Yanovsky Reaction of η^6-Arene-η^5-cyclopentadienyliron Cations with Carbanions derived from Ketones. Regiospecific Attack *ortho* to Electron Withdrawing Functions

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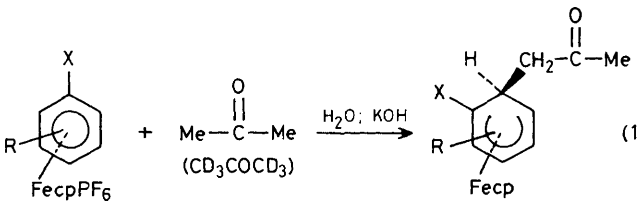
η^6-Arene-η^5-cyclopentadienyliron salts containing electron withdrawing groups such as nitro, halogeno, benzoyl, cyano, and sulphonyl on the arene ring react with carbanions to give electroneutral adducts of the Yanovsky type; these adducts give the corresponding substituted benzene on treatment with buffered cerium(IV) ammonium nitrate.

The reactions of nitroarenes with nucleophiles continue to be the topic of many investigations and have been the subject of several recent reviews.[1] One of the more intriguing of such reactions is the Yanovsky reaction[2] in which carbanions derived from ketones such as acetone react with nitroarenes *ortho* to the nitro function to form a carbon–carbon bond. Although unactivated arenes do not react with nucleophiles under normal conditions, it is known that arene–metal complexes can react with nucleophiles[3] to give, eventually, substituted arenes *via* anionic or neutral cyclohexadienyl intermediates. Recently we have reported[4] the synthesis of η^6-nitroarene-η^5-cyclopentadienyliron cations and have noted[5] that such nitro groups undergo nucleophilic replacement when treated with O, S, or N containing nucleophiles. In this paper we report on the reactions of η^6-arene-η^5-cyclopentadienyliron cations containing electron withdrawing



(1)

cp = cyclopentadienyl

R = H; X = NO_2, Cl, COPh, CN, $SO_2C_6H_4Me$-*p*
R = *o*- or *p*-Me; X = NO_2
R = *o*- or *p*-Cl; X = Cl

groups with carbanions derived from ketones to give stable complexes resulting from a regiospecific attack of the reagent *ortho* to the electron withdrawing group as shown in equation (1). These adducts are also observed with polycyclic complexes, *e.g.* the anthraquinone complex. These reactions occur under very mild conditions. In a typical experiment the cationic complex (3 mmol) was dissolved in the ketone (15 ml) and water (10 ml) containing potassium hydroxide (1.12 g, 20 mmol). After stirring for 15—20 minutes, the mixture was extracted with chloroform, the extract dried ($MgSO_4$), and then passed through a short column (5 cm) of deactivated alumina before evaporation at room temperature. The adducts from the complexes are highly coloured ranging from blue to orange and those from nitroarenes crystallize as dark blue needles. The yields depend on the nature of the carbonyl component and the electron withdrawing substituent but are in the range of 55 to 80%. The metal can be removed using buffered cerium(IV) ammonium nitrate[6] when the corresponding arene is obtained in good yield, *e.g.* the adduct obtained from the *p*-dichlorobenzene complex and acetone gives 1-(2,4-dichlorophenyl)propan-2-one in 50% yield; this particular compound has not previously been prepared although its isomers find use as agricultural chemicals.

The carbanion attacks the benzene ring from the *exo* side and, in every case examined, the carbon *ortho* to the substituent (nitro, chloro, benzoyl, cyano, sulphonyl) is the exclusive site of attack. The *endo* hydrogen is observed in the range δ 3.35—3.38 in the ^1H n.m.r. spectrum and the sp^3 hybridized carbon at δ 30—45 in the ^{13}C n.m.r. spectrum. Cyclopentadienyl protons are found at δ 4.2—4.4 with carbons in the range δ 76—79. In accord with related work[7] signals of proton and carbon adjacent to the sp^3 carbon are shifted upfield by *ca.* 2 p.p.m. (proton) and 40 p.p.m. (carbon) and appear at δ 3.30—3.37 and 36—40 respectively. The i.r. spectra exhibits a ν_{CO} band at 1720 cm^{-1} while the mass spectra shows the presence of the molecular ion with a consistent fragmentation pattern.

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References

1 F. Terrier, *Chem. Rev.*, 1982, **82**, 77; M. Makosza, in 'Current Trends in Organic Synthesis,' ed. H. Nozaki, Pergamon Press, Oxford, 1983, p. 401; E. Buncel, M. R. Crampton, M. V. Strauss, and F. Terrier, 'Electron Deficient Aromatic and Heteroaromatic–Base Interactions,' Elsevier, Lausanne, 1984.
2 For a review devoted entirely to this reaction, see S. S. Gitis and A. Ya. Kaminskii, *Russ. Chem. Rev.*, 1978, **47**, 1061.
3 M. F. Semmelhack, H. T. Hall, Jr., R. Farina, M. Yoshifuji, G. Clark, T. Bargar, K. Hirotsu, and J. Clardy, *J. Am. Chem. Soc.*, 1979, **101**, 3535; A. C. Knipe, S. J. McGuiness, and W. E. Watts, *J. Chem. Soc., Perkin Trans. 2*, 1981, 193.
4 C. C. Lee, U. S. Gill, M. Iqbal, C. I. Azogu, and R. G. Sutherland, *J. Organometal. Chem.*, 1982, **231**, 151.
5 R. L. Chowdhury, C. C. Lee, A. Piórko, and R. G. Sutherland, *Synth. React. Inorg. Met.-Org. Chem.*, accepted for publication.
6 A. J. Pearson, P. R. Bruhn, and I. C. Richards, *Isr. J. Chem.*, 1984, **24**, 93.
7 For examples, see D. Astruc, R. Hamon, E. Roman, and P. Michaud, *J. Am. Chem. Soc.*, 1983, **105**, 5951; N. A. Vol'kenau and V. A. Petrakova, *J. Organomet. Chem.*, 1982, **223**, C7.