

**Preliminary communication**

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**APPLICATION OF ULTRASOUND TO THE PREPARATION OF  
TRICARBONYLIRON DIENE COMPLEXES**

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**Summary**

The reaction of nonacarbonyldiiron with 1,3-conjugated dienes is promoted by ultrasound and has been shown to give high yields of the corresponding  $\eta^4$ -(diene)tricarbonyliron complexes. In addition, 3-chloro-2-chloromethyl-prop-1-ene reacts with nonacarbonyldiiron in the presence of ultrasound to give a quantitative yield of the trimethylenemethanetricarbonyliron complex.

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Recent investigations into the properties of  $\eta^4$ -(diene)tricarbonyliron complexes have begun to demonstrate their potential for use as synthetic intermediates [1]. Their interesting chemistry and the number of methods available for ready removal of the tricarbonyliron moiety [2, 3] has led to their exploitation as both protecting and stabilising groups for conjugated dienes. However, the major stumbling block to their general acceptance lies in the problems encountered in their preparation.

The sensitivity of both products and starting materials to aerial oxidation dictates that reactions must be carried out under inert atmospheres. Many examples of the reaction of dienes with carbonyliron species under the influence of heat or ultraviolet radiation have been published [2, 4]. The most commonly employed procedure involves heating the diene with pentacarbonyliron in a high boiling inert solvent, such as di-n-butyl ether, for long periods of time. Sensitivity of the product to peroxides present in these solvents often requires that the solvent be filtered through basic alumina immediately prior to use. However, despite all these precautions, yields of the diene complexes are seldom better than low to moderate [5] which therefore constitutes a major barrier to their general acceptance as synthetic intermediates. This is especially true where the demands of modern organic synthesis impose extremely high competitive standards. Similarly, the chemistry of trimethylenemethanetricar-

bonyliron complexes remains unexplored despite the elegant use that Trost et al. [6] have made of the analogous palladium complexes.

Here we report a convenient high yielding method for the synthesis of both trimethylenemethanetricarbonyliron and a variety of  $\eta^4$ -(diene)tricarbonyliron complexes as a result of the exposure of a mixture of the substrate and nona-

SCHEME 1

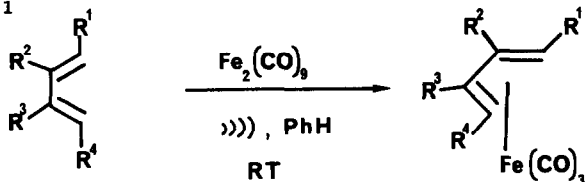


TABLE 1

Diene	Complex	Yield
		100 %
		70 %
		50 %
		62 %
		100 %
		51 %
		95 %

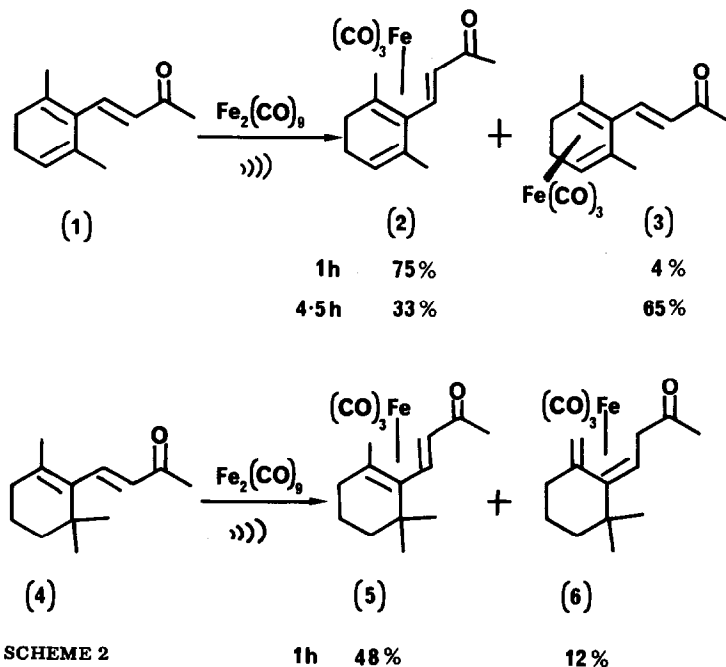
carbonyldiiron to ultrasound (Scheme 1)\*. This method has also previously found application in the preparation of ferrilactone complexes from vinyl epoxides [7].

#### Preparation of $\eta^4$ -(diene)tricarbonyliron complexes

Nonacarbonyldiiron (1.1 eq) was added to a solution of the relevant diene (see Table 1) in benzene and the mixture sonolysed for 1 h, or until all the solid carbonyl had disappeared. Concentration of the reaction mixture and column chromatography of the residue on silica (40/60° petroleum ether/diethyl ether gradient) separated the required complex from any inorganic species. Yields in these reactions were essentially quantitative and limited solely by the volatility of the product.

The method was applied to a variety of dienes and the yields were consistently higher than previous literature preparations despite the fact that no attempt was made at optimisation.

The reaction with pseudionone (1) is of interest in that after 1 h it was possible to isolate a 75% yield of the kinetic product 2 which, on further exposure to ultrasound, isomerised to give a 1/2 ratio of the kinetic 2 and thermodynamic products 3, Scheme 2. Storing the 3,5-diene complex 2 overnight at  $-20^\circ\text{C}$  resulted in almost complete conversion to the 5,9-diene complex 3. Hence, variation of the reaction time allows access to good yields of both isomers selectively. This was not possible by other conventional methods. The reaction of  $\beta$ -ionone (4) with  $\text{Fe}_2(\text{CO})_9$  gave a 4/1 mixture of the *endo* to



SCHEME 2

\* In our previous paper ref. 7a we incorrectly reported that dienes failed to react with  $\text{Fe}_2(\text{CO})_9$  under ultrasonic conditions.

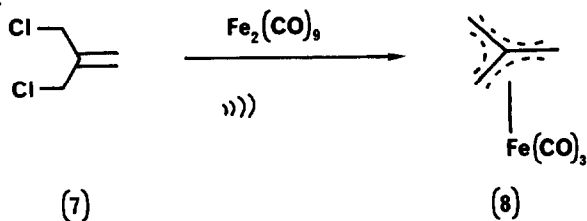
All sonolysis reactions were carried out in a Semat 80W 50KHz ultrasonic bath.

*exo* diene complexes 5 and 6 (Scheme 3) in contrast to Cais and Maoz [8] who obtained a 3/1 ratio in favour of the *exo* isomer 6 via the thermal reaction of  $\beta$ -ionone with  $\text{Fe}(\text{CO})_5$ . However, it should also be noted that the combined overall yield of this reaction was only 21%.

#### Preparation of trimethylenemethanetricarbonyliron

Equimolar amounts of nonacarbonyldiiron and 3-chloro-2-chloromethylprop-1-ene (7) were sonolysed together in 30/40° petroleum ether for 1 h. Careful concentration of the solution and Kugelrohr distillation of the residue gave a remarkable 90% yield of the desired product 8 (Scheme 3). The previous best recorded yield was a meagre 30% described by Emerson et al. [9].

SCHEME 3



In conclusion, having demonstrated the ease with which high yields of these complexes can now be obtained, we hope that this will promote increased use of such species as synthetic intermediates.

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#### References

- 1 For examples see: (a) D.H.R. Barton, A.A.L. Gunatilaka, T. Nakanishi, H. Patin, D.A. Widdowson and B.R. Worth, *J. Chem. Soc., Perkin Trans. I*, (1976) 821; (b) M. Franck-Neumann, F. Brion and D. Martina, *Tetrahedron Lett.*, (1978) 5033; (c) A.J. Pearson and D.C. Rees, *ibid.*, (1980) 3937.
- 2 For a general review see: (a) S.G. Davies, *Organotransition Metal Chemistry: Applications to Organic Synthesis*, 1982, Pergamon Press; (b) A.J. Pearson, *Metallo-organic chemistry*, 1985, John Wiley and Sons, Chapter 8.
- 3 J.M. Kern, D. Martina and M.P. Heitz, *Tetrahedron Lett.*, 26 (1985) 737.
- 4 R. Pettit and G.F. Emerson, *Adv. Organomet. Chem.*, 1 (1964) 1.
- 5 A.J. Deeming, in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.) *Comprehensive organometallic chemistry*, Pergamon Press, Vol. 4, 1982, p. 377.
- 6 B.M. Trost and D.M.T. Chan, *J. Am. Chem. Soc.*, 101 (1979) 6429 and 6432; 102 (1980) 6359.
- 7 (a) A.M. Horton, D.M. Hollinshead and S.V. Ley, *Tetrahedron* 40 (1984) 1737; (b) A.M. Horton and S.V. Ley, *J. Organomet. Chem.*, 285 (1985) C17.
- 8 M. Cais, and N. Maoz, *J. Organomet. Chem.*, 5 (1966) 370.
- 9 G.F. Emerson, K. Ehrlich, W.P. Giering and P.C. Lautebar, *J. Am. Chem. Soc.*, 88 (1966) 3172.