Azo-coupling and Arylation Reactions of Co-ordinated Polyolefins with Arenediazonium Ions

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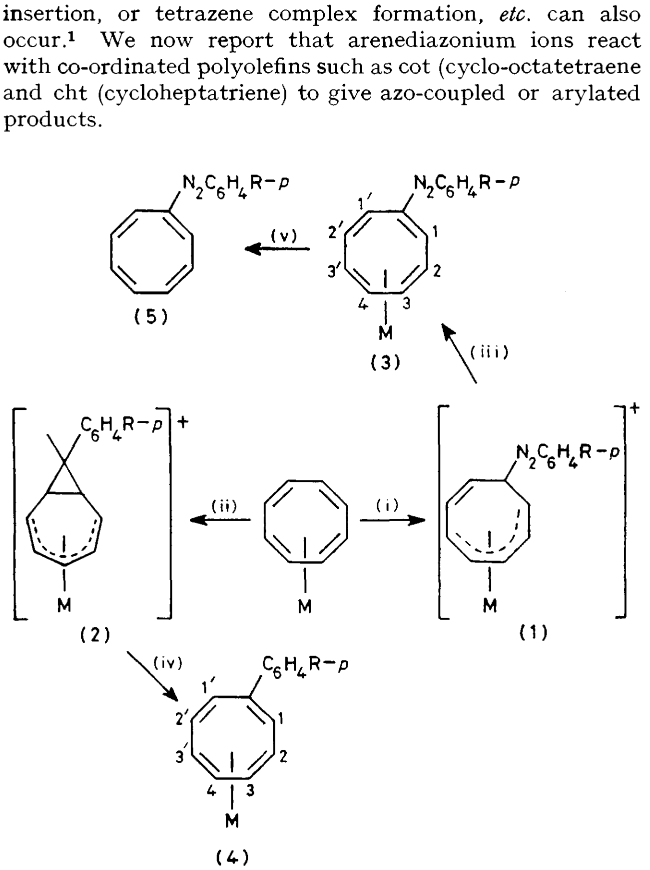
Summary Reaction of arenediazonium ions with [Fe(CO)L_2(η^4-polyene)] [L = CO or P(OMe)$_3$, polyene = cyclo-octatetraene or cycloheptatriene], and subsequent deprotonation gives either azo-coupled or arylated compounds such as [Fe(CO){P(OMe)$_3$}$_2$(η^4-$C_8H_7N_2C_6H_4F$-*p*)] and [Fe(CO)$_3$(η^4-$C_8H_7C_6H_4NO_2$-*p*)] respectively.

THE reaction between an arenediazonium ion and a transition metal compound usually results in co-ordination at the metal centre although one-electron oxidation, insertion, or tetrazene complex formation, *etc.* can also occur.[1] We now report that arenediazonium ions react with co-ordinated polyolefins such as cot (cyclo-octatetraene and cht (cycloheptatriene) to give azo-coupled or arylated products.



SCHEME. i, $[N_2C_6H_4R\text{-}p]\,[BF_4]$ (R = F or NO$_2$) in CH_2Cl_2, $n = 1$ or 2; ii, $[N_2C_6H_4NO_2\text{-}p]\,[BF_4]$ in acetone, $n = 0$; iii, Al_2O_3 or $NaHCO_3$; iv, pyridine; v, $Me_3NO,2H_2O$. M = $Fe(CO)_{3-n}\{P(OMe)_3\}_n$.

The complex $[Fe(CO)_{3-n}\{P(OMe)_3\}_n(\eta^4\text{-cot})]$ reacts rapidly with $[N_2C_6H_4R\text{-}p][BF_4]$ in CH_2Cl_2 ($n = 1$, R = NO$_2$, 0 °C, 90 min, 45%; $n = 2$, R = F, −78 °C, 40 min, 40%) to give the yellow salt $[Fe(CO)_{3-n}\{P(OMe)_3\}_n(\eta^5\text{-}C_8H_8N_2C_6H_4R\text{-}p)][BF_4]$ (**1**) *via* C–N bond formation; ^{1}H and ^{13}C n.m.r. spectroscopy† verified that the iron is bonded to a monosubstituted cyclo-octatrienyl ring (Scheme). By contrast, the tricarbonyl $[Fe(CO)_3(\eta^4\text{-cot})]$ is efficiently arylated by $[N_2C_6H_4NO_2\text{-}p][BF_4]$ (acetone, −20 °C, 15 min, 49%) to give the yellow, bicyclo[5.1.0]octadienyl complex $[Fe(CO)_3(\eta^5\text{-}C_8H_8C_6H_4NO_2\text{-}p)][BF_4]$ (**2**, Scheme).

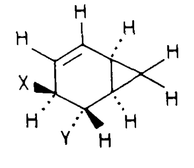
Complex (**1**) is readily deprotonated on Brockman Activity II alumina ($n = 2$, R = F, 13%) or, more effectively, with NaHCO$_3$ in 40% aqueous acetone ($n = 1$, R = NO$_2$, 82%) to give purple-black crystals of the fluxional, substituted-cot compound $[Fe(CO)_{3-n}\{P(OMe)_3\}_n(\eta^4\text{-}C_8H_7N_2C_6H_4R\text{-}p)]$ (**3**). The symmetry of the room-temperature ^{1}H n.m.r. spectrum of (**3**) results from oscillation of the η^4-bonded metal group between $C^2C^3C^4C^{3'}$ and $C^{2'}C^{3'}C^4C^3$ (Scheme).

In the absence of acetone (**1**, $n = 1$, R = NO$_2$) reacts with aqueous NaHCO$_3$ to give low yields of a yellow crystalline product [ν(CO) (hexane) 1 993, 1 937 cm^{-1}; *cf.* (**3**, $n = 1$, R = NO$_2$), ν(CO) (hexane) = 2 001, 1 949 cm^{-1}] which is not fully characterised but which mass spectroscopy suggests to be the disubstituted cyclo-octatriene complex $[Fe(CO)_2\{P(OMe)_3\}\{\eta^4\text{-}C_8H_8(OH)(N_2C_6H_4NO_2\text{-}p)\}]$.

Deprotonation of (**2**) by pyridine in acetone (30 °C, 30 min, 50%) results in opening of the three-membered ring, and formation of red crystalline $[Fe(CO)_3(\eta^4\text{-}C_8H_7C_6H_4NO_2\text{-}p)]$ (**4**) with fluxional properties similar to those of (**3**). In certain cases (**3**) or (**4**) can be isolated directly from the reaction between $[N_2C_6H_4R\text{-}p]^+$ and $[Fe(CO)_{3-n}\{P(OMe)_3\}_n(\eta^4\text{-cot})]$. Thus $[Fe(CO)_3(\eta^4\text{-cot})]$ and $[N_2Ph][BF_4]$ (acetone, 25 °C, 24 h) give low yields of $[Fe(CO)_3(\eta^4\text{-}C_8H_7N_2Ph)]$. The formation of the azo-coupled product in this reaction reveals that C–N bond formation rather than arylation is not only enhanced by replacement of the CO ligands of $[Fe(CO)_3(\eta^4\text{-cot})]$ by P(OMe)$_3$ but also by using arenediazonium ions with less electron-withdrawing substituents.

Displacement of the arylazo-cot ligand from (**3**, $n = 2$, R = F) is effected by $Me_3NO,2H_2O$ in refluxing benzene. The air-stable, yellow-orange crystalline solid (5) (m.p. 86—88 °C, *m/e* 226) has a variable-temperature (−60 to +55 °C) ^{1}H n.m.r. spectrum consistent[2] with the fluxional, mono-substituted cot ring undergoing both inversion and bond shifts.

Free cot and $[N_2C_6H_4R\text{-}p][BF_4]$ (R = F or NO$_2$) in either water or acetone give neither azo-coupled nor arylated cot derivatives. However, whereas $[Fe(CO)_3(\eta^4\text{-cht})]$ undergoes reactions similar to those shown in the Scheme, and $C_7H_7N_2C_6H_4NO_2\text{-}p$, related to (**5**), can be cleaved from $[Fe(CO)_3(\eta^4\text{-}C_7H_7N_2C_6H_4NO_2\text{-}p)]$, free cht and $[N_2C_6H_4NO_2\text{-}p][BF_4]$ in H$_2$O give high yields of (**6**) (orange solid, m.p. 170—172 °C, *m/e* 259).



(**6**) X, Y = OH, $N_2C_6H_4NO_2\text{-}p$

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† For the sake of brevity, ^{1}H and ^{13}C n.m.r. spectral data and the results of ^{1}H–^{1}H and ^{31}P-decoupling experiments, which verify the structures shown in the Scheme, are not given.

[1] D. Sutton, *Chem. Soc. Rev.*, 1975, **4**, 443.

[2] G. I. Fray and R. G. Saxton, 'The Chemistry of Cyclo-octatetraene and its Derivatives,' Cambridge University Press, 1978, pp. 93—94.