Journal of

The Chemical Society,

Chemical Communications

NUMBER 21/1974 6 NOVEMBER

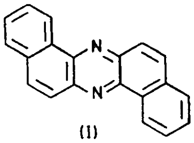
Thermal and Photolytic Decomposition of α- and β-Naphthyl Azides

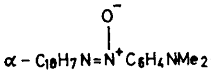
By Susan E. Hilton, Eric F. V. Scriven,* and Hans Suschitzky

(*The Ramage Laboratories, Department of Chemistry and Applied Chemistry, University of Salford, Salford* M54WT)

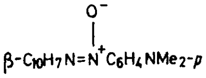
Summary Thermal decomposition of α- and β-naphthyl azide gives dibenzo[*a,h*]phenazine (I), and photoylsis of the latter azide yields 1-amino-2-*NN*-diethylaminonaphthalene (V); the formation of these and other products is discussed in terms of nitrene intermediates.

Thermolysis of naphthyl azides has so far been singularly unproductive since only naphthylamines and sometimes azonaphthalenes, in small yields, have been reported.[1] We have now found that thermolysis of α- and β-naphthyl azide in various solvents could be of potential synthetic interest by virtue of the nature and yield of the resulting products (*cf.* Table). The formation of dibenzo[*a,h*]phenazine (I)† is of particular significance as phenazine formation from two molecules of an azide precursor has so far remained peculiar to the decomposition of *p*-methoxyphenyl azide. Walker and Waters[2] ascribed the formation of 2,7-dimethoxyphenazine on thermolysis of this azide in cumene to the dimerization of anilino-radicals derived from the triplet nitrene by hydrogen abstraction. The complete suppression of the phenazine (I) which we observed on thermolysis in the presence of *p*-nitroso-*NN*-dimethylaniline (a radical quencher and spin-trap[3]) is consistent with this mechanism. Conversely, the notable increase in yield of the phenazine (I), α-azonaphthalene (IX), and the azoxy-compound (II) on thermolysis in bromobenzene is presumably due to the heavy atom effect of bromine promoting singlet → triplet intersystem crossing.[4] This further supports the essential role of a triplet nitrene‡ in the formation of phenazines. We have observed a similar effect[5] on the yield of 2,7-dimethoxyphenazine (and also on dimethoxyazobenzene) in the decomposition of *p*-methoxyphenyl azide in cumene and bromobenzene in the presence and absence of (VII). This suggests that azo-compounds and phenazines are formed from triplet arylnitrenes in aryl azide thermolysis. The small yields of azobenzene (IV) and


(I)


$\alpha\text{-}C_{10}H_7N{=}\overset{O^-}{\overset{|}{N^+}}C_6H_4NMe_2\text{-}p$

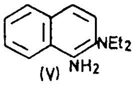
(II)


$\beta\text{-}C_{10}H_7N{=}\overset{O^-}{\overset{|}{N^+}}C_6H_4NMe_2\text{-}p$

(III)

Ph-N=N-Ph

(IV)


(V)

p-$Pr^iC_6H_4$-$C_6H_4Pr^i$-*p*

(VI)

p-$ONC_6H_4NMe_2$

(VII)

α- or β-$C_{10}H_7NH_2$

(VIII)

α- or β-$C_{10}H_7N{=}NC_{10}H_7$-α or -β

(IX)

$C_{10}H_7$= naphthyl

---

† Structure confirmed by comparison with an authentic sample.

‡ That naphthylnitrenes are produced in these reactions has been confirmed by the kinetic method used previously (J. Ashby, E.F.V. Scriven, and H. Suschitzky, *J.C.S. Chem. Comm.*, 1972, 366).

bicumenyl (VI) formed during decomposition of the naphthyl azides in aniline and cumene respectively, are probably due to dimerizations of the appropriate radicals formed by reaction of triplet arylnitrenes with solvent molecules.

Table

Thermolysis and photolysis of α- and β-naphthyl azide

			Products, yield (%)			
Naphthyl azide	Solvent	Conditions[a]	(IX)	(VIII)	Phenazine (I)	Others
α	Bromobenzene	T	20(α)	10(α)	12	—[b]
α	Cumene	T	11(α)	28(α)	5	(VI) 2[b]
α	Bromobenzene + (VII) ..	T	—	Trace	—	(II) 92[c]
α	Cumene + (VII)	T	—	Trace	—	(II) 61[b]
β	Bromobenzene	T	21(β)	40(β)	23	—[b]
β	Bromobenzene + (VII) ..	T	—	Trace	—	(III) 93[c]
α	Aniline	T	4(α)	33(α)	3	(IV) 3[b]
β	Aniline	T	1(β)	63(β)	4	(IV) 11[b]
β	Diethylamine	P	—	46(β)	—	(V) 37[c]
β	Diethylamine + pyrene ..	P	—	45(β)	—	(V) 50[c]

[a] T indicates thermolysis at 155 °C for 8 h under nitrogen; P indicates photolysis in a quartz vessel with a low-pressure Hanovia lamp for 30 h (10 h with added pyrene). [b] This reaction involved much tarring. [c] This reaction involved little tarring.

The absence of singlet derived products from the thermolysis of α- and β-naphthyl azides in aniline led us to photolyse them in diethylamine under a wide range of conditions. From α-naphthyl azide we could only identify α-naphthylamine (10—15%) and α-azonaphthalene (2—12%) These photolyses were accompanied by excessive tarring. More significantly, photolysis of β-naphthyl azide gave compound (V) in fair yield, which was increased by the presence of pyrene, a singlet sensitizer. Thus, β-naphthylnitrene can undergo a singlet reaction, which leads to formation of the diamine (V) by attack of diethylamine on an azirine intermediate, the latter being in equilibrium with the singlet nitrene.[6]

We thank the University of Salford for a research Studentship (to S.E.H.).

(*Received*, 25th *July* 1974; *Com.* 937.)

---

[1] P. A. S. Smith and J. H. Boyer, *J. Amer. Chem. Soc.*, 1951, **73**, 2626; R. Huisgen, D. Vossius, and M. Appl, *Chem. Ber.*, 1958, **91**, 1; G. Boshev, L. K. Dyall, and P. R. Sadler, *Austral. J. Chem.*, 1972, **25**, 599.

[2] P. Walker and W. A. Waters, *J. Chem. Soc.*, 1962, 1632.

[3] E. G. Janzen, *Accounts Chem. Res.*, 1971, **4**, 31; B. Nay, B.Sc. Thesis, University of Salford, 1974.

[4] A. G. Anastassiou, *J. Amer. Chem. Soc.*, 1967, **89**, 3184.

[5] E. F. V. Scriven, unpublished work.

[6] B. Iddon, H. Suschitzky, and D. S. Taylor, *J.C.S. Perkin I*, 1974, 579.