COOC_2H_5$ afforded Rh(PPh_3)$_2$(CO)-Cl. No evidence for the formation of (η^5-C_5H_5)Fe-(CO)(PPh_3)[C(O)CH=CHR] was found [1]. The vinyl complexes were purified as above. Yields:

R	*Vinyl Complex*	*Starting Acyl*	*Rh(PPh$_3$)$_2$(CO)Cl*
CH_3	15%	34%	10%
C_6H_5	14%	11%	44%

Results and Discussion

The complexes *trans*-FpC(O)CH=CHR, where Fp = (η^5-C_5H_5)Fe(CO)$_2$ and R = CH_3 and C_6H_5, are easily prepared according to King's general method [5]. It is interesting that three bands in the terminal carbonyl stretching region of the infrared spectrum for R = C_6H_5 have been reported by both King (in halocarbon oil mull) and Nesmeyanov [9] (in cyclohexane), while Alexander [1] reports only two bands (in $CHCl_3$). A simple dicarbonyl should have only two bands in this region. We also observed three such bands not only for R = C_6H_5 but also for R = CH_3 in hexane; however, no splitting was noticeable in $CHCl_3$ which is known to broaden such bands. Multiplicity of bands has been observed for several different types of metal–acyl complexes [10, 11]. It is believed to be due to conformational isomerism about the metal–acyl bond. In this case, the resolution of the bands due to the conformers is not complete, with only the high frequency band showing splitting. The other carbonyl-stretching and acyl-stretching bands are slightly broadened singlets. The bands in the NMR spectrum are sharp and well resolved, consistent with interconversion of the conformers which is rapid on the NMR time scale, as has been previously found [10, 11]. The vinyl complexes *trans*-FpCH=CHR, where R = CH_3 and C_6H_5, show no detectable splitting of the carbonyl bands in the infrared. Metal acyl complexes seem particularly disposed to displaying this type of conformational isomerism. It is probable that both electronic [12] and steric factors contribute to the barrier.

Treatment of Na^+Fp^- with the *cis*-acid chlorides gave only the *trans*-FpC(O)CH=CHR complexes despite repeated attempts under different reaction conditions, including low temperatures. The *cis*-acid chlorides do not isomerize under the reaction conditions in the absence of the iron species. It is not clear when isomerization occurs. Metal hydrides isomerize olefins and the presence of minute amounts of water or carboxylic acid impurities could lead to the formation of an iron–hydride from Na^+Fp^-. A small amount of such a species could catalytically isomerize the olefin before or after acyl complex formation. On the other hand, Fp^- itself is a nucleophile and might be capable of causing isomerization. Molecular models indicate that the *cis*-acyl complexes would be very sterically crowded. Nevertheless, *cis*-$CH_3CH{=}CHCH_2Cl$ reacts with $NaMn(CO)_5$ to give $Mn(CO)_5$[*cis*-$CH_2CH{=}CHCH_3$] which is stable [6].

The assignment of *cis* and *trans* geometry is based on the coupling constant of the vinyl protons [5, 9, 13]. For the compounds *cis*-RCH=CHC(O)X, where R = C_6H_5 and CH_3, X = OH and Cl, the coupling constant is 12 Hz while in the *trans*-compounds it is 16 and 15 Hz for R = C_6H_5 and CH_3 respectively. Photochemical decarbonylation of *trans*-FpC(O)CH=CHR, R = C_6H_5 (J = 16 Hz) and CH_3 (J = 15 Hz), gave the vinyl complexes *trans*-FpCH=CHR, R = C_6H_5 (J = 16 Hz) and CH_3 (J = 15 Hz). Therefore, decarbonylation has resulted in retention of olefin geometry. The results for R = C_6H_5 agree with an earlier photochemical study on this single compound [9].

The stereochemical outcome (retention *vs.* inversion at carbon) of the electrophilic cleavage of the Fe–C bond in *threo*-FpCHDCHDR′ by halogens depends on whether R′ is an aryl or alkyl group [2, 14]. No such dependence was observed in this case. It had also been reported that no vinyl product was isolated when *trans*-FpC(O)CH=CHC_6H_5 was treated with $Rh(PPh_3)Cl$ in CH_2Cl_2, despite the isolation of $Rh(PPh_3)_2COCl$ in high yield [1]. We have been able to isolate vinyl products for R = C_6H_5 and CH_3, albeit in low yields, when the reactions were carried out in THF. Care in the choice of solvents seems to be required to make use of this method [15]. In both cases the *trans*-vinyl complexes were isolated.

The isomerization during the attempted preparation of the *cis*-acyl complexes prevents definitive comparisons at this time. It is also not possible to rule out initial formation of *cis*-vinyl complexes upon decarbonylation of the *trans*-acyl compounds, followed by rapid *cis* → *trans* isomerization [16]. Further studies are needed to answer these interesting stereochemical questions.

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