Nitrene Capture by Iron Carbonyls

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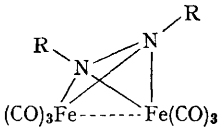
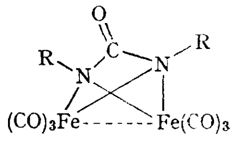
THE thermal decompositions of many azido-compounds in inert media, even at temperatures up to 195°, are very slow processes,[1] and these are reflected in the rather high ΔE values (*e.g.*, cyclohexylazide $\Delta E_{\text{arr}} = 47{\cdot}5$ kcal./mole). Azidobenzene produces less than 2% azobenzene and only a little more aniline after being heated under reflux in benzene for 24 hr. Nitrenes are assumed to be the immediate decomposition products of azido-compounds. We have found that iron carbonyls catalyse this type of decomposition under exceptionally mild conditions. Products are obtained which indicate for the first time that nitrenes may be trapped as ligands in metal carbonyl complexes.

Azidobenzene and nonacarbonyldi-iron react rapidly at room temperature in benzene solution, but the yield of azobenzene is negligible. The principal product is an orange complex $(PhN)_2Fe_2(CO)_6$, m.p. 116—117°, assigned structure (I; R=Ph) on the basis of mass, ^1H n.m.r., i.r., and Mössbauer spectroscopy, the last indicating the equivalent electronic environment of both iron atoms.† This complex, which is based upon an azobenzene skeleton, is not an intermediate in the formation of the *o*-semidine complex from azobenzene and $Fe_2(CO)_9$.[2] Instead, spontaneous decomposition of (I; R=Ph) in solution leads to the urea-based complex (II; R=Ph).[3] Another product from the catalysed decomposition of azidobenzene is an orange complex $(PhNH)_2Fe_2(CO)_6$, m.p. 103°, assigned structure (III; R=Ph), and obtained in low yield in only one of the expected isomeric forms. This material is likely to have the "semi-*trans*" configuration shown, if the thermodynamic stabilities of this type of compound parallels those of the related $[RS\,Fe(CO)_3]_2$ complexes.[4] The μ-phenylamido-complex (III; R=Ph) is not an artefact from the decomposition of (I; R=Ph) and must therefore come directly from the decomposition of azidobenzene. Decomposition of azidobenzene in benzene under reflux is rapid when $Fe_3(CO)_{12}$ is added, but the products now contain a significant quantity of azobenzene (and azoxybenzene if the decomposition is allowed in air).

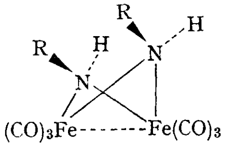
Methyl azide gives an extensive range of products with $Fe_2(CO)_9$. A purple complex, $(CH_3N)_2Fe_3(CO)_9$, is assigned structure (IV) by analogy to the known $S_2Fe_3(CO)_9$,[5] and among the minor products are isomeric forms of the μ-methylamido-complex (III; R=Me). The principal product of this reaction is (II; R=Me) [better obtained from methyl isocyanate and $Fe_2(CO)_9$]. It is assumed that this product is an artefact, possibly derived from (I; R=Me), although the latter could not be detected. A stable very volatile orange–red solid, m.p. 47°, obtained in about 20% yield had the unexpected composition $Me_2N_4Fe(CO)_3$. The i.r. spectrum of this complex resembles that of tricarbonyliron–butadiene in the metal carbonyl region, but shows no N–H, –N=N–, or >C=N– absorptions.



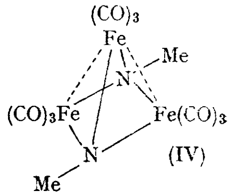
(I)



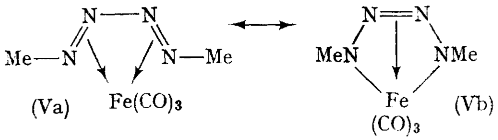
(II)



(III)



(IV)

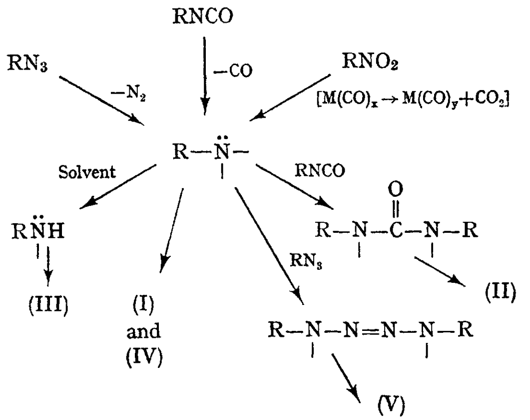


(Va) (Vb)

Mass spectrometry also indicates the absence of NH groups but ions corresponding to $[P - n\text{CO}]^+$ ($n = 0 \rightarrow 3$), $[MeN_3]^+$, and $[MeN]^+$ are prominent. The complex is characterised by a single sharp ^1H n.m.r. signal at τ 5·6. This evidence is consistent with structures (V). No examples of a free tetrazadiene, R–N=N–N=N–R, are known, and their stability is questionable. This compound thus represents a remarkable example of stabilisation by complex formation.

The trinuclear species (IV) is obtained in good yield from the violent reaction occurring between nitromethane and $Fe_2(CO)_9$; (II; R=Me) and (III, R=Me) are minor products from this reaction

† We are indebted to Mr. R. Greatrex and Professor N. N. Greenwood for this determination.



which is notable for the reduction of a nitro-compound by a metal carbonyl.

Each of the above reactions involving azido-, isocyanate, and nitro-compounds is indicative of the catalytic generation of nitrenes. The schemes opposite can account for the formation of the products.

The nature of the products strongly suggests triplet nitrenes, and are thus comparable with the various complexes derived from triplet carbenes recently described.[6]

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