**Reactive Intermediates. Part XVI.** Dihydrobenz[cd]indazoles and Attempted Routes to Benz[cd]indazole

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Attempted synthesis of 1,2-dihydrobenz[cd]indazole from dimethyl 1,2-dihydrobenz[cd]indazole-1,2-dicarboxylate yielded only the more stable 1,3- and 1,5-dihydro-forms, (7) and (8), with the indazole rather than the naphthalene nucleus aromatic. These indazoles can be reconverted into NN-disubstituted dihydrobenzindazole derivatives but cannot be oxidised to benz[cd]indazole. Several other unsuccessful attempts to obtain the elusive benz[cd]indazole system are described.

**BENZ[cd]INDAZOLE** (1) is of interest as a simple, as yet unreported,† heterocyclic system, particularly since its thermolysis or photolysis might lead to different electronic states of the meta-dehydroaromatic species, 1,8-dehydronaphthalene.‡ peri-Substituted naphthalene compounds have recently been reviewed by Balasubramaniyan§ and it would appear that strain in molecules such as (1) should not be prohibitive. In certain acenaphthene derivatives the distortion of the naphthalene nucleus can be considerable. The only authenticated examples of the benzindazole system are the mono (2) and di-N-oxide (3) obtained by pyrolysis of 1-azido-8-nitronaphthalene and by peroxy-acid oxidation of 1,8-diaminonaphthalene.

A promising route to benz[cd]indazole would seem to be oxidation of its dihydro-derivative (4; R¹ = R² = H). 1,2-Dihydrobenz[cd]indazole has been reported previously by Vorozhtsov and Koslov⁷ as being obtained from the reduction of 1,8-dinitronaphthalene. More recently Beecken⁸ claimed to have obtained an identical product from the thiadiazine (5) by reduction and by adsorption on neutral alumina. We were unable to repeat the Russian work and, independently, Hoffmann⁹ has shown that the compound reported by Beecken is the dimethyldehydroperimidine (6). In our hands, 1,8-diaminonaphthalene was always the primary product isolated from Beecken's reactions in the absence of acetone. The dehydroperimidine (6) is formed rapidly from 1,8-diaminonaphthalene and acetone on a neutral alumina column and Beecken's product almost certainly arose in this way.

We have previously reported the NN-diester (4; R¹ = R² = CO₂Me), obtained from cycloaddition of 1,8-dehydronaphthalene to dimethyl azodicarboxylate,⁴ as the only authenticated example of a dihydrobenzindazole. Although only small amounts of the diester were available from this reaction, its hydrolysis and decarboxylation seemed an ideal route to the parent dihydrobenzindazole (4; R¹ = R² = H). However, treatment of the colourless diester (4; R¹ = R² = CO₂Me) with ethanolic potassium hydroxide rapidly gave a deep purple solution from which two colourless isomeric compounds, C₁₀H₈N₂, were isolated. These isomers were separable by preparative t.l.c. but were inter-

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‡ Ekstrand first suggested a benz[cd]indazole type of structure as a possibility for a product of partial reduction of 4,5-dinitro-1-naphthoic acid.
⁷ N. N. Vorozhtsov and V. V. Koslov, J. Gen. Chem. (U.S.S.R.), 1937, 7, 739.
⁹ R. W. Hoffmann, personal communication.
converted slowly at room temperature and rapidly on heating alone or in the presence of acid or base. The

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\begin{align*}
(1) & \quad \text{(1)} \\
(2) & \quad \text{(2)} \\
(3) & \quad \text{(3)} \\
(4) & \quad \text{(4)} \\
(5) & \quad \text{(5)} \\
(6) & \quad \text{(6)} \\
(7) & \quad \text{(7)} \\
(8) & \quad \text{(8)} \\
(9) & \quad \text{(9)} \\
(10) & \quad \text{(10)} \\
(11) & \quad \text{(11)}
\end{align*}
\]

i.r., n.m.r., and mass spectral data for both isomers were very similar and accorded with the two indazole structures (7) and (8). The u.v. spectra were significantly different but not diagnostic and at present a definite assignment of either structure (7) or (8) to one particular isomer is not possible. Cryoscopic molecular weight determination indicated typical indazole association behaviour\(^{10}\) in non-polar solvents. Compounds (7) and (8) were only moderately stable and decomposed, particularly in solution, to give intensely coloured polymers; indeed the formation of a deep purple colouration is diagnostic of the presence of these substances. Alder, Niazi, and Whiting\(^6\) obtained a very similar mixture of (7) and (8) by reduction of the N-oxides (2) and (3). It appears that dihydrobenzindazole (4; \(R^1 = R^2 = H\)) prefers to exist in the thermodynamically more stable tautomeric forms which have an aromatic indazole system with a three-atom peri-bridge, rather than a naphthalene system with a two-atom peri-bridge.

It is tempting to speculate that this type of tautomerism of 1,8-bridged naphthalenes may be general (see ref. \(^{11}\) for a carbocyclic example). However the n.m.r. spectrum of dihydrobenz[cd]indole (9) indicates that it exists in the form shown, although, perhaps significantly, it readily decomposes to purple polymers as do the indazoles.

Further support for the proposed structures (7) and (8) came from the formation of an identical mixture by diazotisation of 5,8-dihydro-1-naphthylamine, in a standard type of indazole preparation. The best procedure involved decomposition of the diazonium chloride in chloroform containing equimolar amounts of triethylamine and acetic acid at room temperature for 24 h. Yields were however low and variable but the directness of the approach made this a convenient source of compounds (7) and (8). The vapour phase pyrolysis of 1-amino-8-azidonaphthalene provides a third route to the dihydrobenzindazoles (7) and (8). Insertion of the nitrene into the adjacent peri-amino N-H bond only proceeds smoothly in the gas phase at high temperature, and numerous pyrolysces and photolyses in solution gave no trace of the indazoles (see following paper).

In view of the possibility of a mobile tautomeric equilibrium (4) \(\rightleftharpoons\) (7) \(\rightleftharpoons\) (8), attempts were made to convert the indazoles (7) and (8) into NN-disubstituted derivatives of form (4). Treatment of the mixture of (7) and (8) with excess of methyl chloroformate in the presence of triethylamine gave dimethyl 1,2-dihydrobenz[cd]indazole-1,2-dicarboxylate (4; \(R^1 = \text{Me, } R^2 = \text{CO}_2\text{Me}\)), identical with that obtained by addition of 1,8-dehydronaphthalene to dimethyl azodicarboxylate, thus providing a new route to 1,2-dihydrobenzindazoles in three steps from 1-aminonaphthalene.

Treatment with phthaloyl chloride gave the NN-disubstituted derivative (10) in low yield, but other di-N-substitution reactions were less successful. Thus use of excess of benzoxy chloride, or of phenacyl bromide, gave only the mono N-substituted derivatives. No indication of a dimethyl derivative was found on treatment with dimethyl sulphate. Other routes to NN-dialkyldihydrobenz[cd]indazoles, such as generation of 1,8-dehydronaphthalene in the presence of azoisobutane, and reduction of the diester (4; \(R^1 = R^2 = \text{CO}_2\text{Me}\)) and the N-acetyl-N-methyl derivative (4; \(R^1 = \text{Me, } R^2 = \text{Ac}\)) (see following paper) with lithium aluminium hydride and diborane also failed.

Although 1,2-dihydrobenz[cd]indazole (4; \(R^1 = R^2 = \text{H}\)) itself was not available it seemed possible that oxidation of its tautomers (7) and (8) could lead to benz[cd]-indazole (1). However oxidations [with lead tetaacetate, mercury(II) oxide, silver(II) oxide, manganese dioxide, or t-butyl hypochlorite] and dehydrogenations (with N-bromosuccinimide, dichlorodicyano-o-benzquinone, and palladium in \(p\)-xylene) under a variety of conditions gave no isolable, stable product. Furthermore, no evidence was obtained from appropriate trapping experiments for 1,8-dehydronaphthalene, which might have been generated by spontaneous decompositions of benz[cd]indazole. Finally attempts to intercept benz[cd]indazole, assuming it to be a strained, highly
reactive cis-azo-compound also failed. Thus no adduct was isolated from oxidations in 2,3-dimethylbutadiene or in the presence of tetraphenylcyclopentadienone (cf. cis-azobenzene) and no [2 + 2] adduct was obtained from oxidations in the presence of diphenylketen. Analogous attempts to isolate or trap benz[cd]indazole or to detect, 1,8-dehydroazaphthalene in the deoxygenation of the mono- (2) and di-N-oxide (3) with phosphorus trichloride, triethyl phosphate, and dichlorocarbene also failed. Our own observations therefore support those reported independently by Alder, Niazl, and Whiting.

Our numerous other attempts to obtain benz[cd]-indazole were directed to forming the internal peri-azo-linkage by standard azo-compound syntheses from 1,8-disubstituted naphthalenes, although an attempt to prepare (1) by reduction of 1,8-dinitronaphthalene with carbon monoxide and iron pentacarbonyl (reagents which normally give good yields of azo-compounds) failed. Oxidation of 1,8-diaminonaphthalene under a variety of conditions was unsuccessful (see also ref. 6). Treatment with manganese dioxide gave only the intermolecular azo-derivative 8,8'-diamino-1,1'-azonaphthalene in low yield, and other oxidants gave only intractable material. Pyrolysis and sensitised and unsensitized photolysis of 1,8-diazidonaphthalene gave only polymeric material and small amounts of 1,8-diaminonaphthalene (see also ref. 6). The failure to obtain benzindazole by this method is analogous to the failure to obtain the known, stable benzo[c]cinnoline from 2,2'-diazidobiphenyl. Standard attempts to convert 1-amino-8-nitronaphthalene into 1-amino-8-nitroanaphthalene and hence into benz[cd]indazole also failed. More speculative routes were equally unsuccessful. Oxidation of 2-aminonaphtho[1,8-de]triazine (11) could lead to loss of 1 mol of nitrogen by analogy with similar oxidation of 2-aminobenzotriazoles where ring opening occurs to give cis,cis-1,4-dicyanoazabutadienides. Since such ring opening is impossible for 2-aminonaphthotriazine, collapse to form benzo[c]indazole was detected. The attempted autoxidation of NN'-bistriphenylphosphorylidenenaphthalene-1,8-diamine failed because of its stability to oxidation; the analogous bisphosphonate readily gives acenaphthylene.

EXPERIMENTAL

The petroleum refers to the fraction of b.p. 40—60°.

1,3- and 1,5-Dihydrobenz[cd]indazoles (7) and (8).—(a) From dimethyl 1,2-dihydrobenz[cd]indazole-1,2-dicarboxylate. A mixture of dimethyl 1,2-dihydrobenz[cd]indazole-1,2-dicarboxylate (500 mg) and ethanolic 0.5-M-sodium hydroxide (10 ml) was left for 2 h under nitrogen. The resulting purple solution was poured into water (250 ml) and extracted with ether (3 × 75 ml). The combined extracts were dried (MgSO₄) and evaporated to give a mixture of 1,3- and 1,5-dihydrobenzindazoles (7) and (8) (71 mg, 40%).

(b) From 5,8-dihydro-1-naphthylamine. (i) 5,8-Dihydro-1-naphthylamine hydrochloride (5 g, 0.0275 mol) was suspended in acetic acid (50 ml) and pentyl nitrite (4 ml 0.0295 mole) was added during 10 min while the temperature was kept as low as possible. After a further 10 min, cold ether (400 ml; —20°) was added to give a precipitate of the diazoniun chloride. The ether was decanted and a solution of triethylamine (2 g) and acetic acid (1.2 g) in chloroform (200 ml), cooled to —20°, was added to the diazonium chloride. The mixture was then set aside in the dark under nitrogen at room temperature for 15 h. The solvent was evaporated off and the residue was extracted with 2N-hydrochloric acid (2 × 50 ml). The acid extracts were neutralised with sodium carbonate and re-extracted with ether. After drying, evaporation gave an identical mixture of 1,3- and 1,5-dihydrobenzindazoles (12%) (after sublimation). (ii) 1-Acetamido-5,8-dihydrobenzophenanthraquinone (5 g) was dissolved in hot acetic anhydride (50 ml); the solution was then cooled to give a suspension. Dry nitrosyl chloride was passed into the suspension, maintained at 0—5°, until a clear solution was obtained. This was poured into ice-water (500 ml) to give an oil which solidified to a pale yellow solid after washing with water. This solid was dissolved in benzene (50 ml) and after being dried (MgSO₄) the solution was refluxed for 1 h under nitrogen. The benzene was then evaporated off and the residue treated as before to give a mixture of 1,3- and 1,5-dihydrobenzindazoles (11%).

Separation of 1,3- and 1,5-Dihydrobenz[cd]indazoles (7) and (8).—This was carried out by preparative t.l.c. on silica gel under nitrogen. The plate was eluted three times with ether to give a pure separation. The separated isomers, in their order of elution, had the following characteristics: (i) m.p. 148—151° (decomp.); λ max 3160 br cm⁻¹ (NH, becoming sharp in dilute solution); λ max 328 br (log ε 3.81), 310 (3.88), and 225 (4.20) nm, τ 1-0 br (1H, s, NH), 2-5—4.0 (5H, m, aromatic and vinyl H), and 6-1 br (unsolved m, 2H, allylic H, m/e 156); (ii) m.p. 153—156° (decomp.); λ max 3160 br cm⁻¹ (NH, becoming sharp in dilute solution); λ max 337 (log ε 3.67), 323 (3.76), 311 (3.60), 298 (3.46), 287 (3.34), and 225 (3.98) nm, τ 0-85 br (1H, s, NH), 2-5—4.0 (5H, m, aromatic and vinyl H), and 6-1 br (unsolved m, 2H, allylic H, m/e 156).

Osmometric molecular weight determinations carried out on the mixture of (7) and (8) gave the following results (molar concentration, apparent molecular weight, association of monomer): 0.022, 158, 1-0; 0.068, 184, 1-2; 0.123, 198, 1.3.

Dihydrobenzindazoles (7) and (8) refers to the mixture of 1,3- and 1,5-dihydroisomers obtained by sublimation of the crude reaction product. Dimethyl 1,2-Dihydrobenz[cd]indazole-1,2-dicarboxylate (4; R¹ = R² = CO₂Me).—Methyl chloroformate (310 mg, 3.3 mmol) in methylene chloride (2.5 ml) was added dropwise below 5° to a mixture of dihydrobenzindazoles (7) and (8).


Sublimation followed by crystallisation from benzene gave needles, m.p. 156—158° (sealed tube) (Found: C, 77.2; H, 5.2; N, 17.4). Calc. for C₁₉H₁₄N₂: C, 76.9; H, 5.15; N, 17.9%.

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(250 mg, 1-6 mmol) and triethylamine (350 mg, 3-5 mmol) in methylene chloride (5 ml). The mixture was allowed to warm to room temperature and left for 1-5 h. Evaporation left a residue which was subjected to preparative t.l.c. on silica gel. Elution with 1:1 ether–petroleum gave dimethyl 1,2-dihydrobenz[c]indazole-1,2-dicarboxylate (25%), m.p. and m.p. of dimethyl 128–130° (lit., 131–132°).

**Naphtho[1,8′:3,4,5]pyrazolo[1,2-b:6,7-diphenylphthalazine-8,13-dione**

(10).—A mixture of dihydrobenz[c]indazoles (7) and (8) (135 mg) and phthaloyl chloride (177 mg) was maintained at 100° for 1 h. The resulting mixture was chromatographed on silica gel. Elution with 30% ether–petroleum gave the naphthopyrazolophthalazine (20%), pale yellow needles (from ether–petroleum), m.p. 239–240° (Found: C, 74.8; H, 3.4; N, 9.1. C_{34}H_{30}N_{8}O_{2} requires C, 75.7; H, 3.5; N, 9.8%). vmax 1670 cm⁻¹ (C=O), m/e 286 (required M, 286).

**Benzosylation of Dihydrobenz[c]indazoles (7) and (8).**—Benzoyl chloride (150 mg) was added to a solution of dihydrobenz[c]indazoles (7) and (8) (150 mg) in methylene dichloride containing a little pyridine. After 2 h evaporation, followed by preparative t.l.c. of the residue, gave, on elution with 1:1 ether–petroleum, 1-benzoyl-1,3(5)-dihydrobenz[c]indazole (20%). This was a single homogeneous product (t.l.c.), m.p. 116–117° (from ether) (Found: C, 78.3; H, 5.0; N, 10.9. Calc. for C_{18}H_{16}N_{2}O: C, 78.8; H, 4.65; N, 10.2%). vmax 1670 cm⁻¹ (C=O), m/e 260 (required M, 260).

**Phenacylation of Dihydrobenz[c]indazoles (7) and (8).**—Phenacyl bromide (2.4 g, 0.012 mol) in benzene (10 ml) was added dropwise at room temperature to a mixture of dihydrobenzindazoles (7) and (8) (936 mg, 0.006 mol) in benzene (35 ml) containing pyridine (316 mg). After 30 min pyridine hydrobromide was filtered off and the benzene solution was washed with dilute hydrochloric acid to remove unchanged indazoles. Evaporation left a residue which was chromatographed on silica gel. Elution with 1:1 ether–petroleum gave 1-phenacyl-1,3(5)-dihydrobenz[c]indazole (17%). This was a single homogeneous product (t.l.c.), plates, m.p. 136–137° (from ether–petroleum) (Found: C, 78.2; H, 5.6; N, 10.3. Calc. for C_{18}H_{14}N_{2}O: C, 78.8; H, 5.15; N, 10.2%). vmax 1685 cm⁻¹ (C=O), m/e 286 (required M, 286).

**Diphenylacetylation of Dihydrobenz[c]indazoles (7) and (8).**—Excess of diphenylketen (3 mmol) was added to a solution of dihydrobenzindazoles (7) and (8) (150 mg) in methylene dichloride containing a little pyridine. After 2 h evaporation, followed by preparative t.l.c. of the residue, gave, on elution with 1:1 ether–petroleum, 1-benzoyl-1,3(5)-dihydrobenz[c]indazole (20%). This was a single homogeneous product (t.l.c.), plates, m.p. 116–117° (from ether) (Found: C, 78.3; H, 5.0; N, 10.9. Calc. for C_{18}H_{16}N_{2}O: C, 78.8; H, 4.65; N, 10.2%). vmax 1670 cm⁻¹ (C=O), m/e 260 (required M, 260).

**Chromatography of Naphtho[1,8-c]-1,2,6-thiadiazine.**—The thiazone in carbon tetrachloride solution was adsorbed onto a neutral alumina column. Elution with ether gave 1,8-diaminonaphthalene (70%), identical with an authentic sample. Similar adsorption followed by elution with acetone gave 2,3-dihydro-2,2-dimethylperimidine (6) (86%), m.p. 116–117° (Found: C, 78.6; H, 7.0; N, 14.3).


C_{13}H_{13}N_{2} requires C, 78.75; H, 7.1; N, 14.15%. vmax 3350 and 3280 cm⁻¹ (N–H), m/e 198 and 182 (M – CH_{2}).

1,8-Diaminonaphthalene was adsorbed on to neutral alumina. Elution with acetone gave an identical sample of 2,3-dihydro-2,2-dimethylperimidine (76%).

1,8-Diachidazonaphthalene.—Hydrogen chloride was passed into a solution of 1-amino-8-azidonaphthalene (552 mg, 3 mmol) in ether to give a precipitate of the amine hydrochloride. This was filtered off and suspended in 0.1N-hydrochloric acid (30 ml, 3 mmol). Sodium nitrite (210 mg, 3 mmol) in water (10 ml) was added dropwise to this suspension and the resulting solution was treated with sodium azide (260 mg, 4 mmol). The precipitate was collected and recrystallised from ether–petroleum to give 1,8-diachidazonaphthalene (450 mg, 80%), needles, m.p. 127° (lit., 199–100°) (Found: C, 57.2; H, 3.0; N, 39.7. C_{19}H_{14}N_{4} requires C, 57.1; H, 2.9; N, 40.0%).

The diazide was also prepared directly from 1,8-diaminonaphthalene by basically the same procedure as that reported by Hoffmann.

Pyrolysis and photolysis gave only intractable polymeric material.

NN'-Bistriphenylphosphoranylidenedi benz-1,8-diamine.—(a) From 1,8-diaminonaphthalene. Triphenyl phosphine (13.1 g, 0.05 mol) in dry benzene (140 ml) was stirred at 0° while a solution of bromine (8 g, 0.05 mol) in benzene (20 ml) was added under nitrogen. Triethylamine (10.1 g, 0.1 mol) in benzene (20 ml) was added at 0–5° followed by 1,8-diaminonaphthalene (3.95 g, 0.025 mol). The mixture was heated to 80° for 20 min, cooled, and then filtered. The residue was warmed with 2N-sodium hydroxide at 40–45° for 5 min, causing the grey solid to turn yellow. The bisphosphoranylidenedi benzine (14 g, 82%) was filtered off. Recrystallisation was unsatisfactory; reprecipitation from chloroform solution by ether gave a greenish yellow solid, m.p. 275–280° (decomp.) (Found: C, 81.2; H, 5.5; N, 4.0. C_{41}H_{27}N_{4}P_{2} requires C, 81.4; H, 4.1%).

(b) From 1,8-diachidazonaphthalene. Triphenylphosphine (3.75 g, 14.3 mmol) in benzene (40 ml) was added dropwise to 1,8-diachidazonaphthalene (1.5 g, 7.1 mmol) in benzene (50 ml). The mixture was refluxed for 15 min. On cooling a dark purple solid (750 mg) separated and was filtered off. Addition of ether to the filtrate gave greenish yellow crystals of the phosphoranylidenedi benzine (1 g, 20%).

Attempted purification of the product by chromatography on basic alumina gave 8-triphenylphosphoranylidenedi benz-1,8-naphthyamine, yellow crystals, m.p. 150–155° (Found: C, 80.6; H, 5.7; N, 6.5. C_{41}H_{27}N_{4}P requires C, 80.4; H, 5.1; N, 6.7%). vmax 3450 and 3230 cm⁻¹ (NH). This compound was also prepared directly (77%) from triphenylphosphine and 1-amino-8-azidonaphthalene, by the method of Mosby and Silva.

The bisphosphoranylidenedi benzine was recovered unchanged after oxygen was bubbled through its solution in dimethyl sulphoxide at 80° for 36 h.

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