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Iron-promoted coupling reaction of homohypostrophene

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Abstract

Thermolysis of homohypostrophene (HHS) with $Fe(CO)_5$ yields four major products which are diastereomeric ketones formed by coupling of one CO with two units of HHS. Their structures were confirmed by NMR and mass spectroscopy analyses. The proposed mechanism for the reaction involves the sequence: iron coordination to HHS, carbonylation of HHS, followed by reductive elimination to give the dimer ketones.

Introduction

Thermolysis of homohypostrophene (HHS) with $Mo(CO)_6$ has been found to yield two types of stable complexes, viz. $Mo(HHS)(CO)_4$ and $Mo(HHS)_2(CO)_2$ [1]. Prolonged heating of these complexes at ca. 150 °C results in retrocyclization of HHS to its isomer dicyclopentadienylmethane. This is somewhat different from that shown by norbornadiene (NBD) and its 7-substituted derivatives, which undergo, and regiospecific *endo–cis–endo* dimerization [2–5]. It is well known that both the readiness to undergo, and the selectivity of, these reactions may be drastically altered if the substituents on double bonds are changed [6]. Another equally important factor is the nature of the metal used as the catalyst. For example, reactions of NBD with $Fe(CO)_5$ proceed more rapidly than those with $Mo(CO)_6$, but are less regioselective [7,8]. Other metal complexes have also been known to show wide ranges of reactivity and selectivity [10,11]. Significant differences have been found between the reactions of NBD with either $Mo(CO)_6$ or $Fe(CO)_5$. Herein we describe the comparison of the reaction of HHS with $Fe(CO)_5$ with that of HHS with $Mo(CO)_6$. Several isomeric dimer ketones are isolated from the reaction. Since the structure of the products is known, the geometry of the Fe-HHS coordinated intermediates can be depicted.

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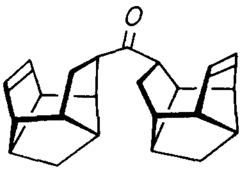
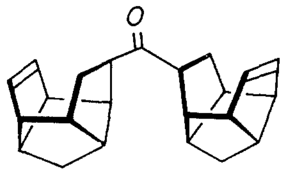
Results and discussion

A solution of $Fe(CO)_5$ and HHS [12] (molar ratio = 2.5/1) in di-n-butyl ether was heated to reflux for 3 d. From the products two sets of isomeric mixtures were isolated. Further separation of each isomer pair could not easily be achieved, so that the isomers in each pair were analyzed together. These are identified as Ia,b (yield 20%) and IIa,b (yield ca. 2%) respectively, the basic units of which are *exo* and *endo* hydrocarbonylated HHS moieties.

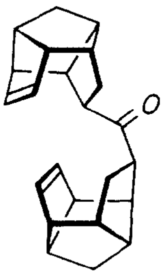


(Ia)

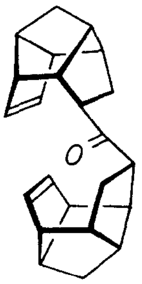


(Ib)

The ^{13}C NMR spectrum of the Ia,b mixture consists of twelve narrowly separated pairs of signals (Fig. 1). One of these signal pairs at low field corresponds to the carbon in the C=O groups. The other eleven signal pairs correspond to the eleven non-equivalent carbons of HHS. The duality of signals implies the presence of two types of HHS moieties in the sample, i.e. Ia and Ib; however, the narrow spacing indicates a high similarity between their chemical environments. The absorption band at 1700 cm^{-1} in IR confirms the presence of a C=O in each molecule. The parent peak in the mass spectrum appears at 318 (relative intensity of 14%), along with two strong fragment peaks at 173 (62%) and 145 (89%). The mass unit of 145 derives from the cation of monohydro-HHS (MW of HHS = 144), and the mass unit of 173 corresponds to the addition of a C=O group to the last fragment. The ^{13}C DEPT NMR spectrum shows the presence of two $-CH_2-$ units in each HHS segment. One of the two double bonds of HHS must have been saturated in the reaction. It was on the basis of these data that the structures of Ia and Ib were deduced.



(IIa)



(IIb)

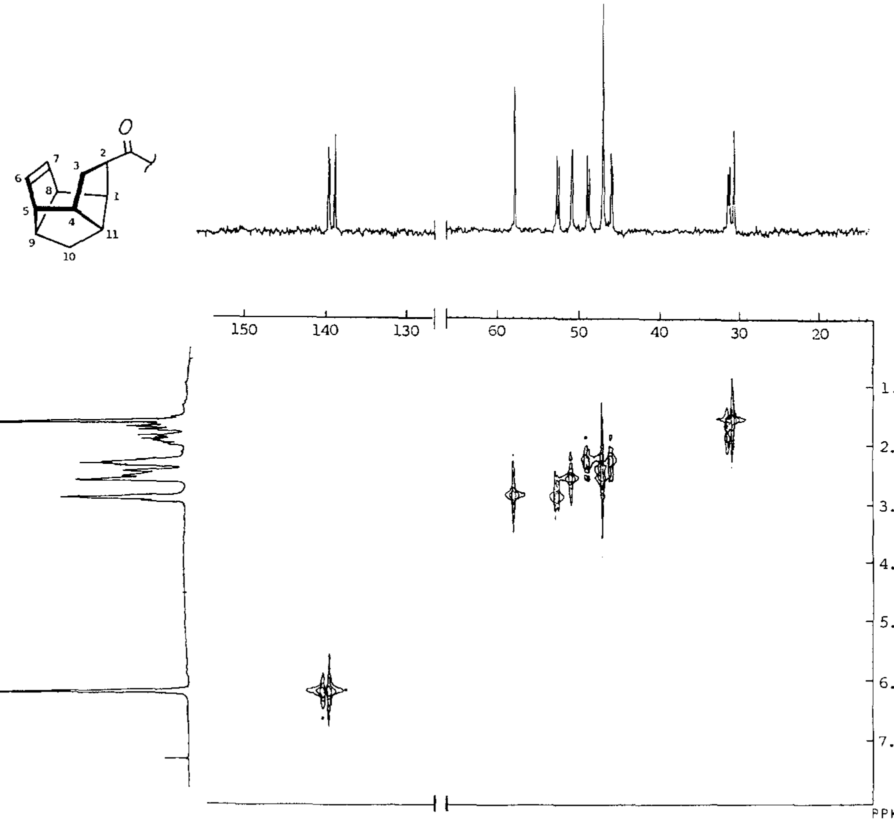


Fig. 1. The ^1H–^{13}C COSY NMR spectrum of Ia,b in $CDCl_3$. Tetramethylsilane was used as internal standard.

Examination of the stereochemistry of Ia,b reveals that the two HHS moieties of either Ia or Ib are chemically equivalent. Ia exists in a *meso* form and Ib exists as a *d*,*l*-pair. Relative yields of the two isomers, within experimental error, is 1/1. Either the ^1H or ^{13}C NMR chemical shifts of both Ia and Ib should be very similar yet distinguishable. The proposed structures of Ia,b were further confirmed by two-dimensional ^1H–^1H COSY and ^1H–^{13}C COSY (Fig. 1) spectroscopy, all of the signals corresponding to hydrogens and carbons were assigned. Details of the assignments are given in the experimental section.

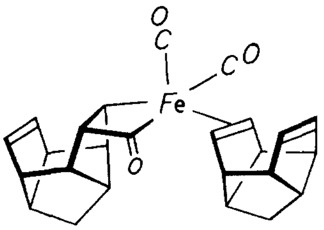
The structural determination for the minor product IIa,b was much more difficult, due in part to its low yield and in part to the complexity of their spectra. The fragmentation patterns of IIa,b in the mass spectrum are almost identical to those of Ia,b, which indicate that they are structurally very similar. The strong infrared absorption at 1700 cm^{-1} confirms the presence of C=O. The most obvious spectroscopic difference between Ia,b and IIa,b was found in their ^1H NMR spectra in the vinyl protons region. the vinyl signal of Ia,b appears as a broad singlet at δ 6.13, while those of IIa,b appear as three separate multiplets centered at δ 5.61, 5.83, and 6.05 (ratio 1/1/2). Some of the vinyl groups of IIa,b must therefore be in asymmetric chemical environments. Isomers with an *endo*-carbonyl group are proposed on account of the reaction mechanism. The signals at 5.61 and 5.83 are assigned to a pair of vinyls split by the *endo*-carbonyl group, which induces a fairly strong yet polarized diamagnetic effect towards the nearby vinyl group. The 46 signals in the ^{13}C NMR spectrum is consistent with the structure proposed. ^{13}C DEPT experiments confirms that their multiplicities (coupling with hydrogens) are correct, i.e. 8 triplets ($-CH_2-$), 28 doublets for saturated carbons ($-CH-$), 8 doublets for vinylic carbons ($=CH-$), and two singlets ($C=O$). The complex ^{1}H NMR spectrum can be resolved by correlation with a 2D ^{1}H–^{13}C COSY plot. Exact assignment of each proton to its NMR signal was not possible owing to serious overlapping of signals.

In order to confirm further the proposed structures of Ia,b and IIa,b, IIa,b were treated so as to convert them into Ia,b. The *endo*-carbonyl group experiences strong steric repulsion by the proximate vinyl group, hence the energy of IIa,b should be higher than that of Ia,b, and epimerization of the *endo*-carbonyl group to an *exo*-form would release such a strain. Therefore, conversion of IIa,b to Ia,b should be readily attainable upon treatment with base, and would provide unequivocal evidence for the isomeric relationship between the two types of structures.

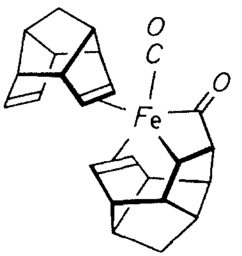
The conversion proceeded as expected and was carried out as follows: Treatment of IIa,b with ethanol containing 10% KOH, with stirring at room temperature for 24 h, quantitatively yielded Ia,b, identical in all respects with the authentic sample.

$$\text{IIa,b} \xrightarrow{10\%\ \text{KOH, EtOH, RT}} \text{Ia,b}$$

The mechanism of the reaction can be inferred from the analogous reaction shown by NBD. Carbonylations from both the *exo* and *endo* faces of NBD have been observed in the dimerization reactions catalyzed by $Fe(CO)_5$ [13]. *Exo*-coordination of HHS to metal should be more kinetically favored than *endo*-coordination; however, *endo*-coordination produces chelates which are more stable [2]. Complexes of types III and IV are proposed as intermediates prior to the coupling of HHS. Reductive elimination after coupling produces the observed products. Although no evidence for the hydrogen source is available, the hydrogens may derive from moisture contaminated in the reagents, or from water added during the aqueous work-up procedure. The ratio of isolated Ia,b to IIa,b (ca. 10/1) reflects the ratio of III to IV present in the reaction if epimerization is negligible.



(III)



(IV)

Experimental

^{1}H and ^{13}C NMR spectra were recorded either on a Bruker AW 80 CW spectrometer or on a Bruker MSL-200 FT spectrometer. Chemical shifts are in parts per million (ppm) downfield from tetramethylsilane in δ units and coupling constants are in hertz (Hz). Results of DEPT experiments for ^{13}C NMR are indicated as multiplicities (s, d, t, q) in parentheses. Infrared spectra were recorded on a Perkin–Elmer 297 infrared spectrophotometer. Melting points were determined by use of a Yamato model MP-21 melting point apparatus and were uncorrected. Elemental analyses were carried out by use of a Perkin–Elmer 240 EA instrument. Mass spectra were recorded on a JEOL JMS-D300 mass spectrometer.

Pentacarbonyliron was purchased from Merck. Homohypostrophene was prepared by a published procedure [12].

2,2′-Bis(tetracyclo[6.3.0.0.^{4,11}0.^{5,9}]-6-undecenyl)ketone derivatives (Ia,b and IIa,b)

A 25-ml two-neck round bottom flask was fitted with a refluxing condenser and a septum through which liquid samples can be injected. The system was purged with nitrogen first and then into it was injected homohypostrophene (730 mg, 5.1 mmol), di-n-butyl ether (15 ml), and pentacarbonyliron (2.48 g, 12.7 mmol). While the solution was being heated under reflux for 3 days, dark precipitates formed. The liquid was decanted and the solids were extracted with ethyl acetate (15 ml × 5). The liquid portions were combined and dried over anhydrous $MgSO_4$, filtered, and then concentrated in a rotary evaporator. Products Ia,b and IIa,b were isolated as two sets of isomers by HPLC on a column packed with silica gel using ethyl acetate/hexane as the eluent. Isomers Ia,b (177 mg, 22%), m.p. 165–167.5 °C; ^{1}H NMR ($CDCl_3$): δ 1.52 (br s, 4H; H(10)), 1.60–1.66 (m, 2H, H(3)), 1.75–1.95 (m, 2H, H(3)), 2.20–2.28 (m, 4H, H(1) and H(4)), 2.35–2.55 (m, 6H, H(5), H(8) and H(11)), 2.82–2.85 (m, 4H, H(2) and H(9)), 6.13 (br s, 4H, H(6) and H(7)); ^{13}C NMR ($CDCl_3$): δ 31.02 (t, 2C, C(10)), 31.62, 31.81 (2t, C(3)), 46.18, 46.32 (2d, C(1) or C(4)), 47.32 (d, 4C, C(5) and C(8)), 49.08, 49.34 (2d, C(1) or C(4)), 51.14, 51.25 (2d, C(11)), 52.83, 53.09 (2d, C(2)), 58.23 (2C, d, C(9)), 138.46, 138.52 (2d, C(6) or C(7)), 139.19, 139.32 (2d, C(6) or C(7)), 216.40, 216.58 (2s, CO); IR (KBr): 1700 cm^{-1} (C=O); MS (relative intensity): m/z 318 (14, M^+), 252 (6.7), 173 (62), 145 (89), 117 (24), 79 (100), 67 (75); Anal. Found: C, 86.58; H, 8.21. $C_{23}H_{26}O$ calc: C, 86.75; H, 8.22%. Isomers IIa,b (15 mg, 1.9%), ^{1}H NMR ($CDCl_3$): δ 1.50 (m, 10H), 1.60–1.70 (m, 1H), 1.80–1.95 (m, 4H), 2.05–2.25 (m, 7H), 2.30–2.55 (m, 14H), 2.76 (br s, 4H), 2.90–3.00 (m, 4H), 5.58–5.64 (m, 2H), 5.80–5.86 (m, 2H), 6.00–6.10 (m, 4H); ^{13}C NMR ($CDCl_3$): δ 30.25 (t), 30.36 (t), 30.85 8t), 30.97 (t), 31.09 (t), 31.40 (t), 31.61 (t), 32.46 (t), 42.38 (d), 42.61 (d), 46.20 (d), 46.31 (d), 46.89 (d), 46.96 (d), 47.19 (d), 47.29 (d, 2C), 47.44 (d), 47.54 (d), 47.58 (d), 48.91 (d, 2C), 49.19 (d), 50.70 (d), 50.88 (d), 51.53 (d), 51.89 (d), 52.17 (d), 53.37 (d), 53.50 (d), 54.48 (d), 54.59 (d), 58.11 (d), 58.18 (d), 58.21 (d), 58.29 (d), 138.16 (d), 138.54 (d), 138.65 (d), 139.05 (d), 139.16 (d), 139.80 (d, 2C), 140.15 (d), 216.2 (s), 216.5 (s); IR (CH_2Cl_2): 1700 cm^{-1} (C=O); MS (relative intensity): m/z 318 (20, M^+), 252 (8.0), 173 (79), 145 (97), 117 (28), 91 (26), 79 (100).

Acknowledgement

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