

Ferrocenyl Radical and Nitrene: Formation of Nitroferrocene with Oxygen

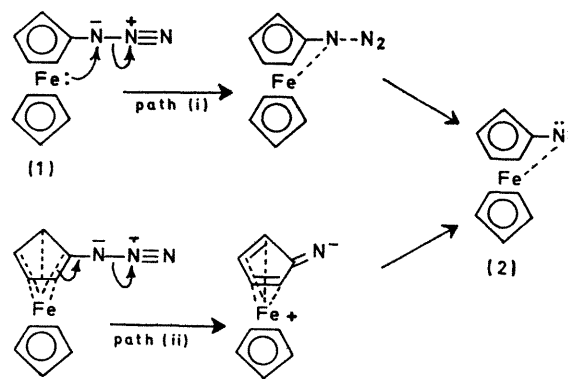
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Summary Photolysis and thermolysis of ferrocenyl azide produce the ferrocenyl radical and the nitrene which in the presence of oxygen give nitroferrocene in reasonable yields, while with cyclohexane an aziridine is formed.

THE thermal and photochemical decomposition of aromatic azides has been of interest in recent years¹ and it is generally believed that these reactions involve a discrete nitrene intermediate which can react either as the singlet or the triplet. It is also known that transition-metal carbonyls are capable of promoting the decomposition of aryl azides under mild conditions to form aryl nitrene complexes.² Theoretical studies³ have predicted that singlet nitrenes might be stabilised by atoms having low-lying *d*-orbitals. We report the results of a study of the thermolysis and photolysis of ferrocenyl azide (**1**) in cyclohexane, C₆H₆, and cyclohexene.

While aryl azides normally decompose between 140–170°, (**1**) eliminates N₂ smoothly at 70–80°, which



SCHEME 1

suggests participation by the metal in formation of the nitrene either *via* the non-bonding pair of electrons on the

iron atom [path (i), Scheme 1] or by a σ - π carbon-metal hyperconjugation mechanism [path (ii)] of the type suggested⁴ for metal participation in metallocenyl carbonium

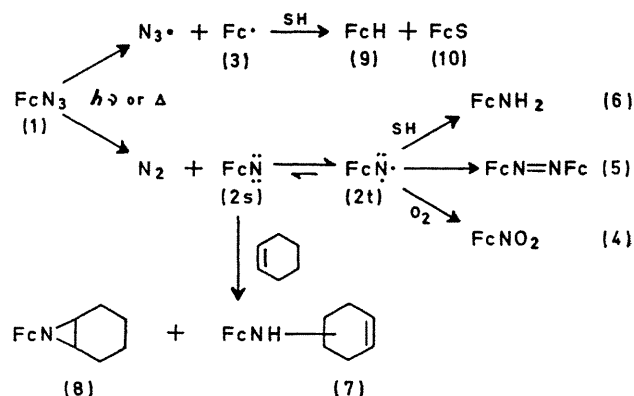
aziridine. Triazoline formation prior to nitrogen elimination or concerted addition and elimination from the azide is possible for the thermal reaction, but highly unlikely in

Thermolysis and photolysis of ferrocenyl azide (% yields)

Under N ₂				FcN=NFC	FcNH ₂ (6)	FcNO ₂ (4)	FcNHS	(8)	FcH (9)	FcS (10)
Solvent		$\Delta/h\nu$		(5)						
C ₆ H ₁₂	Δ	20.5					7.3	
			$h\nu$	42.2					9.0	
C ₆ H ₆	Δ	17.8	16.9				13.6	1.9
			$h\nu$	16.4	16.1				34.9	2.8
C ₆ H ₁₀	Δ	4.0	35.2		2.4	4.8	1.4	
			$h\nu$	6.2	8.2		2.9	4.4	4.4	
Under O ₂										
C ₆ H ₁₂	Δ	5.4		9.4			trace	
			$h\nu$	6.2		21.2			3.3	
C ₆ H ₆	Δ	3.5		4.1			3.8	
			$h\nu$	4.5		21.2			4.8	
C ₆ H ₁₀	Δ	2.7		1.3	1.3	1.9	trace	
			$h\nu$	4.8		8.2	2.2	3.4	trace	

ions. Thermolysis in C₆H₆ under N₂ gave the expected triplet nitrene products [azoferrocene (5) and aminoferrocene (6)]. In addition, products of C-N₃ cleavage were isolated [ferrocene (9) and phenylferrocene], suggesting the intervention of the ferrocenyl radical (3) (see Scheme 2) as well as ferrocenyl nitrene (or nitrenoid) (2), as an intermediate in these reactions. There are a few reports in the literature of C-N₃ bond cleavages on photolysis⁵ or thermolysis⁶ of azides. In two of these cases, C-N₃ homolysis competes with N-N₂ rupture to give delocalised radicals. This suggests that (3) may be stabilised by delocalisation of the odd electron, possibly on to the iron atom. The radical nature of the C-N₃ bond cleavage is confirmed by the reactions carried out under O₂, when the yield of (9) is drastically reduced and no phenylferrocene was detected in C₆H₆.

The effect of O₂ upon the nitrene pathway was dramatic. Formation of the hydrogen-abstraction product was completely suppressed and the yield of azo-compound dropped markedly, as expected for a triplet nitrene. Nitroferrocene (4), identical with an authentic sample,⁷ was formed in all cases, the yields obtained on photolysis in C₆H₆ or cyclohexane suggesting that this is the best method available to date for the preparation of (4). If this is indeed a trapping of the triplet nitrene by molecular O₂, it is the first example of such an interception.† Ferrocenyl nitrene does not insert into the C-H bond of cyclohexane. Very low yields of the C-H insertion products (7) of cyclohexene were isolated,§ as was the aziridine (8) formed by addition across the double bond. This is the first reported example of the addition of an aryl nitrene to an olefin to give an



SCHEME 2

the photochemical process since no reaction took place between the azide and cyclohexene at room temperature in the absence of light. The yields of (7) and (8) are not appreciably affected by the presence of O₂ and it may be concluded that these products are derived mainly from singlet nitrene. The similarity in the thermal and photochemical results (Table) suggests that ferrocenyl nitrene is probably involved in both modes of decomposition.

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† The possibility of indirect formation of nitroferrocene by photolysis of ferrocenylamine or azoferrocene under oxygen was disposed of in separate experiments.

§ Identified after hydrogenation to *N*-cyclohexylferrocenylamine.

¹ For reviews of the literature see R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, 1964, **64**, 149; P. A. S. Smith, "Nitrenes," ed. W. Lwowski, Interscience, New York, 1970, p. 99.

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