

Preliminary communication

REACTIONS OF DIIRON ENNEACARBONYL WITH PYRYLIUM IODIDES

RUSSELL P. HUGHES

Department of Chemistry, Dartmouth College, Hanover, NH 03755 (U.S.A.)

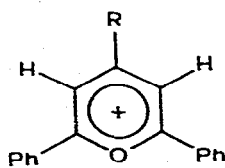
(Received August 12th, 1977)

Summary

Reaction of $\text{Fe}_2(\text{CO})_9$ with 2,4,6-triphenylpyrylium iodide or 2,6-diphenylpyrylium iodide affords tricarbonyliron products derived from apparent reductive coupling of the pyrylium cation. The regioselectivity of coupling differs in each case.

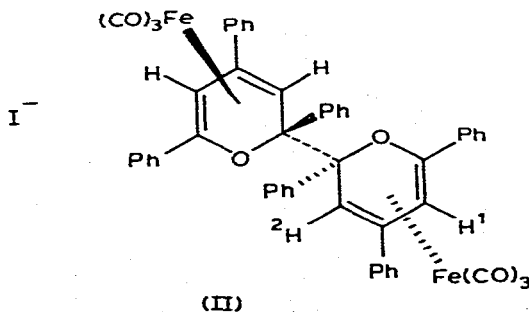
The organometallic chemistry of the heteroaromatic pyrylium cations remains almost totally unexplored. A recent report concerned the reactions of 2,6-disubstituted pyrylium cations with palladium(II) systems [1]. However, only acyclic η^3 -allyl complexes derived from the pseudo-bases of the cations could be isolated from these systems [1]. As part of a general study of the possible oxidative addition reactions of pyrylium iodides with low-valent transition metal compounds, their reactions with diiron enneacarbonyl were examined. We now report on organometallic products of these reactions in which the integrity of the ring is maintained.

Treatment of 2,4,6-triphenylpyrylium iodide (Ia)* with an excess of $\text{Fe}_2(\text{CO})_9$ (benzene; 25°C) afforded, after chromatography, a yellow crystalline complex (76%; $\nu(\text{CO})$ (hexane), 2040s, 1986s, 1974s cm^{-1} ; $^1\text{H NMR}$ (90 MHz; C_6D_6), τ 4.52 (d, $J = 2$ Hz) H^1 , 5.59 (d, $J = 2$ Hz) H^2 , 2.90m ppm phenyl; m/e 898 (P^+)).



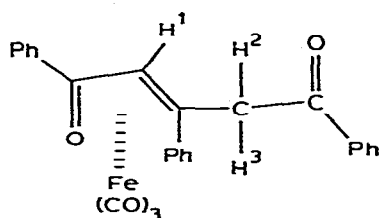
(Ia) R = Ph

(Ib) R = H

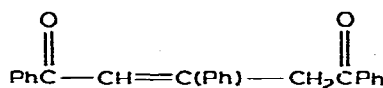


* Prepared from the tetrafluoroborate salt [2] by treatment with concentrated aqueous HI.

These data, together with confirmatory ^{13}C NMR and microanalytical results establish the structure of this complex as the bis(tricarbonyliron) complex II, derived from the net reductive coupling of two pyrylium moieties. Notably the reaction is regiospecific; only 2,2'-coupling is observed. Traces of an orange product were obtained in this reaction (1–2%; $\nu(\text{CO})(\text{hexane})$, 2040s, 1978s, 1964s, 1610m; ^1H NMR (90 MHz; C_6D_6), τ 4.85s H^1 , 5.58 (d, $J = 20$ Hz) H^2 , 6.64 (d, $J = 20$ Hz) H^3 , 2.40m ppm phenyl; m/e 466 (P^+)). These spectroscopic data, together with supporting microanalysis results, indicate the structure of this orange complex to be III, derived from the pseudobase [3] of the 2,4,6-triphenylpyrylium cation. Rigorous exclusion of moisture from the reaction system eliminated III as a reaction product. Complex III was also prepared in 65% yield by treating the pseudo-base IV with an excess of $\text{Fe}_2(\text{CO})_9$ in benzene at 25°C .

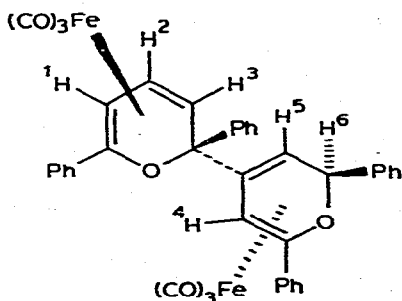


(III)

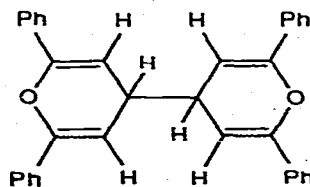


(IV)

In contrast to Ia, reaction of 2,6-diphenylpyrylium iodide Ib* with excess $\text{Fe}_2(\text{CO})_9$ (benzene; 25°C) afforded a single yellow crystalline complex (66%; $\nu(\text{CO})(\text{hexane})$, 2048s, 1990s, 1976s cm^{-1} ; ^1H NMR (90 MHz; C_6D_6), τ 4.66 (m, H^1), 4.90 (m, H^2 and H^6), 5.11 (m, H^4), 6.34 (m, H^3 and H^5), 2.90 ppm (m, phenyl); m/e 746 (P^+)). These data, together with supporting ^{13}C NMR and microanalysis results could only be explained in terms of structure V. The organic skeleton in this complex thus derives from the formal reductive coupling of two pyrylium moieties in a regiospecific, yet unsymmetrical fashion. No evidence for species arising from a 2,2'-coupling reaction was observed in this system.



(V)

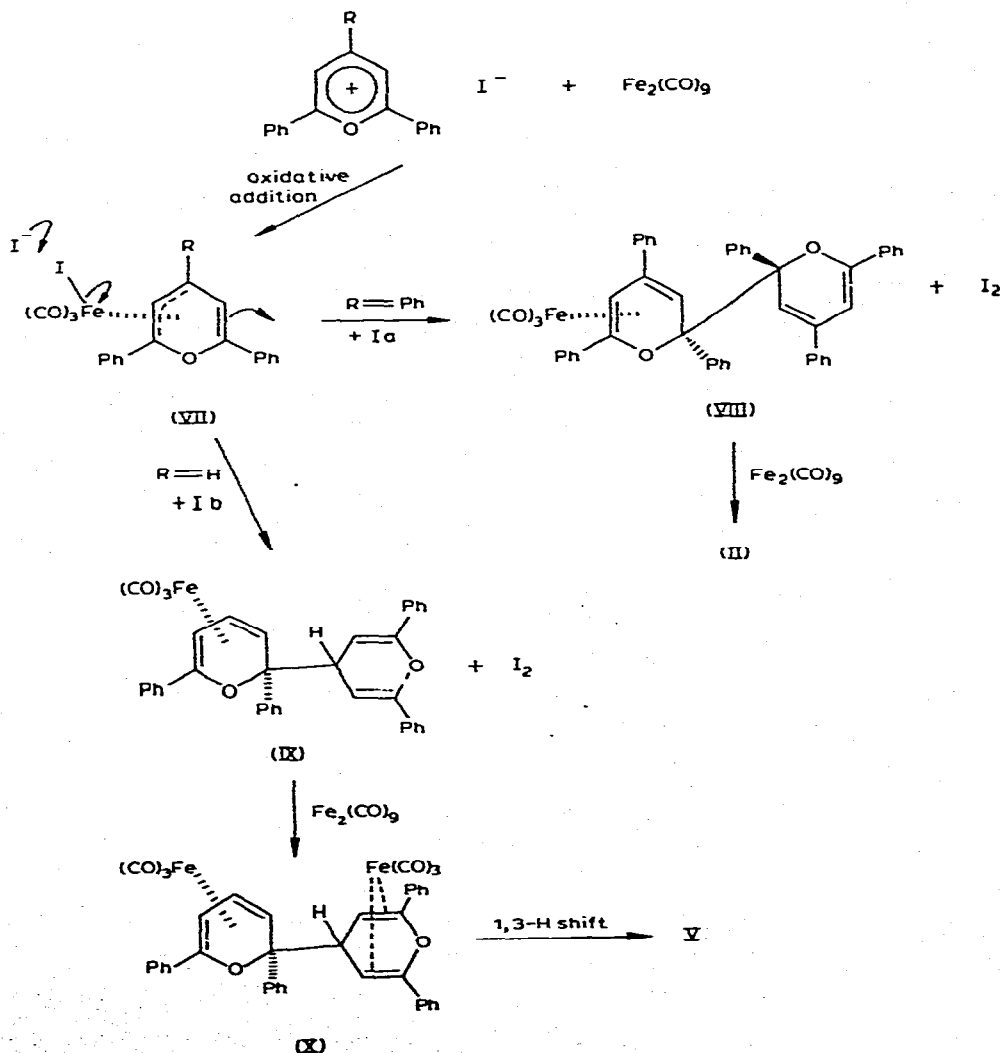


(VI)

*Prepared from the tetrafluoroborate salt by treatment with concentrated aqueous HI. The tetrafluoroborate salt was prepared using the method previously described for the perchlorate salt [4].

The coupling reactions leading to the formation of II and V have no precedence in the reduction chemistry of cations Ia and Ib. One-electron reduction of Ia with Zn is reported to afford a stable radical [5], while the analogous one-electron reduction of Ib affords the bipyran VI, derived from exclusive 4,4'-coupling of the corresponding radical [6]. Clearly the regioselectivity encountered here is determined by the coordinating presence of an iron carbonyl fragment.

A mechanism which rationalizes these results is shown in Scheme 1. Oxidative addition of the pyrylium iodide species with $\text{Fe}_2(\text{CO})_9$ might reasonably generate an η^3 -allyl species VII, by analogy with the oxidative addition reactions of allyl iodides with $\text{Fe}_2(\text{CO})_9$, [7]. The nature of the final products is then determined



SCHEME 1

by the expected regioselectivity of electrophilic attack by free pyrylium cation on the uncoordinated olefinic function of VII. If Ia is the attacking electrophile, attack is expected at the 2-carbon of the free cation [3] to afford VIII, whereas attack by cation Ib is expected to occur at the 4-carbon of the free cation to afford IX. The point of attachment of the attacking electrophile to the coordinated pyrylium system in VII is expected to be at the 2-position in either case affording the stable η^3 -1,3-dieneiron tricarbonyl system. Intermediates VIII and IX can then react with excess $\text{Fe}_2(\text{CO})_9$ to afford the final products. Notably reaction of IX must involve an additional intermediate X which is expected to undergo a facile 1,3-H shift [8] to afford the observed product V.

This system clearly demonstrates the profound effect that coordination of unsaturated substrates to transition metals can have upon the specificity of their reactions. These reactions represent the only route to these skeletal systems, which are synthetically unapproachable from free pyrylium cations.

Further studies of oxidative addition reactions, and the electrophilic behavior of pyrylium cations towards transition metal systems are in progress.

I am grateful to Professor J.F. Harrod (McGill University) in whose laboratory part of this work was carried out, and also to the Research Corporation and the National Research Council of Canada for financial support.

References

- 1 L.Yu. Ukhin, V.I. Il'in, Zh.I. Orlova, N.G. Bokii and Yu.T. Struchkov, *J. Organometal. Chem.*, 113 (1976) 167.
- 2 K. Dimroth, C. Reichardt and K. Vogel, *Org. Synth.*, 49 (1969) 121.
- 3 A.T. Balaban, W. Schroth and G. Fischer, *Advan. Heterocyclic Chem.*, 10 (1969) 241.
- 4 H. Stetter and A. Reischl, *Chem. Ber.*, 93 (1960) 1253.
- 5 V.A. Palchakov, Yu.A. Shdanov and C.N. Dorofeevko, *Zh. Org. Khim.*, 1 (1965) 1171.
- 6 S.N. Baranov, M.A. Dumbai and S.V. Krivun, *Chem. Heterocyclic Comp.*, 10 (1972) 1185.
- 7 A.N. Nesmeyanov and I.I. Kritskaya, *J. Organometal. Chem.*, 14 (1968) 387.
- 8 M. Green and R.P. Hughes, *J. Chem. Soc. Dalton Trans.*, (1976) 1907.