1*H*- and 2*H*-Indazoles by Thermal and Photolytic Decomposition of *o*-Azidobenzoic Acid and *o*-Azidobenzaldehyde Derivatives

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Ethyl *o*-azidobenzimidate (6) and *o*-azidobenzamidine (7) on thermolysis yield 3-ethoxy- (9; X = OEt) and 3-amino-1*H*-indazole (9; X = NH_2), respectively. The former product is also obtained on irradiation of the imidate in methanol–tetrahydrofuran solution.

2-Aryl- and 2-heteroaryl-3-chloro-2*H*-indazoles have been prepared by the action of hot thionyl chloride on *o*-azidoanilides. The trichloro-2*H*-indazoles obtained by the action of phosphorus pentachloride on *o*-azidobenzanilide (12) and by the action of thionyl chloride on *N*-(*o*-azidobenzoyl)-2-aminopyridine have been identified as the 3,5,7-trichloro derivatives. The reductive dehalogenation, nitration, and reactivity of the halogen towards nucleophiles, of 3-chloro-2-phenyl-2*H*-indazole (19) are reported.

A new practicable synthesis of *o*-azidobenzaldehyde (31; X = O) is described. Thermolysis of its phenylhydrazone and semicarbazone derivatives yields 2*H*-indazoles.

The thermolysis of aryl azides bearing unsaturated *ortho* substituents is a useful route to many heterocycles. For example *o*-azido ketones, azo compounds, and nitroarenes yield 2,1-benzisoxazoles,[1] 2*H*-benzotriazoles,[2] and benzofuroxans [3] respectively. The low decomposition temperatures (<100 °C), the absence of typical ' nitrene by-products ' (azo compounds and amines),[4] and the low activation energies (E_a = 80—110 kJ mol^{-1}) of these cyclisations are indicative of anchimerically assisted loss of nitrogen, most probably *via* a pericyclic mechanism [5] of the type illustrated in formula (12a), rather than a discrete nitrene intermediate. Related, but not as mechanistically well defined,[6] are the syntheses of 2-aryl-2*H*-indazoles and 2-arylbenzimidazoles by the thermolysis of the anils (1; $R^1 = N_3$, R^2 = H) and (1; R^1 = H, $R^2 = N_3$) respectively.[7]

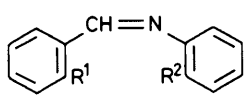
However, attempts to obtain 3-alkoxy- (3; R = OMe), 3-aryloxy- (3; R = OAr), 3-chloro- (3; R = Cl), or 3-amino-2,1-benzisoxazole (3; R = NH_2 or NHAr) by decomposition (thermal or photo) of *o*-azidobenzoates (2; R = OMe and OAr),[8,9] *o*-azidobenzoyl chlorides (2; R = Cl),[9] *o*-azidobenzamides † (2; R = NH_2), or benzanilides (2; R = NHAr) [10] have been singularly unsuccessful. In contrast, in the *p*-benzoquinone series thermal azide cyclisations onto an adjacent ester grouping are well established *e.g.* (4) ⟶ (5).[12,13]

We now report on the successful cyclisation of the nitrogen analogues of these wayward carboxylic acid derivatives, namely the *o*-azidobenzimidate (6) and the *o*-azidobenzamidine (7), and on further examples of the cyclisation of the elusive *o*-azidobenzimidoyl chlorides.[14]

The imidate (6) and the amidine hydrochloride (7) were prepared by standard procedures as outlined in Scheme 1.

The imidate decomposed in boiling *o*-dichlorobenzene to give 3-ethoxy-1*H*-indazole (9; X = OEt) in practicable yield, probably *via* a [1,5] H shift of the 2*H*-indazole (8) formed initially. Similarly, the amidine hydrochloride gave 3-amino-1*H*-indazole (9; X = NH_2) although in poor yield and accompanied by much tar.

The behaviour of the imidate is worthy of comment as the oxygen analogues (2; R = OMe, OEt, OPh, SPh, or OCOPh) on thermolysis yield only triplet nitrene derived products, *i.e.* azo compounds and aminobenzoates.[8,9] Contrary behaviour



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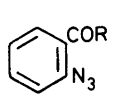

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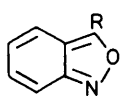

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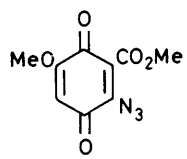

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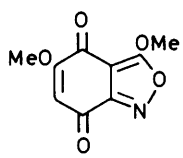


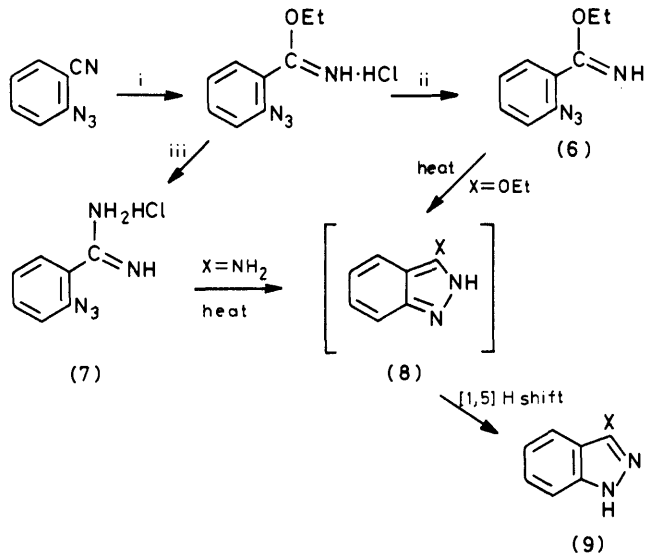
(5)

is also shown by the imidate during photolysis in methanol–tetrahydrofuran solution. Unlike methyl *o*-azidobenzoate (2; R = OMe), which furnishes methyl 2-methoxy-3*H*-azepine-3-carboxylate,[15] the imidate again yields only 3-ethoxy-1*H*-indazole.

Dyall [5] has discussed the reluctance of *o*-azido esters to yield 3-alkoxy-2,1-benzisoxazoles in terms of the loss of resonance energy of the ester function on going to the transition state, and the delocalisation energy of the resulting *o*-quinonoid heterocycle. It may be that the success of the imidate and amidine cyclisations reflects the formation of the fully benzenoid 1*H*-indazoles rather than the *o*-quinonoid 2*H*-isomers. Efforts to substantiate this point were thwarted, however, by the fact that all attempts to synthesise *N*-substituted imidates (10), which would be expected to cyclise to 2-substituted 3-alkoxy-2*H*-indazoles (11), from the *o*-azidobenzimidoyl chlorides (12a), were unsuccessful owing to the ease with which the imidoyl chlorides cyclised to 2-aryl-3-chloro-2*H*-indazoles.[14]

Obviously, the formation of a 2*H*-indazole is no handicap in these cyclisations and the behaviour of the imidoyl chlorides is in stark contrast to that of the *o*-azidobenzoyl chlorides which, in our hands, have so far yielded only tars and trace amounts of uncharacterised materials.[9] These results highlight the greater receptiveness of C=N over that of C=O to enter into reaction with azides (or nitrenes), and is in accord with the behaviour of imidoyl azides, which in many cases exist as the tetrazole form,[16] whereas, to the best of our knowledge, acyl azides show no tendency towards oxatriazole formation.

† A low yield (15%) of 3-amino-6-nitro-2,1-benzisoxazole has been reported [11] from the irradiation of 2-azido-4-nitrobenzamide in methanol.

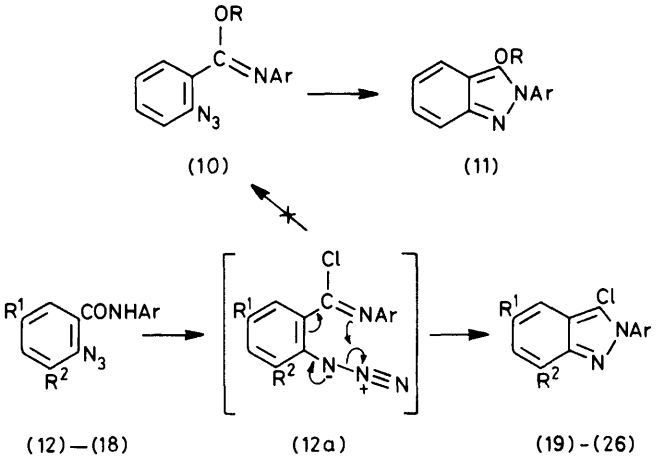


Scheme 1. *Reagents:* i, $HCl_{(g)}$–MeOH, 0 °C; ii, Et_3N, Et_2O; iii, 10M-NH_3–MeOH

derivative was confirmed by synthesis from the azidodichlorobenzanilide (13) with hot thionyl chloride.* Other likely structures, *viz.* (21) and (22) for the trichloro compound, were eliminated on the basis of their non-identity with the products obtained from the cyclisation of the azidochloroanilides (14) and (15), respectively, with thionyl chloride. Extraneous chlorination of the indazole nucleus has been noted [18] during the preparation of indazolinones by cyclisation of *o*-azobenzene carboxylic acids with phosphorus pentachloride.

The behaviour of the *o*-azidobenzoylpyridylamine (16) was unexpected in that of all the anilides studied it alone gave a trichloroindazole on treatment with hot thionyl chloride. Alternative synthesis from the azidodichloropyridylamide (17) confirmed its structure as the 3,5,7-trichloro derivative (23).

We were interested in the nucleophilic reactivity of the chlorine in 3-chloro-2-aryl-2*H*-indazoles, particularly as the analogous 3-chloro-1*H*-indazoles, unlike 2-chlorobenzimidazoles,[20] are reported [21] to be resistant towards hydrolysis. As vinylogous imidoyl halides, 3-chloro-2-aryl-2*H*-indazoles might be expected to show some reactivity towards halogen displacement *via* stabilisation of the transition state as shown in Scheme 3. Against this are the results of SCF calculations which indicate that C-3 is an electron-rich centre; this conclusion is borne out by experiment, *e.g.* electrophilic halogenation occurs readily at the 3-position.[21a]



(12) $R^1 = R^2 = H$, Ar = Ph
(13) $R^1 = R^2 = Cl$, Ar = Ph
(14) $R^1 = Cl$, $R^2 = H$, Ar = *p*-ClC_6H_4
(15) $R^1 = R^2 = H$, Ar = 2,4-$Cl_2C_6H_3$
(16) $R^1 = R^2 = H$, Ar = 2-pyridyl
(17) $R^1 = R^2 = Cl$, Ar = 2-pyridyl
(18) $R^1 = NO_2$, $R^2 = H$, Ar = *p*-$NO_2C_6H_4$
(19) $R^1 = R^2 = H$, Ar = Ph
(20) $R^1 = R^2 = Cl$, Ar = Ph
(21) $R^1 = Cl$, $R^2 = H$, Ar = *p*-ClC_6H_4
(22) $R^1 = R^2 = H$, Ar = 2,4-$Cl_2C_6H_3$
(23) $R^1 = R^2 = Cl$, Ar = 2-pyridyl
(24) $R^1 = NO_2$, $R^2 = H$, Ar = *p*-$NO_2C_6H_4$
(25) $R^1 = R^2 = H$, Ar = *o*-$NO_2C_6H_4$
(26) $R^1 = R^2 = H$, Ar = *p*-MeC_6H_4

Scheme 2.

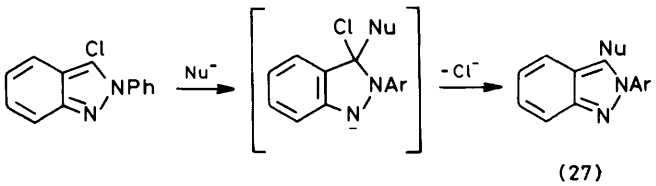
Imidoyl chlorides are usually obtained by the action of halogenating agents (*e.g.* $SOCl_2$, $POCl_3$, or PCl_5) on benzanilides.[17] We have found,[14] however, that *o*-azidobenzanilide (12) with hot thionyl chloride yields not the expected *o*-azidobenzimidoyl chlorides (12a) but directly and in excellent yield the 2-aryl-3-chloro-2*H*-indazoles (19), most probably *via* an assisted loss of nitrogen as illustrated in Scheme 2.

This cyclisation, which constitutes a useful synthesis of the 2*H*-indazole system, can also be achieved, although in reduced yield, *e.g.* (19) (44%), with phosphorus oxychloride. Prolonged (24 h) treatment of the *o*-azidobenzanilide (12) with phosphorus pentachloride at 100 °C, however, is accompanied by further chlorination and yields the known 3,5,7-trichloro-2-phenyl-2*H*-indazole (20). The structure of the trichloro

In the event, we found that 3-chloro-2-phenyl-2*H*-indazole suffers displacement of chloride on prolonged boiling with sodium ethoxide in ethanol, and with pyrrolidine in dimethylformamide, but not with potassium hydroxide in ethanol (with or without 18-crown-6), benzylamine in boiling dimethylformamide, thiophenol in methanol, or ammonia in phenol at 180 °C.[22]

Nitration of 3-chloro-2-phenyl-2*H*-indazole with a mixture of fuming nitric acid and concentrated sulphuric acid at 0 °C

* Synthesis was prompted by a discrepancy (174 °C [18] and 205 °C [19]) in the literature m.p. of this compound.



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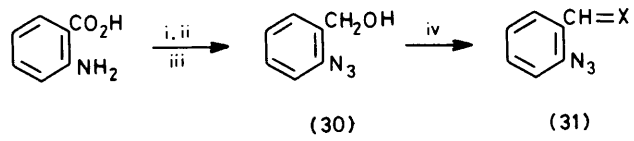
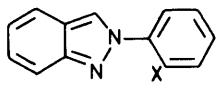
Scheme 3.



(30) (31)

Scheme 4. *Reagents:* i, $LiAlH_4$, Et_2O; ii, $NaNO_2$–HCl, 0 °C; iii, NaN_3–NaOAc–H_2O; iv, $C_5H_5NHCrO_3Cl$



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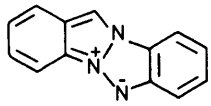

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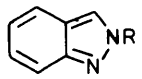

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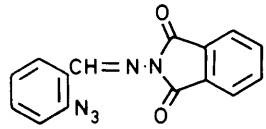

(33)

produced a dinitro derivative, the structure of which was shown by alternative synthesis to be not the known 3-chloro-5,7-dinitro derivative, but 3-chloro-5-nitro-2-(*p*-nitrophenyl)-2*H*-indazole (24). On the basis of this result it is tempting to suggest that the two uncharacterised isomeric mononitro derivatives obtained by the action of cold fuming nitric acid on 2-phenyl-2*H*-indazole [21b] are the 2-(*p*-nitrophenyl) and 5-nitro-2-phenyl derivatives.

Hydrodehalogenation of 3-chloro-2-aryl-2*H*-indazoles is readily achieved using zinc dust and acetic acid. Under these conditions 3-chloro-2-(*o*-nitrophenyl)-2*H*-indazole (25) suffers dehalogenation and reduction of the nitro group to give 2-(*o*-aminophenyl)-2*H*-indazole (28; X = NH_2). Diazotisation of the amine followed by azidation gave 2-(*o*-azidophenyl)-2*H*-indazole (28; X = N_3), the thermolysis of which to give the azapentalene (29) has recently been described.[23,24] Attempts to prepare azapentalenes by deoxygenation of 3-chloro-2-(*o*-nitrophenyl)-2*H*-indazole (25) with triethyl phosphite gave only tarry materials.

As mentioned earlier, the thermolysis of the anils of *o*-azidobenzaldehyde [7] is a useful route to 2-aryl-2*H*-indazoles, and recently the oximes of *o*-azidoacetophenones have been pyrolysed to yield 2-hydroxy-2*H*-indazoles.[25] We have extended this process to include the synthesis of 2-amino-2*H*-indazoles by thermolysing and/or photolysing the phenylhydrazone and semicarbazone derivatives of *o*-azidobenzaldehyde.

o-Azidobenzaldehyde has been prepared either by diazotisation of *o*-aminobenzaldehyde oxime [26] or by hydrolysis of *o*-azidobenzaldehyde azine.[27] Both of these methods are somewhat tedious, particularly the former, which in our hands proved to be messy and unreliable. Consequently, we have developed a new, convenient, high-yield route to *o*-azidobenzaldehyde (31; X = O) as outlined in Scheme 4. Oxidation of *o*-azidobenzyl alcohol (30) with pyridinium chlorochromate [28] in dichloromethane furnishes *o*-azidobenzaldehyde in excellent yield (90%) and sufficiently pure for direct use

The phenylhydrazone (31; X = NNHPh) and semicarbazone (31; X = $NNHCONH_2$) derivatives were prepared by standard procedures. On thermolysis, the phenylhydrazone behaved as expected and gave 2-anilino-2*H*-indazole (32; R = NHPh) in useful yield (54%). In contrast, the semicarbazone gave not the expected ureido derivative (32; R = $NHCONH_2$) but 2-amino-2*H*-indazole (32; R = NH_2). Loss of the $CONH_2$ unit appears to be a thermal process, since on photolysis in methanol–tetrahydrofuran the semicarbazone did give the ureido derivative (32; R = $NHCONH_2$) albeit in low yield (14%). Its structure was confirmed by addition of 2-amino-2*H*-indazole, prepared from the phthalimide (33),[27] to potassium cyanate.

Experimental

I.r. and mass spectra were measured on a Perkin-Elmer 257 and an AEI MS12 or MS9 spectrometer, respectively. ^1H and ^{13}C N.m.r. spectra were recorded on a Perkin-Elmer R32 90 MHz and a Varian Associates CFT20 spectrometer, and were calibrated with reference to tetramethylsilane and deuteriochloroform, respectively, as internal standards.

Ethyl 2-Azidobenzimidate (6).—In a 50-ml two-necked flask fitted with a gas bubbler and a condenser with drying tube ($CaCl_2$), was placed a suspension of *o*-azidobenzonitrile [29] (0.88 g) in anhydrous ethanol (10 ml). The stirred suspension was cooled to 0 °C in an ice–salt bath and then hydrogen chloride was bubbled through the mixture until a clear solution was obtained (*ca.* 90 min). The gas flow was stopped, the flask stoppered, and the mixture allowed to stand overnight in the refrigerator. Addition of anhydrous diethyl ether (*ca.* 50 ml) to the ethanol solution brought about precipitation of *ethyl 2-azidobenzimidate hydrochloride* (1 g) as white needles, m.p. 97 °C (decomp.) (Found: C, 47.7; H, 4.9; N, 24.7. $C_9H_{11}ClN_4O$ requires C, 47.42; H, 4.92; N, 24.79%); $\nu_{max.}$ (Nujol) 2 800—2 600 ($NH_2^+Cl^-$), 2 145 (N_3), 1 650 cm^{-1} (C=N).

Treatment of a suspension of the hydrochloride (0.5 g) in diethyl ether with triethylamine liberated *ethyl 2-azidobenzimidate* (6) which, after removal of triethylamine hydrochloride (by filtration) and ether (by distillation), was obtained as an orange oil (0.35 g, 84%), $\nu_{max.}$ (Nujol) 3 450 (NH), 2 140 (N_3), 1 640 cm^{-1} (C=N); δ($CDCl_3$) 1.2—1.3 (3 H, t, Me), 4.1—4.4 (2 H, q, CH_2), 7.0—8.0 (4 H, m, ArH), and 8.3 (1 H, bs, NH).

2-Azidobenzamidine Hydrochloride (7).—Ethyl 2-azidobenzimidate (1 g) was added to a stirred 10M-methanolic ammonia solution (15 ml). After 1 h the solution was evaporated to leave a brown residue. Recrystallisation of the residue from ethanol–methyl ethyl ketone gave *2-azidobenzamidine hydrochloride* (7) (0.52 g) as white prisms, m.p. 175—180 °C (decomp.) (Found: C, 42.7; H, 4.2; N, 35.2. $C_7H_8ClN_5$ requires C, 42.54; H, 4.08; N, 35.43%), $\nu_{max.}$ (Nujol) 2 120 (N_3), 1 670 cm^{-1} (C=N).

3-Ethoxy-1H-indazole (9; X = OEt).—(*a*) Ethyl 2-azidobenzimidate (6) (2 g) in *o*-dichlorobenzene (50 ml) was heated under reflux (178 °C) for 30 min. Removal of the solvent under reduced pressure followed by purification of the semisolid residue on an alumina column, with benzene–diethyl ether (3 : 1) as eluant, gave *3-ethoxy-1H-indazole* (9; X = OEt) (1.2 g) as a pale-brown solid which crystallised from benzene or toluene as off-white rosettes, m.p. 83 °C (Found: C, 66.5;

Table. *o*-Azidobenzanilides (13)—(17) and 2-aryl- and 2-heteroaryl-3-chloro-2*H*-indazoles (20)—(24)

Compd.	M.p. (°C)	Yield (%)	Found (%)			Molecular formula	Requires (%)		
			C	H	N		C	H	N
(13)	108 [a]	79	51.1	2.8	18.1	$C_{13}H_8Cl_2N_4O$	50.8	2.6	18.2
(14)	129 [a]	68	50.8	2.6	18.6	$C_{13}H_8Cl_2N_4O$	50.8	2.6	18.2
(15)	111 [b]	72	50.6	2.9	18.3	$C_{13}H_8Cl_2N_4O$	50.8	2.6	18.2
(16)	118 [b]	75	46.8	2.3	22.7	$C_{12}H_7Cl_2N_5O$	46.8	2.3	22.7
(17)	168 [a]	75	47.6	2.9	25.6	$C_{13}H_8N_6O_5$	47.6	2.45	25.6
(20)	168 [c]	60	52.3	2.4	9.4	$C_{13}H_7Cl_3N_2$	52.5	2.4	9.4
(21)	163 [c]	71	52.2	2.3	9.2	$C_{13}H_7Cl_3N_2$	52.5	2.4	9.4
(22)	74 [c]	92	52.7	2.6	9.6	$C_{13}H_7Cl_3N_2$	52.5	2.4	9.4
(23)	205 [c]	67	48.1	2.2	14.3	$C_{12}H_6Cl_3N_3$	48.2	2.0	14.3
(24)	198 [d]	73	49.0	2.3	17.6	$C_{13}H_7ClN_4O_4$	49.0	2.2	17.6

[a] Pale-yellow crystals from ethanol. [b] White crystals from ethanol. [c] White crystals from light petroleum (b.p. 60—80 °C). [d] Pale-yellow crystals from toluene–light petroleum (b.p. 100—120 °C).

H, 6.2; N, 17.3. $C_9H_{10}N_2O$ requires C, 66.64; H, 6.21; N, 17.27%), $\nu_{max.}$ (Nujol) 3 400 (NH), 1 620 cm^{-1} (C=N); δ(CCl_4) 12.02 (1 H, bs, NH), 7.65 (1 H, d, ArH, *J* 7.5 Hz), 7.4—6.8 (3 H, m, ArH), 4.35 (2 H, q, OCH_2), and 1.4 (3 H, t, Me); *m*/*z* 162 (M^+).

(*b*) Indazolinone [30] (1 g) was added to a stirred solution of triethyloxonium tetrafluoroborate [31] (1.7 g) in dichloromethane (50 ml). After 12 h the solvent was removed by distillation and the residue boiled with water (2 ml) for 5 min, and then cooled. 3-Ethoxy-1*H*-indazole (9; X = OEt) (0.4 g), m.p. 81 °C was obtained as a white solid identical with the product obtained by procedure (*a*).

(*c*) A solution of ethyl 2-azidobenzimidate (6) (1.1 g) in methanol (150 ml) and dry tetrahydrofuran (150 ml) was photolysed (110-W medium-pressure lamp with Pyrex filter) in a water-cooled Hanovia photochemical reactor under nitrogen, until ν(N_3) at 2 140 cm^{-1} had disappeared (*ca.* 4 h). The solvent was removed under reduced pressure and the oily residue distilled (Kügelrohr) to give 3-ethoxy-1*H*-indazole (0.45 g, 47%), b.p. 130—140 °C/0.5 Torr, as a pale-yellow oil which crystallised as pale-yellow rosettes, m.p. 81 °C.

3-*Amino*-1H-*indazole* (9; X = NH_2).—A suspension of 2-azidobenzamidine hydrochloride (7) (1.3 g) in *o*-dichlorobenzene (100 ml) was heated under reflux (178 °C) for 30 min. The resulting mixture was filtered in order to remove the black cindery residue, and the filtrate evaporated to dryness under reduced pressure. Purification of the residue on a silica column, with toluene–ethyl acetate (1 : 1) as eluant, gave 3-amino-1*H*-indazole as a pale-brown solid (0.03 g) which crystallised from light petroleum (b.p. 60—80 °C)–ethyl acetate, m.p. 152 °C. The product was identical with an authentic sample of 3-amino-1*H*-indazole prepared by the action of hydrazine hydrate on ethyl *o*-azidobenzoate.[30]

3,5,7-*Trichloro*-2-*phenyl*-2H-*indazole* (20).—A mixture of *o*-azidobenzanilide [14] (1.5 g) and phosphorus pentachloride (5 g) was heated on a boiling water bath for 16 h. The reaction mixture was cooled, poured onto crushed ice, and extracted with chloroform (3 × 25 ml). The chloroform extracts were dried ($MgSO_4$), the solvent removed under reduced pressure, and the residue chromatographed on alumina (toluene as eluant). 3,5,7-Trichloro-2-phenyl-2*H*-indazole (20) (1.2 g, 65%) was obtained as a white solid which crystallised from light petroleum (b.p. 60—80 °C), m.p. 168 °C (Found: C, 52.0; H, 2.4; N, 9.4. Calc. for $C_{13}H_7Cl_3N_2$: C, 52.47; H, 2.37; N, 9.41%) (lit., m.p. 174 °C [18] and 205 °C [19]).

When the reaction was stopped after 2 h, and worked up as directed above, a mixture of two products was obtained, the mass spectrum of which indicated the presence of a dichloro and a trichloro derivative.

Preparation of o-*Azidobenzoic Acids. General Method.*—2-*Azido*-3,5-*dichlorobenzoic acid.* To a solution of 2-amino-3,5-dichlorobenzoic acid (6.18 g) in concentrated hydrochloric acid (60 ml) and water (60 ml) was added dropwise a solution of sodium nitrite (2.3 g) in water (30 ml) at a rate such that the temperature of the reaction mixture remained below 5 °C. After completion of nitrite addition the diazonium solution was filtered (cold sinter) and added dropwise to a stirred solution of sodium azide (2 g) and sodium acetate (30 g) in water (60 ml). The yellow solution was stirred for 15 min, then acidified by addition of concentrated hydrochloric acid to give 2-*azido*-3,5-*dichlorobenzoic acid* (77%), which crystallised from toluene as white needles, m.p. 155 °C (Found: C, 36.5; H, 1.4; N, 18.2. $C_7H_3Cl_2N_3O_2$ requires C, 36.21; H, 1.30; N, 18.11%), $\nu_{max.}$ (Nujol) 2 120 (N_3), 1 680 cm^{-1} (C=O).

Prepared similarly were 2-*azido*-5-*chlorobenzoic acid* (70%), white prisms from toluene, m.p. 149 °C (Found: C, 42.5; H, 2.2; N, 21.4. $C_7H_4ClN_3O_2$ requires C, 42.55; H, 2.04; N, 21.26%) and 2-*azido*-5-*nitrobenzoic acid* (62%), white crystals from toluene, m.p. 151 °C; $\nu_{max.}$ (Nujol) 2 140 (N_3), 1 705 cm^{-1} (C=O); *m*/*z* 208 (M^+).

Preparation of o-*Azidobenzanilides.—General method.* The azidobenzoic acid (4 g) and freshly distilled thionyl chloride (15 ml) were heated under reflux for 2 h. The excess of thionyl chloride was removed by co-distillation with benzene (2 × 25 ml) to leave a residue of the *o*-azidobenzoyl chloride which was not purified further (**CAUTION**: it is most inadvisable to attempt the distillation of *o*-azidobenzoyl chlorides even under reduced pressure) but added dropwise to a stirred solution of the arylamine in pyridine (15—25 ml). The reaction mixture was stirred for 30 min at room temperature and then poured into water, whereupon the azidoanilide was precipitated. Physical and spectroscopic details of the azidoanilides are given in the Table.

N-(2-*Pyridyl*)-o-*azidobenzamide* (16). A solution of 3-(2-pyridyl)-1,2,3-benzotriazin-4(3*H*)-one (6.75 g) [32] and sodium azide (7.8 g) in glacial acetic acid (50 ml) was heated under reflux for 1 h. (**CAUTION**: this operation must be carried out in an efficient fume-hood as copious amounts of HN_3, a toxic gas, are evolved.) The cold reaction mixture was then basified ($NaHCO_3$) and extracted with chloroform (3 × 30 ml). The dried ($MgSO_4$) chloroform extracts were evaporated under reduced pressure to give N-(2-*pyridyl*)-o-*azidobenzamide* (16)

(68%) as a white solid which crystallised from light petroleum (b.p. 60—80 °C) as white prisms, m.p. 78—80 °C (Found: C, 60.3; H, 3.9; N, 29.3. $C_{12}H_9N_5O$ requires C, 60.25; H, 3.79; N, 29.27%); $\nu_{max.}$ (Nujol) 2 120 (N_3), 1 665 cm^{-1} (C=O).

3-*Chloro*-2-*aryl*-2H-*indazoles* (19)—(23).—The 3-chloro-2-aryl-2*H*-indazoles were prepared from the azidoanilides in hot thionyl chloride as described previously.[14] Analytical data are given in the Table.

3-*Ethoxy*-2-*phenyl*-2H-*indazole* (27; Nu = OEt, Ar = Ph).—3-Chloro-2-phenyl-2*H*-indazole (0.5 g) was heated under reflux for 8 h with a solution of sodium ethoxide [sodium (0.5 g) in ethanol (20 ml)]. The reaction mixture was cooled, and the solvent removed by distillation under reduced pressure. The residue was adsorbed onto alumina and chromatographed. Elution with toluene–light petroleum (b.p. 80—100 °C) (1 : 1) gave 3-*ethoxy*-2-*phenyl*-2H-*indazole* (0.52 g, 99%) as a pale-yellow oil, b.p. 180—185 °C/0.5 Torr (Found: C, 75.5; H, 5.8; N, 11.5. $C_{15}H_{14}N_2O$ requires C, 75.60; H, 5.92; N, 11.75%); δ($CDCl_3$) 7.0—8.0 (9 H, m, ArH), 4.2—4.7 (2 H, q, CH_2), and 1.2—1.5 (3 H, t, Me).

2-*Phenyl*-3-*pyrrolidinyl*-2H-*indazole* (27; Nu = C_4H_8N, Ar = Ph).—3-Chloro-2-phenyl-2*H*-indazole (0.5 g) was heated under reflux with an excess of pyrrolidine (5 ml) in dimethylformamide (10 ml) for 8 h. Treatment of the reaction mixture as in the previous experiment gave 2-*phenyl*-3-*pyrrolidinyl*-2H-*indazole* (0.37 g, 64%) as a yellow oil, b.p. 170—175 °C/0.5 Torr (Found: C, 77.3; H, 6.5; N, 15.9. $C_{17}H_{17}N_3$ requires C, 77.53; H, 6.50; N, 15.95%); δ($CDCl_3$) 7.1—7.8 (9 H, m, ArH), 3.2—3.5 [4 H, m, $N(CH_2)_2$], and 1.7—2.0 (4 H, m, CH_2CH_2).

On heating the 3-chloro-2-phenyl-2*H*-indazole (0.5 g) with KOH–MeOH, or with KOH–MeOH–18-crown-6, benzylamine–DMF, or thiophenol–MeOH under reflux for 24 h, or in phenol at 180 °C with ammonia for 2 h, only unchanged chloroindazole was obtained.

3-*Chloro*-2-(p-*nitrophenyl*)-5-*nitro*-2H-*indazole* (24).—To a stirred solution of 3-chloro-2-phenyl-2*H*-indazole (0.5 g) in concentrated sulphuric acid (5 ml) maintained at 0—5 °C was added dropwise during 5 min a mixture of concentrated sulphuric acid (2 ml) and fuming nitric acid (s.g. 1.5) (1 ml). The reaction mixture was stirred for 2 h then poured onto crushed ice (25 g) in order to precipitate the nitro compound as a pale-yellow solid. Isolation of the product by filtration and crystallisation from light petroleum (b.p. 100—120 °C)–toluene gave 3-*chloro*-5-*nitro*-2-(p-*nitrophenyl*)-2H-*indazole* (0.55 g, 79%) as pale-yellow prisms, m.p. 198 °C, identical (mixed m.p., superimposable i.r. spectrum) with the product (24) obtained by the action of hot thionyl chloride on the azidodinitroanilide (18).

2-(o-*Aminophenyl*)-2H-*indazole* (28; X = NH_2).—To a solution of 3-chloro-2-(*o*-nitrophenyl)-2*H*-indazole [14] (2.73 g) in glacial acetic acid (20 ml) was added zinc dust (3.9 g). The stirred mixture was heated under reflux for 2 h, filtered hot, and the residue washed with cold water (2 × 20 ml). The combined filtrate and water washings were diluted by addition of water (50 ml) and extracted with diethyl ether (3 × 25 ml). The ether extracts were dried ($MgSO_4$) and the ether removed by distillation, to leave the semi-solid product which was purified by column chromatography (Al_2O_3), with light petroleum (b.p. 40—60 °C) as eluant. 2-(*o*-Aminophenyl)-2*H*-indazole (1.2 g, 60%) crystallised from light petroleum (b.p. 60—80 °C) as white prisms, m.p. 92 °C (Found: C, 74.8; H, 4.9; N, 20.2. $C_{13}H_{11}N_3$ requires C, 74.62; H, 5.30; N, 20.08%) (lit.,[24] m.p. 136 °C). However, incorrect analysis figures are cited for this compound.

2-Phenyl-2*H*-indazole (90%), m.p. 82 °C (lit.,[33] m.p. 84 °C), and 2-(*p*-tolyl)-2*H*-indazole (87%), m.p. 98 °C (lit.,[34] m.p. 100 °C) were prepared similarly from 3-chloro-2-phenyl- and 3-chloro-2-(*p*-tolyl)-[14] 2*H*-indazole, respectively.

o-*Azidobenzaldehyde* (31; X = O).—*o*-Aminobenzyl alcohol (12 g), m.p. 81 °C, prepared by reduction of anthranilic acid with lithium aluminium hydride,[35] was diazotised and subsequently converted into *o*-azidobenzyl alcohol (11.26 g), m.p. 50—52 °C (lit., [36] m.p. 53 °C) by the method used for the preparation of 2-azido-3,5-dichlorobenzoic acid.

To a solution of the azidobenzyl alcohol (4.2 g) in dichloromethane (60 ml) was added, with stirring, a suspension of freshly prepared pyridinium chlorochromate (10.45 g) [28] in dichloromethane (60 ml). The reaction mixture became black and was stirred at room temperature until t.l.c. (alumina) indicated complete disappearance of the azido alcohol. Diethyl ether (200 ml) was then added to the reaction mixture and the mixture filtered through anhydrous $MgSO_4$. The black gum remaining in the reaction flask was extracted with boiling diethyl ether (2 × 50 ml). The filtrate and the combined ether extracts were evaporated to yield a semi-solid residue of *o*-azidobenzaldehyde. Purification by column chromatography (Al_2O_3), with light petroleum (b.p. 40—60 °C) as eluant, gave *o*-azidobenzaldehyde (3.7 g, 90%) as pale-yellow prisms, m.p. 34 °C (lit.,[26] m.p. 36.5 °C); $\nu_{max.}$ (Nujol) 2 130 (N_3), 1 700 cm^{-1} (C=O); phenylhydrazone, m.p. 97 °C (lit.,[26] m.p. 102 °C); *semicarbazone*, prisms (EtOH), m.p. 193 °C (Found: C, 47.0; H, 3.9; N, 40.7. $C_8H_8N_6O$ requires C, 47.05; H, 3.92; N, 41.17%); $\nu_{max.}$ (Nujol) 3 450, 3 300, 3 100 (NH), 2 130 (N_3), 1 690 cm^{-1} (C=O); *m/z* 204 (M^+).

2-*Anilino*-2H-*indazole* (32; R = NHPh).—*o*-Azidobenzaldehyde phenylhydrazone (1.5 g) was added in portions to boiling *o*-dichlorobenzene (25 ml) contained in a two-necked, round-bottomed flask. After being heated under reflux for 1 h, the reaction mixture was cooled, and the solvent removed under reduced pressure (40 °C/1—2 Torr). The residue was adsorbed onto alumina and purified by column chromatography. Elution with toluene–ethyl acetate (2 : 1) gave 2-anilino-2*H*-indazole as a pale-brown solid (0.72 g, 54%) which crystallised from benzene–light petroleum (b.p. 60—80 °C) as colourless needles, m.p. 165 °C (lit.,[37] m.p. 164 °C) (Found: C, 74.3; H, 5.3; N, 20.2. Calc. for $C_{13}H_{11}N_3$: C, 74.62; H, 5.29; N, 20.08%).

2-*Amino*-2H-*indazole* (32; R = NH_2).—*o*-Azidobenzaldehyde semicarbazone (1.5 g) was added in portions to boiling (230 °C) diphenyl ether. After being heated at this temperature for 5 min, the reaction mixture was cooled and treated as in the previous experiment. Purification of the product by column chromatography (Al_2O_3, ethyl acetate as eluant) gave 2-amino-2*H*-indazole (0.24 g, 25%), which crystallised from toluene as colourless plates, m.p. 98 °C (lit.,[27] m.p. 98 °C). The product was identical with a sample of 2-amino-2*H*-indazole prepared by the method of Anselme and Sakai.[27]

A similar result was obtained on thermolysing the semicarbazone in boiling 1-methylnaphthalene (b.p. 240 °C).

2-*Ureido*-2H-*indazole* (32; R = $NHCONH_2$).—(*a*) A solution of *o*-azidobenzaldehyde semicarbazone (0.8 g) in a mixture of methanol (40 ml) and tetrahydrofuran (40 ml) was irradiated using a 125-W medium-pressure mercury lamp and Pyrex filter, for 9 h. The solvent was removed under reduced pressure and the residue chromatographed on alumina.

Elution with ethyl acetate gave unchanged azide (0.1 g). Further elution with ethyl acetate–methanol gave 2-*ureido*-2H-*indazole* (0.2 g) as a white solid that crystallised from methanol, m.p. 205 °C (Found: C, 52.0; H, 5.7; N, 26.7. $C_8H_8N_4O$ requires C, 51.9; H, 5.7; N, 26.9%); $\nu_{max.}$ (Nujol) 3 350, 3 250, 3 170 (NH), 1 680 cm^{-1} (C=O). *m/z* 176 (M^+).

(*b*) To a solution of 2-amino-2*H*-indazole (0.5 g) in glacial acetic acid (3 ml) containing one drop of concentrated sulphuric acid, was added, with shaking, a solution of potassium cyanate (0.3 g) in water (2 ml). The reaction mixture was left overnight, and then filtered to yield 2-ureido-2*H*-indazole as a white residue (0.3 g), which crystallised from methanol, m.p. 205 °C, and which was identical with the product obtained in the previous experiment.

Acknowledgements

We thank the S.E.R.C. for a research studentship (to R. H. S.).

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Received 7th March 1983; *Paper* 3/354