

342. *The Reaction between Phenylhydrazine and 2-Naphthol, studied with Nitrogen-15.*

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2-Naphthol reacts with phenyl[2-¹⁵N]hydrazine in the presence of sulphur dioxide to give ammonia and benzo[*c*]carbazole which retains some of the nitrogen-15. The reaction probably involves the formation of a phenyl-naphthylhydrazine which is converted into the carbazole through an *oo'*-benzidine rearrangement (main reaction) and through an *o*-semidine rearrangement. The intermediate 1-*o*-aminophenyl-2-[¹⁵N]naphthylamine produced in the main reaction eliminates nitrogen-15 exclusively on decomposition under the conditions used for the overall reaction.

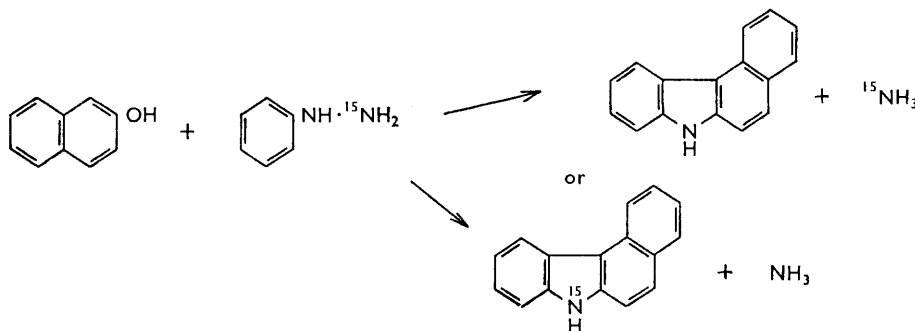
PHENYLHYDRAZINE and 2-naphthol when refluxed in aqueous solution in the presence of sulphur dioxide give¹ benzo[*c*]carbazole (I), ammonia, and 1-*o*-aminophenyl-2-naphthylamine (II). The diamine (II) may be an intermediate in the formation of the carbazole

¹ Japp and Maitland, *J.*, 1903, 269.

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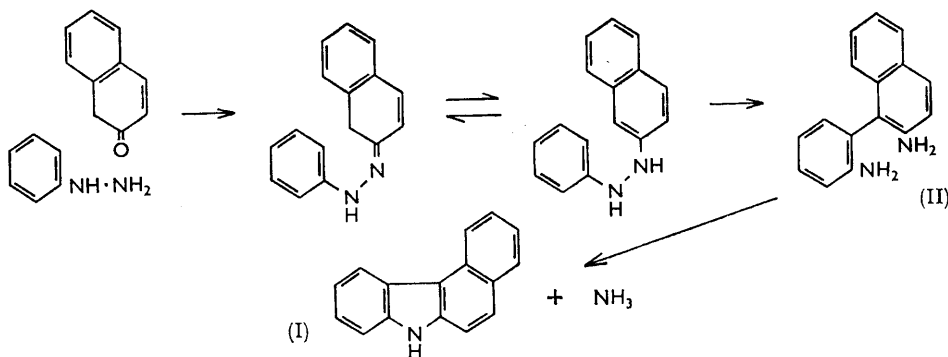
since, if the reaction is arrested after 30 hours the yield of diamine is only 5% whereas after 12 hours it is 20%. Further evidence is that the diamine gives ² benzo[*c*]carbazole under conditions similar to those used for the overall reaction.

The reaction has been studied by using as starting material phenyl[2-¹⁵N]hydrazine, synthesised from aniline and potassium[¹⁵N]nitrite. The reaction might proceed either by elimination of the nitrogen from the 1-position of phenylhydrazine to yield unlabelled ammonia and labelled benzo[*c*]carbazole, or from the 2-position, to give labelled ammonia and an unlabelled carbazole:



In reactions carried out at 100° some 6% of the benzo[*c*]carbazole produced from phenyl[2-¹⁵N]hydrazine retained nitrogen-15. Rather less nitrogen-15 was retained at a higher temperature (see the Table). The ammonia was labelled in a corresponding manner and varied correspondingly with temperature.

The reaction between phenylhydrazine and 2-naphthol was discovered in an attempt to show that polycyclic phenols can react in a tautomeric keto-form and the mechanism was explained^{1,3} in terms of this tautomer. The stages suggested, (a) formation of a hydrazone followed by its tautomeric rearrangement to a hydrazine, (b) an *oo'*-benzidine rearrangement of the hydrazine to an *oo'*-diaminobiaryl, and (c) ring closure by deamination, are shown below. The stages subsequent to the formation of the hydrazine are analogous to a Fischer indolisation:



By this mechanism phenyl[2-¹⁵N]hydrazine would yield unlabelled benzo[*c*]carbazole and ammonia labelled to twice the extent of the phenylhydrazine.

The diamine (II), formed by an *oo'*-benzidine rearrangement would be labelled in the amino-group attached to the 2-naphthyl position. Such a group is more labile⁴ than when attached to the phenyl system. Evidence for assigning the label to the naphthyl

² Fuchs and Niszel, *Ber.*, 1927, **60**, 209.

³ Schopff, *Ber.*, 1896, **29**, 265; Japp and Findlay, *J.*, 1897, 1117.

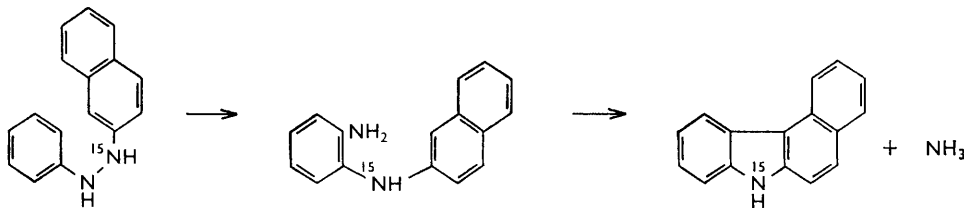
⁴ Corbett and Holt, *J.*, 1960, 3646.

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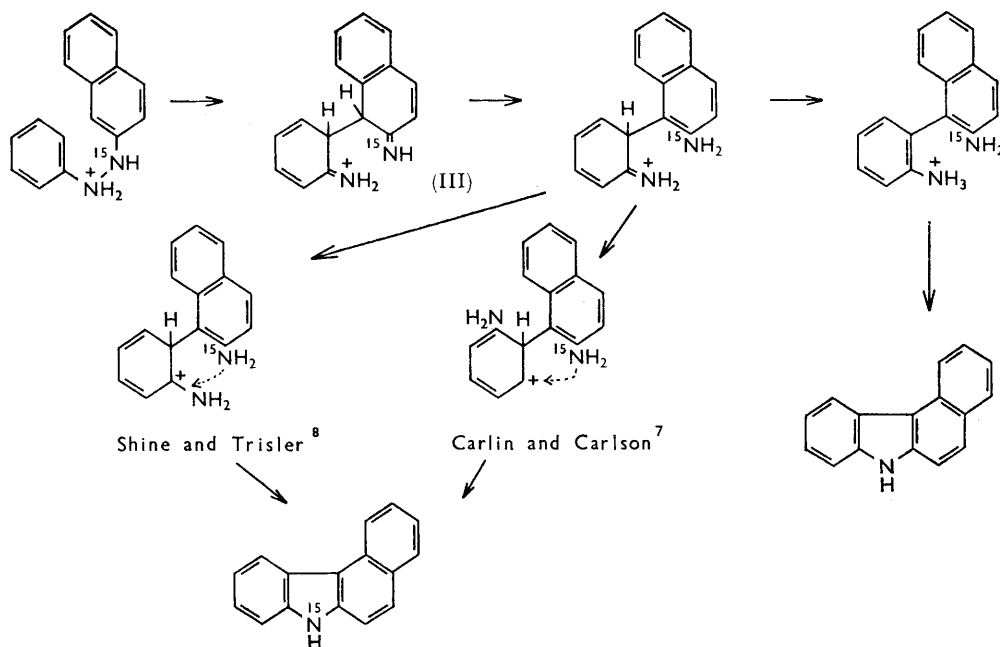
and 2-Naphthol, studied with Nitrogen-15.

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substituent was obtained by isolating the labelled diamine (II) and preparing from it benzo[*c*]carbazole under the conditions of the overall reaction. Benzo[*c*]carbazole thus formed was virtually unlabelled. It was shown that part of the benzo[*c*]carbazole derived from phenyl[2-¹⁵N]hydrazine is formed with retention of nitrogen-15. The present evidence shows that the formation of this labelled benzocarbazole does not involve the diamine (II). The probable route⁵ is *via* a simultaneous *o*-semidine rearrangement at stage (*b*) thus:



The results can also be interpreted in terms of the current views on the Fischer indolisation reaction, reviewed by Robinson.⁶ The formation of the C-C bond during Fischer indolisation is believed⁷ to involve a "non-aromatic" intermediate similar to (III) which could yield the carbazole system by losing either nitrogen atom. A similar intermediate was suggested⁸ for the *oo'*-benzidine rearrangement. Thus the observation that benzo[*c*]carbazole is obtained in the present reaction by two mechanisms is compatible with current views. The routes to the labelled and unlabelled carbazoles would then be represented by the following scheme:



Significance of Results.—The assumption of two simultaneous mechanisms for the formation of benzo[*c*]carbazole is justified only if the ratio *R* for the carbazole differs

⁵ Clusius and Barsh, *Helv. Chim. Acta*, 1954, **37**, 2013.

⁶ Robinson, *Chem. Rev.*, 1963, **63**, 376.

⁷ Carlin and Carlson, *J. Amer. Chem. Soc.*, 1959, **81**, 4673.

⁸ Shine and Trisler, *J. Amer. Chem. Soc.*, 1960, **82**, 4054.

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significantly from zero. Seven analyses of samples of ammonium salts having known atom-% of nitrogen-15 gave a maximum error of 1.6%. The sum of the values R for benzocarbazole and for ammonia in any experiment should be 2. The value ΣR is a measure of the self consistency of experiments. Satisfactory values are indicated in the Table. The values R may be regarded as differing significantly from zero.

TABLE I.

Reaction temp.	Atom-% ^{15}N in:			R for		ΣR
	phenylhydrazine	benzo[c]carbazole	ammonia	benzo[c]carbazole	ammonia	
80°	3.35	0.765	6.00	0.13	1.86	1.99
100	3.43	0.755				
	2.48	0.600	4.22	0.12	1.89	2.01
120	2.43	0.636				
	4.03	0.612	7.48	0.07	1.95	2.02
120	4.00	0.617				
	9.13	1.08	16.9	0.08	1.91	1.99
	9.29		17.1			
	8.89					

$$R = \frac{\text{Excess } ^{15}\text{N in product}}{\text{Excess } ^{15}\text{N in reactant}}$$

Atmospheric abundance, 0.37 atom-% ^{15}N .

EXPERIMENTAL.

Reaction of Phenyl[2- ^{15}N]hydrazine with 2-Naphthol.—Phenyl[2- ^{15}N]hydrazine was prepared by diazotising aniline with labelled nitrous acid and reducing the product with stannous chloride.⁹ An excess of sodium hydroxide was added and the free base was extracted with ether. The ether was removed.

In a typical experiment phenyl[2- ^{15}N]hydrazine (0.992 g., 3.39 atom-% of nitrogen-15), 2-naphthol (1.2 g.), and water (10 g.) was saturated with sulphur dioxide, then heated on a steam-bath for 7 hr., or at 80° for 42 hr., or at 120° in a sealed tube for 4 hr.

The aqueous layer was decanted from the brown oil and made alkaline. The solution was extracted three times with benzene, after which ammonia was distilled from the solution and assayed.

The brown oil produced by the reaction was dissolved in benzene and extracted consecutively with 2N-sodium, with 3N-hydrochloric acid, and with water. The acidic extracts were basified with sodium carbonate and the precipitate was boiled in ethanol with charcoal. The solution was filtered and allowed to deposit crystals which, after recrystallisation twice from ethanol, gave 1-*o*-aminophenyl-2-naphthylamine, (8%) m. p. 156° (lit., 156°).

The benzene solution was filtered through alumina, and the eluate evaporated and crystallised thrice from aqueous acetic acid, to give benzo[c]carbazole (2%), m. p. 135° (lit., 135°).

*Conversion of 1-*o*-Aminophenyl-2-[^{15}N]naphthylamine into Benzo[c]carbazole.*—1-*o*-Aminophenyl-2-[^{15}N]naphthylamine (0.10 g.), prepared from phenyl[2- ^{15}N]hydrazine (3.39 atom-% of nitrogen-15), in water (15 ml.) was saturated with sulphur dioxide then heated on a steam-bath. After 30 hr. a solid was separated and recrystallised, giving benzo[c]carbazole, m. p. 135° (0.060 g.; 0.453 atom-% of nitrogen-15), in almost quantitative yield. The ratio R of the excess of nitrogen-15 in the product to that in the reactant was 0.027.

Isotopic Assay.—Nitrogen was prepared from the samples by the method of Holt and Hopson-Hill,¹⁰ for assay in the mass spectrometer.

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⁹ Clusius and Hoch, *Helv. Chim. Acta*, 1950, **33**, 2122.

¹⁰ Holt and Hopson-Hill, *J.*, 1952, 4251.