Metal Carbonyl-induced Reactions of Azirines.[1] A Significant Effect of the Metal Carbonyl on the Reaction Pathway

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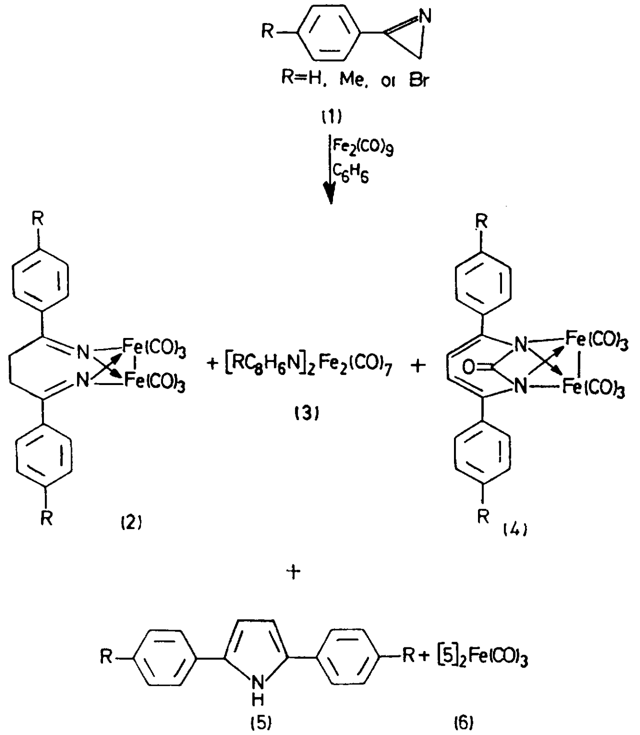
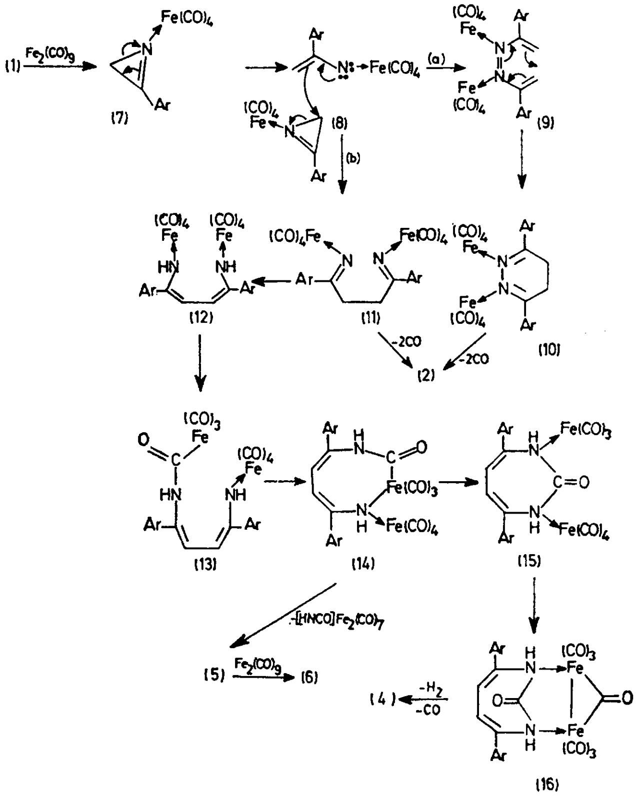
Summary 2-Aryl azirines react with di-iron enneacarbonyl to give 2,5-diarylpyrroles, and several binuclear iron carbonyl complexes, but no pyrazines or dihydropyrazines, as obtained with group VI metal carbonyls.

It has recently been shown that the reaction of group VI metal carbonyls [$M(CO)_6$, M=Cr, Mo, W] with 2-aryl azirines at room temperature results in dimerization to 2,5-diarylpyrazines, and isomeric diaryl-3,6-dihydropyrazines.[1] These products probably arise *via* carbon–carbon bond cleavage of the azirine ring. We now report that a remarkable change in reaction pathway occurs when di-iron enneacarbonyl, $Fe_2(CO)_9$, is used instead of group VI metal carbonyls.



Scheme 1

Treatment of 2-phenyl azirine (**1**, R = H), 2-*p*-tolyl azirine (**1**, R = Me), or 2-*p*-bromophenyl azirine (**1**, R = Br)[2] with $Fe_2(CO)_9$ [1·5: 1·0 mole ratio of $Fe_2(CO)_9$: (**1**)] in anhydrous benzene at 50 °C (oil bath temperature) for 3—4 h, gave the following products in order of elution from a chromatographic column; the di-iron hexacarbonyl complex (**2**); a trace amount of an unidentified complex (**3**), the urea complex (**4**), 2,5-diarylpyrrole (**5**); and bis(2,5-diaryl) pyrrole iron tricarbonyl (**6**).†



Scheme 2

Terminal metal carbonyl stretching bands for (**2**; R = H, Me, Br) are in good accord with literature data for the related phthalazine complex.[3]

Both the urea and metal carbonyl absorptions for (**4**) are in agreement with data for urea complexes derived from nitro compounds.[4] The pyrroles (**5**; R = H, Me), are known compounds [(**5**, R = Br) was identified by analytical as well as by mass and n.m.r. spectral data]. No pyrazines or dihydropyrazines, free or complexed, were isolated in any of the reactions described above. The $Fe_2(CO)_9$-azirine reactions are therefore occurring *via* a different reaction sequence from that observed using group VI metal carbonyls as reagents. We suggest that $Fe_2(CO)_9$ induces

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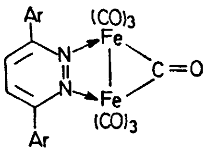
† Satisfactory analytical data were obtained for new compounds. The following yields of pure products (crude yields were much higher) were obtained (R, %): (**2**) (H, 7·8; Me, 4·5; Br, 2·4), (**3**) (H, Me, Br, < 1%), (**4**) (H, 3·0; Me, 2·0; Br, 4·5), (**5**) (H, 12·8; Me, 19·7; Br, 16·5), (**6**) (H, 1·0; Me, 1·0). Spectral data for (**2**)—(**6**), R = Me: (**2**), $\nu_{C\equiv O}$ 2070, 2030, 1994, 1950 sh cm^{-1}, ^1H n.m.r. ($CDCl_3$) δ 2·35 (6H), 2·65(4H), 6·75—7·30(8H), (*m/e*) 542, 514, 486, 458, 458, 430, 402, 374; (**3**), $\nu_{C\equiv O}$ 2080, 2040, 1990, $\nu_{C=O}$ 1733 cm^{-1}, ^1H n.m.r. ($CDCl_3$) δ 2·40(6H), 5·20(4H), 7·10—8·00(8H); (**4**), $\nu_{C\equiv O}$ 2080, 2045, 2000, 1990, $\nu_{C=O}$ 1728 cm^{-1}, ^1H n.m.r. ($CDCl_3$) δ 2·41(6H), 6·85—7·60(10H), (*m/e*) 568, 540, 512, 484, 456, 428, 400, 372; (**5**), ^1H n.m.r. δ 2·33(6H), 6·55(2H), 7·20—7·50(8H), 8·70(1H), (*m/e*) 247; (**6**), $\nu_{C\equiv O}$ 2030, 1982 cm^{-1}; ^1H n.m.r. ($CDCl_3$) δ 2·37(6H), 6·5(4H), 7·10—8·10(16H), 8·40(1H), (*m/e*) 634, 606, 578, 550. Analogous spectral data were obtained for (**2**)—(**6**), R=H, Br.

carbon–nitrogen rather than carbon–carbon bond cleavage of the azirine ring. Such a cleavage (C–N) would account for the formation of complexes of structural type (**2**) and (**4**). A possible reaction sequence is outlined in Scheme 2.

Initial *n*-donor complexation of (**1**) would give (**7**). Carbon–nitrogen bond cleavage of (**7**) would afford the nitrene-type complex (**8**) which can be converted into (**2**) by either dimerization to the azo complex (**9**), Cope rearrangement (**10**), followed by loss of two carbonyl groups [path (a)]; or by addition of (**8**) to the reactant azirine to give the di-iron octacarbonyl complex (**11**), which can then collapse to (**2**) [path (b)]. Alternatively, (**11**) can tautomerize to (**12**), which on ligand migration (**13**) and subsequent cyclization, would provide (**14**). Pyrrole (**5**) can then result from collapse of (**14**). The latter could also serve as a precursor to the urea complex (**15**), which on successive elimination of carbon monoxide and hydrogen would give (**4**).



(A)

It is conceivable that preferential *n*- or π-donor complexation, in the initial step of the proposed mechanism, is responsible for the different sites of cleavage of the azirine ring by Group VI carbonyls as compared to $Fe_2(CO)_9$. We are, at present, attempting to obtain definitive mechanistic results regarding this point.

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[1] For previous paper in this series, see H. Alper and S. Wollowitz, *J. Amer. Chem. Soc.*, 1975, **97**, 3541.

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[4] H. Alper, *Inorg. Chem.*, 1972, **11**, 976. The bridging carbonyl stretching absorption for the isomeric complex, (A), would occur at significantly higher frequency.[3,5]

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