Journal of Organometallic Chemistry, 208 (1981) C31—C35
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

TRICARBONYLIRON COMPLEXES OF SOME BLOCKED CYCLOHEXADIENES

B.M. RATNAYAKE BANDARA, ARTHUR J. BIRCH*, BRIAN CHAUNCY, and LAWRENCE F. KELLY

Research School of Chemistry, Australian National University, P.O. Box 4, Canberra, A.C.T. 2600 (Australia)

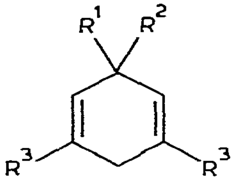
(Received November 27th, 1980)

Summary

Complexation commencing with some substituted 1,3- or 1,4-cyclohexadienes with $Fe(CO)_5$ indicates that the steric direction is controlled by classical hindrance with groups such as alkyl, but probably involves transmission of the entering group through intermediate complexation with CO_2Me. The results help to define methods of obtaining desired stereoisomers in the series.

Regio- and stereo-specific reactions of substituted tricarbonyl(η^4-cyclohexa-1,3-diene)iron complexes together with the easy removal of the metal, enable these compounds to be used in the form of the derived dienyl salts as synthetic equivalents for dienyl, aryl or enone fragments in organic synthesis [1]. The complexes can be prepared starting with 1,3- or 1,4-cyclohexadienes or their equivalents [2]. Although 1,4-cyclohexadienes are readily available from the Birch reduction of aromatic substrates [3], the complexation usually results in a mixture of isomeric products because of the involvement of several possible allyl intermediates in the process [4]. Major synthetic capabilities are based on the often complete stereospecificities of reaction of complexes [5] so that definitions of methods of forming given stereoisomers, as well as structural isomers, are desirable. For examination of both features we have complexed some 1,4-cyclohexadienes with gem-substituents using $Fe(CO)_5$ in refluxing di-n-butyl ether. These dienes are readily available from Birch reduction intermediates by alkylations [6], e.g. **1**, **2**, **4**, **5**, **6** and **8**. The diene acid corresponding to **3** was formed by quenching with solid CO_2 the anion which results from the treatment with n-BuLi of the metal/ammonia reduction-product of biphenyl [7].

0022-328X/81/0000—0000/$ 02.50, © 1981, Elsevier Sequoia S.A.



(1) $R^1 = R^2 = CO_2Me$, $R^3 = H$

(2) $R^1 = CO_2Me$, $R^2 = Me$, $R^3 = H$

(3) $R^1 = CO_2Me$, $R^2 = Ph$, $R^3 = H$

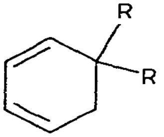
(4) $R^1 = CO_2Me$, $R^2 = CH_2Ph$, $R^3 = H$

(5) $R^1 = CO_2Me$, $R^2 = CH_2CO_2Me$, $R^3 = H$

(6) $R^1 = Ph$, $R^2 = Me$, $R^3 = H$

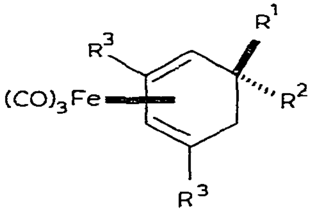
(7) $R^1 = CO_2Me$, $R^2 = H$, $R^3 = H$

(8) $R^1 = CO_2Me$, $R^2 = Me$, $R^3 = OMe$



(9) $R = Me$

(10) $R = Ph$



(11) $R^1 = R^2 = CO_2Me$, $R^3 = H$

(12) $R^1 = CO_2Me$, $R^2 = Me$, $R^3 = H$

(13) $R^1 = CO_2Me$, $R^2 = Ph$, $R^3 = H$

(14) $R^1 = CO_2Me$, $R^2 = CH_2Ph$, $R^3 = H$

(15) $R^1 = CO_2Me$, $R^2 = CH_2CO_2Me$, $R^3 = H$

(16) $R^1 = CH_2CO_2Me$, $R^2 = CO_2Me$, $R^3 = H$

(17) $R^1 = Me$, $R^2 = Ph$, $R^3 = H$

(18) $R^1 = Ph$, $R^2 = Me$, $R^3 = H$

(19) $R^1 = CO_2Me$, $R^2 = H$, $R^3 = H$

(20) $R^1 = H$, $R^2 = CO_2Me$, $R^3 = H$

(21) $R^1 = CO_2Me$, $R^2 = Me$, $R^3 = OMe$

(22) $R^1 = Me$, $R^2 = CO_2Me$, $R^3 = OMe$

(23) $R^1 = R^2 = Me$, $R^3 = H$

(24) $R^1 = R^2 = Ph$, $R^3 = H$

The conjugated dienes **9** and **10** were available from the corresponding 5,5-disubstituted cyclohexa-2-ene-1-ones [8].

Single products were observed from the dienes **1**—**4**, although two isomers could have resulted by alternative attack on the two faces of the ring. The dienes **5** and **6** gave two products. The diester complex **11** showed in its ^1H NMR spectrum two resonances at δ 3.73 and 3.63 ppm corresponding to CO_2Me protons. The latter signal was absent in the product formed by the alkaline hydrolysis of **11** under mild conditions (aq. NaOH/MeOH/5—10°C/2 h) indicating that only one CO_2Me had been cleaved. β-CO_2Me groups, on the same side as the iron, usually resonate at lower fields than those on the opposite, α-, side [9,10,11]. The β-CO_2Me group of **11** was, therefore, unaffected in the hydrolysis. The ester complexes **12** and **14** did not react with NaOH even under rather more rigorous conditions at room temperature. Based on this result, and the similarities of their ^1H NMR spectra (see Table 1) to that of **17** whose configuration has been confirmed by X-ray crystallography [12], β-CO_2Me structures were assigned to **12** and **14**.

The fact that the dienes **5** and **6** gave on complexation two stereoisomers (TLC, ^1H NMR, mass spec.), while the esters **1**—**4** gave one isomer only is probably an indication of the directive effect of CO_2Me [9,13]. In the case of the diester **5**, the β-CO_2Me (**15**): α-CO_2Me (**16**) ratio of the products is 6/1 (^1H

TABLE 1

^1H NMR SPECTRA

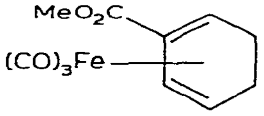
Diene/Product	^1H NMR (δ, ppm)[a] resonances of the product	Diene/Product	^1H NMR (δ, ppm)[a] resonances of the product
1/11[b]	5.38 m 2- and 3-H 3.73 s β-CO_2Me 3.63 s α-CO_2Me 3.31 d J 6 Hz 4-H 3.18 m 1-H 2.53—2.13 m 6-H	5/15, 16[b] (6/1)[d]	5.37 m 2- and 3-H 3.79 s β-CO_2Me of 15 3.69, 3.67 s,s CO_2Me of 16 3.65 s CH_2CO_2Me of 15 3.3—2.3 m 1-, 4- and 6β-H and CH_2CO_2Me 1.7 dd J 16, 3 Hz 6α-H of 15 1.95 dd, J 16, 3 Hz 6α-H of 16
2/12[b]	5.30 m 2- and 3-H 3.66 s CO_2Me 3.37 dd J 6, 2 Hz 4-H 3.06 m 1-H 2.58 dd J 16, 3.5 Hz 6β-H 1.52 dd J 16, 2.7 Hz 6α-H 1.20 s Me	6/17, 18[c] (2/1)[d,e]	7.3—7.0 m Ph 5.34 m 2- and 3-H 3.45—3.05 m 1- and 4-H 2.45—2.00 m 6-H 1.43 s Me of 17 1.30 s Me of 18
3/13[c]	7.14 s Ph 5.34 m 2- and 3-H 3.63 s CO_2Me 3.16 m 1- and 4-H 3.08 dd J 17, 4 Hz 6β-H 2.04 dd J 17, 2.5 Hz 6α-H	8/21, 22[b] (1/1)[d]	5.27 d J 2.5 Hz 2-H 3.76 s CO_2Me of 21 3.63 s 3-OMe of 21 and CO_2Me of 22 3.62 s 3-OMe of 22 3.49 d J 2.5 Hz 4-H of 21 3.44 s 1-OMe of 21 3.42 s 1-OMe of 22 3.07 d J 15 Hz 6β-H of 21 3.04 d J 2.5 Hz 4-H of 22 2.46—1.97 AB q 6-H of 22 1.51 d J 15 Hz 6α-H of 21 1.36 s Me of 21 1.28 s Me of 22
4/14[b]	7.10 m Ph 5.27 m 2- and 3-H 3.63 s CO_2Me 3.30 dd J 6, 2 Hz 4-H 3.03 m 1-H 2.77 s CH_2Ph 2.53 dd J 16, 4 Hz 6β-H 1.77 dd J 16, 2.7 Hz 6α-H	10/24[c]	7.4—6.7 m Ph 5.44, 5.20 m, m 2- and 3-H 3.38 m 1- and 4-H 2.92 dd J 16, 4 Hz 6β-H 2.46 dd J 16, 3 Hz 6α-H

[a] Me_4Si (internal reference). [b] $CDCl_3$ (NMR solvent). [c] CCl_4 (NMR solvent). [d] Isomer ratio (by ^1H NMR). [e] Isomer ratio (by GLC).

NMR), the CO_2Me closer to the diene bonds being more effective in directing the stereochemistry than that in CH_2CO_2Me. Already noted is that alkyl groups exert a classical type of steric hindrance on the approach to the nuclear bonds of the coordinatively unsaturated iron species, $Fe(CO)_n$ (n = 3 [14] or 4 [15]), e.g. complexation of "α"-phellandrene [5]. A composite of this steric effect by alkyl or aryl groups and the initial coordination of $Fe(CO)_n$ (n = 3 or 4) to CO_2Me, is probably the explanation of the formation of single isomers in the above examples.

The same directive influence of the ester group is not observed in complexation of diene **8**, which results in formation of complexes **21** and **22** in about equal proportions. This suggests that competition for the electron-deficient coordinating iron species occurs between the ester group and π-donation from the double bonds. For reasons discussed elsewhere [16] the demethoxylation observed with precursor lacking CO_2Me is not observed during formation of **21** and **22**.

In complexation of the unblocked diene ester **7** [9] the 5β-CO_2Me isomer **19** has been found as the major product, the 5α-CO_2Me (**20**) and the 2-CO_2Me (**25**) being minor products. This result is in agreement with the above conclusions. A detailed examination [11] of this reaction has shown that **20** and **25** have been formed by the α-approach of $Fe(CO)_n$ rather than by a thermal isomerisation of an initially formed **19**.



(25)

As expected, the conjugated dienes **9** and **10** gave single products **23** [17] and **24**, respectively.

All the new compounds have been characterised by spectral data (IR, ^1H NMR, mass spect.) and in key instances by elemental analysis.

References

1 A.J. Birch, B.M.R. Bandara, K. Chamberlain, B. Chauncy, P. Dahler, A.I. Day, I.D. Jenkins, L.F. Kelly, T.-C. Khor, G. Kretschmer, A.J. Liepa, A.S. Narula, W.D. Raverty, E. Rizzardo, C. Sell, G.R. Stephenson, D.J. Thompson, and D.H. Williamson, Tetrahedron, Woodward Memorial Issue, accepted for publication.

2 R. Pettit, G.F. Emerson, and J.E. Mahler, J. Chem. Ed., 40 (1963) 175; B.F. Hallam and P.L. Pauson, J. Chem. Soc., (1958) 642; M. Slupczynski, I. Wolszczak, and P. Kosztolowicz, Inorg. Chim. Acta, 33 (1979) L97; A.J.P. Domingos, J.A.S. Howell, B.F.G. Johnson, and J. Lewis, Inorg. Synth., 16 (1976) 103.

3 A.J. Birch and G.S. Subba Rao, Advan. Org. Chem., 8 (1972) 1; E.M. Kaiser, Synthesis, (1972) 391.

4 H. Alper, P.C. LePort, and S. Wolfe, J. Amer. Chem. Soc., 91 (1969) 7553; T.H. Whitesides and J.P. Neilan, J. Amer. Chem. Soc., 98 (1976) 63.

5 A.J. Birch, Anals N.Y. Acad. Sci., 333 (1980) 107; and ref. therein.

6 A.J. Birch, J. Chem. Soc., (1950) 1551; A.J. Birch and J. Slobbe, Aust. J. Chem., 30 (1977) 1045; I.K. Zhurkovich and D.V. Ioffe, Zh. Org. Khim., 10 (1974) 212, Chem. Abstr., 80 (1974) 120375w; R.J. Cregge, J.L. Herman, C.S. Lee, J.E. Richman, and R.H. Schlessinger, Tetrahedron Lett., (1973) 2425; D.F. Lindow, C.N. Cortez, and R.G. Harvey, J. Amer. Chem. Soc., 94 (1972) 5406; H. van Bekkum, C.B. van den Bosch, G. van Minnen-Pathius, J.C. de Mos, and A.M. van Wijk, Recl. Trav. Chim. Pays-Bas, 90 (1971) 137.

7 A.J. Birch and G. Nadamuni, J. Chem. Soc. Perkin I, (1974) 545.
8 H.E. Zimmerman and G.A. Epling, J. Amer. Chem. Soc., 94 (1972) 8749; C. Walling and A.A. Zavitsas, J. Amer. Chem. Soc., 85 (1963) 2084.
9 A.J. Birch and A.J. Pearson, J. Chem. Soc. Perkin I, (1978) 638.
10 A.J. Pearson, Aust. J. Chem., 29 (1976) 1101; A.L. Burrows, B.F.G. Johnson, J. Lewis, and D.G. Parker, J. Organometal. Chem., 127 (1977) C22;
11 B.M.R. Bandara, A.J. Birch, and W.D. Raverty, unpublished results.
12 B.F. Anderson and G.B. Robertson, unpublished results.
13 T.H. Whitesides, R.W. Slaven, and J.C. Calabrese, Inorg. Chem., 13 (1974) 1895.
14 D.H. Gibson, T.-S. Ong, and F.G. Khoury, J. Organometal. Chem., 157 (1978) 81.
15 S.M. Nelson and M. Sloan, J. Chem. Soc., Chem. Commun., (1972) 745; E.K. von Gustorf and J.C. Hogan, Tetrahedron Lett., (1969) 3191.
16 A.J. Birch, L.F. Kelly, and D.J. Thompson, J. Chem. Soc. Perkin I, accepted for publication.
17 W.G. Dauben and M.E. Lorber, Org. Mass. Spectrom., 3 (1970) 211.