

## Pyrolysis of 2,3-Diazidonaphthalene

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2,3-Diazidonaphthalene gives *trans*-1,2-dicyano-1,2-dihydrobenzocyclobutene on flash pyrolysis in the vapour phase. No evidence for the formation of 2,3-didehydronaphthalene was found in the vapour phase or in solution.

Treatment of methyl 3-azido-2-naphthoate with hydrazine gave 1,2-dihydrobenz[f]indazol-3-one in high yield rather than the expected hydrazide.

1,2-DIAZIDOBENZENE has been considered as a potential source of benzyne since loss of three molecules of nitrogen is formally possible.<sup>1</sup> However on pyrolysis only two molecules of nitrogen were eliminated, resulting in cleavage of the aromatic ring to give *cis,cis*-1,4-dicyanobuta-1,3-diene.<sup>1</sup>

2,3-Diazidonaphthalene (1) remains of interest however, since analogous ring cleavage to give a dicyanodiene would involve formation of an unstable *o*-quinodimethane (2) and therefore the alternative pathway leading to aryne formation might be favoured. The dicyano-*o*-quinodimethane (2) would itself be of interest since no simple *o*-quinodimethanes have yet been isolated and there is the possibility that the cyano-substituents might stabilise the system sufficiently to allow its isolation at low temperatures from a vacuum pyrolysis of the diazide (1).

2,3-Diazidonaphthalene cannot be obtained by the route used so successfully for other aromatic 1,2-diazides<sup>1</sup> because of the inaccessibility of 2-amino-3-nitronaphthal-

ene. 2-Amino-3-naphthoic acid<sup>2</sup> is available in quantity however and this was converted into the diazide by the following sequence. The amino-acid was esterified and treated with hydrazine to give the amino-hydrazide. Rapid addition of 2 equiv. of sodium nitrite to this in aqueous acid followed by addition of sodium azide gave 3-azido-2-naphthoyl azide. This was converted into 3-azido-2-naphthylamine *via* the azido-isocyanate and thence, by diazotisation and addition of sodium azide, into the diazide (1).

Pyrolysis of the diazide in refluxing diglyme in the presence of an excess of tetraphenylcyclopentadienone gave no trace of tetraphenylanthracene; thus the formation of 2,3-didehydronaphthalene can be ruled out.<sup>3</sup> The only product isolated was an unidentified buff solid for which elemental analysis, u.v., i.r., and mass spectral data were consistent with the dimeric structure (4) expected by analogy with dimerisation of other *o*-quinodimethanes and benzocyclobutenes.<sup>4,5</sup> However,

<sup>3</sup> C. W. Rees and R. C. Storr, *J. Chem. Soc. (C)*, 1969, 765.

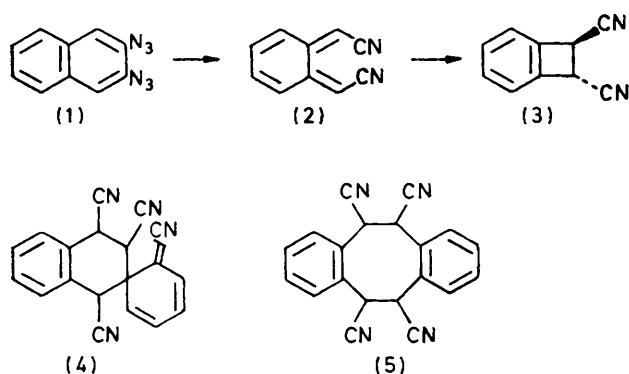
<sup>4</sup> A. T. Blomquist, Y. C. Meinwald, C. G. Bottomley, and P. W. Martin, *Tetrahedron Letters*, 1960, 13.

<sup>5</sup> L. A. Errede, *J. Amer. Chem. Soc.*, 1961, **83**, 949; M. P. Cava and A. A. Deana, *ibid.*, 1959, **81**, 4266.

<sup>1</sup> J. H. Hall and E. Patterson, *J. Amer. Chem. Soc.*, 1967, **89**, 5856.

<sup>2</sup> C. F. H. Allen and A. Bell, *Org. Synth.*, Coll. Vol. III, 1955, p. 78.

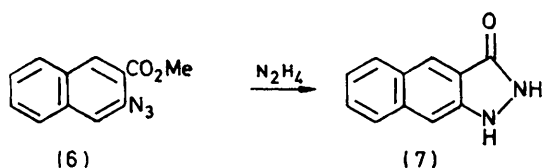
the n.m.r. spectrum in  $\text{CDCl}_3$  showed only aromatic proton absorptions, thus excluding this structure and its alternative <sup>4</sup> rearrangement product (5).



When the diazide was flash pyrolysed by sublimation through a tube at  $400^\circ$  and 0.05 mmHg and the pyrolysate collected at *ca.*  $-50^\circ$ , *trans*-1,2-dicyano-1,2-dihydrobenzocyclobutene (3) was obtained (55%). No dibenzo[*b,h*]biphenylene was detected, again suggesting that no 2,3-didehydronaphthalene had been generated. At a higher temperature ( $650^\circ$ ) some *cis*-1,2-dicyano-1,2-dihydrobenzocyclobutene was also produced, by isomerisation of the *trans*-isomer. A similar loss of stereospecificity has been reported in the thermal desulphonylation of 1,3-dihydrobenzo[*c*]thiophen 2,2-dioxides to give 1,2-dihydrobenzocyclobutenes.<sup>6</sup>

Significantly, the *trans*-dicyanide (3) is expected from orbital symmetry controlled conrotatory closure of the presumed intermediate *cis,cis*-dicyanoquinodimethane (2). The benzylic proton absorptions of the *trans*-dicyanodihydrobenzocyclobutene occur at slightly higher field than those of the *cis*-isomer, as is the case for the corresponding dihalodihydrobenzocyclobutenes.<sup>7</sup> The relative polarities of the two dicyanides as observed in column chromatography (*trans* less polar than *cis*) is as expected and also parallels that of the two dibromides.

*trans*-1,2-Dicyano-1,2-dihydrobenzocyclobutene (3) decomposes under the conditions of the solution pyrolysis of the diazide to give a complex mixture of products from which no dimers of dicyano-*o*-quinodimethane could be isolated.



During the course of an attempted synthesis of 2,3-diazidonaphthalene we discovered an unusual reaction. We planned to prepare 3-azido-2-naphthoyl azide from

<sup>6</sup> J. R. Manoir, J. F. King, and R. R. Fraser, *J.C.S. Chem. Comm.*, 1972, 541.

<sup>7</sup> G. Fraenkel, Y. Asahi, M. J. Mitchell, and M. P. Cava, *Tetrahedron*, 1964, **20**, 1179.

<sup>8</sup> H. Suschitzky, personal communication.

<sup>9</sup> S. Bradbury, M. Keating, C. W. Rees, and R. C. Storr, *Chem. Comm.*, 1971, 827.

3-azido-2-naphthoylhydrazide but when methyl 3-azido-2-naphthoate (6) was treated with hydrazine hydrate in ethanol 1,2-dihydrobenzo[*f*]indazolin-3-one (7) was formed in high yield, rather than the expected hydrazide. The formation of indazolinones from *o*-azidobenzoate esters and hydrazine under very mild conditions has been independently observed by Suschitzky and his co-workers.<sup>8</sup> This curious reaction is probably closely related to the mechanistically intriguing formation of indazoles from *o*-azidophenyl ketones and hydrazine, which we have reported previously.<sup>9</sup> Intramolecular nucleophilic displacement of the azide by the hydrazide or hydrazone group is very unlikely in view of the ease of conversion of (6) into (7), and the ease of conversion of 2-azido-3-benzoylnaphthalene by hydrazine into 3-phenylbenzo[*f*]indazole. Furthermore, this mechanism is almost certainly disproved by the observation that 1-substituted indazoles are not formed when hydrazine is replaced by methyl or phenylhydrazine. Significantly the corresponding azidohydrazone appear to be converted into indazoles only in the presence of hydrazine; other bases such as triethylamine do not suffice. Further work is obviously necessary to unravel the mechanisms of these reactions.

#### EXPERIMENTAL

The pyrolysis apparatus has been described previously.<sup>10</sup> 2-Amino-3-naphthoylhydrazide<sup>11</sup> was obtained from 2-amino-3-naphthoic acid<sup>2</sup> by treatment of its methyl ester<sup>12</sup> with hydrazine.

**3-Azido-2-naphthoyl Azide.**—Solid sodium nitrite (1.38 g, 0.02 mol) was added rapidly at  $0^\circ$  to a vigorously stirred suspension of 2-amino-3-naphthoylhydrazide (2.01 g, 0.01 mol) in 2*N*-hydrochloric acid (10 ml). Some solid separated out and, after stirring at  $0^\circ$  for 1 h, the solution was filtered and sodium azide (0.98 g, 0.015 mol) in water (15 ml) was added to the filtrate. The resulting solid was filtered off, dried, and recrystallised from light petroleum (b.p.  $40\text{--}60^\circ$ ) to give pale yellow plates of 3-azido-2-naphthoyl azide (1.30 g, 55%), m.p.  $61\text{--}62^\circ$ ,  $\lambda_{\text{max}}$  266 and 290sh nm ( $\epsilon$  36,300 and 12,900),  $\nu_{\text{max}}$  2100 and 2150  $\text{cm}^{-1}$ ,  $m/e$  238 ( $M^+$ ), 210 ( $M - \text{N}_2$ ), and 182 ( $M - 2\text{N}_2$ ). Ready decomposition to 3-azido-2-naphthoyl isocyanate made satisfactory analysis impossible.

**3-Azido-2-naphthylamine.**—A solution of 3-azido-2-naphthoyl azide (2.38 g, 0.07 mol) in dry benzene (25 ml) was heated under reflux for 1 h to give 3-azido-2-naphthoyl isocyanate which was not isolated. The solution was cooled and then boiled with aqueous potassium hydroxide solution (50%; 25 ml) for a further 1 h. After cooling, the organic layer was washed with water, dried ( $\text{Na}_2\text{SO}_4$ ), and evaporated to give 3-azido-2-naphthylamine as almost colourless needles from light petroleum (1.43 g, 78%), m.p.  $103\text{--}104^\circ$  (lit.<sup>13</sup>  $103\text{--}104^\circ$ ).

**2,3-Diazidonaphthalene (1).**—Sodium nitrite (0.069 g, 0.01 mol) in water (15 ml) was added dropwise at  $0^\circ$  to a solution of 3-azido-2-naphthylamine (1.84 g, 0.01 mol) in

<sup>10</sup> D. J. Anderson, T. L. Gilchrist, D. C. Horwell, C. W. Rees, and E. Stanton, *J.C.S. Perkin I*, 1972, 1317.

<sup>11</sup> K. Fries, R. Walter, and K. Schilling, *Annalen*, 1935, **516**, 248.

<sup>12</sup> A. N. Hambly and B. V. O'Grady, *Austral. J. Chem.*, 1962, **16**, 459.

<sup>13</sup> C. W. Rees and R. C. Storr, *J. Chem. Soc. (C)*, 1969, 756.

2N-hydrochloric acid. After 1 h the cold solution was filtered into a solution of sodium azide (0.098 g, 0.015 mol) in water (15 ml). The resulting solid was filtered off and recrystallised from light petroleum (b.p. 40–60°) to give the *diazide* (1) (1.82 g, 87%), as needles, m.p. 63–64° (Found: C, 57.3; H, 2.6; N, 39.8.  $C_{10}H_6N_6$  requires C, 57.15; H, 2.9; N, 40.0%),  $\lambda_{\max}$  262 nm ( $\epsilon$  31,000),  $\nu_{\max}$  2100  $cm^{-1}$ ,  $m/e$  210 ( $M^+$ ), 182 ( $M - N_2$ ), and 154 ( $M - 2N_2$ ).

*trans*-1,2-Dicyano-1,2-dihydrobenzocyclobutene (3).—2,3-Diazidonaphthalene (0.105 g, 0.5 mmol) was sublimed at 0.05 mmHg through a Pyrex tube maintained at 400°, the product being collected on an acetone–Drikold cooled trap (–50 to –60°) as a yellow solid. Preparative t.l.c. on silica gel gave *trans*-1,2-dicyano-1,2-dihydrobenzocyclobutene which crystallised from light petroleum (b.p. 40–60°) as needles (0.042 g, 55%), m.p. 88–91° (Found: C, 77.6; H, 4.2; N, 18.2.  $C_{10}H_6N_2$  requires C, 77.9; H, 3.9; N, 18.2%),  $\lambda_{\max}$  256, 262, 268, and 287 nm ( $\epsilon$  1300, 1700, 1600, and 600),  $\nu_{\max}$  2220  $cm^{-1}$ ,  $\tau$  ( $CDCl_3$ ) 2.4–2.8 (4H, m, aromatic) and 5.4 (2H, s, benzylic).

*cis*-1,2-Dicyano-1,2-dihydrobenzocyclobutene.—2,3-Diazidonaphthalene (0.105 g, 0.5 mmol) was sublimed at 0.05 mmHg through a quartz tube maintained at 650°, the product being collected as above. Preparative t.l.c. gave *trans*-1,2-dicyano-1,2-dihydrobenzocyclobutene (0.036 g, 47%) and *cis*-1,2-dicyano-1,2-dihydrobenzocyclobutene which crystallised from light petroleum (b.p. 40–60°) as pale yellow needles (0.006 g, 8%), m.p. 54–57°,  $\nu_{\max}$  2050  $cm^{-1}$ ,  $\tau$  ( $CDCl_3$ ) 2.4–2.8 (4H, m, aromatic) and 5.25 (2H, s, benzylic),  $m/e$  154 ( $M^+$ ), 127 ( $M - HCN$ ), and 105 (Found:  $M^+$ , 154.0515.  $C_{10}H_6N_2$  requires  $M$ , 154.0515).

*Pyrolysis of 2,3-Diazidonaphthalene in Solution.*—2,3-Diazidonaphthalene (0.210 g, 1 mmol) in diglyme (5 ml) was added dropwise to refluxing diglyme. After 0.5 h the solution was allowed to cool and poured into water (500 ml). The resulting mixture was extracted with dichloromethane and after thorough washing with water and drying ( $Na_2SO_4$ ), the dichloromethane was removed to give buff crystals, after purification by chromatography on silica gel (0.052 g, 34%), m.p. 128–131° (Found: C, 77.5; H, 4.2; N, 17.9. Calc. for  $C_{20}H_{12}N_4$ : C, 77.9; H, 3.9; N, 18.2%),  $\lambda_{\max}$  253

and 347 nm ( $\epsilon$  12,000 and 7800) [the dimer from diethyl 1,2-dihydrobenzocyclobutene-1,2-dicarboxylate shows  $\lambda_{\max}$  347 nm ( $\epsilon$  9300)\*],  $\nu_{\max}$  2200 and 2250  $cm^{-1}$ ,  $\tau$  ( $CDCl_3$ ) 2.5–3.0 (m),  $m/e$  308 ( $M^+$ ), 281 ( $M - HCN$ ), 254 ( $M - 2HCN$ ), and 227 ( $M - 3HCN$ ).

*Pyrolysis of trans-1,2-Dicyano-1,2-dihydrobenzocyclobutene in Solution.*—*trans*-1,2-Dicyano-1,2-dihydrobenzocyclobutene (0.072 g, 0.5 mmol) in diglyme (5 ml) was added dropwise to refluxing diglyme (10 ml). The solution was refluxed for 0.5 h and worked up as above to give the same product (0.033 g, 43%).

*Vapour Phase Pyrolysis of trans-1,2-Dicyano-1,2-dihydrobenzocyclobutene.*—*trans*-1,2-Dicyano-1,2-dihydrobenzocyclobutene was sublimed at 0.05 mmHg through a quartz tube maintained at 650° to give a mixture of *trans*- and *cis*-dicyanodihydrobenzocyclobutenes. The n.m.r. spectrum of the pyrolysate indicated an isomer ratio *trans* : *cis* of 5 : 1.

*Methyl 3-Azido-2-naphthoate* (6).—Methyl 2-amino-3-naphthoate (6.03 g, 30 mmol) in 2N-hydrochloric acid (30 ml) was cooled to 0° and treated with sodium nitrite (2.07 g, 30 mmol) in water (15 ml). The resulting solution was stirred for 1 h at 0°, and sodium azide (2.76 g, 40 mmol) in water (15 ml) was added dropwise to give a solid which was filtered off and crystallised from ether–light petroleum to give *methyl 3-azido-2-naphthoate* (4.76 g, 70%), m.p. 57–58° (Found: C, 63.4; H, 4.1; N, 18.8.  $C_{12}H_9N_3O_2$  requires C, 63.4; H, 4.0; N, 18.5%),  $\nu_{\max}$  2109 and 1720  $cm^{-1}$ ,  $\tau$  ( $CDCl_3$ ) 2.2–2.9 (6H, m) and 6.14 (3H, s),  $m/e$  227 ( $M^+$ ), 199 ( $M - N_2$ ), 169, and 140.

*1,2-Dihydrobenz[f]indazol-3-one* (7).—The ester (6) (4.54 g, 20 mmol) in absolute ethanol (25 ml) was treated with hydrazine hydrate (1.9 g, 20 mmol), heated under reflux for 1 h, and cooled. The yellow solid which separated immediately was filtered off, dried, and sublimed at 175° and 0.03 mmHg to give 1,2-dihydrobenz[f]indazol-3-one (1.6 g, 44%) as a pale yellow solid, m.p. and mixed m.p. 315–318° (decomp.) [lit.,<sup>14</sup> 320° (decomp.)].

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<sup>14</sup> J. Adamson, D. L. Forster, T. L. Gilchrist, and C. W. Rees, *J. Chem. Soc. (C)*, 1971, 981.