Phenyl Participation as a Mechanistic Probe in the Electrophilic Cleavage of the Iron–Carbon Bond

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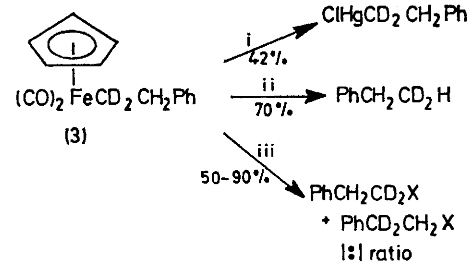
Summary Electrophilic cleavage of the Fe–C bond of (**3**) by halogens involves the formation of phenonium ion (**4**), while cleavage by HgX_2 and HX does not, nor does halogen cleavage of the Co–C bond in (**5**).

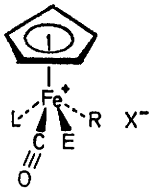
STUDIES of the stereochemistry of metal–carbon σ-bond cleavage by electrophiles have shown both retention[1–4] and inversion[4–7] of configuration at carbon. Stereochemical investigations of such cleavage reactions at chiral pseudo-tetrahedral iron centres[8] implicate attack by the electrophile directly at iron to form an intermediate (**1**) ($E = H^+$, HgX^+, or X^+; $L = CO$ or PPh_3) whose subsequent fate depends on the nature of the electrophile, E.

We report experiments which establish the role of iron as a leaving group in the halogen cleavage reaction, thereby further substantiating attack at the metal with resultant M–C bond activation, rather than an S_E2 (open) type of mechanism. In the reactive intermediate (**1**), the neutral fragment $[(\eta^5\text{-}C_5H_5)Fe(CO)LE]$, (**2**) could function as a stable leaving group. Then, S_N2 displacement on carbon by X^- would result in inversion of configuration at carbon, consistent with observations of Whitesides *et al.*[4] in the cleavage of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2CHDCHDC(CH_3)_3]$. Recently, the cleavage of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2CHDCHDPh]$ by Br_2 was reported to proceed with retention of configuration at carbon.[1] We believe these two seemingly contradictory stereochemical results are understandable in the light of the above mechanism and the following facts.

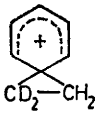


SCHEME. Reagents: i, $HgCl_2$ in tetrahydrofuran 15 h, 45°; ii, HBr in CS_2, 25°; iii, Br_2 in CS_2 at 0° or in CH_2Cl_2 at $-78°$ or I_2 in CS_2 at 0°.

When compound (**3**) (>98% [$^2H_2$]†) was cleaved by Br_2 or I_2 under a variety of conditions, β-phenethyl bromide or iodide was obtained as a *ca.* 1 : 1 mixture of [αα-$^2H_2$]- and [ββ-$^2H_2$]-isomers, which could be distinguished and estimated by their n.m.r. spectra. Cleavage of [(η⁵-C_5H_5)Fe$(CO)_2CH_2CH_3$] by excess of Br_2 in the presence of $PhCH_2CD_2Br$ led to no rearrangement of the phenethyl bromide, establishing that the rearrangement upon cleavage of (**3**) was on the reaction co-ordinate. The equivalence of the two methylene groups is most consistent with the interpretation that (**2**) (L = CO, E = Br^+ or I^+) is a good enough leaving group for the phenyl group to compete with X^- in attack from the rear at carbon, resulting in the formation of the phenonium ion (**4**). This cation may undergo attack by X^- at either methylene group, thus leading to the observed distribution of deuterium in the β-phenethyl halides. Also, the double inversion at carbon resulting from this mechanism explains the overall retention reported for the reaction of [(η⁵-C_5H_5)Fe$(CO)_2$CHDCHDPh].[1] Initial attack by electrophiles at iron appears to be reversible.[8] The leaving of (**2**) to form the phenonium ion (**4**), however, apparently is not, since cleavage of (**3**) by a deficiency of Br_2 does not lead to any rearrangement of recovered (**3**).



(1)



(4)

For reasons that are not clear, when the electrophile in (**1**) is H^+ or HgX^+, elimination of R–E from iron appears to be faster than attack from the rear at carbon either by Ph or by X^-. Thus, cleavage of the Fe–C bond by HBr or $HgCl_2$ leads to isomerically pure CHD_2CH_2Ph or $ClHgCD_2Ph$ respectively.‡

We have also examined [Co(py)$(Hdgy)_2CD_2CH_2Ph$] (Hdgy = dimethylglyoximato; py = pyridyl) (**5**).§ Cleavage of (**5**) by I_2 in CH_2Cl_2 at 25° overnight produced $PhCH_2CD_2I$ (73% yield) which was isomerically pure. Since evidence suggests[6] that halogen cleavage of the Co–C bond proceeds by one-electron oxidation of the complex followed by S_N2 attack at carbon, it is possible that activation of the phenyl group by suitable substituents may be necessary in order to observe phenyl participation in cases where oxidation of the metal does not sufficiently activate the M–C bond.

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† Compound (**3**) was prepared from [(η⁵-C_5H_5)Fe$(CO)_2$Na] and $PhCH_2CD_2OTs$ in 78% yield. The tosylate was prepared by a known procedure (>98% [$^2H_2$] by mass spectrometry of the alcohol) (W. H. Saunders, S. Asperger, and D. H. Edison, *J. Amer. Chem. Soc.*, 1958, **80**, 2421).

‡ While these results are also consistent with an S_E2 (cyclic) mechanism, studies of stereochemistry at chiral iron argue against this alternative.[8]

§ Compound (**5**) was prepared from $PhCH_2CD_2OTs$ by a standard procedure. (G. N. Schrauzer and R. L. Windgassen, *J. Amer. Chem. Soc.*, 1966, **88**, 3738.)

[1] D. Slack and M. C. Baird, *J.C.S. Chem. Comm.*, 1974, 701.
[2] R. W. Johnson and R. G. Pearson, *Chem. Comm.*, 1970, 986.
[3] P. K. Wong and J. K. Stille, *J. Organometallic Chem.*, 1974, **70**, 121.
[4] P. L. Bock, D. J. Boschetto, J. R. Rasmussen, J. P. Demers, and G. M. Whitesides, *J. Amer. Chem. Sec.*, 1974, **96**, 2814.
[5] F. R. Jensen, V. Madan, and D. H. Buchanan, *J. Amer. Chem. Soc.*, 1971, **93**, 5283.
[6] S. M. Anderson, D. H. Ballard, J. Z. Chrastowski, D. Dodd, and M. D. Johnson, *J.C.S. Chem. Comm.*, 1972, 685.
[7] H. L. Fritz, J. H. Espenson, D. A. Williams, and G. A. Molander, *J. Amer. Chem. Soc.*, 1974, **96**, 2378.
[8] T. C. Flood, D. L. Miles, and F. J. DiSanti, manuscript in preparation; T. A. Attig and A. Wojcicki, *J. Amer. Chem. Soc.*, 1974, **96**, 252.