648. *Studies on the Possible Interconversion of Phenylhydrazones and Phenylazoalkanes. Part II* [1a]

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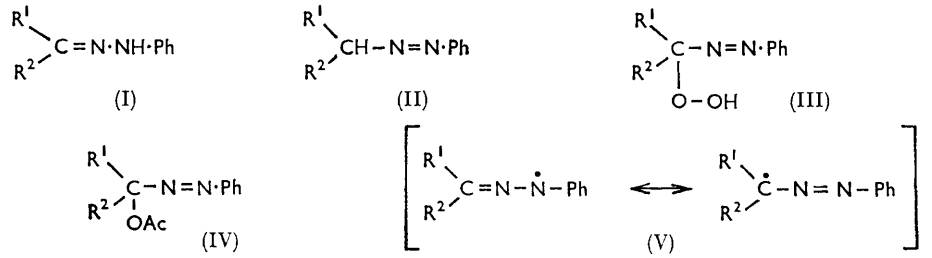
Phenylazoalkanes have been converted into phenylhydrazones using acidic, basic, and radical-initiated conditions. Conditions under which phenylhydrazones are converted into indoles have been used to convert phenylazoalkanes into indoles, without isolation of the intermediate phenylhydrazones.

In recent work [1] it has been shown that the rearrangement in neutral solvents of phenylhydrazones (I) to phenylazoalkanes (II), as reported by O'Connor,[2] does not occur, and the yellow coloration observed by him was attributed to the autoxidation of the phenylhydrazones giving 1-hydroperoxy-1-phenylazoalkanes (III).



The mechanism for the autoxidation of phenylhydrazones (see Part I [1a]) proposed by Pausacker [3] and by Criegee and Lohous [4] is very similar to the mechanism proposed by Iffland, Salisbury, and Schafer [5] for the formation of 1-acetoxy-1-phenylazoalkanes (IV) from phenylhydrazones and lead tetra-acetate. In the latter case, it was assumed that the lead tetra-acetate effects cleavage of the N–H bond of the phenylhydrazone, generating the pseudo-allylic radical (V), and the latter abstracts an acetate group from the lead

[1] (*a*) Part I, A. J. Bellamy and R. D. Guthrie, *J.*, 1965, 2788; (*b*) G. J. Karabatos and R. A. Taller, *J. Amer. Chem. Soc.*, 1963, **85**, 3624.
[2] R. O'Connor, *J. Org. Chem.*, 1961, **26**, 4375.
[3] K. H. Pausacker, *J.*, 1950, 3478.
[4] R. Criegee and G. Lohous, *Chem. Ber.*, 1951, **84**, 219.
[5] D. C. Iffland, L. Salisbury, and W. R. Schafer, *J. Amer. Chem. Soc.*, 1961, **83**, 747.

triacetate radical, produced in the first stage, giving the azoacetate (IV) and lead diacetate. In both reactions, the radical derived from the phenylhydrazone reacts at carbon.

It therefore seemed reasonable that if the radical (V) could be generated from a phenylhydrazone using a radical initiator in the absence of other reactive species, intermolecular hydrogen abstraction might occur, leading to phenylazoalkanes if the radical reacted at carbon. The abstracted hydrogen could originate from other phenylhydrazone molecules if the reaction were performed in an inert solvent, or from the solvent itself if a suitable solvent, such as chloroform, were used.

To test these ideas, cyclohexanone phenylhydrazone (I; R^1, R^2 = $-[CH_2]_5$) in chloroform was treated with benzoyl peroxide in an evacuated sealed tube at 100°. The dark product which was obtained after 24 hr. was chromatographed on alumina, but no phenylazocyclohexane (II; R^1, R^2 = $-[CH_2]_5$) was isolated. Unchanged cyclohexanone phenylhydrazone appeared to be the major product.

When a control reaction was performed to test the stability of the expected product, phenylazocyclohexane, under the reaction conditions, only a small amount of phenylazocyclohexane (11%) was recovered; the major product was cyclohexanone phenylhydrazone (54%). Similarly, when phenylazoethane (II; R^1 = Me, R^2 = H) was treated with benzoyl peroxide in chloroform, β-acetaldehyde phenylhydrazone (I; R^1 = Me, R^2 = H; 37%) was obtained. On using hexane as the reaction solvent instead of chloroform, the yields of the phenylhydrazones were considerably increased, the yield of cyclohexanone phenylhydrazone being raised to 71% and that of β-acetaldehyde phenylhydrazone to 51%. Acetaldehyde phenylhydrazone was isolated as the β-isomer since this is more readily purified than the α-isomer.[2] 2-Methyl-2-phenylazopropane was recovered almost quantitatively after treatment with benzoyl peroxide in hexane.

Although Edward and Samad[6] reported that phenylazodiphenylmethanol benzoate was produced on treatment of benzophenone phenylhydrazone with benzoyl peroxide, we did not expect products of this type, as only catalytic amounts of benzoyl peroxide were used in our experiments.

From the apparently negative result for the treatment of cyclohexanone phenylhydrazone with benzoyl peroxide, it is reasonable to assume that the radical (V) is being generated, but hydrogen abstraction, in contrast to the reactions with oxygen and lead tetra-acetate, takes place at nitrogen and not at carbon. Similarly, the radical when generated from phenylazocyclohexane also reacts at nitrogen. The abstracted hydrogen in the reaction performed in hexane is certainly derived from other phenylazoalkane molecules, but in chloroform its origin is less certain.

There are few reports of the treatment of phenylazoalkanes with base.[7] We have treated a series of primary and secondary phenylazoalkanes (see Experimental section) with sodium methoxide in methanol (1M). In every case, the colour of the solution changed from bright yellow to very pale yellow in a few minutes and the corresponding phenylhydrazones were isolated in 45—80% yield. Since phenylhydrazones are rapidly autoxidised in the presence of air, the reaction and most of the work-up procedure was performed in an atmosphere of nitrogen. For the reactions of phenylazocyclohexane and phenylazoethane with base, no starting material was detected in the product. The other reaction products were not examined for the presence of starting material. 2-Methyl-2-phenylazopropane was unchanged after similar treatment. Application of this rearrangement to phenylazo-sugars has led to a new route for the synthesis of keto-sugars.[8]

The base-catalysed conversion of phenylazoalkanes into phenylhydrazones presumably proceeds *via* the conjugate base of the phenylazoalkane, followed by reprotonation on the nitrogen adjacent to the phenyl group.

Base-catalysed rearrangements of alkylazoalkanes to the corresponding alkylhydrazones

[6] J. T. Edward and S. A. Samad, *Canad. J. Chem.*, 1963, **41**, 1638.
[7] H. Zollinger, " Diazo and Azo Chemistry," Interscience Publ., Inc., New York, 1961, p. 327.
[8] G. J. F. Chittenden and R. D. Guthrie, *Proc. Chem. Soc.*, 1964, 289.

have been reported by Fodor and Szarves [9] for dibenzylazo-compounds, and by Hutton and Steel [10] for *cis*- and *trans*-azomethane.

Except for the reported conversion of phenylazoethane into acetaldehyde phenylhydrazone using 60% sulphuric acid,[11] and the conversion of a 17-phenylazo-steroid into the corresponding phenylhydrazone in the presence of perchloric acid,[12] there are few reports in the literature of the treatment of phenylazoalkanes with acid.[7] Using concentrated sulphuric acid in ethanol at 0°, we have converted phenylazoalkanes into phenylhydrazones (see Experimental section) in 50—70% yield. The reaction was quenched when the colour of the solution had changed from bright yellow to very pale yellow. Primary phenylazoalkanes appeared to react more quickly than the secondary compounds. As in the base-catalysed rearrangement, the reaction and most of the work-up procedure was performed in an atmosphere of nitrogen. 2-Methyl-2-phenylazopropane was unchanged after treatment with concentrated sulphuric acid in ethanol at 80° during 4 hr. The reaction probably proceeds by protonation of the nitrogen adjacent to the phenyl group, followed by loss of a proton from the carbon atom adjacent to the other nitrogen.

When phenylhydrazones are treated with proton or Lewis acids under conditions more drastic than those described above, indoles are formed.[13] As expected, therefore, we have shown for a number of examples that phenylazoalkanes under these conditions give the same indole as from the corresponding phenylhydrazone (see Experimental section).

On treating n-butyraldehyde phenylhydrazone with concentrated sulphuric acid in ethanol at 50°, the solution turned bright yellow after 3 minutes. To determine if this were due to the formation of 1-phenylazobutane, the reaction was quenched at this stage and the product was chromatographed on alumina. No 1-phenylazobutane was isolated.

In 1943, Snyder and Smith [14] commented on the *immediate* cherry-red coloration in a Fischer indole synthesis with cyclohexanone phenylhydrazone, using boron trifluoride as catalyst, and also on the fact that this effect was absent during the same reaction with cyclohexanone 1-methyl-1-phenylhydrazone. As an explanation, they suggested that in the reaction with cyclohexanone phenylhydrazone an equilibrium is set up between the phenylhydrazone and the azo-form, both forms being complexed with boron trifluoride, the azo-form producing the deep colour. An equilibrium of this sort would not be possible with the 1-methyl-1-phenylhydrazone.

We have repeated these experiments and agree with their results. We also repeated the reaction, stopping it when the cherry-red colour was observed. The crude product, which was mainly cyclohexanone phenylhydrazone as judged from the infrared spectrum, was chromatographed on alumina. No phenylazocyclohexane was isolated.

When phenylazocyclohexane was treated with boron trifluoride–ether in glacial acetic acid, the colour of the solution changed from orange-yellow to cherry-red during 10 *minutes* and the product was largely cyclohexanone phenylhydrazone with a small amount of unchanged phenylazocyclohexane. If the coloration were due to the formation of a phenylazocyclohexane–boron trifluoride complex, then this reaction should also have given an immediate colour. Since this was not so, and since phenylazocyclohexane was shown to be stable under the work-up conditions, the explanation advanced by Snyder and Smith [14] appears doubtful.

It is noteworthy that in a control reaction in which boron trifluoride was not added, cyclohexanone phenylhydrazone in glacial acetic acid gave 1,2,3,4-tetrahydrocarbazole in increased yield (86%). In this case, therefore, the role of the boron trifluoride is doubtful.

Our results on the interconversion of phenylhydrazones and phenylazoalkanes using

[9] G. V. Fodor and P. Szarvas, *Ber.*, 1943, **76**, 334.
[10] R. F. Hutton and C. Steel, *J. Amer. Chem. Soc.*, 1964, **86**, 745.
[11] E. Fischer, *Ber.*, 1896, **29**, 793.
[12] A. F. Chaplin, D. H. Hey, and J. Honeyman, *J.*, 1959, 3194.
[13] B. Robinson, *Chem. Rev.*, 1963, **63**, 373.
[14] H. E. Snyder and C. W. Smith, *J. Amer. Chem. Soc.*, 1943, **65**, 2452.

acidic, basic, and radical-initiated conditions, suggests that the phenylhydrazone isomer is the thermodynamically more stable, since it is almost certain that some, if not all, of these reactions are equilbrium controlled.

Experimental

Alumina was of type H, 100—200 mesh, supplied by Peter Spence Ltd. Light petroleum refers to the fraction b. p. 40—60°. The identity of compounds was proved where necessary by mixed m. p. and by infrared spectrometry.

Treatment of Phenylazoalkanes * *with Benzoyl Peroxide.*—A mixture of the phenylazoalkane (2×10^{-3} mole) and benzoyl peroxide (0·024 g.) in chloroform (0·66 ml.) or hexane (0·5 ml.) was sealed under vacuum and heated at 100° during 24 hr. The mixture became dark, and in the case of reactions performed in hexane, some product crystallised during the reaction. The product was transferred in ether and evaporation *in vacuo* gave the crude product, which was purified as stated below.

(*a*) *Phenylazocyclohexane.* Treatment of phenylazocyclohexane with benzoyl peroxide in chloroform gave cyclohexanone phenylhydrazone (54%), m. p. 70·5—74·5° (from aqueous ethanol) (lit.,[2] m. p. 74—76°). Chromatography on alumina of the crude reaction mixture from a similar reaction gave unchanged phenylazocyclohexane (11%), eluted with light petroleum. Elution with ether gave 1-hydroperoxy-1-phenylazocyclohexane (75%). Cyclohexanone phenylhydrazone (71%) was also isolated from a reaction performed in hexane.

(*b*) *Phenylazoethane.* Treatment of phenylazoethane with benzoyl peroxide in chloroform gave β-acetaldehyde phenylhydrazone (37%), m. p. 53—56° (from 70% aqueous ethanol containing a trace of hydrochloric acid) (lit.,[15] m. p. 56°). β-Acetaldehyde phenylhydrazone (51%) was also isolated from a reaction performed in hexane.

(*c*) *2-Methyl-2-phenylazopropane.* The crude product from 2-methyl-2-phenylazopropane and benzoyl peroxide in hexane was dissolved in light petroleum and chromatographed on alumina. Elution with light petroleum gave the starting material (94%).

Treatment of Cyclohexanone Phenylhydrazone with Benzoyl Peroxide.—A mixture of cyclohexanone phenylhydrazone (0·189 g.) and benzoyl peroxide (0·006 g.) in chloroform (0·33 ml.) was sealed under vacuum and heated at 100° during 24 hr. The dark product was chromatographed on alumina (20 g.). No phenylazocyclohexane was isolated on elution with light petroleum. Elution with light petroleum–ether (1 : 1) gave a colourless product (cyclohexanone phenylhydrazone) which produced 1-hydroperoxy-1-phenylazocyclohexane (0·116 g.) when the eluent was allowed to stand in the presence of air.[1a] Elution with ether gave more 1-hydroperoxy-1-phenylazocyclohexane (0·046 g.). Pure cyclohexanone phenylhydrazone behaved in a similar manner on chromatography on alumina.

Treatment of Phenylazoalkanes with Sodium Methoxide in Methanol.—The phenylazoalkane ($1—3{\cdot}5 \times 10^{-3}$ mole) was added to a refluxing solution of sodium methoxide in methanol (20 ml.; 1M) under nitrogen. After a few minutes the colour of the solution had changed from bright yellow to very pale yellow. The solution was heated under reflux during a further 1 hr. As far as possible the work-up was performed in an atmosphere of nitrogen. The mixture was cooled and glacial acetic acid (5 ml.) was added followed by sodium carbonate (6 g.) in brine (75 ml.). Finally ether (100 ml.) was added and the mixture was shaken vigorously. The organic layer was separated, dried briefly, and evaporated *in vacuo* to give the crude product, which was purified as stated below.

(*a*) *Phenylazocyclohexane.* Treatment of phenylazocyclohexane with sodium methoxide in methanol gave cyclohexanone phenylhydrazone (45%), m. p. 67—71° (from aqueous ethanol). The mother-liquor from the recrystallisation was evaporated and chromatographed on alumina (20 g.). No phenylazocyclohexane was isolated on elution with light petroleum.

(*b*) *Phenylazoethane.* The colour of the solution changed from bright yellow to very pale yellow during 2—3 min. and β-acetaldehyde phenylhydrazone (52%), m. p. 57—59° (from 70% aqueous ethanol containing a trace of hydrochloric acid), was isolated. No phenylazoethane was isolated on chromatography of the mother-liquor.

(*c*) *2-Phenylazopropane.* The solution changed from bright yellow to very pale yellow

* The phenylazoalkanes were prepared as described in ref. 1(*a*).

[15] E. G. Laws and N. V. Sidgwick, *J.*, 1911, 2085.

during 5—10 min. and acetone phenylhydrazone (47%), b. p. 152—153°/25 mm. n_D^{24} 1·577, was isolated (lit.,[2] b. p. 108—109°/1·6 mm.).

(*d*) 1-*Phenylazobutane.* The solution changed from bright yellow to very pale yellow during 1—2 min. and n-butyraldehyde phenylhydrazone (78%), b. p. 96—97°/0·6 mm. $n_D^{24\cdot5}$ 1·5705, was isolated (lit.,[4] b. p. 167°/24 mm.).

(*e*) 2-*Methyl*-2-*phenylazopropane.* The yellow colour of the solution was not discharged on treating 2-methyl-2-phenylazopropane with sodium methoxide in methanol and the starting material (81%) was recovered after 2 hr.

Treatment of Phenylazoalkanes with Concentrated Sulphuric Acid in Ethanol.—The phenylazoalkane (4×10^{-3} mole) was added to concentrated sulphuric acid (2·4 ml.) in dry ethanol (21·6 ml.) at 0° under nitrogen. The mixture was stirred at this temperature until the bright yellow colour of the solution was discharged. At this stage the reaction was quenched by the addition of sodium carbonate (8 g.) in water (150 ml.). As far as possible the work-up was performed in nitrogen. Ether (100 ml.) was added and the mixture shaken vigorously. The organic layer was separated, shaken with brine, dried briefly, and evaporated to give the crude product which was purified as stated below.

(*a*) 1-*Phenylazopropane.* The solution changed from bright yellow to very pale yellow during 20 min. and acetone phenylhydrazone (64%), b. p. 88—89°/0·8 mm. $n_D^{23\cdot5}$ 1·585, was isolated.

(*b*) 1-*Phenylazobutane.* The solution changed from bright yellow to very pale yellow during 5 min. and n-butyraldehyde phenylhydrazone (64%), b. p. 98—99°/0·7 mm. n_D^{24} 1·5705, was isolated.

(*c*) *Phenylazoethane.* The bright yellow colour was discharged after 5 min. and β-acetaldehyde phenylhydrazone (60%), m. p. 54—56° (from 70% aqueous ethanol containing a trace of hydrochloric acid), was isolated.

(*d*) *Phenylazocyclohexane.* The solution changed from bright yellow to very pale yellow during 20 min. and cyclohexanone phenylhydrazone (47%), m. p. 71—75° (from aqueous ethanol), was isolated.

In a similar reaction, the mixture was heated under reflux during 4 hr. The colour changed from bright yellow to very pale yellow (2—3 min.) and then slowly to red. The reaction mixture was worked up as before and 1,2,3,4-tetrahydrocarbazole (50%), m. p. 111·5—114·5° (from methanol as white crystals), was isolated (lit.,[16] m. p. 116—118°).

(*e*) 2-*Methyl*-2-*phenylazopropane.* The yellow colour of the solution was maintained on heating under reflux during 4 hr. and the starting material (95%) was recovered.

Treatment of Cyclohexanone Phenylhydrazone with Concentrated Sulphuric Acid in Ethanol.—Cyclohexanone phenylhydrazone (0·375 g.) was added to concentrated sulphuric acid (1·2 ml.) in dry ethanol (10·8 ml.) under nitrogen and the solution was heated under reflux during 4 hr.; a red colour developed. Sodium carbonate (2·5 g.) in water (10 ml.) was added, the mixture was poured into water (150 ml.), and the product was isolated with ether. Evaporation of the solvent and recrystallisation gave 1,2,3,4-tetrahydrocarbazole (0·213 g.; 62%), m. p. 112—115° (from methanol as white crystals).

Attempts to prepare 2-methylindole and 3-ethylindole from acetone phenylhydrazone and n-butyraldehyde phenylhydrazone, respectively, under similar conditions were unsuccessful for 2-methylindole and only moderately successful for 3-ethylindole (12%).

Treatment of Phenylazoalkanes with Anhydrous Zinc Chloride.—(*a*) 2-*Phenylazopropane.* A mixture of 2-phenylazopropane (0·75 g.) and anhydrous zinc chloride (3·75 g.) under nitrogen was heated to 180° and the mixture became dark. The product was steam-distilled under nitrogen. The first few ml. of distillate contained unchanged 2-phenylazopropane (0·007 g.). The second fraction (250 ml.) was extracted with ether to give a white solid (0·40 g.) which was recrystallised to give 2-methylindole (0·19 g.; 27%), m. p. 54—56° (from aqueous ethanol), identified by comparison with an authentic sample prepared from acetone phenylhydrazone and anhydrous zinc chloride (37%; m. p. 56—59°) (lit.,[17] m. p. 60°).

(*b*) 1-*Phenylazobutane.* A mixture of 1-phenylazobutane (0·75 g.) and anhydrous zinc chloride (3·75 g.) under nitrogen was heated to 180°. The mixture became dark before heating and yellow again at 60—80°. It darkened once more as 180° was approached. On cooling, water (30 ml.) and dilute hydrochloric acid (5 ml.) were added and the product was steam-distilled under nitrogen. The distillate (250 ml.) was saturated with sodium chloride and

[16] C. Y. Rogers and B. B. Corson, *J. Amer. Chem. Soc.*, 1947, **69**, 2910.
[17] E. Fischer, *Ann.*, 1886, **236**, 127.

extracted with ether to give slightly impure 3-ethylindole (0·31 g.; 46%), identified by comparison with an authentic sample prepared from n-butyraldehyde phenylhydrazone and anhydrous zinc chloride (30%; b. p. 125—133°/3·75 mm.) (lit.,[18] b. p. 150—156°/20 mm.).

Treatment of n-Butyraldehyde Phenylhydrazone with Concentrated Sulphuric Acid in Ethanol.—n-Butyraldehyde phenylhydrazone (0·33 g.) was added to concentrated sulphuric acid (1·2 ml.) in dry ethanol (10·8 ml.) at 50° under nitrogen. The temperature was kept at 50° and the colour changed from pale yellow to bright yellow during 3 min. At this stage, the mixture was rapidly cooled in ice and the reaction was quenched by the addition of sodium carbonate (2·5 g.) in water (10 ml.). The mixture was poured into water (150 ml.) and the product was isolated with ether. No 1-phenylazobutane was obtained on chromatography of the crude product on alumina.

Use of Boron Trifluoride–Ether Complex to effect Fischer Indole Syntheses.—The procedure was that described by Snyder and Smith.[14]

(*a*) 1,2,3,4-*Tetrahydrocarbazole.* Boron trifluoride–ether complex (0·755 g.) was added to cyclohexanone phenylhydrazone (1·00 g.) in glacial acetic acid (2·5 ml.). The solution *immediately* turned cherry-red and became warm. On heating at 65°, the solution refluxed vigorously during 1—2 min. and became light brown. Boron trifluoride–ammonia was precipitated. The mixture was heated under reflux during a further 20 min. Isolation of the product in the manner described by Snyder and Smith [14] gave 1,2,3,4-tetrahydrocarbazole (0·65 g.; 76%), m. p. 119—121° (from methanol) (lit.,[14] m. p. 118°). In a control reaction, cyclohexanone phenylhydrazone (0·50 g.) in glacial acetic acid (1·25 ml.) was heated under reflux during 20 min. without the addition of boron trifluoride–ether. The solution changed to light brown and 1,2,3,4-tetrahydrocarbazole (0·38 g.; 86%), m. p. 117—120°, was isolated.

(*b*) 9-*Methyl*-1,2,3,4-*tetrahydrocarbazole.* Boron trifluoride–ether (0·378 g.) was added to cyclohexanone 1-methyl-1-phenylhydrazone [0·537 g.; b. p. 106—110/0·5 mm.; n_D^{26} 1·569 (lit.,[2] b. p. 126—127°/1·7 mm.; n_D^{20} 1·5703] in glacial acetic acid (1·25 ml.). After 2—3 min., the solution changed from yellow to medium reddish-brown accompanied by refluxing. Boron trifluoride–ammonia was precipitated. The mixture was heated under reflux during a further 20 min. Isolation of the product as described by Snyder and Smith [14] gave 9-methyl-1,2,3,4-tetrahydrocarbazole (0·255 g.; 52%), m. p. 47·5—49·5° (from ethanol) (lit.,[19] m. p. 50°).

Attempt to Isolate Phenylazocyclohexane from the Reaction of Cyclohexanone Phenylhydrazone with Boron Trifluoride–Ether Complex.—The addition of boron trifluoride–ether (0·38 g.) to the green solution obtained by dissolving cyclohexanone phenylhydrazone (0·50 g.) in glacial acetic acid (1·25 g.) produced a cherry-red solution with slight evolution of heat. The mixture was allowed to stand during 10 min. and was then poured into water (50 ml.) containing sodium carbonate (1·5 g.). Isolation of the product with ether gave a yellow solid (0·48 g.) which was mainly cyclohexanone phenylhydrazone and did not contain any 1,2,3,4-tetrahydrocarbazole or 1-hydroperoxy-1-phenylazocyclohexane as judged from its infrared spectrum. No phenylazocyclohexane was obtained on chromatography of the crude product on alumina. In a control work-up, phenylazocyclohexane (0·10 g.) was recovered quantitatively after brief treatment with sodium carbonate (0·3 g.) in water (10 ml.).

Treatment of Phenylazocyclohexane wtih Boron Trifluoride–Ether Complex.—Boron trifluoride–ether (0·38 g.) was added to phenylazocyclohexane (0·5 g.) in glacial acetic acid (1·25 ml.). The colour of the solution changed from orange-yellow to cherry-red during 10 min. with slight evolution of heat. At this stage, the mixture was poured into water (50 ml.) containing sodium carbonate (1·5 g.) and the product was isolated with ether. From its infrared spectrum, the product appeared to be largely cyclohexanone phenylhydrazone. A small amount (0·034 g.) of phenylazocyclohexane was also isolated by chromatography of the crude product on alumina.

Treatment of Phenylazocyclohexane with Acetic Acid.—Phenylazocyclohexane (0·50 g.) in glacial acetic acid (1·25 ml.) was heated under reflux during 20 min. The solution changed from yellow to brown. After diluting with glacial acetic acid (0·5 ml.), the product was allowed to crystallise. The filtrate was reheated, diluted with hot water, and on cooling, more product crystallised. The combined product was recrystallised to give 1,2,3,4-tetrahydrocarbazole (0·36 g.; 80%), m. p. 117·5—120° (from methanol).

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[18] R. H. Cornforth and R. Robinson, *J.*, 1942, 680.
[19] W. H. Perkin and S. G. P. Plant, *J.*, 1921, 1825.