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Stereoselectivity in the formation of tricarbonyliron complexes of some dihydrobiphenyls

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Abstract

Ratios of isomeric products in complexation of some substituted cyclohexa-1,4- and 1,3-dienes, using $Fe(CO)_5$ or $Fe_3(CO)_{12}$ are significantly affected by the nature of an allylic substituent: CO_2Me tends to direct the metal to its occupied face, Ph less so and Me is inhibitory. An appropriately substituted cyclohexadiene gives a single stereoisomer.

1. Introduction

Efficient regio- and stereo-selective formations and isolations of substituted tricarbonyl(η^4-cyclohexa-1,3-diene)iron complexes are needed for use as synthetic intermediates in organic synthesis [1]. One successful method to provide a range is by introduction of nucleophiles into their cations [2], another is to generate directly the desired isomers. The organic precursors are frequently the Birch reduction products of aromatic compounds, which are cyclohexa-1,4-dienes with specifically placed substituents. These yield, with iron carbonyls, mixtures of isomeric substituted tricarbonyl (η^4-cyclohexa-1,3-diene)iron complexes, in processes which we have shown [3] to be kinetically controlled and defined by the initial diene-substitution pattern. Alkyl substituents in "allylic" situations sterically tend to acquire a less crowded α(exo)-disposition [4], which could result by initial addition of the Fe on the ring opposite to alkyl and subsequent consummation with exclusive hydrogen-migration on the β(endo)-face via the metal during the 1,4- into 1,3-diene conversion.

To supplement the previous studies on the influences of substituents such as CO_2Me or alkyl [3,4], we examine here chiefly Ph located in an allylic situation on the parent diene. Ph has a large bulk which may exercise classical hindrance, but also a π-electron system which may direct sterically on the same face by interaction with the reactive iron species. The present and previous results suggest that the mode of direction of the Fe species is dominantly through electronic effects for CO_2Me, much less so for Ph and purely due to spatial hindrance with Me.

2. Results and discussion

The diene **1** [5] gave good yields (78%–90%) of a mixture of the isomeric complexes 2-Ph (**5**), 5α(exo)-Ph (**7**) and 5β(endo)-Ph (**8**) in the ratios 13:23:10 (from pentacarbonyliron) and 9:10:5 (from dodecacarbonyltriiron); the ratios were determined by GLC analysis. The compound **5** was obtained pure by chromatographic separation of the mixture. From the product of treatment with triphenylcarbenium tetrafluoroborate of a fraction containing **7** and **8**, the latter gave the 1-Ph cation **15** and the former was recovered pure because hydride abstraction from it is sterically inhibited. The compound **7** was identical in spectra with that formed from the unsubstituted cation salt **14** with Ph_2Cd [6], and its α(exo)-stereochemistry is confirmed from the CH_2-splitting pattern characteristic of an adjacent α(exo)-substituent [7].

That the only unreacted hydrocarbons recovered are the 1,4-diene **1** and biphenyl is consistent with previous

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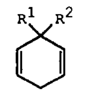
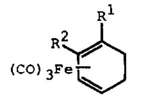


(1) R^1 = Ph, R^2 = H

(2) R^1 = CO_2Me, R^2 = H

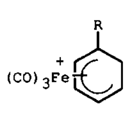
(3) R^1 = Ph, R^2 = Me

(4) R^1 = Ph, R^2 = CO_2Me



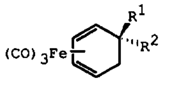
(5) R^1 = H, R^2 = Ph

(6) R^1 = Ph, R^2 = H



(14) R = H

(15) R = Ph



(7) R^1 = H, R^2 = Ph

(8) R^1 = Ph, R^2 = H

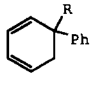
(9) R^1 = Ph, R^2 = Me

(10) R^1 = Me, R^2 = Ph

(11) R^1 = CO_2Me, R^2 = Ph

(12) R^1 = CO_2Me, R^2 = H

(13) R^1 = R^2 = Ph



(16) R = H

(17) R = Ph

conclusions [8] that preconjugated free 1,3-dienes are not intermediates in the complexation. The "conjugation" of the initial 1,4-diene structure during complexation probably involves η^3-allyl-$HFe(CO)_3$ intermediates [8], with removal and back-donation of H via the metal atom. Three regioisomeric complexes may be formed from a cyclohexa-1,4-diene with one substituent. Stereoisomers α(exo)- or β(endo)- can also result in the relevant structures with substituents "allylic" to the complexed system, the configuration being defined by the influence of the substituent on the direction of consummated attack of the complexed iron intermediate. The 2-Ph (**5**) and the 5α(exo)-Ph (**7**) both result from the approach of the iron species on the opposite face to the bulky Ph; the diene ring may be considered approximately planar [9]. As therefore expected, the sum of **5** plus **7** is higher than **8**. But it is surprising on steric grounds that the latter is formed at all. To achieve these proportions the Ph must provide some electronic assistance in opposition to its dominant steric effect. The absence in the product of the 1-Ph isomer **6** is an indication that thermal equilibration of isomeric complexes [10] does not occur under these conditions [3a,11].

The formation of 2-Ph (**5**) and 5α(exo)-Ph (**7**) corresponds to the migration in the diene precursor of benzylic H and the other allylic H on the same face, respectively. The proportion of **5** was less than that of **7**, and this is surprising in view of the greater classical reactivity of the benzylic position in 1,4-dihydrobiphenyl. The β(endo)-complex **12** was preponderant with the analogous CO_2Me diene **2**, and both types of allylic H of this diene appeared to be of about equal probability of migration during complexation [3a].

To assess the relative directing effects of the substituents Ph, Me and CO_2Me, the dienes **3**, **4** and **16** were required as precursors. The 1,3-diene **16** was prepared by detachment of Fe with cupric chloride in ethanol from a mixture of 5α(exo)-Ph (**7**) and 5β(endo)-Ph (**8**) complexes, and was characterized by its maleic anhydride adduct. The blocked diene **3** was available from the reductive methylation of biphenyl [12]. The diene **4** was formed by quenching the Li anion corresponding to **1** (biphenyl and lithium) with carbon dioxide followed by diazomethane.

The reaction of the 1,3-diene **16** with either $Fe(CO)_5$ or $Fe_3(CO)_{12}$ furnished in 73%–84% yield the 5α(exo)-Ph complex **7** and its 5β(endo)-Ph isomer **8** in about 3:1 ratio (GLC). The result confirms a considerable degree of addition to the hindered face of the diene. The reaction of the blocked diene **3** with $Fe(CO)_5$ afforded in 80% yield the 5α(exo)-Me,5β(endo)-Ph complex **9** and its 5β(endo)-Me,5α(exo)-Ph isomer **10** in the ratio 2:1 (GLC and ^1H NMR). The former is the major product, based on the ratio of two ^1H NMR signals for Me, one at δ 1.43, the other at δ 1.30, because β(endo)-substituents resonate at lower field than the corresponding α(exo)-substituents [7,13]. Surprisingly, on classical grounds, the major isomer is the more sterically crowded one. Only a single isomer (**11**) was observed in moderate yield (44%) from the reaction of **4** with $Fe(CO)_5$. The assignment of stereochemistry could not be made unambiguously from ^1H NMR using the correlation $\delta_\beta CO_2Me \geq 3.63 \geq \delta_\alpha CO_2Me$ [7] because the CO_2Me of **11** resonated at δ 3.63. However, the 5β(endo)-CO_2Me, 5α(exo)-Ph structure **11** was established by X-ray analysis [14].

The directive effects can be rationalized with CO_2Me greater than Ph in assisting against steric hindrance, and Me acting solely through hindrance. The most likely reason for the effect is intermediate passage of the complexing group such as $Fe(CO)_n$ (where $n = 3$ [11a] or 4 [11b]) via the π-electrons of the unsaturated substituent.

The isolation of 5α(exo),5β(endo)-Ph_2 complex (**13**) in 95% yield from the preconjugated diene **17** [15] indicates that complexation is not unduly subjected to steric hindrance.

The separation of **7** and **8** demonstrated hydride abstraction with triphenylcarbenium tetrafluoroborate of 5α(exo)-H from the latter, 5β(endo)-isomer, forming the 1-Ph cation **15**. This result differs from the analogous 5β-CO_2Me complex **12** which loses hydride from the 6-(presumably α-) position [7,16], indicating different electronic effects of the two classes of substituents on hydride removal.

3. Experimental details

For general conditions see ref. 2. Volatile complexes were analysed by GLC using a Perkin–Elmer model 881 instrument with glass columns (6 feet × 0.25 inches outer diameter). The stationary phases used were 5% Carbowax 20M on acid washed Chrom W (System A) and 1.5% SE30 on acid washed Chrom W (System B).

3.1. Tricarbonyliron complexes from 3-phenylcyclohexa-1,4-diene (1)

The diene precursor (**1**) was prepared by the Birch reduction of biphenyl [5]. A mixture of **1** (5.00 g, 32 mmol) and $Fe(CO)_5$ (12 ml, 91 mmol) was heated in refluent di-*n*-butyl ether (100 ml) for 36 h, and worked up as described previously [17]. The product (9.00 g, 90%) was identified after separation and ^1H NMR analysis (see below) as a mixture of **5**, **7** and **8** in a ratio of 13:23:10 (GLC, System A, 160°C, retention times 1.00:1.34:1.54).

Chromatography on silica and elution with light petroleum gave tricarbonyl(η^4-2-phenylcyclohexa-1,3-diene)iron (**5**) [10] as a yellow oil, UV (hexane) λ_{max}: 224 nm (log ϵ 4.39); IR (CCl_4) ν: 2060, 1980 cm^{-1}; ^1H NMR (CCl_4): δ 7.6–7.2 (5H, m, Ph), 5.75 (1H, dd, *J* 7 and 2 Hz, H-3), 3.70 (1H, br s, H-1), 3.16 (1H, m, H-4), 2.1–1.5 (4H, m, H-5,6); MS *m/z*: 296 (M), 268 (M–CO), 240 (M–2CO), 212 (M–3CO); M calculated for $C_{15}H_{12}FeO_3$ 296.01328. Found 296.01351. The less mobile band gave a mixture of tricarbonyl(η^4-5α-phenylcyclohexa-1,3-diene)iron (**7**) and tricarbonyl(η^4-5β-phenylcyclohexa-1,3-diene)iron (**8**), IR (CCl_4): 2055, 1980 cm^{-1}; ^1H NMR (CCl_4): δ 7.4–6.9 (m, Ph), 5.6–5.1 (m, H-2,3), 3.45–3.05 (m, H-5 of **7**, H-1,4), 2.87 (br t, *J* 7 Hz, H-5 of **8**), 2.55–2.10 (m, H-6β), 2.05–1.50 (m, H-6α). Anal. Found: C, 60.8; H, 4.0. $C_{15}H_{12}FeO_3$ calcd.: C, 60.85; H, 4.08%. The ratio of **7** and **8** was found to be 3.8:1 from the integration of the resonances at δ 5.6–5.1, 3.45–3.05 and 2.87 in the ^1H NMR spectrum.

A solution of **7** and **8** (3.8:1, 2.30 g, 7.77 mmol) in CH_2Cl_2 (5 ml) was cooled to 0°C and treated with triphenylcarbenium tetrafluoroborate (1.25 g, 3.79 mmol) for 15 min. Dilution with Et_2O resulted in a yellow precipitate (555 mg, 19%) which was identified as tricarbonyl(η^5-1-phenylcyclohexadienyl)iron tetrafluoroborate (**15**) [10], dec. > 150°C (from CH_2Cl_2); IR (nujol) ν: 2100, 2060 cm^{-1}; ^1H NMR (CF_3CO_2H): δ 7.62 (5H, s, Ph), 7.46 (1H, t, *J* 7 Hz, H-3), 6.20 (2H, br d, *J* 7 Hz, H-4,2), 4.50 (1H, t, *J* 7 Hz, H-5), 3.87 (1H, dd, *J* 16 and 7 Hz, H-6β), 2.66 (1H, d, *J* 16 Hz, H-6α). Anal. Found: C, 47.3; H, 2.7. $C_{15}H_{11}BF_4FeO_3$ calcd.: C, 47.18; H, 2.90%. The filtrate was washed with water, dil $NaHCO_3$ and brine, dried ($MgSO_4$), and solvent removed. The residue was dissolved in light petroleum (5 ml) and cooled to −30°C to precipitate out the bulk of triphenylmethane. Chromatography of the mother liquor on silica and elution with light petroleum gave the pure 5α(exo)-Ph **7** [6] as a yellow oil, UV (hexane) λ_{max}: 226 nm (log ϵ 4.5); IR (CCl_4) ν: 2055, 1975 cm^{-1}; ^1H NMR (CCl_4): δ 7.3–7.0 (5H, m, Ph), 5.5 (2H, m, H-2,3), 3.5–3.1 (3H, m, H-1,4,5), 2.36 (1H, m#, H-6β), 1.64 (1H, m#, H-6α). M found 296.01351. #CH_2-splitting pattern characteristic of an adjacent α(exo)-substituent [7].

With $Fe_3(CO)_{12}$/benzene/reflux, 16 h, the product (78% yield) from the diene **1** analysed for a mixture of **5**, **7** and **8** in a ratio of 9:10:5 (GLC, System A, 160°C).

3.2. 5-Phenylcyclohexa-1,3-diene (16)

A solution of **7** and **8** (3.8:1, 362 mg) in EtOH (5 ml) was treated with a saturated solution of $CuCl_2 \cdot 2H_2O$ in EtOH (10 ml) at room temperature for 1.5 h. The mixture was poured into dil NH_4Cl, extracted with light petroleum, and the organic layer washed, dried ($MgSO_4$), concentrated and distilled to give a mixture (151 mg) of the diene **16** and biphenyl in a ratio of 73:27 (GLC, System A, 120°C). The diene was characterized as the maleic anhydride adduct, m.p. 143–144°C (from light petroleum and Et_2O); MS *m/z*: 254 (M). Anal. Found: C, 75.5; H, 5.6. $C_{16}H_{14}O_3$ calcd.: C, 75.58; H, 5.55%.

3.3. Complexation of 5-phenylcyclohexa-1,3-diene (16)

The diene **16** (304 mg), contaminated with biphenyl, gave ($Fe(CO)_5$/$^nBu_2O$/reflux, 5 h) a mixture of compounds, shown by GLC (System A, 120°C until elution of biphenyl, 160°C) to consist of the starting diene (12%), biphenyl (27%), **5** (1%), **7** (45%) and **8** (15%).

With $Fe_3(CO)_{12}$/benzene/reflux, 16 h, the diene **16** (309 mg) contaminated with biphenyl, gave a mixture of complexes, shown by GLC (System A, 160°C) to be **5** (1%), **7** (40%) and **8** (12%).

3.4. Complexation of 3-methyl-3-phenylcyclohexa-1,4-diene (3)

The diene **3** (2.20 g, 12.94 mmol), prepared by reductive methylation of biphenyl [12], was treated with $Fe(CO)_5$ ($^nBu_2O$/reflux, 36 h) to obtain, after chromatography on silica and elution with light petroleum and benzene (9:1), a yellow oil (3.20 g, 80%). The product was identified as a mixture of tricarbonyl(η^4-5α-methyl-5β-phenylcyclohexa-1,3-diene)iron (**9**) and tricarbonyl(η^4-5β-methyl-5α-phenylcyclohexa-1,3-diene) iron (**10**) in a ratio of 2:1 (GLC, System A, 170°C; System B, 150°C); UV (pentane) λ_{max}: 223 nm (log ϵ 4.35); IR (CCl_4) ν: 2040, 1970 cm^{-1}; ^{1}H NMR (CCl_4): δ 7.35–7.00 (m, Ph), 5.45–5.20 (m, H-2,3), 3.45–3.00 (m, H-1,4), 2.45–2.00 (m, H-6), 1.43 (s, Me of **10**), 1.30 (s, Me of **9**), the signals at δ 1.43 and 1.30 integrated to 1:2; MS m/z: 310 (M), 282 (M–CO), 254 (M–2CO), 226 (M–3CO). Anal. Found: C, 62.1; H, 4.5 $C_{16}H_{14}FeO_3$ calcd.: C, 61.97; H, 4.55%.

3.5. Methyl 1-phenylcyclohexa-2,5-diene-1-carboxylate (4)

A solution of **1** (2.00 g, 12.82 mmol) in a mixture of THF (50 ml) and HMPA (5 ml) was cooled to −70°C and treated with ^{n}BuLi (1.66 M in hexane, 8.5 ml). After stirring for 15 min, dry CO_2 was introduced at −70°C until the brown colour disappeared. The clear solution was allowed to warm to room temperature and poured into aq $NaHCO_3$. The aq layer was washed with Et_2O, acidified (dil HCl), and extracted with Et_2O. The Et_2O extract was washed with brine and water, and dried ($CaCl_2$). Removal of Et_2O gave a viscous oil which solidified on cooling. The crude carboxylic acid was esterified with diazomethane in Et_2O and the ester **4** purified by filtration through a short column of neutral alumina (activity 3). The yield of **4**, a colourless oil, was 1.32 g, 48%; UV (EtOH) λ_{max}: 221, 251 (shoulder) nm (log ϵ 3.66, 3.07); IR (film) ν: 1735 cm^{-1}; ^{1}H NMR (CCl_4): δ 7.16 (5H, s, Ph), 6.1–5.7 (4H, m, olefinic H), 3.64 (3H, s, CO_2Me), 2.66 (2H, br s, 4-H); MS m/z: 214 (M). Anal. Found: C, 78.5; H, 6.5. $C_{14}H_{14}O_2$ calcd.: C, 78.48; H, 6.59%.

3.6. Tricarbonyl(η^4-5β-methoxycarbonyl-5α-phenylcyclohexa-1,3-diene)iron (11)

The diene **4** (1.31 g, 6.12 mmol) on treatment with $Fe(CO)_5$ [$^nBu_2O$/reflux, 24 h] gave, after eluting through silica with light petroleum and benzene (1:1), a yellow oil (960 mg, 44%) which solidified on cooling. ^{1}H NMR spectrum and GLC analysis (System A, 190°C; System B, 170°C) showed the product to be a single compound which was identified as **11**, m.p. 69–70°C (from pentane); UV (pentane) λ_{max}: 233, 281 nm (log ϵ 4.22, 3.59); IR (CCl_4) ν: 2055, 1980 cm^{-1}; ^{1}H NMR (CCl_4): δ 7.14 (5H, s, Ph), 5.32 (2H, m, H-2,3), 3.63 (4H, s with a shoulder, CO_2Me and H-4), 3.16 (1H, m, H-1), 3.08 (1H, dd, J 17 and 4 Hz, H-6β), 2.02 (1H, dd, J 17 and 2.5 Hz, H-6α); MS m/z: 354 (M), 326 (M–CO), 298 (M–2CO), 270 (M–3CO). Anal. Found: C, 57.9; H, 4.1. $C_{17}H_{14}FeO_5$ calcd.: C, 57.66; H, 3.98%. The steric structure and atomic coordinates of **11** have been determined from a single-crystal X-ray diffraction study [14].

3.7. Tricarbonyl(η^4-5α,5β-diphenylcyclohexa-1,3-diene) iron (13)

The diene **17** (500 mg, 2.16 mmol) prepared from the reaction of the tosylhydrazone of 4,4-diphenylcyclohexa-2-en-1-one with ^{n}BuLi [15], was treated with $Fe(CO)_5$ ($^nBu_2O$/reflux, 16 h) to afford, after chromatography on silica and elution with light petroleum and benzene (9:1), **13** as a yellow solid (760 mg, 95%), m.p. 126–127°C (from light petroleum); IR (CCl_4) ν: 2055, 1970 cm^{-1}; ^{1}H NMR (CCl_4): δ 7.2–6.7 (10H, m, Ph), 5.44 (1H, m, H-3), 5.16 (1H, m, H-2), 3.4 (2H, m, H-1,4), 2.92 (1H, dd, J 16 and 3 Hz, H-6β), 2.46 (1H, dd, J 16 and 2.5 Hz, H-6α); MS m/z: 372 (M), 344 (M–CO), 316 (M–2CO), 288 (M–3CO). Anal. Found: C, 67.5; H, 4.2. $C_{21}H_{16}FeO_3$ calcd.: C, 67.77; H, 4.33%.

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