

## Synthesis and Characterization of a Dendrimer Like Coupling Product, $[C_6(CH_2)_6(CH_3OCC=CCOOCH_3)_3]$

F R Alam<sup>1\*</sup>, S S Ullah<sup>2</sup> and M R Haque<sup>3</sup>

**Abstract :** A dendrimer like coupling product,  $[C_6(CH_2)_6(CH_3OCC=CCOOCH_3)_3]$  (IV) has been synthesized by the oxidation of 1,2,3,4,5,6-hexamethylenecyclohexanenonacarbonyltriiron (III) with ceric ammonium sulphate followed by coupling with dimethylacetylene-dicarboxylate at  $-10^\circ C$ . The compound has been characterized by IR,  $^1H$  NMR,  $^{13}C$  NMR, mass spectra and elemental analysis.

**Key words:** Dendrimer, IR,  $^1H$  NMR,  $^{13}C$  NMR.

### Introduction

Synthesis and reactions of transition metal olefin complexes constitute a vast expanding area of organometallic chemistry [1]. Diene irontriacarbonyl complexes can be readily decomposed at low temperature with liberation of the free diene upon treatment with oxidizing agents such as ferric or ceric ions [2,3]. Previous studies showed that cyclobutadieneirontriacarbonyl decomposed in the presence of ceric ions to give, along with other materials, a dimer or cyclobutadiene [2,3]. Watts *et al.* [4] also reported the isolation of cyclobutadiene compound and when such decomposition was carried out in presence of acetylenic compounds, the demetallation leads to the formation of Dewar benzene derivatives (I & II) as expected from the addition of an acetylene to “free” cyclobutadiene (Scheme 1). Following that work we have investigated the oxidation reaction of  $\pi$ -bonded complex 1,2,3,4,5,6-hexamethylenecyclohexanenonacarbonyltriiron (III) with ceric ammonium sulphate followed by coupling with dimethylacetylenedicarboxylate in order to study its potential use in the synthesis of dendrimer like coupling product and the results are described in the present paper.

### Experimental

The reactions were carried out under dry nitrogen atmosphere. The solvents were dried and distilled prior to use. IR spectra were recorded on Shimadzu 8010 spectrometer. NMR spectra were recorded on Bruker AR-250 and 500 MHz spectrophotometers and Mass spectra on a high resolution mass spectrometer.  $Na_2[Fe(CO)_4]$  [5] and 1,2,3,4,5,6-hexamethylenecyclohexanenonacarbonyltriiron [6] were prepared by the previously reported method. Dimethylacetylenedicarboxylate and ceric ammonium sulphate were purchased from Aldrich and used as received.

<sup>1</sup> Associate Professor, Department of Chemistry, National University, Gazipur-1704, Bangladesh.

<sup>2</sup> Professor, Department of Chemistry, Jahangirnagar University, Savar, Dhaka-1342, Bangladesh.

<sup>3</sup> Inorganic and Environmental Research Laboratory, Department of Chemistry, Jahangirnagar University, Savar, Dhaka-1342, Bangladesh.

\* Author to whom all correspondence may be made.

The oxidation reaction of 1, 2, 3, 4, 5, 6- hexamethylenecyclohexanenonacarbonyl-triiron (III) with ceric ammonium sulphate followed by coupling with dimethylacetylenedicarboxylate:

Ceric ammonium sulphate (200 mg, 0.41 mmol) in ethanol (20 mL) and a solution of dimethylacetylenedicarboxylate (60 mg, 0.41 mmol) in ethanol (10 mL) were added dropwise to a cold ethanolic solution (20 mL) of 1,2,3,4,5,6-hexamethylenecyclohexanenonacarbonyltriiron (III) (80 mg, 0.14 mmol) with vigorous stirring under nitrogen atmosphere at  $-10^{\circ}\text{C}$ . The reaction mixture was stirred for 6 hours. The solvent was removed under reduced pressure and the residue chromatographed first on a silica column and then on silica TLC plates, eluting with diethylether-dichloromethane (2:1; v/v) to give  $[\text{C}_6(\text{CH}_2)_6(\text{CH}_3\text{OOC}=\text{CCOOCH}_3)_3]$  (IV) as colourless solid with melting zone in the range  $124\text{--}130^{\circ}\text{C}$  (24 mg, 29%) [Found: C, 62.5; H, 5.3.  $\text{C}_{30}\text{H}_{30}\text{O}_{12}$  requires: C, 61.85; H, 5.19%]. IR (KBr):  $\nu_{\text{CO}}$ ,  $1734\text{ cm}^{-1}$ ;

$^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  3.76 (bs, 18H) and 3.55 (s, 12H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  151.070, 105.142, 85.146, 57.137 and 43.533.

MS :  $m/z$  582  $[\text{M}^+]$ , 567  $[\text{M}^+-\text{CH}_3]$ , 551  $[\text{M}^+-\text{OCH}_3]$ , 523  $[\text{M}^+-\text{COOCH}_3]$ , 508  $[\text{M}^+-\text{COOCH}_3 + \text{CH}_3]$ , 492  $[\text{M}^+-\text{(COOCH}_3 + \text{OCH}_3)]$ , 464  $[\text{M}^+-\text{(2COOCH}_3)]$ , 449  $[\text{M}^+-\text{(2COOCH}_3 + \text{CH}_3)]$ , 433  $[\text{M}^+-\text{(2COOCH}_3 + \text{OCH}_3)]$ , 436  $[\text{M}^+-\text{(2COOCH}_3 + \text{CO})]$ , 390  $[\text{M}^+-\text{(3COOCH}_3 + \text{CH}_3)]$ , 374  $[\text{M}^+-\text{(3COOCH}_3 + \text{OCH}_3)]$ , 346  $[\text{M}^+-\text{(4COOCH}_3)]$ , 331  $[\text{M}^+-\text{(4COOCH}_3 + \text{CH}_3)]$ , 315  $[\text{M}^+-\text{(3COOCH}_3 + \text{OCH}_3)]$ , 287  $[\text{M}^+-\text{(5COOCH}_3)]$ , 272  $[\text{M}^+-\text{(5COOCH}_3 + \text{CH}_3)]$ , 256  $[\text{M}^+-\text{(5COOCH}_3 + \text{OCH}_3)]$ , 228  $[\text{M}^+-\text{(6COOCH}_3)]$ , 59  $[\text{COOCH}_3]^+$ , 44  $[\text{CO}_2]^+$ , 31  $[\text{OCH}_3]^+$  & 28  $[\text{CO}]^+$ .

## Results and Discussion

The oxidation of 1, 2, 3, 4, 5, 6- hexamethylenecyclohexanenonacarbonyltriiron (III) with ceric ammonium sulphate followed by coupling with dimethylacetylenedicarboxylate in ethanol at  $-10^{\circ}\text{C}$  afforded the coupling compound  $[\text{C}_6(\text{CH}_2)_6(\text{CH}_3\text{OOC}=\text{CCOOCH}_3)_3]$  (IV). The IR spectrum of IV in KBr exhibits a peak at  $1734\text{ cm}^{-1}$  due to ester groups, which is similar to those reported for the related ester compounds [7-9]. The  $^1\text{H NMR}$  spectrum of IV in  $\text{CDCl}_3$  exhibits two singlets at  $\delta$  3.76 and 3.55 in a relative intensity of 3:2. The singlet at  $\delta$  3.76 is assigned to methyl protons of the ester groups,  $\delta$  3.55 is due to the methylene protons. The low field shifts of methylene protons of IV compared to that of the starting M-C  $\pi$ -bonded complex [6,10] [ $\delta$  0.02 (d,  $J_{\text{H-H}}$  2.5 Hz, 6H) and 2.63 (d,  $J_{\text{H-H}}$  2.5 Hz, 6H)] and slight high field shift of methyl protons compared to those of free dimethylacetylenedicarboxylate<sup>11</sup> ( $\delta$  3.9) indicates the formation of the dendrimer like coupling compound through methylene and olefinic carbon atoms. The upfield resonance of methyl protons of IV is similar to those reported for the related ester compounds [9,12]. The  $^{13}\text{C NMR}$  spectrum of IV in  $\text{CDCl}_3$  showed resonances at  $\delta$  151, 105, 85, 57 and 43. The assignment of the five resonances to the five types of carbon nuclei present in the molecule is very straightforward [13,14]; the resonance at  $\delta$  151 is obviously in the C=O region,  $\delta$  105 is due to aromatic carbon,  $\delta$  85 is due to  $>\text{C}=\text{C}<$ ,  $\delta$  57 is due to  $\text{OCH}_3$  and  $\delta$  43 is due to  $\text{CH}_3$  groups. The mass spectrum of IV showed the molecular ion peak

at  $m/z$  582, which is consistent with the molecular formula  $[C_{30}H_{30}O_{12}]$  (**IV**). Other characteristic peaks are due to successive loss of six ester groups, six methylene groups from molecular ion peak. The mass fragmentation pattern is in agreement with the proposed formula for **IV**. The elemental analysis is also in agreement with the proposed molecular formula for **IV**. Thus on the basis of the spectroscopic evidences the structure **IV** is suggested for this dendrimer like coupling compound (Scheme 2).

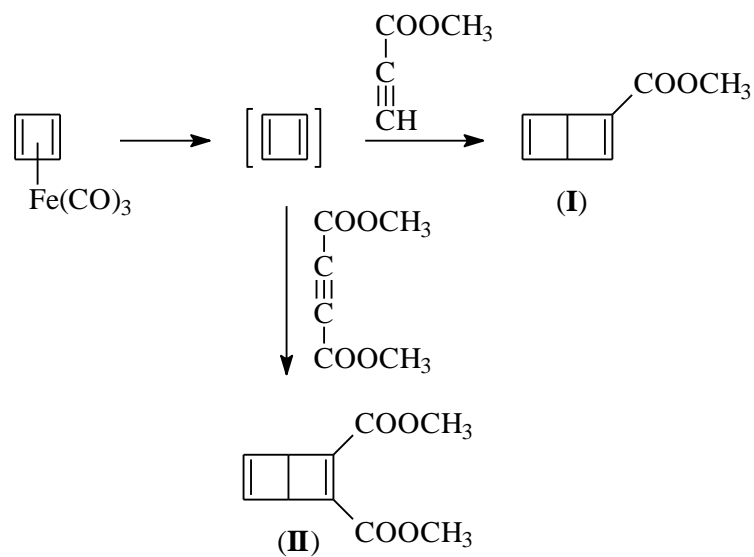
Compound **IV** is remarkable both from structural and functional points of view in that it has a planar core with symmetrically surrounding six carboxylate and three olefinic groups. These groups may be amenable to further transformation by conventional organic chemistry. Compound **IV** may be viewed as a dendrimer of first generation, which is capable of further coupling with acetylenedicarboxylate to give a second generation dendrimer. The reaction of **III** with excess (1:6) dimethylacetylenedicarboxylate results in the formation a higher molecular weight coupling product which points towards the reaction being carried further to second generation stage. The product is being fully characterized and will be reported in a further communication.

### Acknowledgement

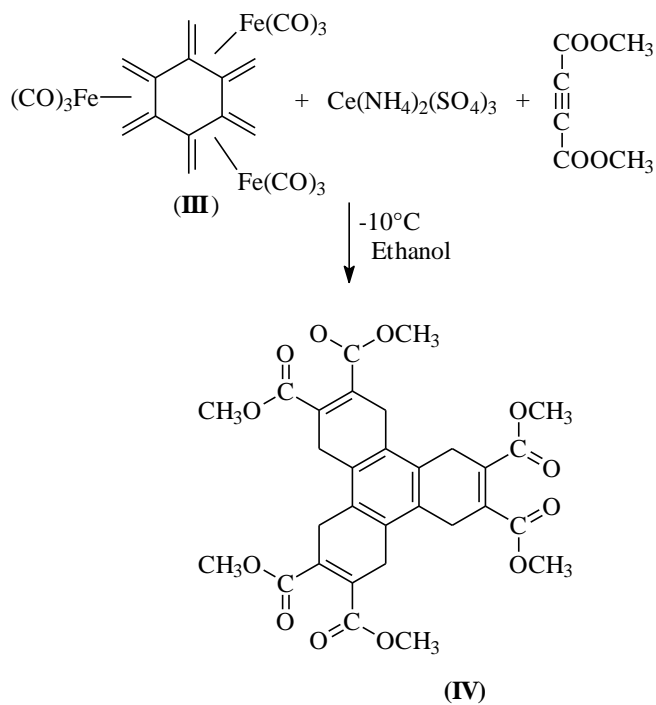
The authors are thankful to Prof. M Elias Molla and Prof. M M Karim, at the Laboratorium fur Aniganische Chemie II, Bayreuth Universitat, D-95440, Bayreuth, Germany for providing  $^1H$  NMR,  $^{13}C$  NMR, mass spectra and elemental analysis.

### References

1. (a) Stone F. G. A. and West R., 2005, *Advances in Organometallic Chemistry*, Academic Press, New York, **10**, 273; (b) M. A. Esteruelas and A. M. Lopeg, 2005, *Organometallics*, **24**, 3584; (c) I. J. Blackmore, X. Jin and P. Legzdins, 2005, *Organometallics*, **24**, 4088; (d) Q. Y. Hu, W. X. Lu, H. D. Tang, H. H. Y. Sung, T. B. Wen, I. D. Williams, G. K. L. Wong, Z. Lin and G. Jia, *Organometallics*, **24**, 3966.
2. Emerson G. F., Watts L. and Petit R., 1965, *J. Am. Chem. Soc.*, **87**, 31.
3. Cava M. P. and Napier D. R., 1957, *J. Am. Chem. Soc.*, **79**, 1701.
4. Watts L., Fitzpatrick J. D. and Petit R., 1965, *J. Am. Chem. Soc.*, **87**, 3253.
5. Collman J. P., 1975, *Ace. Chem. Res.*, **8**, 342.
6. Ullah S. S., Azam K. A., Kabir S. E., Rahman A. K. F. and Begum R., 1990, *Indian J. Chem.*, **29A**, 22.
7. Chounan Y., Ibuka T. and Yamamoto Y., 1994, *J. Chem. Soc., Chem. Commun.*, **17**, 2003.
8. Mehta G. and Reddy S. H. K., 1994, *J. Chem. Soc., Perkin Trans.*, **20**, 2949.
9. Atkinson J. G., Ayer D. E., Buchi G. and Ernest W. R., 1963, *J. Am. Chem. Soc.*, **85**, 2257 and references therein.
10. Ullah S. S., Azam K. A., Kabir S. E. and Alam F. R., 1994, *Indian J. Chem.*, **33A**, 420.
11. Charles J. P., *The Aldrich Library of NMR Spectra*, ed. **II**, p 960.
12. Ullah S. S., Kabir S. E., Molla M. E. and Karim M. M., 1984, *Indian J. Chem.*, **23A**, 404.
13. Benwell C. N., 1992, *Fundamentals of Molecular Spectroscopy*, 3rd ed., 286.
14. Morrison R. T. and Boyd R. N., 1989, *Organic Chemistry*, **5th** ed., 612.



Scheme 1



Scheme 2