623. *Polyazabicyclic Compounds. Part II.* Further Derivatives of Benzo-1 : 2 : 4-triazine.*

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A number of 3-arylbenzo-1 : 2 : 4-triazines have been prepared from formazans, and their *N*-oxidation studied.

3-Aminobenzo-1 : 2 : 4-triazines can be converted into 1 : 4-di-*N*-oxides.

Some derivatives of 8-hydroxybenzo-1 : 2 : 4-triazine have been obtained.

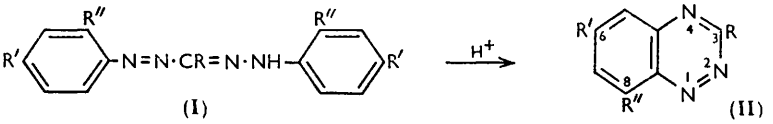
(*A*) It was shown previously * that the Bamberger [1] synthesis of benzo-1 : 2 : 4-triazines from suitably substituted formazans (I ⟶ II) was widely applicable, and was favoured by a 3-aryl group (R = Ar in I). To delineate the range of the reaction further, and to provide substances potentially of therapeutic interest, new examples, particularly of the cyclisation of formazans having electron-attracting substituents, have been studied.

The yields of benzo-1 : 2 : 4-triazines obtained from appropriate formazans are listed in Table 2 and accord with the character of the reaction as an intramolecular electrophilic substitution. Nitro-groups in the 1- and 5-aryl groups of the formazan greatly hinder the cyclisation, but even the poor yields obtained in some of the cases listed do not completely negate the utility of the reaction, for the formazans are relatively easy to obtain. In only one instance could we detect phenazine formation. Although we could not obtain pure

* Part I, *J.*, 1955, 2326.

[1] Bamberger and Wheelwright, *Ber.*, 1892, **25**, 3201.

1 : 3 : 5-tri-*p*-nitrophenylformazan, experiments with a crude specimen suggest that the degree of electronegative substitution prevented triazine formation. The cyclisations listed were all effected by means of a mixture of sulphuric and acetic acids, and optimum yields were obtained only by careful adherence to the described conditions. Polyphosphoric acid was used successfully in some cases, but offered no advantage.



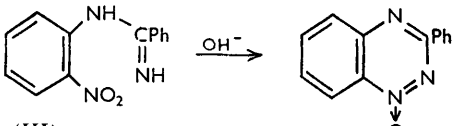
(I) (II)

3-*p*-Nitrophenyl-, 6-methoxy-3-*p*-nitrophenyl-, and 6-nitro-3-phenyl-benzo-1 : 2 : 4-triazine were reduced to the corresponding amines. Anhydrous stannous chloride [2] was the only reagent suitable for this purpose. 6-Amino-3-phenylbenzo-1 : 2 : 4-triazine could also be obtained, but in very poor yield, by the reduction of *N*-benzoyl-*N*′-2 : 4-dinitrophenylhydrazine.

(*B*) Little is known of benzo-1 : 2 : 4-triazine *N*-oxides. Their reported antimalarial activity [3,4] and, by analogy with other heterocyclic *N*-oxides,[5,6] their potential value as antibacterial reagents, prompted an investigation of these compounds. Our products fall into two groups, those without a 3-amino-group and those with this feature.

With peracetic acid, benzo-1 : 2 : 4-triazine gave a poor yield of the 1-oxide, whose structure was proved by synthesis (see below). Neither benzo-1 : 2 : 4-triazine itself, nor any of its derivatives lacking the 3-amino-group, could be converted into dioxides, either with peracetic or with performic acid. 8-Methoxybenzo-1 : 2 : 4-triazine with peracetic acid gave what appears to be a 1 : 2 : 4-triazinecarboxylic acid.

Peracetic acid at room temperature converted 3-phenylbenzo-1 : 2 : 4-triazine into a monoxide, m. p. 105—107°, whilst oxidation at 45—50° gave an isomeric substance, m. p. 132—133°. The two products were isomeric monoxides, and not merely polymorphic forms of one compound, as was shown by their different ultraviolet extinction curves. The lower-melting monoxide was unchanged by heat, or by mineral acids, but peracetic acid converted it into the higher-melting isomer. The latter we proved to be 3-phenylbenzo-1 : 2 : 4-triazine 1-oxide by its synthesis from *N*-*o*-nitrophenylbenzamide (III ⟶ IV), and, in view of its easy isomerisation, we suggest that the lower-melting compound is the 2-oxide. This type of migration seems not to have been observed previously in heterocyclic *N*-oxides, but similar transformations occur in some azoxybenzenes. Migration of oxygen from one nitrogen to the other sometimes happens under the conditions of the Wallach rearrangement,[7] while β-*p*-nitroazoxybenzene changes to the α-isomer on treatment with chromic acid.[8]

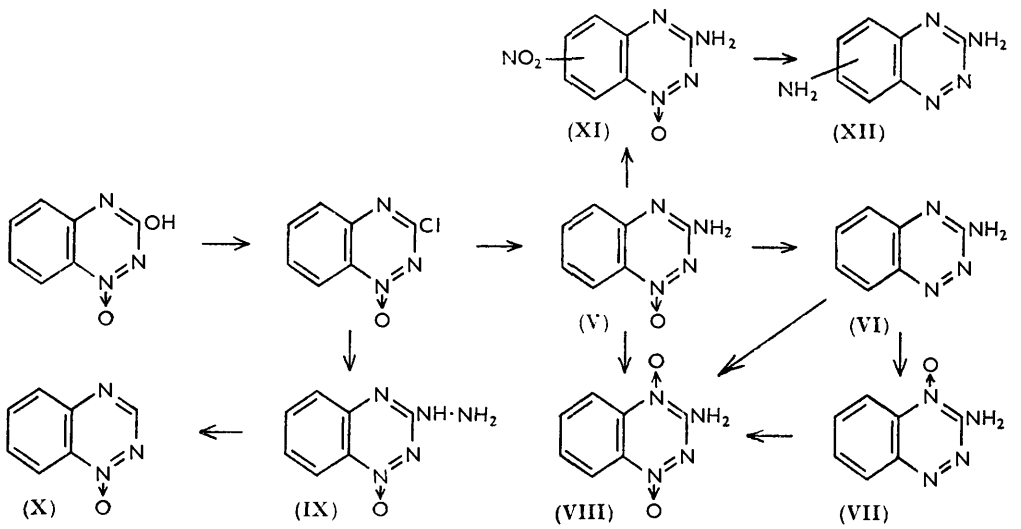


(III) (IV)

Mild oxidation of 3-*p*-chlorophenylbenzo-1 : 2 : 4-triazine gave a mixture, probably of isomeric monoxides with some of the parent compound. Oxidation of 3-*p*-acetamidophenyl- and 3-*p*-acetamidophenyl-6-methoxy-benzo-1 : 2 : 4-triazine, followed by hydrolysis, gave monoxides which are assumed to be the 1-isomers.

[2] Albert and Linnell, *J.*, 1936, 1617.
[3] Wolf, Pfeister, Wilson, and Robinson, *J. Amer. Chem. Soc.*, 1955, **76**, 3552.
[4] Wolf, Wilson, Pfeister, and Tishler, *ibid.*, p. 4611.
[5] McIlwain, *J.*, 1943, 322.
[6] Landquist, *J.*, 1953, 2816 *et seq.*
[7] Angeli, *Gazzetta*, 1916, **46**, II, 82.
[8] *Idem*, *ibid.*, 1916, **46**, II, 79.

In the most convenient preparation [9,10] of 3-amino- or 3-hydroxy-benzo-1 : 2 : 4-triazines use is made of the cyclisation by alkali of *o*-nitrophenyl-guanidines or -ureas (of which reactions the above synthesis of 3-phenylbenzo-1 : 2 : 4-triazine 1-oxide is an extension). The guanidine can be prepared from an *o*-nitroaniline and cyanamide in



hydrochloric acid, a recent modification [3] enabling otherwise unreactive anilines to be used. *o*-Nitrophenylureas are less readily available, although 4-chloro-2-nitrophenylurea can be easily obtained [4] by reaction of carbonyl chloride with 4-chloro-2-nitroaniline followed by treatment with ammonia. We have used an analogous series of reactions for the preparation of *o*-nitrophenylurea, thus making easily available in quantity 3-hydroxy- and 3-amino-benzo-1 : 2 : 4-triazine 1-oxide. 3-Hydroxybenzo-1 : 2 : 4-triazine 1-oxide could be converted into the 3-chloro-compound without destroying the oxide group, and the chloro-compound readily provided 3-aminobenzotriazine 1-oxide (V), previously obtained by Arndt and Rosenau [10] from *o*-nitrophenylguanidine. Reduction of the oxide (V) to the base (VI) and oxidation with peracetic acid gave the compound regarded by Arndt and Rosenau [10] as 3-aminobenzo-1 : 2 : 4-triazine 2-oxide. Although under similar conditions 3-benzamido-1 : 2 : 4-triazine was not oxidised, Adams and Mujano [11] have shown that 2-amino-pyridine and -quinoline are not affected by peracetic acid, and it seems likely that only the ring-nitrogen atoms are oxidised when the base (VI) is treated with this reagent. Further oxidation of the oxide (V) and of its isomer gave the same di-*N*-oxide. 3-Acetamidobenzo-1 : 2 : 4-triazine 1-oxide also gave this dioxide, losing its acetyl group in the reaction. We suggest that Arndt and Rosenau's monoxide is probably 3-aminobenzo-1 : 2 : 4-triazine 4-oxide (VII), and that further oxidation converts both (V) and (VII) into the 1 : 4-di-*N*-oxide (VIII). An attempt to cyclise nitroformaldehyde *o*-nitrophenylhydrazone to 3-aminobenzo-1 : 2 : 4-triazine 4-oxide failed.

3-Amino-7-chloro and 3-amino-7-methoxy-benzo-1 : 2 : 4-triazine were converted into the 4(?)-monoxides and the 1 : 4(?)-dioxides analogous to (VII) and (VIII). The dioxides gave yellow solutions in acid, but red ones in aqueous or alcoholic alkali. The monoxides did not give red solutions in alkali.

3-Chlorobenzo-1 : 2 : 4-triazine 1-oxide was readily converted into 3-hydrazinobenzo-1 : 2 : 4-triazine 1-oxide (IX). This was oxidised to benzotriazine 1-oxide (X), identical with the compound formed from benzo-1 : 2 : 4-triazine. The chloro-compound did not

[9] Arndt, *Ber.*, 1913, **46**, 3522.
[10] Arndt and Rosenau, *Ber.*, 1917, **50**, 1248.
[11] Adams and Mujano, *J. Amer. Chem. Soc.*, 1954, **76**, 2785.

react with toluene-*p*-sulphonhydrazide, but the required derivative was obtained by acylation of 3-hydrazinobenzo-1 : 2 : 4-triazine 1-oxide. With alkali it gave no recognisable product.

A number of experiments were made with the object of preparing diaminobenzo-1 : 2 : 4-triazines. 2 : 4-Dinitroaniline could not be converted into 2 : 4-dinitrophenylurea, and both this compound [12] and 4-acetamido-2-nitrophenylurea failed to cyclise with alkali.

Benzo-1 : 2 : 4-triazine itself and 3-hydroxybenzo-1 : 2 : 4-triazine 1-oxide could not be nitrated, even under forcing conditions, and 3-benzamidobenzo-1 : 2 : 4-triazine 1-oxide gave the 3-*m*-nitrobenzamido-compound. However, the oxide (V) readily gave 3-amino-*x*-nitrobenzo-1 : 2 : 4-triazine 1-oxide (XI). That this product was not a nitramine was proved by its reduction to 3 : *x*-diaminobenzo-1 : 2 : 4-triazine (XII) which differed from 3-hydrazinobenzo-1 : 2 : 4-triazine prepared from (IX). The crystalline red diamine could not be obtained analytically pure, probably because of its sensitivity to oxidation, but it gave a pure monoacetyl derivative (probably the *Bz*-acetamido-derivative, in view of the difficulty met in acetylating 3-aminobenzo-1 : 2 : 4-triazine).

(*C*) In preparing analogues of oxine by demethylating 8-methoxy-, 8-methoxy-3-methyl-, and 8-methoxy-3-phenyl-benzo-1 : 2 : 4-triazine with aluminium chloride in benzene it was previously noticed (Part I, *loc. cit.*) from analytical evidence that the phenolic product must either contain benzene of crystallisation or have been substituted by a phenyl group. Sublimation did not change the compositions of the compounds and the second possibility seemed the more likely. It is now borne out by the observation that 3-phenylbenzo-1 : 2 : 4-triazine, when heated with aluminium chloride in benzene, is converted into 3 : *x*-diphenylbenzo-1 : 2 : 4-triazine. We know of no comparable reaction with other heterocyclic systems, but similar phenylation may occur initially in the conversion of azobenzene into *p*-aminodiphenyl by the action of aluminium chloride in benzene.[12, 13]

Hydrobromic acid, although satisfactory as a demethylating agent for preparing 8-hydroxy-3-phenyl- and 8-hydroxy-3-*p*-chlorophenyl-benzo-1 : 2 : 4-triazine, caused decomposition when used with 5-ethoxy-3-amino-, 8-methoxy-3-methyl-, and 8-methoxy-benzo-1 : 2 : 4-triazine. The two 3-aryl-8-hydroxy-compounds formed sparingly soluble red sodium salts, giving brilliant red aqueous solutions. Working up the products in attempted dealkylation of 5-ethoxy-3-amino-, 8-methoxy-3-methyl-, and 8-methoxy-benzo-1 : 2 : 4-triazine gave red alkaline extracts which darkened when kept, probably because of the ready oxidation of the phenol produced.

Experimental

Ultraviolet extinction data refer to solutions in 95% ethanol.

For many of the triazine derivatives good analyses could not be obtained, perhaps owing to difficulty in purifying these insoluble compounds or owing to their instability or high nitrogen content.

Preparation of Formazans.[14]—The appropriate diazonium chloride solution (10—20% excess) was added during *ca.* 30 min. to a stirred solution of the phenylhydrazone in a large excess of pyridine. Stirring was continued overnight and the mixture was then poured into water. The product was collected, washed, and recrystallised (Table 1).

Preparation of Benzo-1 : 2 : 4-triazines.—The following general method gave the best results. Concentrated sulphuric acid was added, as quickly as possible, to the stirred, cooled solution of the formazan in glacial acetic acid. The temperature was not allowed to rise above 15°, but it was essential to avoid separation of the formazan by overcooling. The resulting blue solution

[12] Reudler, *Rec. Trav. chim.*, 1914, **33**, 4044.
[13] Thomas, "Anhydrous Aluminium Chloride in Organic Chemistry," Reinhold Publ. Corp., New York, 1941, p. 660.
[14] Ashley, Davis, Nineham, and Stack, *J.*, 1953, 3881.

was heated on the water-bath. When it became brownish-yellow it was immediately poured on ice. The product was washed well and recrystallised (see Table 2).

3-p-*Aminophenylbenzo*-1 : 2 : 4-*triazine*.—3-*p*-Nitrophenylbenzo-1 : 2 : 4-triazine (1·75 g.) and an anhydrous stannous chloride reagent [15] (35 c.c.) were heated on the water-bath for 15 min. After dilution with water (100 c.c.) and basification with 2N-sodium hydroxide the mixture was extracted with benzene. Evaporation of the dry (Na_2SO_4) extract gave 3-p-*aminophenylbenzo*-1 : 2 : 4-*triazine* (1·4 g., 91%), scarlet needles, m. p. 186—188° (from methanol) (Found : C, 70·2; H, 5·0. $C_{13}H_{10}N_4$ requires C, 70·3; H, 4·5%). It formed an acetamido-derivative (yellow powder, m. p. 238—241°) and its diazotisation followed by coupling with alkaline β-naphthol gave a red dye.

3-p-*Aminophenyl*-6-*methoxybenzo*-1 : 2 : 4-*triazine*.—6-Methoxy-3-*p*-nitrophenylbenzo-1 : 2 : 4-triazine (1·5 g.) and an anhydrous stannous chloride reagent [15] (30 c.c.) were heated on the water-bath for 15 min. The precipitated solid was dissolved in water, concentrated hydrochloric acid (5 c.c.) was added, and the mixture heated for a further 10 min. Worked up as in the previous experiment but with continuous ether-extraction the mixture gave 3-p-*aminophenyl*-6-*methoxybenzo*-1 : 2 : 4-*triazine* (0·6 g., 44·7%) as golden needles, m. p. 190—192° (Found : C, 65·6; H, 4·6. $C_{14}H_{12}ON_4$ requires C, 66·7; H, 4·6%), from ethanol. This triazine gave an acetamido-derivative (yellow powder, subliming at 245—255°) and its diazotisation followed by coupling with alkaline β-naphthol gave a red dye.

3-*Chlorobenzo*-1 : 2 : 4-*triazine* 1-*Oxide*.—3-Hydroxybenzo-1 : 2 : 4-triazine (2·5 g.) (prepared by a method similar to that used for the 7-chloro-compound [4]), pure dimethylaniline (5 c.c.), and pure phosphorus oxychloride (10 c.c.) were refluxed for 45 min. The mixture was then poured on ice. The product crystallised from methanol, giving 3-*chlorobenzo*-1 : 2 : 4-*triazine* 1-*oxide* (1·8 g., 64%) as white plates, m. p. 117—118° (Found : C, 46·7; H, 2·3. $C_7H_4ON_3Cl$ requires C, 46·3; H, 2·2%).

3-*Hydrazinobenzo*-1 : 2 : 4-*triazine* 1-*Oxide*.—3-Chlorobenzo-1 : 2 : 4-triazine 1-oxide (2·5 g.) and 90—95% w/w hydrazine hydrate (10 c.c.) in ethanol (100 c.c.) were refluxed gently for 1 hr. Removal of the solvent by careful evaporation under a vacuum, and recrystallisation of the residue from methanol, gave yellow needles, m. p. 201—203° (decomp.) (Found : C, 47·4; H, 4·0. $C_7H_7ON_5$ requires C, 47·5; H, 4·0%), of 3-*hydrazinobenzo*-1 : 2 : 4-*triazine* 1-*oxide* (1·75 g., 72%). With toluene-*p*-sulphonyl chloride in pyridine it gave impure 3-toluene-*p*-sulphonylhydrazinobenzo-1 : 2 : 4-triazine 1-oxide, yellow needles, m. p. 223—225° (decomp.) (from 2-methoxyethanol) (Found : C, 52·5; H, 4·1. Calc. for $C_{14}H_{13}O_3N_5S$: C, 50·8; H, 4·0%).

3-*Hydrazinobenzo*-1 : 2 : 4-*triazine*.—3-Hydrazinobenzo-1 : 2 : 4-triazine 1-oxide (0·56 g.) in hot concentrated hydrochloric acid (28 c.c.) was treated with stannous chloride dihydrate (2·24 g.) and heated on the water-bath for 5 min. It was basified and extracted continuously with chloroform. Evaporation of the dry ($CaSO_4$) extract and crystallisation of the residue from methanol gave yellow needles of 3-*hydrazinobenzo*-1 : 2 : 4-*triazine*, m. p. 168—170° (Found : C, 52·4; H, 4·7. $C_7H_7N_5$ requires C, 52·2; H, 4·4%).

3-*Aminobenzo*-1 : 2 : 4-*triazine* 1-*Oxide*.—Anhydrous ammonia was passed into a stirred, refluxing solution of 3-chlorobenzo-1 : 2 : 4-triazine 1-oxide (5 g.) in ethanol (200 c.c.) for 7 hr. After 12 hr. there was collected a yellow powder (2·42 g., 54%), m. p. 269—271°, undepressed on admixture with 3-aminobenzo-1 : 2 : 4-triazine 1-oxide prepared by Arndt's method.[9] With acetic anhydride in pyridine it gave 3-*acetamidobenzo*-1 : 2 : 4-*triazine* 1-*oxide* (60%), yellow needles, m. p. 191—192° (from methanol) (Found : C, 53·2; H, 3·9. $C_9H_8O_2N_4$ requires C, 52·9; H, 4·0%), and with benzoyl chloride in pyridine the corresponding benzamido-derivative, m. p. 206—209°.

3-*Aminobenzo*-1 : 2 : 4-*triazine* 1 : 4-*Dioxide*.—3-Acetamidobenzo-1 : 2 : 4-triazine 1-oxide (1·3 g.) in acetic acid (32 c.c.) containing 30% hydrogen peroxide (16 c.c.) was kept at 45—50° for 17 hr. Neutralisation, continuous extraction with ether and evaporation of the dry (Na_2SO_4) extract gave the crude dioxide (1·035 g., 72%) which from methanol formed orange needles, m. p. 229—230° (decomp.) (rate of heating 10°/min.) of 3-*aminobenzo*-1 : 2 : 4-*triazine* 1 : 4-*dioxide* (Found : C, 46·5; H, 3·8. $C_7H_6O_2N_4$ requires C, 47·2; H, 3·4%), $\lambda_{max.}$ 272, 474 mμ ($\log_{10}\varepsilon$ 4·24; 3·52), inflexion at 226 mμ ($\log_{10}\varepsilon$ 3·10). The dioxide was also formed by the similar oxidation of 3-aminobenzo-1 : 2 : 4-triazine and of 3-aminobenzo-1 : 2 : 4-triazine 1- or 4-oxide.

Nitroformaldehyde o-*Nitrophenylhydrazone*.—A slurry of *o*-nitroaniline (10 g.), sodium

[15] Albert and Linnell, *J.*, 1936, 1617.

TABLE 1. *Formazans* (I).

Formazan R	Formazan R′	Formazan R″	Yield (%)	M. p.	Appearance [f]	Formula	Found (%) C	Found (%) H	Required (%) C	Required (%) H
Ph	Cl	H [a]	50	183—184°	Needles, green reflex [c]	$C_{19}H_{14}N_4Cl_2$	62·2	4·0	62·0	3·8
p-C_6H_4·OMe	Cl	H	43	190—191	Needles, green reflex [c]	$C_{20}H_{16}ON_4Cl_2$	60·1	4·1	60·3	4·0
p-C_6H_4·NO_2	OMe	H	51	188—189 *	Needles, green reflex [d]	$C_{21}H_{19}O_4N_5$	62·2	4·6	62·2	4·7
Ph	NO_2	H	8	212—214 *	Black prisms, green reflex [e]	$C_{19}H_{14}O_4N_6$	58·0	3·5	58·5	3·5
p-C_6H_4·OMe	NO_2	H [b]	14·5	210—212 *	Black flakes [e]	$C_{20}H_{14}O_5N_6$	61·8	4·1	57·1	3·8
p-C_6H_4Cl	H	OMe	44	128—129	Black rhombs, green reflex [d]	$C_{21}H_{19}O_2N_4Cl$	63·6	4·8	63·9	4·8

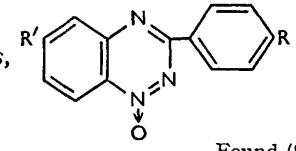
[a] *p*-Anisaldehyde *p*-chlorophenylhydrazone, m. p. 151—153° (from MeOH). [b] *p*-Chlorobenzaldehyde *o*-methoxyphenylhydrazone, m. p. 111—112° (from MeOH). [c] From acetone. [d] From ethanol. [e] From 2-methoxyethanol; a pure specimen could not be obtained. [f] Dark red unless otherwise stated. * With decomp.

TABLE 2. 3-*Arylbenzo*-1 : 2 : 4-*triazines*.

Derivative	Formazan (g.)	H_2SO_4 (c.c.)	AcOH (c.c.)	Time (min.)	Yield (g.)	M. p.	Formula	Found (%) C	Found (%) H	Calc. (%) C	Calc. (%) H
3-*p*-Nitrophenyl	6·4	54	280	17	1·75 [aeg]	241—243°	$C_{13}H_8O_2N_4$	62·5	3·3	61·9	3·2
3-*p*-Chlorophenyl	10·0	40	150	7	3·1 [bh]	151—152	$C_{13}H_8N_3Cl$	64·5	3·5	64·5	3·3
3-*p*-Methoxyphenyl	2·0	10	50	,,	1·05 [ch]	139—140	$C_{14}H_{11}ON_3$	70·8	4·9	70·9	4·7
6-Chloro-3-phenyl	10·0	150	400	20	3·2 [cfg]	134—135	$C_{13}H_8N_3Cl$	64·7	3·3	64·6	3·3
6-Chloro-3-*p*-methoxyphenyl	,,	,,	,,	13	3·6 [cg]	147—148	$C_{14}H_{10}ON_3Cl$	63·4	3·6	63·3	3·8
6-Methoxy-3-*p*-nitrophenyl	13·4	,,	450	30	3·2 [dg]	228—229	$C_{14}H_{10}O_3N_4$	59·1	4·0	59·6	3·6
6-Nitro-3-phenyl	1·0	20	10	5	0·10 [ch]	187—189	$C_{13}H_8O_2N_4$	60·9	3·1	61·9	3·2
3-*p*-Methoxyphenyl-6-nitro	,,	,,	,,	,,	0·30 [di]	314—315 [e]	$C_{14}H_{10}O_3N_4$	61·6	4·0	59·6	3·6
3-*p*-Chlorophenyl-8-methoxy	16·2	81	24·3	4·5	4·15 [dg]	259—260	$C_{14}H_{10}ON_3Cl$	62·2	4·0	61·9	3·7

[a] From benzene. [b] From MeOH. [c] From EtOH. [d] From dioxan. With decomp. above 300°. [f] Together with 0·85 g. of 2 : 7-dichlorophenazine, m. p. 261—263°. [g] Yellow needles. [h] Orange needles. [i] Yellow flakes.

TABLE 3. *Benzo*-1 : 2 : 4-*triazine* 1-*oxides*,



Oxide R	Oxide R′	M. p.	Appearance	Solvent	Formula	Found (%) C	Found (%) H	Required (%) C	Required (%) H
Cl	H [a]	215—216°	Needles	EtOH	$C_{13}H_8ON_3Cl$	60·7	3·3	60·6	3·2
OMe	H	139—140	Needles	C_6H_6	$C_{14}H_{11}O_2N_3$	65·8	4·3	66·4	4·4
NO_2	H [b]	247—248	Needles	$CHCl_3$	$C_{13}H_8O_3N_4$	58·1	2·9	58·2	3·1
NH_2	H [c]	235—237 *	Orange		$C_{13}H_{10}ON_4$	65·0	4·8	65·5	4·2
H	Cl [d]	148—150	Flakes	EtOH	$C_{13}H_8ON_3Cl$	60·2	3·1	60·6	3·1
OMe	Cl [d]	187—188	Needles	EtAc	$C_{14}H_{10}O_2N_3Cl$	58·3	3·6	58·4	3·8
NO_2	OMe [e]	199·5—200·5	Needles	AcOH	$C_{14}H_{10}O_4N_4$	56·2	3·5	56·4	3·4
NH_2	OMe	245—246 *	Red needles	EtOH	$C_{14}H_{12}O_2N_4$	61·6	4·7	62·7	4·5

[a] Conditions as for 3-phenylbenzo-1 : 2 : 4-triazine 2-oxide give a mixture, m. p. 167—182° (Found: C, 62·5; H, 3·1%). [b] 4 Days at 45—50°. [c] The acetamido-derivative was treated for 3 days at 45—50° and then hydrolysed. The amine was not crystallisable. It was isolated by precipitation from hydrochloric acid solution with sodium hydroxide. [d] 3 Days at 45—50°. [e] 5 Days at 45—50°. [f] Yellow unless otherwise stated.

nitrite (5 g.), and water (15 c.c.) was added all at once to a stirred mixture of concentrated hydrochloric acid (14 c.c.) and crushed ice (50 g.). After 15 min. the filtered diazonium salt solution was added to a mixture of nitromethane (4·5 g.), ethanol (10 c.c.), water (40 c.c.), sodium hydroxide (2·9 g.), and crushed ice (150 g.) stirred at 0°. After 30 min. the solid was collected, washed, and recrystallised from ethanol, giving maroon needles of the *hydrazone* (9·1 g., 77%), m. p. 135—137° (Found: C, 40·7; H, 3·4. $C_7H_6O_4N_4$ requires C, 40·0; H, 2·9%).

3-Amino-7-chlorobenzo-1 : 2 : 4-triazine 4-Oxide.—3-Amino-7-chlorobenzo-1 : 2 : 4-triazine[3] (0·285 g.), acetic acid (53 c.c.), and 30% hydrogen peroxide (13 c.c.) were kept at room temperature for 84 hr. Neutralisation, and recrystallisation of the precipitate from dioxan gave *3-amino-7-chlorobenzo-1 : 2 : 4-triazine 4-oxide* (0·2 g., 64%) as yellow needles, m. p. 213—215° (Found: C, 43·4; H, 2·7. $C_7H_5ON_4Cl$ requires C, 42·8; H, 2·6%).

3-Amino-7-methoxybenzo-1 : 2 : 4-triazine 4-Oxide.—3-Amino-7-methoxybenzo-1 : 2 : 4-triazine[3] (0·33 g.), acetic acid (30 c.c.), and 30% hydrogen peroxide (10 c.c.) as above gave the *4-oxide* (0·14 g., 39%) as orange needles, m. p. 182—183° (decomp.) (from methanol) (Found: C, 49·4; H, 3·8. $C_8H_8O_2N_4$ requires C, 50·0; H, 4·2%).

3-Amino-7-chlorobenzo-1 : 2 : 4-triazine 1 : 4-Dioxide.—3-Amino-7-chlorobenzo-1 : 2 : 4-triazine 1-oxide[3] (0·5 g.), acetic acid (200 c.c.), and 30% hydrogen peroxide (50 c.c.) after 40 hr. at 45—50° gave, after evaporation under a vacuum, a residue which crystallised from 2-ethoxyethanol as orange needles of *1 : 4-dioxide* (0·2 g., 34%), m. p. 293—295° (decomp.) (10°/min.) (Found: C, 42·4; H, 3·2. Calc. for $C_7H_5O_2N_4Cl$: C, 39·6; H, 2·4. $C_7H_5O_2N_4Cl,\frac{1}{2}C_4H_{10}O_2$ requires C, 42·0; H, 3·9%).

3-Amino-7-methoxybenzo-1 : 2 : 4-triazine 1 : 4-Dioxide.—3-Amino-7-methoxybenzo-1 : 2 : 4-triazine 1-oxide[3] (1 g.), acetic acid (100 c.c.), and 30% hydrogen peroxide (40 c.c.) after 72 hr. at 20—25° and 24 hr. at 45—50° gave, after evaporation under vacuum, a residue which crystallised from water as orange needles of the *1 : 4-dioxide* (0·52 g., 47%), m. p. 213—214° (decomp.) (Found: C, 46·6; H, 3·8. $C_8H_8O_3N_4$ requires C, 46·2; H, 3·9%).

7-Acetyl-3-aminobenzo-1 : 2 : 4-triazine 1-Oxide.—3-Nitro-4-aminoacetophenone[16] (0·5 g.) and cyanamide hydrochloride (1 g.) were heated at 150—180° for 5 min. and then at 180—190° for a further 5 min. After dilution with water and basification the alkaline solution was left at room temperature for 2 days. The product (0·36 g.) was collected and sublimed (180—200°/0·1 mm.), giving *7-acetyl-3-aminobenzo-1 : 2 : 4-triazine 1-oxide* (0·07 g.; 12·4%) which formed yellow needles, m. p. 272—273° (decomp.) (Found: C, 52·6; H, 3·4. $C_9H_8O_2N_4$ requires C, 52·9; H, 4·0%), from dioxan.

3-Amino-5-ethoxybenzo-1 : 2 : 4-triazine 1-Oxide.—2-Amino-3-nitrophenetole[17] (1·4 g.) and cyanamide hydrochloride (2·8 g.) were heated at 180—190° for 10 min. The mixture was made strongly alkaline with 30% aqueous sodium hydroxide and boiled for 5 min. The product gave yellow needles of *3-amino-5-ethoxybenzo-1 : 2 : 4-triazine 1-oxide* (0·85 g., 54%), m. p. 245·5—247·5° (from methanol) (Found: C, 51·9; H, 4·7. $C_9H_{10}O_2N_4$ requires C, 52·4; H, 4·9%).

Benzo-1 : 2 : 4-triazine 1-Oxide.—(*a*) Benzo-1 : 2 : 4-triazine (0·25 g.) in acetic acid (25 c.c.) and 30% hydrogen peroxide (2·2 c.c.) at room temperature for 5 days gave, after neutralisation and recrystallisation of the precipitate from methanol, pale yellow flakes of the *1-oxide* (0·045 g., 16%), m. p. 138—140° (Found: C, 57·4; H, 3·8. $C_7H_5ON_3$ requires C, 57·1; H, 3·4%), $\lambda_{max.}$ 275, 346 mμ ($\log_{10}\varepsilon$ 3·76, 3·80), inflexion at 293 mμ ($\log_{10}\varepsilon$ 3·54), intense absorption below 240 mμ.

(*b*) 3-Hydrazinobenzo-1 : 2 : 4-triazine 1-oxide (0·2 g.) in water (10 c.c.) was treated with 10 c.c. of 10% copper sulphate pentahydrate solution and the mixture was heated on the water-bath for 3 hr. Filtration, extraction of the filtrate with chloroform, and evaporation of the dry (Na_2SO_4) extract followed by recrystallisation of the residue from methanol gave pale yellow flakes (0·01 g., 6%), m. p. 138—140° undepressed on admixture with the oxide from (*a*).

Oxidation of 8-Methoxybenzo-1 : 2 : 4-triazine.—The methoxy-compound (100 mg.), 30% hydrogen peroxide (0·7 c.c.), and acetic acid were kept for 3 days at room temperature. Neutralisation and extraction with chloroform, followed by evaporation of the dry (Na_2SO_4) extract, gave a yellow powder. Recrystallisation from water gave a *yellow substance*, m. p. 208—210° (decomp.) (Found: C, 35·8, 35·8; H, 3·8, 3·5. $C_5H_3O_4N_3$ requires C, 35·5; H, 1·8%).

3-Phenylbenzo-1 : 2 : 4-triazine 2(?)-Oxide.—3-Phenylbenzo-1 : 2 : 4-triazine (1 g.), acetic acid (40 c.c.), and 30% hydrogen peroxide (6 c.c.), after 2 days at room temperature gave in the usual

[16] Gibson and Levin, *J.*, 1931, 2403.
[17] Blanksma, *Chem. Weekblad*, 1908, **5**, 789.

way 3-*phenylbenzo*-1 : 2 : 4-*triazine* 2(?)-*oxide* (0·52 g., 48%), yellow needles (from methanol), m. p. 105—107° (Found : C, 69·2; H, 5·4. $C_{13}H_9ON_3$ requires C, 69·9; H, 4·1%), $\lambda_{max.}$ 260, 276, 360 mμ ($\log_{10}\varepsilon$ 4·53, 4·53, 3·68).

3-*Phenylbenzo*-1 : 2 : 4-*triazine* 1-*Oxide*.—(*a*) 3-Phenylbenzo-1 : 2 : 4-triazine (1 g.), acetic acid (40 c.c.), and 30% hydrogen peroxide gave after 20 hr. at 45—50° the 1-*oxide* (0·93 g., 86%), orange plates (from ethanol), m. p. 132—133° (Found : C, 70·2; H, 4·2%), $\lambda_{max.}$ 278, 370 mμ ($\log_{10}\varepsilon$ 4·56, 3·65, inflexion at 255 mμ ($\log_{10}\varepsilon$ 4·42). The figures for 3-phenylbenzo-1 : 2 : 4-triazine were $\lambda_{max.}$ 258, 354 mμ ($\log_{10}\varepsilon$ 4·53, 3·68), inflexion at 276 mμ ($\log_{10}\varepsilon$ 4·47).

(*b*) 3-Phenylbenzo-1 : 2 : 4-triazine 2(?)-oxide (0·1 g.), acetic acid (5 c.c.), and 30% hydrogen peroxide (5 c.c.) after 40 hr. at 45—50° gave orange plates (0·07 g.), m. p. 132—133°, undepressed on admixture with 3-phenylbenzo-1 : 2 : 4-triazine 1-oxide.

(*c*) *N*-*o*-Nitrophenylbenzamidine picrate [18] (1 g.) was shaken with 2N-sodium hydroxide (5 c.c.) for 5 min. The free amidine was heated on the water-bath for 5 min. with 2N-sodium hydroxide (25 c.c.). Extraction with chloroform, careful evaporation of the dry (Na_2SO_4) extract, and recrystallisation from methanol gave orange plates (0·02 g., 2·2%), m. p. 132—133°, undepressed on admixture with 3-phenylbenzo-1 : 2 : 4-triazine 1-oxide.

Preparation of Benzo-1 : 2 : 4-*triazine* 1-*Oxides*.—The appropriate benzo-1 : 2 : 4-triazine was oxidised under conditions (see Table 3) similar to those used for 3-phenylbenzo-1 : 2 : 4-triazine 1-oxide (*a*).

3 : x-*Diphenylbenzo*-1 : 2 : 4-*triazine*.—3-Phenylbenzo-1 : 2 : 4-triazine (1 g.), anhydrous aluminium chloride (4 g.) and dry benzene (50 c.c.) were refluxed for 4 hr. N-Hydrochloric acid (100 c.c.) precipitated an insoluble product which, after crystallisation from ethanol, gave yellow plates of 3 : *x*-diphenylbenzo-1 : 2 : 4-triazine (0·1 g., 7·4%), m. p. 133° (Found : C, 79·5; H, 4·6. Calc. for $C_{19}H_{13}N_3$: C, 80·5; H, 4·6%).

8-*Hydroxy*-3-*phenylbenzo*-1 : 2 : 4-*triazine*.—8-Methoxy-3-phenylbenzo-1 : 2 : 4-triazine (0·15 g.) and hydrobromic acid (10 c.c. ; *d* 1·46) were refluxed under nitrogen for 45 min. 2N-Sodium hydroxide was added to give pH 4—5 and the solution was extracted continuously with benzene. Extraction of the benzene solution with 2N-sodium hydroxide gave a red solution from which 8-hydroxy-3-phenylbenzo-1 : 2 : 4-triazine (0·07 g., 49%) was isolated by acidification with acetic acid, extraction with chloroform, and evaporation of the dry (Na_2SO_4) extract. It formed yellow needles, m. p. 178—179° (Found : C, 68·2; H, 4·3; N, 18·6. Calc. for $C_{13}H_9ON_3$: C, 69·9; H, 4·1; N, 18·8%), from benzene–light petroleum (b. p. 60—80°).

3-p-*Chlorophenyl*-8-*hydroxybenzo*-1 : 2 : 4-*triazine*.—3-*p*-Chlorophenyl-8-methoxybenzo-1 : 2 : 4-triazine (2 g.) and hydrobromic acid (100 c.c. ; *d* 1·46) were refluxed for 30 min. and then poured into water. Crystallisation of the product from ethanol gave 3-p-*chlorophenyl*-8-*hydroxybenzo*-1 : 2 : 4-*triazine* (0·37 g., 19·5%). It formed yellow needles, m. p. 248—249° (Found : C, 60·2; H, 2·8. $C_{13}H_8ON_3Cl$ requires C, 60·6; H, 3·1%), from ethyl acetate.

6-*Amino*-3-*phenylbenzo*-1 : 2 : 4-*triazine*.—*N*-Benzoyl-*N'*-2 : 4-dinitrophenylhydrazine (2 g.) was hydrogenated in ethyl acetate in the presence of 5% palladium–charcoal (2 g.). After filtration the combined filtrate and washings, which rapidly reddened, were evaporated to small bulk, yellow crystals [0·27 g.; m. p. 246—247° (decomp.)] separating. Recrystallisation from methanol gave yellow needles of the amine, m. p. 251—252° (decomp.) (Found : C, 71·3; H, 4·4. Calc. for $C_{13}H_{10}N_4$: C, 70·3; H, 4·5%). Similarly 6-nitro-3-phenylbenzo-1 : 2 : 4-triazine with the anhydrous stannous chloride reagent [15] (15 min. at 95°) gave 6-amino-3-phenylbenzo-1 : 2 : 4-triazine, m. p. and mixed m. p. 251—252°.

Nitration of 3-*Benzamidobenzo*-1 : 2 : 4-*triazine* 1-*Oxide*.—Fuming nitric acid (5 c.c.) was added in 5—10 min. to a solution, at 0—5°, of the oxide (0·5 g.) in concentrated sulphuric acid (5 c.c.). After being stirred for 24 hr. at room temperature the mixture was poured into water. One recrystallisation of the product from aqueous dioxan gave 3-m-*nitrobenzamidobenzo*-1 : 2 : 4-*triazine* 1-*oxide* (0·26 g.), m. p. 233—237°. Hydrolysis with concentrated hydrochloric acid (5 c.c., refluxed for 1 hr.) gave 3-aminobenzo-1 : 2 : 4-triazine 1-oxide and *m*-nitrobenzoic acid, each identified by a mixed m. p. determination.

Nitration of 3-*Aminobenzo*-1 : 2 : 4-*triazine* 1-*Oxide*.—The oxide (5 g.) in concentrated sulphuric acid (50 c.c.) was treated with 15 c.c. of a nitrating mixture [from concentrated sulphuric acid (22·5 c.c.) and nitric acid (2·5 c.c., *d* 1·48)] and heated on the water bath for 30 min. Pouring on ice and recrystallisation of the product (5·74 g., 90%), m. p. 287—289° (decomp.),

[18] Oxley, Partridge, and Short, *J.*, 1947, 1110.

from dioxan gave yellow needles of 3-*amino*-x-*nitrobenzo*-1 : 2 : 4-*triazine* 1-*oxide*, m. p. 291—292° (decomp.) (Found : C, 40·3; H, 2·3. $C_7H_5O_3N_5$ requires C, 40·6; H, 2·4%).

3 : x-*Diaminobenzo*-1 : 2 : 4-*triazine*.—Hydrogenation of the nitro-compound (0·5 g.) as a suspension in ethanol (250 c.c.) with 30% palladium–charcoal (50 mg.) gave, after 4 mols. had been absorbed, a pale yellow solution. After filtration the filtrate, which rapidly reddened, was evaporated under a vacuum. Recrystallisation of the residue (0·34 g.) from water gave small red needles of the diamine. It darkened at 250° and became black at 260—262°. Diazotised and coupled with alkaline β-naphthol it gave a red dye. The *monoacetyl derivative* (Found : C, 53·0; H, 4·7. $C_9H_9ON_5$ requires C, 53·2; H, 4·5%) separated as a yellow powder from dilute acetic acid; it became brown at about 270° and blackened above 293°.

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