

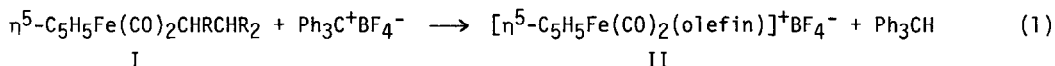
REGIOSPECIFIC FORMATION OF TERMINAL OLEFINS BY A
NOVEL ELIMINATION REACTION

D.E. Laycock and M.C. Baird*

Department of Chemistry, Queen's University,
Kingston, Canada K7L 3N6

The formation of olefins by elimination reactions has long been a central topic in many synthetic and mechanistic discussions^{1,2}. In spite of recent advances in mechanistic interpretations of elimination processes², however, synthetic applications are often of limited value because of the nature or variety of the reaction products. Thus, for instance, base-catalyzed dehydrohalogenation reactions of 1- and 2-haloalkanes can result in the formation of mixtures of both substitution products and isomeric olefins, while dehydration of alcohols can also give mixtures of olefins^{1,2}.

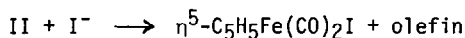
We wish to describe a new, regioselective synthetic route to terminal olefins. The method is based on the long-known^{3,4} but little studied ability of the trityl carbonium ion to abstract a hydride ion from the β -carbon atom of alkyliron compounds of the type $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{-CHRCHR}_2$ (R = H, alkyl, aryl) (I) to form triphenylmethane and the cationic complexes $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2(\text{olefin})]^+$ (II), i.e.



Examples of systems studied to date are listed in Table 1. The alkyliron compounds, Ia-f, are readily prepared in dry THF by displacement of bromide (a,b,c,e), or tosylate (d,f) from the corresponding alkyl bromide or tosylate by the very powerful nucleophile $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]^-$ (as its sodium salt). Compounds of type I are readily purified by removal of the THF in vacuo, extraction of the residue by petroleum ether (30-60°) and elution through a neutral alumina column (80-200 mesh). They are obtained as yellow oils or crystalline solids exhibiting varying degrees of air sensitivity. The yields listed have not yet been optimized, and many certainly can be improved.

Treatment of the compounds, Ia-f, with ~ 1 equivalent of $\text{Ph}_3\text{C}^+\text{BF}_4^-$ in dry methylene chloride at 0°C gives the olefin complexes, IIa-f. The course of the reactions can readily be monitored by following the disappearance of ν_{CO} of I ($\sim 2000, 1950 \text{ cm}^{-1}$) and the appearance of ν_{CO} of II ($\sim 2080, \sim 2040 \text{ cm}^{-1}$) in the infrared spectrum. Addition of cold ethyl ether to the reaction solutions gives the olefin complexes as light yellow, reasonably pure solids; they can be recrystallized from methylene chloride-petroleum ether, but only with considerable reduction in yield.

The olefins are liberated from the complexes, II, quantitatively and *without isomerization* by treatment with sodium iodide in acetone, i.e.



We have previously suggested⁴ that the formation of II involves direct abstraction of hydride from I by the bulky carbonium ion. It thus seemed likely that steric hindrance to attack on a β hydrogen atom by the trityl ion would be a major factor in deciding the course of the reaction. The results listed in Table 1 are generally in agreement with this hypothesis, as with one exception (Ia \rightarrow IIa), the 2-alkyliron compounds yields only the products expected on the basis of abstraction from the methyl rather than the methylene groups. Indeed, the 2-butyl compound, Ia, may well turn out to be unique in this sense, as it is the smallest alkyl group which can lead to more than one olefin.


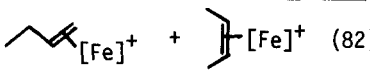


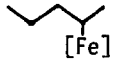

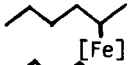


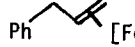
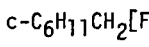
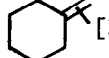
Electronic factors may also on occasion be significant in determining the course of the abstraction reaction as alkyliron compounds containing electronegative substituents (CN, OMe) on the β carbon atom are unreactive⁶; perhaps the β hydrogen atoms in these cases are not sufficiently hydridic in nature to interact with the trityl ion. We are currently investigating the tolerance of other functional groups to the reaction conditions.

Finally we note that Reetz and Stephan⁷ have reported that hydride abstraction from alkyllithium and -magnesium compounds also yields olefins, although their results do not seem to be significantly superior with respect to regioselectivity than more conventional elimination reactions. The method described here has obvious advantages where 1- or 2- substituted alkyl compounds are being employed, and the virtually complete absence of isomerization, substitution or addition⁷ products makes it a viable synthetic approach to the regioselective preparation of terminal olefins.

Acknowledgements

We thank Queen's University and the National Research Council of Canada for support of this research.

Table 1. Yields of Alkyliron(I) of Iron Olefin(II) Cationic Complexes ($[\text{Fe}] = \eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2$)

	I (Yield, %)	II (Yield, %)
a	 (30)	 (82)
b	 (96)	 (50)
c	 (30)	 (74)
d	 (75)	 (60)
e	 (54)	 (79)
f	 (85)	 (50)

References

- 1) M. Schlosser in "Methoden der Organischen Chemie (Houben-Weyl)", Band V/1b, p. 1, Georg Thieme Verlag, Stuttgart, 1972.
- 2) W.H. Saunders and A.F. Cockerill, "Mechanisms of Elimination Reactions", Wiley-Interscience, New York, 1973.
- 3) M.L.H. Green and P.L.I. Nagy, *J. Organometal. Chem.*, **1**, 58 (1963).
- 4) D.A. Slack and M.C. Baird, *J.C.S. Chem. Comm.*, 701 (1974).
- 5) J.J. Eisch and R.B. King, "Organometallic Syntheses", Vol. 1, p. 161, Academic Press, New York, 1965.
- 6) P. Lennon, A.M. Rosan and M. Rosenblum, *J. Amer. Chem. Soc.*, **99**, 8426 (1977).
- 7) M.T. Reetz and W. Stephan, *Angew. Chem. Internat. Ed.*, **16**, 44 (1977).

(Received in USA 16 May 1978; received in UK for publication 4 July 1978)