708. *Cyclic Amidines. Part XVII.*[1] 4-*Imino*-1,2,3-*benzotriazines.*

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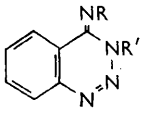
4-Imino-1,2,3-benzotriazines afford, on reduction, 3-aminoindazoles and, on decomposition in acid, 6-aminophenanthridines. The reactions of *o*-cyanophenyltriazens have been studied.

Pyrolysis of 3,4-dihydro-3-phenyl-4-phenylimino-1,2,3-benzotriazine (I; R = R′ = Ph) is said [2] to yield 6-anilinophenanthridine or 1-phenyl-2-phenylimino-3,4-benzazetine. Structurally similar benzotriazinones have recently been reported to afford phenanthridones,[3] and arylnaphthotriazines likewise yield benzacridines.[4] This Paper summarises work related to the conversion of substituted 4-iminobenzotriazines into 3-aminoindazoles and 6-aminophenanthridines.

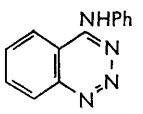
o-Amino-*NN*′-diarylbenzamidines required for the synthesis of substituted benzotriazines have been obtained in small yield by condensation of arylamines with carbon tetrachloride.[2] Such amidines and their *N*-alkyl-*N*′-aryl-substituted analogues were efficiently prepared by reduction of the *o*-nitrobenzamidines, produced from *o*-nitrobenzamides.[5] Treatment of *o*-amino-*NN*′-diarylbenzamidines, having identical *N*-substituents, with nitrous acid gave benzotriazines (I; R = R′ = Ph[2] or C_6H_4·OMe) unambiguously.

[1] Part XVI, Parfitt, Partridge, and Vipond, *J.*, 1963, 3062.
[2] Shah, *J. Indian Inst. Sci.*, 1924, **7**, 205.
[3] Gibson, *Chem. and Ind.*, 1962, 698; *J.*, 1963, 3539; Hey, Rees, and Todd, *Chem. and Ind.*, 1962, 1332.
[4] Waldmann and Back, *Annalen*, 1940, **545**, 52.
[5] Hill and Cox, *J. Amer. Chem. Soc.*, 1926, **48**, 3214.

o-Amino-*N*-phenylbenzamidine, with nitrous acid, furnished a yellow base (I; R = H, R′ = Ph) and a colourless, amphoteric isomer (II). The structure (I) of the base was deduced from the identity of its alkaline hydrolysis product, sodium 2-(phenylaminodiazo)-



(I)



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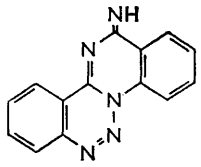

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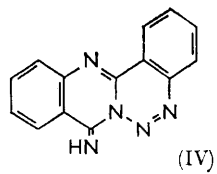


(IV)

benzoate, with that from 3-phenyl-1,2,3-benzotriazin-4-one.[6] In contrast, the isomer (II) with aqueous alkali lost nitrogen to yield *o*-aminobenzanilide; 1,2,3-benzotriazin-4-one behaves similarly.[7] *o*-Cyanobenzenediazonium chloride, coupled at pH 7 with aniline, gave 4′-amino-2-cyanoazobenzene and, as the major product, 1-*o*-cyanophenyl-3-phenyltriazen, the identity of which followed from its hydrolysis to sodium 2-(phenylaminodiazo)benzoate. Confirmation of the structure of the yellow benzotriazine (I; R = H, R′ = Ph) came from its formation when 1-*o*-cyanophenyl-3-phenyltriazen was boiled in aqueous ethanol. The benzyl homologue (I; R = H, R′ = $PhCH_2$) was similarly formed from benzylamine and *o*-cyanobenzenediazonium chloride.

Treatment of *o*-amino-*N*-alkyl-*N*′-phenylbenzamidines with nitrous acid led to benzotriazines having spectroscopic properties very similar to those of the benzotriazines (I; R = H, R′ = Ph or $PhCH_2$) and different from the benzotriazine (II). They were therefore assigned the structures (I; R = Me, Et, Pr^i, or C_6H_{11}; R′ = Ph). The formation of the isomeric benzotriazines (cf. II) was not detected.

1,3-Di-*o*-cyanophenyltriazen,[8] when boiled in aqueous ethanol, gave, not the expected benzotriazine, but 4-amino-2-phenylquinazoline. It is suggested that this resulted from the intermediate tetracyclic compound (III) which behaved as a masked diazo-compound to undergo reduction with ethanol. Diazotisation of 4-amino-2-*o*-aminophenylquinazoline gave this tetracyclic compound (III) or the isomeric tetra-azabenz[*a*]anthracene (IV), which in boiling ethanol also yielded 4-amino-2-phenylquinazoline. Reduction of 1,3-di-*o*-cyanophenyltriazen with hydrazine and Raney nickel gave 4-amino-2-*o*-aminophenylquinazoline, the formation of which could involve as an intermediate the tetracyclic compound (III) or its isomer, 3-*o*-cyanophenyl-3,4-dihydro-4-imino-1,2,3-benzotriazine.

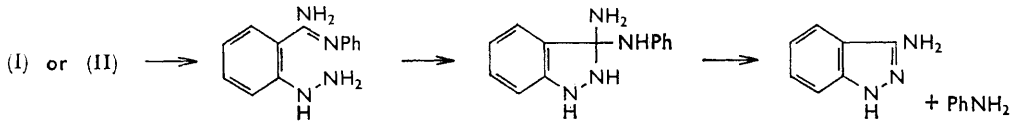
The cyclisation of 1-*o*-cyanophenyl-3-phenyltriazen in aqueous acid to the triazine (II) was accounted for by the observation that the expected cyclisation product (I; R = H, R′ = Ph) was slowly quantitatively converted into its isomer (II) in aqueous acid. Analogous Dimroth rearrangements in similar quinazolines [9] are promoted by alkalis.

3-Aminoindazole has been obtained by reduction of 4-amino-1,2,3-benzotriazine 3-oxide.[10] Reduction of 4-iminobenzotriazines with stannous chloride in ethanol furnished 3-aminoindazoles in high yield. The production of 3-aminoindazole from both isomeric benzotriazines (I; R = H, R′ = Ph) and (II) implied that, in their reduction, fission of the 2,3-bond was followed by cyclisation to an *ortho*-amidine, which then underwent elimination of an amine. Of the two possibilities, ammonia and aniline, the weaker base was eliminated, as shown. In agreement, 4-alkylimino-3-phenylbenzotriazines (I; R = Me, Et, Pr^i, or C_6H_{11}, R′ = Ph) gave 3-alkylaminoindazoles, aniline being eliminated. However, the small difference in the basic strength of ammonia (pK_a 9·27) and of benzylamine (pK_a 9·34) [11]

[6] Mehner, *J. prakt. Chem.*, 1901, **63**, 241.
[7] Finger, *J. prakt. Chem.*, 1888, **37**, 431.
[8] Pinnow and Sämann, *Ber.*, 1896, **29**, 623.
[9] Grout and Partridge, *J.*, 1960, 3540.
[10] Aron and Elvidge, *Chem. and Ind.*, 1958, 1234; Parnell, *J.*, 1961, 4930.
[11] Albert and Serjeant, " Ionisation Constants of Acids and Bases," Methuen, London, 1962, pp. 140, 153.

appears inadequate to account for the formation from the triazine (I; R = H, R′ = $PhCH_2$) of 3-benzylaminoindazole (75%) only, the identity of which was confirmed by comparison with the product of reductive aralkylation of 3-aminoindazole. 3-Anilinoindazole obtained from the triazine (I; R = R′ = Ph) was shown to differ from the isomeric 3-amino-2-phenylindazole, which was synthesised unequivocally by reduction of the product of condensation of *o*-aminobenzonitrile and nitrosobenzene. Certain other 3-amino-2-arylindazoles were analogously prepared from *o*-cyano-azo-compounds.

Decomposition of substituted 4-iminobenzotriazines proceeded rapidly in 30% sulphuric acid with copper powder, or in 100% phosphoric acid, to yield 6-aminophenanthridines,



selected examples of which were degraded to phenanthridone by alkali fusion. Both the triazines (I; R = H, R′ = Ph) and (II) gave the same low yield of 6-aminophenanthridine, possibly as a result of the unfavourable configuration of a common intermediate amidine ion or radical, formed directly by elimination of nitrogen from the triazine (II), or after a Dimroth rearrangement from the triazine (I; R = H, R′ = Ph). The failure of a 3-*p*-methoxyphenylbenzotriazinone to yield a phenanthridone [3] was paralleled by a decrease in the yield of the aminophenanthridine from a similarly substituted iminobenzotriazine.

Experimental

o-*Nitrobenzamides*, prepared by interaction of *o*-nitrobenzoyl chloride in benzene, the amine, and aqueous sodium hydroxide, were as follows: N-*ethyl*-, m. p. 92—93° (Found: C, 55·8; H, 5·1; N, 14·2. $C_9H_{10}N_2O_3$ requires C, 55·7; H, 5·2; N, 14·4%); N-*isopropyl*-, m. p. 138—139° (Found: C, 57·9; H, 5·7. $C_{10}H_{12}N_2O_3$ requires C, 57·7; H, 5·8%); N-*cyclohexyl*-, m. p. 151—152° (Found: C, 62·6; H, 6·6; N, 10·9. $C_{13}H_{16}N_2O_3$ requires C, 62·9; H, 6·5; N, 11·3%).

N-*Cyclohexyl*-o-*nitro*-N′-*phenylbenzamidine*.—Phosphorus pentachloride (31·2 g.) and *N*-cyclohexyl-*o*-nitrobenzamide (37·2 g., 1 mol.) were refluxed together in dry benzene (300 ml.) for 2 hr., cooled, treated with aniline (14 g., 1 mol.), added dropwise, and refluxed again for 1·5 hr. The resin which separated was extracted with N-hydrochloric acid. The clarified (charcoal) extract was poured on to an excess of aqueous sodium hydroxide and ice. The benzamidine (46 g., 94%) separated from concentrated hydrochloric acid as the *hydrochloride*, prisms, m. p. 261—263° (from 2-methoxyethanol) (Found: C, 63·8; H, 6·1; N, 11·3. $C_{19}H_{21}N_3O_2$,HCl requires C, 63·4; H, 6·1; N, 11·7%). Its *picrate* had m. p. 180—181° (Found: N, 15·5. $C_{25}H_{24}N_6O_9$ requires N, 15·2%). In Table 1 are recorded analogous o-*nitrobenzamidines* similarly prepared.

Table 1.

o-Nitrobenzamidines.

Compound	Yield (%)	M. p.	Found (%) C	H	N	Formula	Required (%) C	H	N
NN′-Diphenyl	85	114—115°			13·3	$C_{19}H_{15}N_3O_2$			13·2
N-Methyl-*N*′-phenyl	95	136—137	65·8	5·3	16·2	$C_{14}H_{13}N_3O_2$	65·9	5·1	16·5
N-Ethyl-*N*′-phenyl	95	120—121	66·6	5·4		$C_{15}H_{15}N_3O_2$	66·9	5·6	
N-Isopropyl-*N*′-phenyl	95	113—114			14·9	$C_{16}H_{17}N_3O_2$			14·8
N-Phenyl-*N*′-*p*-tolyl picrate	80	216—218	55·3	3·7	15·2	$C_{26}H_{20}N_6O_9$	55·7	3·6	15·0
N-Phenyl-*N*′-*p*-methoxyphenyl	55	137—138			11·7	$C_{20}H_{17}N_3O_3$			12·1
picrate		207—209	54·0	3·5	14·2	$C_{26}H_{20}N_6O_{10}$	54·2	3·5	14·6
NN′-Di-*p*-methoxyphenyl	25	122—123			10·8	$C_{21}H_{19}N_3O_4$			11·1

o-*Nitro*-N-*phenylbenzamidine*.—*o*-Nitrobenzonitrile (3·7 g.) and aniline toluene-*p*-sulphonate (6·7 g.) were stirred together at 210° for 3 hr., dissolved in 50% ethanol (85 ml.), filtered (charcoal), and made alkaline with aqueous ammonia. The precipitate, when dissolved in 2N-hydrochloric acid (30 ml.) and poured on to 4N-sodium hydroxide (30 ml.) and ice, gave the *amidine*

(3·4 g.), plates, m. p. 116—117° (from aqueous 2-methoxyethanol) (Found: N, 17·7. $C_{13}H_{11}N_3O_2$ requires N, 17·4%).

o-*Amino*-NN′-*diphenylbenzamidine*.—Finely powdered *o*-nitro-*NN*′-diphenylbenzamidine (3·1 g.) was added during 30 min. to a stirred solution of stannous chloride dihydrate (6·8 g.) in concentrated hydrochloric acid (50 ml.). After 90 minutes' stirring at 20—25°, the mixture was poured on to 10N-sodium hydroxide (75 ml.) and ice. The precipitated amino-amidine crystallised from ethanol (1·8 g.) as needles, m. p. 113—115° (lit.,[2] 114°).

Substituted o-*aminobenzamidines*, prepared analogously, are given in Table 2. In certain instances the amino-amidine could be characterised only as a salt.

TABLE 2.

o-Aminobenzamidines.

Compound	Yield (%)	M. p.	Found (%) C	H	N	Formula	Required (%) C	H	N
N-Phenyl	95	148—149°			19·6	$C_{13}H_{13}N_3$			19·9
N-Methyl-*N*′-phenyl	95	107—108	74·5	6·3		$C_{14}H_{15}N_3$	74·6	6·7	
N-Ethyl-*N*′-phenyl picrate	83	174—175	54·0	4·0	18·1	$C_{21}H_{20}N_6O_7$	53·8	4·3	17·9
N-Isopropyl-*N*′-phenyl	79	95—96	75·9	7·2	16·7	$C_{16}H_{19}N_3$	75·9	7·6	16·6
N-Cyclohexyl-*N*′-phenyl	95	88—89	77·4	7·9	14·5	$C_{19}H_{23}N_3$	77·8	7·9	14·3
N-Cyclohexyl-*N*′-phenyl picrate		175—176	57·6	4·8	15·8	$C_{25}H_{26}N_6O_7$	57·5	5·0	16·1
N-Phenyl-*N*′-*p*-tolyl picrate	62	209—210	59·0	4·3	16·2	$C_{26}H_{22}N_6O_7$	58·9	4·2	15·8
NN′-Di-*p*-methoxyphenyl picrate	98	159—160	56·1	4·5	14·6	$C_{27}H_{24}N_6O_9$	56·3	4·2	14·6

1-o-*Cyanophenyl*-3-*phenyltriazen*.—*o*-Aminobenzonitrile (5·9 g.) was diazotised in concentrated hydrochloride acid (75 ml.), buffered with sodium acetate (140 g.), and coupled with aniline (4·7 g.). The red resin so formed solidified after being stirred at 0° for 2 hr. Fractionation of a benzene solution of the dry material on alumina (75 g.) gave the *triazen* (7·4 g.) as an orange-red band by benzene elution, m. p. 107—108° (from light petroleum–benzene), $\lambda_{max.}$ (in EtOH) 237, 300sh., 368 mμ (log ε 4·08, 3·65, 4·31) (Found: C, 70·3; H, 4·7; N, 25·0. $C_{13}H_{10}N_4$ requires C, 70·3; H, 4·5; N, 25·2%). A crimson band, eluted with chloroform, gave 4′-*amino*-2-*cyanoazobenzene* (0·55 g.), m. p. 190—191° (from benzene), $\lambda_{max.}$ 255, 422 mμ (log ε 4·12, 4·34) (Found: C, 70·0; H, 4·7; N, 25·4. $C_{13}H_{10}N_4$ requires C, 70·3; H, 4·5; N, 25·2%).

The triazen (0·75 g.) when refluxed with 2N-sodium hydroxide (30 ml.) for 1 hr. deposited *sodium* 2-(*phenylaminodiazo*)*benzoate* (0·55 g.), yellow needles, m. p. 209—210° (from ethanol) (Found: C, 59·4; H, 3·3; N, 15·9. $C_{13}H_{10}N_3NaO_2$ requires C, 59·3; H, 3·8; N, 16·0%). The same compound (91%) resulted from an analogous alkaline hydrolysis of 3-phenyl-1,2,3-benzotriazin-4-one.

3,4-*Dihydro*-4-*imino*-3-*phenyl*-1,2,3-*benzotriazine* (0·8 g.) was produced when 1-*o*-cyanophenyl-3-phenyltriazen (1 g.) was refluxed in 70% ethanol for 90 min., and crystallised as yellow flakes, m. p. 112—114° (from 2-methoxyethanol) (Found: C, 69·9; H, 4·6; N, 25·0. $C_{13}H_{10}N_4$ requires C, 70·3; H, 4·5; N, 25·2%).

o-Amino-*N*-phenylbenzamidine (10·6 g.) in 2N-sulphuric acid (150 ml.) was treated at 0° during 20 min. with sodium nitrite (3·5 g.) in water (20 ml.) and stirred at 0° a further 1·5 hr. Recrystallisation from aqueous 2-methoxyethanol of the solid precipitated by ammonia afforded the same triazine (6 g.) m. p. and mixed m. p. 112—114°. The mother-liquors, after being concentrated, furnished 4-*anilino*-1,2,3-*benzotriazine* (0·8 g.), m. p. 201° (efferv.) (from ethanol) (Found: C, 70·7; H, 4·5; N, 25·1. $C_{13}H_{10}N_4$ requires C, 70·3; H, 4·5; N, 25·2%). The yields of the two isomers were variable.

The 4-iminobenzotriazine (0·2 g.) was dissolved in 2N-hydrochloric acid (10 ml.) at room temperature, kept for 6 hr., and made alkaline with aqueous ammonia to yield 4-anilinobenzotriazine (0·2 g.), m. p. and mixed m. p. 201° (efferv.) (from ethanol). 1-*o*-Cyanophenyl-3-phenyltriazen (0·2 g.), when stirred for 6 hr. at room temperature with 2N-hydrochloric acid (10 ml.) and basified with ammonia, gave the same 4-anilinobenzotriazine (0·2 g.).

When refluxed in 2N-sodium hydroxide (20 ml.) for 1 hr., the 4-iminobenzotriazine (0·4 g.) yielded sodium 2-(phenylaminodiazo)benzoate, m. p. and mixed m. p. 209—210° (decomp.).

Hydrolysis of the 4-anilinobenzotriazine (0·22 g.) in boiling 2N-sodium hydroxide (10 ml.) for 6 hr. afforded *o*-aminobenzanilide (0·13 g.), m. p. and mixed m. p. 130—131°.

4-*Amino*-2-o-*nitrophenylquinazoline* (with R. T. PARFITT).—Ammonia was passed through a

mixture of 4-chloro-2-*o*-nitrophenylquinazoline [12] (15 g.) and anhydrous copper sulphate (0·3 g.) in phenol (90 g.) at 200—210° for 4 hr. Basification of the cooled solution with 5N-sodium hydroxide and crystallisation of the precipitate from chloroform then butanol gave the *nitro-amine* (10·1 g.), m. p. 172—174° (Found: C, 62·8; H, 3·6; N, 21·2. $C_{14}H_{10}N_4O_2$ requires C, 63·1; H, 3·8; N, 21·0%). Its *hydrochloride*, precipitated from aqueous acetic acid with concentrated hydrochloric acid, had m. p. 307—308° (decomp.) (Found: C, 55·1; H, 3·2; N, 18·5. $C_{14}H_{10}N_4O_2$,HCl requires C, 55·5; H, 3·6; N, 18·5%), and its *picrate* (prisms from acetic acid) had m. p. 216—218° (Found: C, 48·7; H, 2·8. $C_{20}H_{13}N_7O_9$ requires C, 48·5; H, 2·6%).

4-*Amino*-2-o-*aminophenylquinazoline*.—(*a*) (with R. T. Parfitt) Raney nickel (2 g.) was added during 30 min. to the above nitro-amine (1 g.) in ethanol (50 ml.) and hydrazine hydrate (1 ml.) at 60—70°. Addition of 2N-hydrochloric acid (25 ml.) to the hot filtrate furnished the *diamine dihydrochloride* (0·74 g.), yellow needles, m. p. 288—290° (from water) (Found: C, 54·8; H, 4·5; N, 18·2. $C_{14}H_{12}N_4$,2HCl requires C, 54·4; H, 4·5; N, 18·1%).

(*b*) 1,3-Di-*o*-cyanophenyltriazen [8] (2·4 g.), suspended in ethanol (100 l.) and hydrazine hydrate (4 ml.), when treated with Raney nickel (0·5 g.) at 65—70° for 1 hr., gave the same diamine salt, m. p. and mixed m. p. 288—290°.

Diazotisation of 4-*Amino*-2-o-*aminophenylquinazoline*.—The diamine (0·47 g.), suspended in 2N-hydrochloric acid (7 ml.), was treated at 0° with sodium nitrite (0·14 g.) in water (2 ml.); the yellow hydrochloride rapidly dissolved and colourless crystals were deposited. After 15 min. at 0°, the addition of aqueous ammonia liberated either 4b,12-dihydro-12-imino-4b,5,6,11-tetra-azachrysene (III) or 6a,7-dihydro-7-imino-5,6,6a,12-tetra-azabenz[*a*]anthracene (IV), brown prisms, m. p. 148—150° (efferv.) (from hexane), $\lambda_{max.}$ (in hexane) 225, 254sh, 268, 296, 320, 340sh, 350, 364sh mμ (log ε 4·58, 4·32, 4·25, 4·10, 3·88, 3·92, 3·95, 3·90) (Found: C, 68·1; H, 4·0; N, 28·5. Calc. for $C_{14}H_9N_5$: C, 68·0; H, 3·7; N, 28·3%).

4-*Amino*-2-*phenylquinazoline*.—(*a*) 1,3-Di-*o*-cyanophenyltriazen [8] (2·5 g.) was boiled in 75% aqueous ethanol (40 ml.) for 1 hr. and vacuum-evaporated to dryness. The quinazoline (1·2 g.), extracted from the resulting red oil with 2N-sulphuric acid, re-precipitated by ammonia, and crystallised from aqueous ethanol, had m. p. and mixed m. p.[13] 147—148°.

(*b*) The foregoing tetracyclic compound (0·25 g.) was boiled for 1 hr. in 75% aqueous ethanol (4 ml.). After being filtered (charcoal), the red solution deposited the quinazoline (0·15 g.), m. p. and mixed m. p. 147—148° (from aqueous ethanol).

3,4-*Dihydro*-4-*methylimino*-3-*phenyl*-1,2,3-*benzotriazine*.—Sodium nitrite (0·7 g.) in water (10 ml.) was added dropwise during 20 min. at 0—5° to *o*-amino-*N*-methyl-*N'*-phenylbenzamidine (2·25 g.) in 2N-sulphuric acid (50 ml.). After 1 hr. at 0°, the *triazine* (2·3 g., 98%) was precipitated with aqueous ammonia, yellow needles, m. p. 131—132° (from ethanol) (Found: C, 71·4; H, 4·9. $C_{14}H_{12}N_4$ requires C, 71·2; H, 5·1%).

Table 3.

3,4-Dihydro-1,2,3-benzotriazines.

Compound	Yield (%)	M. p.	Found (%) C	H	N	Formula	Required (%) C	H	N
4-Ethylimino-3-phenyl	62	83—84°	71·8	5·6	22·6	$C_{15}H_{14}N_4$	72·0	5·6	22·4
4-Isopropylimino-3-phenyl.....	95	76—77	72·1	6·5	21·2	$C_{16}H_{16}N_4$	72·7	6·1	21·2
4-Cyclohexylimino-3-phenyl	75	94—95	75·2	6·7		$C_{19}H_{20}N_4$	75·0	6·6	
3-*p*-Methoxyphenyl-4-*p*-methoxyphenylimino	53	123—124	70·2	4·9	15·8	$C_{21}H_{18}N_4O_2$	70·4	5·1	15·6

Substituted 3,4-*dihydro*-1,2,3-*benzotriazines*, prepared similarly, are recorded in Table 3.

3-*Benzyl*-3,4-*dihydro*-4-*imino*-1,2,3-*benzotriazine*.—*o*-Aminobenzonitrile (5·9 g.), suspended in concentrated hydrochloric acid (75 ml.), was treated at 0° during 30 min. with sodium nitrite (3·5 g.) in water (15 ml.) and stirred for 1 hr. Hydrated sodium acetate (140 g.) in water (50 ml.) was added, and benzylamine (5·3 g.) added dropwise during 15 min. After 1 hour's stirring at 0°, the solid, m. p. 108—110° (decomp.), was boiled in 70% aqueous ethanol (60 ml.) for 90 min.; the *triazine* (7·6 g.), m. p. 119—120° (from light petroleum–benzene), separated from the cooled solution (Found: C, 71·0; H, 5·3; N, 24·1. $C_{14}H_{12}N_4$ requires C, 71·2; H, 5·1; N, 23·7%).

[12] Partridge, Vipond, and Waite, *J.*, 1962, 2549.
[13] Meerwein, Laasch, Mersch, and Nentwig, *Chem. Ber.*, 1956, **89**, 224.

The light-absorptions of 1,2,3-benzotriazines, determined for ethanol solutions, are given in Table 4.

TABLE 4.

Light-absorption (λ in mμ) of 3,4-dihydro-1,2,3-benzotriazines.

Compound	$\lambda_{max.}$	log ε	$\lambda_{max.}$	log ε	$\lambda_{max.}$	log ε	$\lambda_{max.}$	log ε	$\lambda_{max.}$	log ε
4-Imino-3-phenyl	—	—	260	3·97	268	3·95	307	3·76	318	3·77
3-Benzyl-4-imino	—	—	261	4·03	269	3·10	307	3·72	318	3·73
4-Methylimino-3-phenyl	—	—	262	4·15	270	4·14	310	3·83	—	—
4-Ethylimino-3-phenyl	—	—	263	4·15	271	4·15	312	3·86	—	—
4-Isopropylimino-3-phenyl ...	—	—	263	4·13	271	4·13	317	3·86	—	—
4-Cyclohexylimino-3-phenyl...	—	—	264	4·14	272	4·14	314	3·89	—	—
3-Phenyl-4-phenylimino [2].....	—	—	265	4·10	271	4·11	315	3·88	—	—
6-Methyl-3-*p*-tolyl-4-*p*-tolylimino	230	4·53	265	4·10	272 *	4·09	323	3·94	—	—
3-*p*-Methoxyphenyl-4-*p*-methoxyphenylimino	234	4·49	—	—	270 *	4·13	306	3·92	—	—
4-Anilino-1,2,3-benzotriazine	241 *	4·11	—	—	272	3·85	—	—	334	4·11

* Shoulder.

3-*Aminoindazole*.—3,4-Dihydro-4-imino-3-phenyl-1,2,3-benzotriazine (1·1 g.) was gradually added to a warm solution of stannous chloride dihydrate (3·4 g.) in ethanol (50 ml.), and the solution was refluxed for 2 hr. Solvent (35 ml.) was distilled off and 2N-sodium hydroxide (25 ml.) was added. Basic material, after being collected in ether and recovered, furnished 3-aminoindazole (0·5 g., 76%), m. p. and mixed m. p. 154—155° (from benzene). The 4-anilino-benzotriazine likewise afforded 3-aminoindazole (74%). The *indazoles* listed in Table 5 were

TABLE 5.

Indazoles prepared from the benzotriazines (I).

Indazole	Yield (%)	M. p.	Found (%) C	H	N	Formula	Required (%) C	H	N	Benzotriazine (I) R	R′
3-Methylamino *	70	147—148°	65·1	5·8	28·6	$C_8H_9N_3$	65·3	6·2	28·6	Me	Ph
3-Ethylamino *	80	95—96	66·9	6·8	26·2	$C_9H_{11}N_3$	67·1	6·9	26·1	Et	Ph
3-Isopropylamino *	60	87—88			23·8	$C_{10}H_{13}N_3$			24·0	Pr^i	Ph
3-Cyclohexylamino *	70	123—124	72·7	8·2	19·4	$C_{13}H_{17}N_3$	72·5	8·0	19·5	C_6H_{11}	Ph
3-Benzylamino	75	123—124			18·5	$C_{14}H_{13}N_3$			18·8	H	Ph·CH_2
3-Anilino *	85	170—171	74·6	4·9		$C_{13}H_{11}N_3$	74·6	5·3		Ph	Ph[2]
3-*p*-Methoxyphenyl-amino †	77	161—162			17·6	$C_{14}H_{13}N_3O$			17·6	*p*-C_6H_4OMe	*p*-C_6H_4OMe
5-Methyl-3-*p*-toluidino ‡	78	169—170	76·2	6·1		$C_{15}H_{15}N_3$	75·9	6·4		3,4-Dihydro-6-methyl-3-*p*-tolyl-4-*p*-tolylimino [2]	

* Products included aniline. † Products included *p*-anisidine. ‡ Products included *p*-toluidine.

similarly prepared. 3-Aminoindazole (1·3 g.) and benzaldehyde (1·1 g.) were refluxed in ethanol (5 ml.) for 2 hr., the gum precipitated by water was extracted with chloroform and the extract was dried ($CaCl_2$) and evaporated. Reduction of the residue with magnesium in methanol [14] gave the 3-benzylamino-compound (0·9 g.), m. p. and mixed m. p. 123—124°. *o*-Nitro-*N*-phenylbenzamidine (2·4 g.), reduced with zinc dust (2·6 g.) and ammonium chloride (2 g.) in 80% aqueous ethanol (50 ml.) at 65° for 20 min., gave the 3-anilinoindazole (1·2 g.), m. p. and mixed m. p. 170—171°.

3-*Amino*-2-*phenylindazole*.—A solution of *o*-aminobenzonitrile (2·4 g.) and nitrosobenzene (2·4 g.) in acetic acid (10 ml.) was heated on a steam-bath for 2·5 hr. Vacuum-evaporation of the solvent furnished an oil from which an orange-red fraction was isolated by chromatography in benzene on alumina. This fraction was refluxed for 2 hr. with stannous chloride dihydrate (6·8 g.) in ethanol (50 ml.). After removal of most of the solvent, 5N-sodium hydroxide (40 ml.) was added and the *indazole* (1 g.), m. p. 143—144°, was collected in chloroform, recovered, and crystallised from benzene–light petroleum (Found: C, 74·8; H, 5·4; N, 20·2. $C_{13}H_{11}N_3$ requires C, 74·6; H, 5·3; N, 20·1%).

3-*Amino*-2-p-*dimethylaminophenylindazole*.—*o*-Aminobenzonitrile (11·8 g.) in concentrated hydrochloric acid (120 ml.) was diazotised during 1 hr. at 0°, sodium acetate (165 g.) in water

[14] Zechmeister and Truka, *Ber.*, 1930, **63**, 2883.

(200 ml.) was added, followed by dimethylaniline (12·1 g.) added dropwise. After 1 hr. 2-*cyano*-4′-*dimethylaminoazobenzene* (23·5 g.) was collected, crimson plates, m. p. 150—151° (from aqueous ethanol) (Found: C, 71·8; H, 5·3. $C_{15}H_{14}N_4$ requires C, 72·0; H, 5·6%). This azo-compound (17·5 g.) was refluxed for 2·5 hr. with stannous chloride (47·3 g.) in ethanol (250 ml.) and evaporated to 80 ml. Base, liberated by 2N-sodium hydroxide, collected in chloroform, and recovered, gave the *indazole* (14 g.), needles, m. p. 180—181° (from benzene) (Found: C, 71·6; H, 6·4; N, 22·0. $C_{15}H_{16}N_4$ requires C, 71·4; H, 6·4; N, 22·2%). Treatment with acetic anhydride in boiling acetic acid for 15 min. gave an *acetyl derivative*, m. p. 196—198° (Found: N, 19·1. $C_{17}H_{18}N_4O$ requires N, 19·0%), and, with acetic anhydride alone for 1 hr., a *diacetyl derivative*, m. p. 156—157° (Found: C, 67·2; H, 5·6; N, 16·4. $C_{19}H_{20}N_4O_2$ requires C, 67·8; H, 6·0; N, 16·7%).

3-*Amino*-2-p-*hydroxyphenylindazole* was similarly prepared from *o*-aminobenzonitrile and phenol, and had m. p. 258—260° (from ethanol) (Found: C, 69·2; H, 5·3. $C_{13}H_{11}N_3O$ requires C, 69·3; H, 4·9%); *picrate*, m. p. 201—202° (Found: C, 50·0; H, 3·2. $C_{19}H_{14}N_6O_8$ requires C, 50·2; H, 3·1%); *dibenzoyl derivative*, m. p. 220—221° (from aqueous methanol) (Found: N, 9·8. $C_{27}H_{19}N_3O_3$ requires N, 9·7%). The intermediate 2-*cyano*-4′-*hydroxyazobenzene*, orange needles, had m. p. 212—214° (decomp.) (from aqueous ethanol) (Found: C, 70·6; H, 4·3; N, 18·4. $C_{13}H_9N_3O$ requires C, 69·9; H, 4·1; N, 18·8%).

6-*Isopropylaminophenanthridine*.—(*a*) Copper powder (10 mg.) was added to a suspension of 3,4-dihydro-4-isopropylimino-3-phenyl-1,2,3-benzotriazine (1·3 g.) in 30% sulphuric acid (30 ml.). The mixture was rapidly heated (15 min.) to maintain a steady effervescence, and filtered. Basification of the solid which separated from the cooled solution, with aqueous ammonia, gave the *phenanthridine* (0·63 g., 54%), flakes, m. p. 90—91° (from light petroleum) (Found: C, 81·1; H, 6·6; N, 11·9. $C_{16}H_{16}N_2$ requires C, 81·3; H, 6·8; N, 11·9%).

(*b*) The benzotriazine (1 g.) was stirred into a mixture of phosphoric acid (8 ml.) and phosphorus pentoxide (5 g.) and kept at 120—130° until effervescence ceased (5—10 min.). Base was liberated from the cooled mixture with aqueous ammonia, collected in chloroform, and recovered from the dried (K_2CO_3) extract. A benzene solution of the residue, when chromatographed on alumina (30 g.), afforded as a blue fluorescent band the phenanthridine (0·69 g., 77%), m. p. and mixed m. p. 90—91° (from light petroleum).

The phenanthridine (0·47 g.) and potassium hydroxide (3 g.) were heated together in an iron crucible at 380—400° for 90 min. 5,6-Dihydro-6-oxophenanthridine (0·25 g., 64%), precipitated

TABLE 6.

Phenanthridines.

Compound	Yield (%) (*a*)	Yield (%) (*b*)	Found (%) M. p.	Found (%) C	Found (%) H	Found (%) N	Formula	Required (%) C	Required (%) H	Required (%) N
6-Amino *		17	193—194°							
6-Methylamino †	42	66	184—185	80·9	5·9	13·2	$C_{14}H_{12}N_2$	80·7	5·8	13·5
6-Ethylamino ‡	36	62	131—132	81·2	6·4	12·9	$C_{15}H_{14}N_2$	81·1	6·4	12·6
6-Anilino ‡ §	31	62	156—157	84·0	5·3	10·0	$C_{19}H_{14}N_2$	84·4	5·2	10·4
2,8-Dimethyl-6-*p*-toluidino	30	62	133—134	84·6	6·6	9·3	$C_{22}H_{20}N_2$	84·6	6·5	9·0
2-Methoxy-6-*p*-methoxyphenylamino	9	10	125—126	76·6	5·5	8·7	$C_{21}H_{18}N_2O_2$	76·3	5·5	8·5

* From both triazines (I; R = H, R′ = Ph) and (II). Morgan and Walls (*J.*, 1932, 2225) record m. p. 195·5°. With nitrous acid it gave phenanthridone, m. p. and mixed m. p. 291—293°. † Morgan and Walls (*J.*, 1938, 389) record m. p. 187°. ‡ Alkali fusion gave phenanthridone. § A yellow band, remaining after elution of the phenanthridine, was eluted with chloroform and gave *o*-hydroxy-*NN*′-diphenylbenzamidine (0·6 g., 44%), m. p. and mixed m. p. 155—156° (from aqueous ethanol) (Found: C, 79·1; H, 5·7; N, 9·8. Calc. for $C_{19}H_{16}N_2O$: C, 79·1; H, 5·6; N, 9·7%) (cf. Kirsanov, Levchenko, and Tretykova, *Ukrain. Khim. Zhur.*, 1953, **19**, 622).

by concentrated hydrochloric acid from an aqueous extract of the cooled melt, had m. p. and mixed m. p. 291—292°.[15] Boiling 40% aqueous sodium hydroxide or 20% potassium hydroxide in ethylene glycol did not degrade the phenanthridine.

In Table 6 analogously prepared phenanthridines are recorded.

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[15] Graebe and Wander, *Annalen*, 1893, **276**, 245.