Decomposition of Aromatic Azides by Di-iron Nonacarbonyl

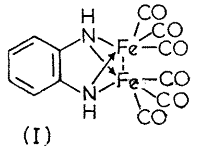
By C. D. CAMPBELL and C. W. REES*

(*Department of Chemistry, The University, Leicester,* LE1 7RH)

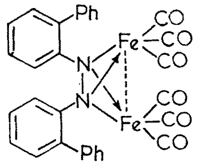
Summary Aromatic azides and diazides are decomposed by di-iron nonacarbonyl to give primary amines, ureas, bis(tricarbonyliron) complexes, and other products, probably *via* nitrenes and nitrene–iron complexes, under very mild conditions; the reactions are more complex than uncatalysed pyrolysis of the azides, however.

DEKKER and KNOX have shown that di-iron nonacarbonyl decomposed methyl and phenyl azide under mild conditions to give interesting tricarbonyliron complexes, possibly derived from nitrene intermediates.[1] We have investigated the reactions of *ortho*-substituted phenyl azides and *peri*-substituted α-naphthyl azides to see if nitrenes really are intermediates and if this catalytic decomposition is a useful synthetic alternative to pyrolysis. All the decompositions were in benzene at 20° under nitrogen in the dark, with slightly more than 1 mole of iron carbonyl per azide group.

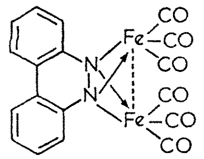
o-Diazidobenzene gave *cis,cis*-mucononitrile (27%), the product of pyrolysis (190°) of this azide[2] and of oxidation of *o*-phenylenediamine and 2-aminobenzotriazole.[3] No iron carbonyl complexes were isolated; presumably the intermediate dinitrene undergoes preferential valence isomerization to the dicyanide. Previous attempts to trap the dinitrene also failed.[3] *o*-Azidoaniline, however, gave the deep red crystalline bis(tricarbonyliron) complex[†] (I) (19%), m.p. 120° (decomp.),[‡] and the hydrogen-abstraction product, *o*-phenylenediamine (10%). Complex (I) was oxidised to *cis,cis*-mucononitrile by lead tetra-acetate; it represents a parent heterocyclic system, the mono-*N*-phenyl derivative of which is formed from azobenzene and di-iron nonacarbonyl.[4]



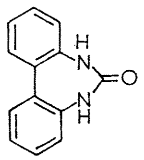
(I)



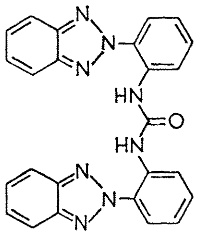
(II)



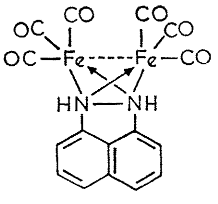
(III)



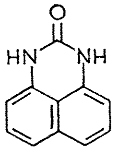
(IV)



(V)



(VI)



(VII)

2-Azidobiphenyl decomposes at 180° to give carbazole in high yield;[5] with the iron carbonyl only 1% of carbazole was formed. The other products were *NN'*-bis-(2-biphenylyl)urea (34%), 2-aminobiphenyl (10%), and the dimeric orange bis(tricarbonyliron) complex (II) (5%), m.p. 140° (decomp.). The analogous monomeric red complex (III) (5%), m.p. 215—220° (decomp.) was similarly obtained from 2,2′-diazidobiphenyl; this complex was oxidised to benzo[*c*]cinnoline (70%) with ferric chloride. The major product from 2,2′-diazidobiphenyl was the cyclic urea (IV) (38%), m.p. 324—326°. Thus, if nitrenes are intermediates in these azidobiphenyl decompositions they abstract hydrogen or carbon monoxide in preference to their normal insertion reactions.

2-Azidoazobenzene gave *o*-aminoazobenzene (18%) and 2-phenylbenzotriazole (32%); the latter is obtained almost quantitatively on heating the azide at 80°. In addition two novel reduction products, azobenzene (3%) and 2,2′-bis(phenylazo)diphenylamine (11%), m.p. 90—91°, were obtained. In the same conditions 2,2′-diazidoazobenzene gave 2-(*o*-aminophenyl)benzotriazole (20%) and 2,2′-bis(benzotriazol-2-yl)carbanilide (V) (10%), m.p. 238—241°. The same two products were also produced (31% and 34%, respectively) when 2-(*o*-azidophenyl)benzotriazole, the initial thermolysis product of 2,2′-diazidoazobenzene,[6] was decomposed with di-iron nonacarbonyl. Surprisingly, dibenzo-1,3a,4,6a-tetra-azapentalene, the very stable pyrolysis product of these two azides,[6] was not detected.

Decomposition of 1,8-diazidonaphthalene with di-iron nonacarbonyl gave the red complex (VI) (2%), m.p. 158° (decomp.), and perimidone (VII) (6%); the same two products (9% and 3%, respectively) were similarly obtained from 1-amino-8-azidonaphthalene. Oxidation of (VI) did not, however, generate the rare benz[*c,d*]indazole ring system (*cf.* ref. 7).

Thus, although the original observation of the striking catalysis of azide decomposition by di-iron nonacarbonyl is general, the catalysed reactions are complex and do not provide an attractive alternative route to nitrene cyclisation products.

We thank the S.R.C. for a Fellowship (C.D.C.) and Drs. T. L. Gilchrist and R. C. Storr for help and advice.

(*Received, March 19th, 1969; Com. 396.*)

[†] Appropriate analytical and spectral data were obtained for all new compounds. Mass spectra of the iron complexes showed parent molecular ions and prominent fragments corresponding to successive loss of all six carbonyl groups. M.ps were taken in open capillaries.

[‡] Complex (I) has also been obtained from *o*-phenylene diamine and di-iron nonacarbonyl in 4·3% yield (M. M. Bagga, W. T. Flannigan, G. R. Knox, and P. L. Pauson, *J. Chem. Soc.* (*C*), in the press). We thank Professor Pauson for kindly disclosing this result prior to publication.

[1] M. Dekker and G. R. Knox, *Chem. Comm.*, 1967, 1243.
[2] J. H. Hall and E. Patterson, *J. Amer. Chem. Soc.*, 1967, **89**, 5856.
[3] C. D. Campbell and C. W. Rees, *J. Chem. Soc.* (*C*), 1969, 742.
[4] P. E. Baikie and O. S. Mills, *Chem. Comm.*, 1966, 707.
[5] P. A. S. Smith and J. H. Hall, *J. Amer. Chem. Soc.*, 1962, **84**, 480.
[6] R. A. Carboni and J. E. Castle, *J. Amer. Chem. Soc.*, 1962, **84**, 2453.
[7] C. W. Rees and R. C. Storr, *J. Chem. Soc.* (*C*), 1969, 760.