4-Methylene-1,2,3-benzotriazines

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Diazotization of 2′-aminoacetophenone, followed by coupling with primary aliphatic amines, affords unstable triazenes which readily undergo cyclodehydration over neutral alumina to give 3-alkyl-4-methylene-1,2,3-benzotriazines (**5***a–d*). 3-Aryl-4-methylene-1,2,3-benzotriazines (**8***a–c*) are likewise obtained by cyclodehydration of the stable 1-(*ortho*-acetylphenyl)-3-aryltriazenes (**7***a–c*). Attempted synthesis of the unsubstituted 4-methylene-1,2,3-benzotriazine (**5***e*), by the same method, did not succeed. 4-Hydroxy-1,2,3-benzotriazines (**4**) are postulated as intermediates in the cyclodehydration; this hypothesis is supported by the isolation of the stable 4-hydroxy-1,2,3-benzotriazine (**12**) from the coupling reaction of methylamine with the diazonium salt derived from *ortho*-aminobenzophenone. An account of a preliminary study of the thermolysis of 3-methyl-4-methylene-1,2,3-benzotriazine (**5***a*) is included.

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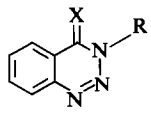
La diazotation de l'amino-2′ acétophénone suivie par un couplage avec des amines aliphatiques primaires conduit aux triazènes instables qui subissent facilement une cyclodéshydratation en présence d'alumine neutre pour donner les alkyl-3 méthylène-4 benzotriazines-1,2,3 (**5***a–d*). De la même manière on peut obtenir les aryl-3 méthylène-4 benzotriazines-1,2,3,(**8***a–c*) par cyclodéshydratation des(*ortho*-acétylphényl-1) aryl-3 triazènes (**7***a–c*) stables. On n'a pas réussi à synthétiser par cette méthode le méthylène-4 benzotriazine-1,2,3 (**5***e*) non-substitué. On fait l'hypothèse que les hydroxy-4 benzotriazines-1,2,3 (**4**) sont des intermédiaires dans la cyclodéshydratation; cette hypothèse se base sur le fait que l'on peut isoler l'hydroxy-4 benzotriazine-1,2,3 (**12**) stable à partir de la réaction de couplage de la méthylamine avec le sel de diazonium dérivé de l'*ortho*-aminobenzophénone. On inclut un rapport préliminaire sur l'étude de la thermolyse du méthyl-3 méthylène-4 benzotriazine-1,2,3 (**5***a*).

[Traduit par le journal]

Introduction

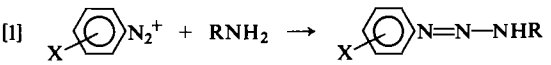
In the series of 1,2,3-benzotriazines represented by **1**, the 4-oxo (**1***a*), 4-thio (**1***b*), and 4-imino (**1***c*) derivatives are well known and have been extensively studied (1).



1 *a* X = O; *b* X = S; *c* X = NR′; *d* X = CH_2

Several methods are available for the synthesis of the 4-oxo derivatives; for example, the diazotization of substituted anthranilamides has long been known to give 1,2,3-benzotriazinones (2). In a similar manner, diazotization of *ortho*-aminothiobenzamide gives rise to 4-mercapto-1,2,3-benzotriazine, the tautomer of **1***b* (R = H) (3). Early work (4) on the diazotization of *ortho*-aminobenzamidines, which affords the 4-imino-1,2,3-benzotriazines (**1***c*), has been extended by Stevens and co-workers (5) to cover a wide variety of *N*-alkyl and *N*-aryl substituents. In contrast to the extent of knowledge of the derivatives **1***a*, **1***b*, and **1***c*, no example of a 4-methylene derivative (**1***d*) has previously been reported.[1]

In a previous report (6), the formation of triazenes, **2**, in the coupling reaction of aryl diazonium salts with primary aliphatic amines was shown to be strongly influenced by the nature of the substituent X [1].



[1]

2

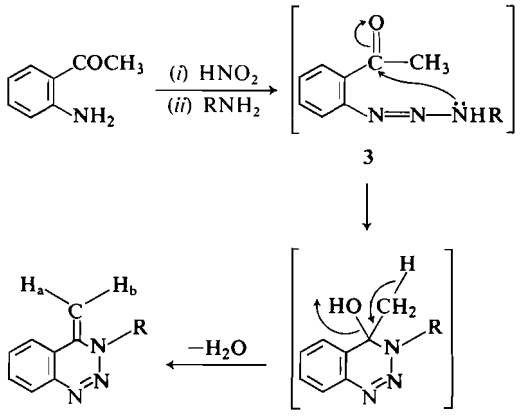
Maximum yields of triazene are obtained when X is a strongly electron-withdrawing group (*i.e.* —NO_2, —COMe, —CO_2Me, —CN), preferably in the *para*-position. However, reaction of *ortho*-substituted diazonium salts with alkylamines frequently afforded unstable triazenes, sometimes giving rise to anomalous products. For example, 1-(*ortho*-carbalkoxyphenyl)-3-alkyltriazenes, **9**,

[1]4-Methyl-1,2,3-benzotriazine, which has been reported recently (ref. 12), could be regarded as the 'tautomer' of the unsubstituted 4-methylene-1,2,3-benzotriazine (**1***d*, R = H).

have previously been shown (7) to undergo facile cyclization to 4-oxo-1,2,3-benzotriazines, **1***a*, and the *ortho*-nitrophenyltriazene (**2**, X = *ortho*-NO_2, R = Me) decomposes in the solid state or in solution (6). In the present work, we describe a study of the coupling reaction of the diazonium salts derived from *ortho*-aminophenyl ketones with primary amines; the triazenes obtained therefrom are the precursors of 4-methylene-1,2,3-benzotriazines (**1***d*), reported here for the first time.

Discussion

Treatment of an aqueous solution of the diazonium salt derived from *ortho*-aminoacetophenone with an excess of methylamine afforded an unstable orange-red solid **A**. Stirring the solid **A** in chloroform solution over neutral alumina gave a high yield of 3-methyl-4-methylene-1,2,3-benzotriazine (**5***a*, R = Me), the expected product of cyclodehydration of the *ortho*-acetylphenyltriazene, **3** (Scheme 1); no other product



5 *a* R = Me
b R = Et
c R = *n*-Pr
d R = $PhCH_2$
e R = H

SCHEME 1

was obtained from the alumina catalyzed reaction. The n.m.r. spectrum of the orange-red solid **A** suggests the presence of the open-chain triazene **3**, as well as the 4-methylenetriazine **5***a*, and at least one other component, which may be the hydroxytriazine intermediate, **4**. The presence of the open-chain triazene **3** is inferred from comparison with the n.m.r. spectrum of the previously reported isomer, 1-(*para*-acetylphenyl)-3-methyltriazene (6). Attempted purification of the orange-red solid **A** by column chromatography on alumina, with CCl_4 as eluent, resulted only in formation of the 4-methylenetriazine **5***a*. Apparently the cyclodehydration of the triazene **3** occurs incompletely during the coupling reaction and is catalyzed by adsorption on alumina during chromatography or in the slurry. Attempted recrystallization of the orange-red solid **A** was unsuccessful, being accompanied by considerable decomposition.

3-Methyl-4-methylene-1,2,3-benzotriazine, **5***a*, is a yellow crystalline solid, which displays the expected spectral characteristics. Carbonyl absorption is absent in the infrared spectrum; the only prominent absorption in the i.r. is at 1620 cm^{-1}, assigned to the exocyclic C=C ethylenic group (8). The most characteristic features of the n.m.r. spectrum of **5***a* are the doublets at 4.40 and 3.83 p.p.m., arising from geminal coupling of the non-equivalent vinylic protons of the 4-methylene-group, H_A and H_B; the observed coupling constant (2.4 Hz) is typical of geminal, vinylic systems (ref. 8, p. 128). The assignment of the resonances at 4.40 and 3.83 p.p.m. to the vinylic protons H_A and H_B respectively is based on consideration of the deshielding effect of the benzene ring; proton H_A is in closer proximity to the π-electron system of the benzene ring and should therefore resonate at lower field. The AB pattern exhibited by **5***a* is typical of all 4-methylene-triazines described here.

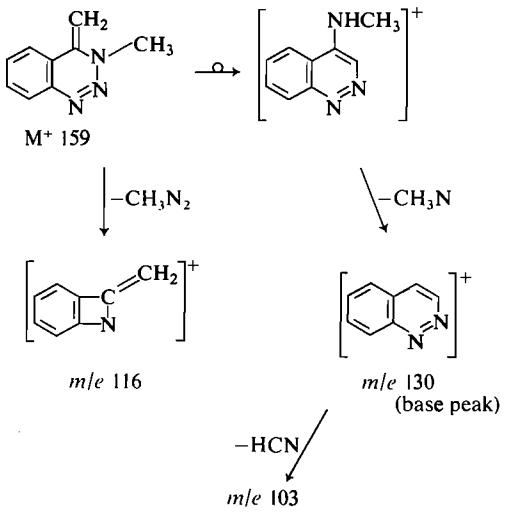
The mass spectrum of **5***a*, surprisingly, does not exhibit a fragment corresponding to direct loss of N_2, which is characteristic of 1,2,3-benzotriazines (9). The initial fragmentation, as indicated by the base peak at *m/e* 130, involves the loss of CH_3N from the molecular ion. The most likely explanation for this unusual mode of fragmentation is that the molecular ion rearranges to give the more stable methylaminocinnoline ion (Scheme 2), which would then readily lose the methylamino group as CH_3N to give the parent cinnoline ion at *m/e* 130. The strong peak at *m/e* 103 in the mass spectrum of **5***a* is invariably observed in the mass spectra of benzodiazines (10), arising in this case by loss of HCN from the cinnoline fragment. An alternative mode of fragmentation of the molecular ion, indicated by a less abundant fragment at *m/e* 116, probably involves loss of the CH_3N_2 grouping from the unrearranged molecular ion.

The formation of 3-alkyl-4-methylene-1,2,3-benzotriazines by the method described above

TABLE 1. Spectral data for 3-alkyl-4-methylene-1,2,3-benzotriazines (5)

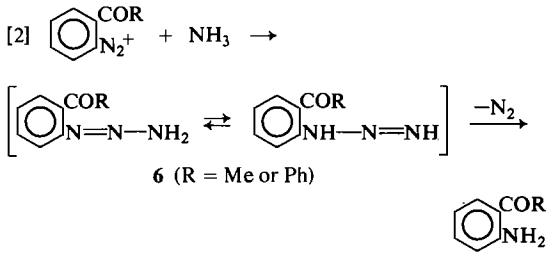
	R	$\nu_{max}(cm^{-1})$	δ (p.p.m.) Aromatic	H_a	H_b	R
5*a*	Me	1620	7.1–7.6 (m)	4.4 (d)*	3.83 (d)*	3.55 (3H, s, N—Me)
5*b*	Et	1620	7.1–7.7 (m)	4.4 (d)*	3.85 (d)*	3.95 (2H, q, CH_2)‡ 1.35 (3H, t, CH_3)‡
5*c*	*n*-Pr	1620	7.2–7.8 (m)	4.4 (d)*	— †	3.7–4.1 (3H, m, H_b+CH_2) 1.8 (2H, m, CH_2) 1.0 (3H, t, CH_3)‡
5*d*	$PhCH_2$	1620	6.9–7.9 (m)	4.4 (d)*	3.80 (d)*	5.2 (2H, s, benzylic CH_2)

*J = 2.4 Hz.
†H_b doublet is masked by the triplet of the N—CH_2 group.
‡J = 7 Hz.



SCHEME 2

has been extended to the 3-ethyl- (**5***b*), 3-*n*-propyl- (**5***c*), and 3-benzyl- (**5***d*) 4-methylene-1,2,3-benzotriazines, which exhibit spectral characteristics analogous to those of 3-methyl-4-methylene-1,2,3-benzotriazine (Table 1). The 3-ethyl- and 3-*n*-propyl derivatives are both oils, with a strong orange color, whereas the 3-benzyl-derivative is, like the 3-methyl analog, a yellow solid. Attempted synthesis of the unsubstituted 4-methylene-1,2,3-benzotriazine, **5***e*, by the same method did not succeed; treatment of the diazonium salt from *ortho*-aminoacetophenone with aqueous ammonia afforded only *ortho*-aminoacetophenone, presumably by formation and fragmentation of the 1-aryltriazene (**6**, R = Me) [2]. Similar treatment of *ortho*-aminobenzophenone likewise resulted in regeneration of starting material.



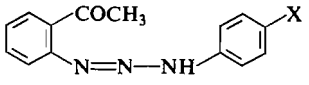
3-Aryl-4-methylene-1,2,3-benzotriazines, **8**, should, by analogy, be available from the cyclization of 1,3-diaryltriazenes, Ar—N=N—NH-Ar′, with an *ortho*-acetyl substituent in one aryl group. A search of the literature determined that no such diaryltriazene had previously been reported. Accordingly, *ortho*-aminoacetophenone was diazotized and coupled, in turn, with aniline, *para*-anisidine, *para*-aminoacetophenone, and methyl *para*-aminobenzoate, affording the 3-aryl-1-(*ortho*-acetylphenyl)-triazenes **7***a* (X = H), **7***b* (X = —OMe), **7***c* (X = —COMe), and **7***d* (X = —CO_2Me) respectively. Unlike the 3-alkyl-1-(*ortho*-acetylphenyl)-triazenes, these diaryltriazenes are stable crystalline solids, which exhibit the expected spectral characteristics (Table 2).

Some difficulty was encountered when cyclization of 3-phenyl-1-(*ortho*-acetylphenyl)-triazene, **7***a*, was attempted over alumina. Experiments carried out with acidic, basic, and neutral alumina, in turn, led to the conclusion that, as in the case of the 3-alkyl analogs, the best catalyst for the cyclization is neutral alumina. Various times for the reaction over neutral alumina were employed; surprisingly, a reaction time of only 2.5 h was necessary to effect complete cyclization. Longer reaction times resulted in a change in the nature of the product, but the exact course

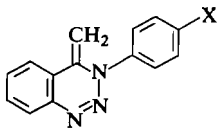
TABLE 2. Spectral data for 1-(*ortho*-acetylphenyl)-3-aryltriazenes (7)

	X	$\nu_{max}(cm^{-1})$	δ (p.p.m.) Aromatic	*ortho*-CH_3CO—	X
7*a*	H	3200 (NH) 1645 (C=O)	6.7–8.0 (m)	2.55 (s)	—
7*b*	CH_3O—	3200 (NH) 1645 (C=O)	6.7–8.0 (m)	2.60 (s)	3.80 (s, O—CH_3)
7*c*	CH_3CO—	3200 (NH) 1680 (C=O, *para*) 1645 (C=O, *ortho*)	7.0–8.2 (m)	2.60 (s)	2.67 (s, *para*-CH_3CO—)
7*d*	CH_3OCO—	3200 (NH) 1730 (C=O, ester) 1645 (C=O, ketone)	7.0–8.2 (m)	2.65 (s)	3.95 (s, CH_3OCO—)

of this apparent decomposition has not been determined. The product of the 2.5 h treatment of 7*a* over neutral alumina is a red oil, which resisted attempts at crystallization and appeared



7 *a* X = H
b X = OMe
c X = COMe
d X = CO_2Me

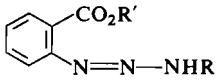


8 *a* X = H
b X = OMe
c X = COMe

to decompose during column chromatography. In spite of these difficulties, the spectral characteristics of the red oil demonstrate unequivocally that it is 3-phenyl-4-methylene-1,2,3-benzotriazine, 8*a*. The carbonyl absorption at 1645 cm^{-1} in the i.r. spectrum of 7*a* is completely absent in the i.r. spectrum of 8*a*. The conversion 7*a* → 8*a* is also accompanied by a characteristic change in the n.m.r. spectrum; the methyl singlet at 2.55 p.p.m. in the n.m.r. spectrum of 7*a* is absent in the n.m.r. spectrum of 8*a*, being replaced by the twin doublets of the vinylic protons, H_A and H_B, at 4.40 and 3.85 p.p.m. respectively.

Likewise, 3-(*para*-methoxyphenyl)-4-methylene-1,2,3-benzotriazine, 8*b*, was obtained as an oil from the corresponding triazene, 7*b*; on the other hand, 3-(*para*-acetylphenyl)-4-methylene-1,2,3-benzotriazine, 8*c*, was obtained as a crystalline solid. Both compounds display spectral characteristics analogous to those of the 3-phenyl derivative (Table 3). However, attempts to cyclize the ester 7*d* by this method did not succeed.

The facile cyclization of the *ortho*-acetylphenyltriazenes, 3, is somewhat different from the previously reported behavior of the unstable 1-(*ortho*-carbalkoxyphenyl)-3-alkyltriazenes, 9,



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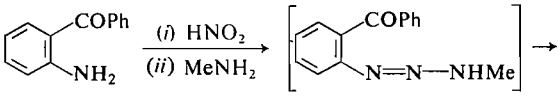
which readily undergo cyclization to the benzotriazinones (1*a*, R = alkyl) (7). The cyclization of the esters is a straight forward example of nucleophilic substitution at the carbonyl group, but analogous cyclization of the ketone 3 (Scheme 1) would afford the 4-hydroxytriazine intermediate 4 which is precluded from formation of an oxo derivative by the nature of the leaving group (*i.e.* CH_3—). Instead elimination of water from the 4-hydroxytriazine, involving the α-hydrogen of the original keto group, can take place, affording the 4-methylenetriazine 5.

Thus, the formation of the 4-methylenetriazines 5 necessitates the presence of α-hydrogen in the acyl group of the *ortho*-aminophenyl ketone used as starting material; absence of an α-hydrogen might well be the condition required for the formation of a stable 4-hydroxytriazine analogous to 4. Accordingly, *ortho*-aminobenzophenone, 10, was diazotized and the resulting diazonium salt solution was treated with an excess of methylamine, whereupon a white solid precipitated immediately. The white solid is quite stable, but does not exhibit the spectral characteristics of the expected triazene 11. Although

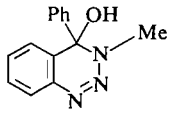
TABLE 3. Spectral data for 3-aryl-4-methylene-1,2,3-benzotriazines (**8**)

	X	$\nu_{max}(cm^{-1})$	δ (p.p.m.) Aromatic	H_a	H_b	X
8*a*	H	1600	7.1–7.9 (m)	4.4 (d)*	3.85 (d)*	—
8*b*	CH_3O—	1610	6.8–7.9 (m)	4.4 (d)*	3.80 (d)*	3.85 (s, O—CH_3)
8*c*	CH_3CO—	1680 (C=O, ketone) 1600	7.1–8.2 (m)	4.5 (d)*	4.05 (d)*	2.67 (s, *para*-CH_3CO—)

*J = 2.4 Hz.



10 **11**



12

the molecular weight of 239, determined by mass spectrometry, correlated with formula **11**, the i.r. spectrum of the white solid does not display a band in the carbonyl region. There is, however, a strong, broad band at 2600–3300 cm^{-1}, indicating the presence of a hydroxyl group. The mass and i.r. spectral evidence clearly show that the white solid is the 4-hydroxy-1,2,3-benzotriazine, **12**; the n.m.r. spectrum of the white solid is also consistent with structure **12**. The 4-hydroxytriazine, **12**, represents the first reported example of a triazine derivative of this type.

Due to the interest in the thermolysis of 1,2,3-benzotriazines reflected in the recent literature (11), the thermal properties of the 4-methylenetriazines **5**, seem to be of potential significance. However, the results obtained so far from thermolysis experiments with the 3-methyl derivative **5***a* are disappointing. Little or no change was observed after refluxing **5***a* in ethanol, benzene, or *para*-xylene. Decomposition did take place when **5***a* was refluxed in diglyme, but this reaction afforded only intractable tar. The 3-methyl derivative **5***a* does decompose in the cold when stored for long periods; the yellow crystalline solid darkens in color and becomes gummy in texture. The exact nature of this decomposition is under further investigation.

Experimental

Melting points were obtained on a hot-stage apparatus and are uncorrected. Infrared spectra were recorded with liquid paraffin mulls on a Perkin-Elmer Model 467 grating spectrophotometer, and u.v. spectra on a Perkin-Elmer Model 402 ultraviolet and visible spectrophotometer. Nuclear magnetic resonance spectra were recorded in deuteriochloroform as solvent, using tetramethylsilane as internal standard, with a Varian EM360 60 MHz spectrometer. Mass spectral data were obtained with a Dupont–C.E.C. Model 21-491 spectrometer.

3-Methyl-4-methylene-1,2,3-benzotriazine, 5a

ortho-Aminoacetophenone (0.85 g, 0.0063 mol) was dissolved in 15 ml of 2 *M* hydrochloric acid and diluted with 15 ml of water. The resulting solution was cooled to 0–5 °C, diazotized by the dropwise addition of an aqueous solution of sodium nitrite (0.45 g, 0.0065 mol), and left stirring for 15 min. Aqueous methylamine (2.8 ml of 40%, 0.036 mol) was then added to the cold diazonium salt solution in one portion. After stirring for a further 10 min, filtration of the resulting mixture afforded a bright orange-red solid (yield 0.91 g, m.p. 59–62 °C).

After drying under suction, the orange-red solid (0.91 g) was dissolved in chloroform (50 ml) and neutral alumina (28 g) was added. The resulting slurry was stirred at room temperature for 4.5 h, after which the alumina was removed by filtration and washed several times with small portions of chloroform. The combined chloroform extract and washings were evaporated to dryness affording 3-methyl-4-methylene-1,2,3-benzotriazine, **5***a*, (0.785 g, 0.0049 mol, 78.5%) m.p. 64–66 °C, as yellow needles; ν_{max} 1620 cm^{-1} (exocyclic C=C); λ_{max} (cyclohexane) 210 (ε 36 500), 268 (ε 14 300), 277 (ε 14 100), 333 (ε 4300), 348 (ε 3500), 375 (ε 1800), and 394 (ε 1800) nm; M^+ 159 ($C_9H_9N_3$), *m/e* 130 ($M - NCH_3$, base), 116 ($M - N_2CH_3$), 103, 89.[2]

The above procedure was repeated with ethylamine, *n*-propylamine, or benzylamine in place of methylamine to afford the 3-alkyl-4-methylene-1,2,3-benzotriazines: **5***b*, R = Et, b.p. 103 °C (2.0 Torr), 60% yield; **5***c*, R = *n*-Pr, b.p. 97 °C (dec.) (1.5 Torr), 90% yield; **5***d*, R = $PhCH_2$, m.p. 80 °C (dec.), 67% yield. Spectral data of these compounds are given in Table 1.

1-(ortho-Acetylphenyl)-3-aryltriazenes, 7

ortho-Aminoacetophenone (0.02 mol) was dissolved in 2 *M* hydrochloric acid (30 ml), and diluted with water (20 ml). The solution was cooled to 0–5 °C, diazotized with sodium nitrite (0.02 mol) in water and stirred for 20 min. A solution of the aromatic amine (0.025 mol) in 2 *M*

[2]Elemental analysis was not attempted, due to the unstable nature of the compound which could only be stored under refrigeration.

hydrochloric acid (30 ml) was added slowly to the diazonium salt solution, and, after stirring for a further 15 min, the resulting mixture was neutralized with an excess of sodium acetate trihydrate (~50 g). The resulting yellow precipitate was filtered and recrystallized from ethanol affording the 1-(*ortho*-acetylphenyl)-3-aryltriazene as follows (aromatic amine, X, % yield, m.p.): **7***a*, aniline, X = H, 63% yield, m.p. 102–104 °C; **7***b*, *p*-anisidine, X = OCH_3, 81% yield, m.p. 136–138 °C; **7***c*, *p*-aminoacetophenone, X = $COCH_3$, 94% yield, m.p. 175–177 °C; **7***d*, methyl *p*-aminobenzoate, X = CO_2CH_3, 51% yield, m.p. 126–128 °C. Spectral data of these compounds are given in Table 2.

3-Aryl-4-methylene-1,2,3-benzotriazines, 8

The 1-(*ortho*-acetylphenyl)-3-aryltriazene **7** (0.003 mol) was dissolved in chloroform (50 ml) and stirred over neutral alumina (25 g) for 2.5–5.0 h. Filtration of the slurry, followed by washing of the alumina with chloroform, and evaporation of the combined chloroform washings afforded the 3-aryl-4-methylene-1,2,3-benzotriazines as follows: **8***a*, X = H, red oil, 70% yield (reaction time 2.5 h); **8***b*, X = OCH_3, red oil, 57% yield (reaction time 4.5 h); **8***c*, X = $COCH_3$, m.p. 121–123 °C ($CHCl_3$), 48% yield (reaction time 5.0 h). Spectral data of these compounds are given in Table 3.

4-Hydroxy-3-methyl-4-phenyl-1,2,3-benzotriazine, 12

ortho-Aminobenzophenone (5.08 g) was suspended in 2 *M* hydrochloric acid (60 ml) and the mixture heated to boiling. Concentrated hydrochloric acid (4.0 ml) was added to bring the amine into solution, which was then diluted with water (80 ml) and cooled to 0–5 °C. At this point, the hydrochloride salt precipitated. The cold slurry was diazotized with sodium nitrite (1.8 g) in a minimum volume of water over a period of 1 h, after which time a clear solution was obtained. Aqueous methylamine (40%, 11.2 ml) was added in one portion, and the resulting white precipitate was filtered, suction dried, and recrystallized from ethanol, affording 4-hydroxy-3-methyl-4-phenyl-1,2,3-benzotriazine, **12** (4.6 g, 76%), m.p. 142–144 °C (EtOH), ν_{max} 2600–3300 cm^{-1} (broad, OH); δ 6.9–7.8 (9H, m, aromatic), 3.6 (1H, s, broad, OH), and 3.3 (3H, s, N—CH_3) p.p.m.; M^+ 239.

Anal. Calcd. for $C_{14}H_{13}N_3O$: C, 70.28; H, 5.48; N, 17.56. Found: C, 70.08; H, 5.37; N, 17.33.

Attempted Synthesis of 1-ortho-Acetylphenyltriazene, 3 (R = H)

ortho-Aminoacetophenone (1.71 g) was dissolved in 2 *M* hydrochloric acid (20 ml), diluted with water (40 ml) and diazotized at 0 °C with sodium nitrite (0.90 g). Concentrated ammonia was added dropwise to the diazonium salt solution until slightly basic and the resulting mixture extracted with chloroform. Evaporation of the dried chloroform extracts afforded *ortho*-aminoacetophenone (quantitative recovery), identical in all respects with the starting material.

Likewise, diazotization of *ortho*-aminobenzophenone followed by neutralization of the diazonium salt solution with ammonia, afforded the starting material, recovery 82%.

Thermolysis of 3-Methyl-4-methylene-1,2,3-benzotriazine, 5a

(*a*) The 4-methylenetriazine (0.67 g) was heated dry over a steam bath for 1.0 h. The residue, although considerably darkened in color, crystallized on cooling and was found to be identical with the starting material.

(*b*) The 4-methylenetriazine (0.53 g) was recovered unchanged after refluxing in absolute ethanol (50 ml) for 3 h.

(*c*) The 4-methylenetriazine (0.94 g) was refluxed in benzene (50 ml) for 24 h and, after evaporation of the solvent, was recovered unchanged (87% recovery).

(*d*) The 4-methylenetriazine (0.74 g) was refluxed in *p*-xylene (25 ml) for 2 h; evaporation afforded unchanged starting material (93%).

(*e*) The 4-methylenetriazine (0.785 g) was refluxed in anhydrous diglyme for 6.5 h; evaporation under vacuum at 100 °C afforded a black oil, which was purified by column chromatography on neutral alumina with chloroform eluent affording unchanged starting material (83% recovery).

(*f*) The 4-methylenetriazine (0.9 g) was refluxed in diglyme for 18 h; the residue, after evaporation, was a black tar, which remained intractable to purification. This residue did not appear to contain starting material.

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