Synthesis and Reactions of 1-Alkyl-3-(*o*-carbalkoxyphenyl)-triazenes

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The reaction of diazotized anthranilate esters with primary aliphatic amines has been reinvestigated, giving rise to a new series of comparatively unstable 1-alkyl-3-(*o*-carbalkoxyphenyl)-triazenes (**3**). The structures of the products have been confirmed by spectroscopic analysis, molecular ion mass measurements, and from the results of chemical degradation. The spectroscopic properties indicate a preference for the tautomer in which the azo-group is non-conjugated with the benzene ring, Ar·NH·N═N·R; this hypothesis is partly supported by the chemical degradation. In general, the triazenes (**3**) break down by fragmentation of the triazene moiety to give anthranilic acid derivatives, or undergo cyclization to 3-alkyltriazinones (**1**). The alkyltriazinones are also obtained directly in the coupling reaction of the diazonium salt with the amine in the presence of a sodium acetate buffer. The cyclization is quantitative when catalyzed by activity V alumina; a wide variation in the product distribution obtained by reaction with different types of alumina has been observed, and the correlation of these results with the known surface structure of alumina is discussed. Finally, an explanation is offered for the difference between the results of the present work and previous reports.

La réaction des esters anthraniliques diazotés sur les amines primaires aliphatiques a été réexaminée, donnant lieu à une nouvelle série d'alkyl-1 (*o*-carbalkoxyphenyl)-3 triazènes (**3**) relativement instables. Les structures des produits ont été confirmées par analyse spectroscopique, mesure de masse des ions moléculaires et à partir des résultats de la dégradation chimique. Les propriétés spectroscopiques indiquent une préférence pour le tantomère dans lequel le groupe azo n'est pas conjugué au cycle benzènique ArNH·N═N·R; cette hypothèse est en partie confirmée par dégradation chimique. En général les triazènes (**3**) se décomposent par fragmentation du reste triazène qui conduit aux dérivés de l'acide anthranilique, ou subissent une cyclisation en alkyl-3 triazinones (**1**). Les alkyltriazinones sont également obtenues par couplage direct du sel de diazonium avec l'amine en présence du tampon acétate de sodium. La cyclisation est quantitative par catalyse sur alumine d'activité V; une grande variété dans la distribution du produit obtenue par réaction avec divers types d'alumine, a été observée; une corrélation de ces résultats avec la surface d'une structure connue d'alumine est discutée. Finalement, une explication est donnée pour la différence entre les résultats de ce travail et ceux rapportés jusqu'ici.

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Generally, the reaction of a diazonium salt with a primary aliphatic amine results in substitution of both amino hydrogen atoms, yielding a 3-alkylpentaz-1,4-diene, Ar·N═N·NR·N═N·Ar, and the intermediate diazoamino compound, Ar·N═N·NHR, is not usually isolated (1). In contrast, 1,3-diaryltriazenes, Ar·N═N·NH·Ar, are readily obtained in high yield from the coupling reaction of the diazonium salt with a primary aromatic amine (2). A much used method of synthesis of 3-aryl-1,2,3-benzotriazin-4-ones (**1**, R = aryl) involves diazotization of an alkyl anthranilate (**2**, R′ = Me or Et), coupling of the diazonium salt solution with a primary aromatic amine, $ArNH_2$, and cyclization of the resulting *o*-carbalkoxyphenyltriazene (**3**, R = aryl, R′ = alkyl) in boiling aqueous ethanol (3). On the other hand, the reaction of diazotized anthranilate esters with primary aliphatic amines has been reported (4–6) to afford directly the 3-alkyl-1,2,3-benzotriazinone (**1**, R = alkyl), although often in low yield. 1-Alkyl-3-(*o*-carbalkoxyphenyl)-triazenes (**3**, R and R′ = alkyl) have been postulated (4, 6) as intermediates in the latter reaction, but in no previously reported case has the intermediate been isolated.

We report a reinvestigation of the reaction of diazotized anthranilate esters with primary aliphatic amines, affording a series of 1-alkyl-3-(*o*-carbalkoxyphenyl)-triazenes (**3**) in good to excellent yields, and an extensive study of the properties and reactions of these compounds.

For example, treatment of a solution of *o*-carbethoxybenzene diazonium salt with excess of methylamine affords an 84% yield of 1-methyl-3-(*o*-carbethoxyphenyl)-triazene (**3***a*); the product must be isolated from the reaction

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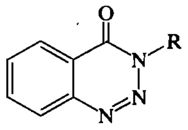
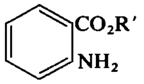
mixture immediately after addition of the amine. 3-Methyl-1,2,3-benzotriazin-4-one (**1**a) is obtained in excellent yield if the reaction mixture is stirred for a while after the addition of methylamine. Evidently, under the strongly basic conditions employed, the intermediate triazene (**3**a) is sufficiently stable to be isolated, but undergoes a slow cyclization when left in the reaction mixture. The cyclization is apparently acid-catalyzed since the methyltriazinone (**1**a) is formed rapidly, when the coupling reaction of the diazonium salt with methylamine is carried out in the presence of a sodium acetate buffer (weak acid). In fact, as described later, the methyltriazinone (**1**a) is one of the products of acid hydrolysis of the triazene (**3**a).



1

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



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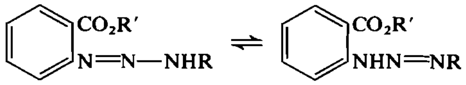
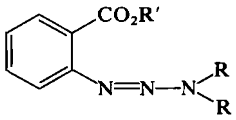


i *ii*

3

a R = Me; R′ = Et
b R = R′ = Et
c R = *n*-Pr; R′ = Et
d R = cyclohexyl; R′ = Et
e $R = PhCH_2$; R′ = Et
f R = Et; R′ = Me
g R = R′ = Me



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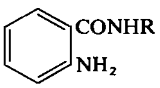

5

The reaction of diazotized anthranilate esters with primary aliphatic amines to give triazenes is not entirely general. 1-Alkyl-3-(*o*-carbalkoxyphenyl)-triazenes (**3**a–g) were obtained in 40–100% yields by diazotization of the alkyl anthranilate (**2**), followed by rapid treatment of the cold diazonium salt solution with an excess of the amine, RNH_2. In the case of reaction of ethylamine with diazotized ethyl anthranilate, a minor yield of the ethyltriazinone (**1**b) was also obtained. In one reaction, that of *iso*-propylamine with the diazonium salt, the intermediate triazene was not isolated, but in that instance an 80% yield of the *iso*-propyltriazinone (**1**d) was obtained. This anomaly does not seem to be a function of the nature of the alkyl group, since reaction of the closely similar cyclohexylamine proceeds normally. In two instances, the reactions of *n*- and *iso*-butylamine, neither the expected triazenes nor the cyclization products were isolated; in both cases a quantitative recovery of the anthranilate ester results.

The triazenes (**3**a–g) were frequently obtained contaminated with anthranilate ester if, in the coupling reaction, the amine was added slowly to the diazonium salt solution or if the temperature of the reaction mixture was not maintained at or close to 0°. van Heyningen (4) also observed anthranilate ester regeneration in these reactions. Since it is unlikely that the amine could be formed directly from the diazonium salt (1), it appears that triazene formation does take place in these reactions and that the regeneration of anthranilate ester arises from a fragmentation of the triazene (see later discussion).

The 1-alkyl-3-(*o*-carbalkoxyphenyl)-triazenes (**3**) (Table 1) are unstable, low melting solids or viscous oils, which decompose on standing, in some instances completely within 48 h, affording the corresponding 3-alkyltriazinone (**1**). The solid triazenes are also prone to decomposition when recrystallization is attempted, in some cases precluding further purification. Attempted distillation of the oils resulted in decomposition at approximately 130°. Attempted purification by column chromatography (alumina or silica) results in rapid decomposition on the column with gas evolution. All efforts to separate mixtures of triazene and anthranilate, obtained in the coupling reactions described above, failed due to decomposition of the triazene. Consequently, some of the physical and spectroscopic data in Table 1 relate to unpurified products, but these data show that the triazenes are obtained quite pure directly from the reaction mixture.

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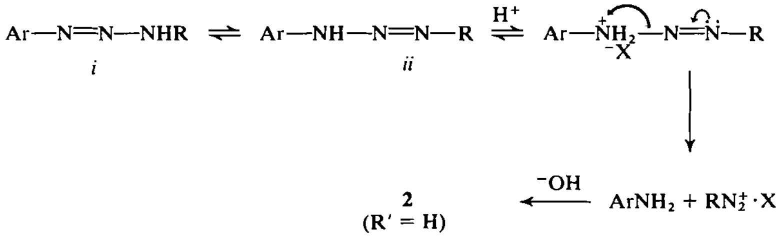
TABLE 1. 1-Alkyl-3-(*o*-carbalkoxyphenyl)-triazenes*

							Molecular ion (mass spectrum)		N.m.r. (CDCl$_3$)		
Compound	R	R′	Yield (%)	m.p. (°C)	b.p. (°C)	Molecular formula	Found	Calcd.	δ(p.p.m.)	Protons	ν_{max} (cm^{-1})
a	Me	Et	84	35–36†	—	$C_{10}H_{13}N_3O_2$	207.1010	207.1008	11.93(1H, s) 6.75–8.09(4H, m) 4.33(2H, q) 3.57(3H, s) 1.37(3H, t)	NH aromatic O—CH$_2$ N—Me C—Me	3300 (NH) 1690 (CO) 1495 (N=N)
b	Et	Et	75	—	dec. 132	$C_{11}H_{15}N_3O_2$	221.1166	221.1164	11.90(1H, s) 6.70–8.05(4H, m) 4.30(2H, q) 3.71(2H, q) 1.30(3H, t) 1.23(3H, t)	NH aromatic O—CH$_2$ N—CH$_2$ O·C·Me N·C·Me	"
c	*n*-Pr	Et	100	—	dec. 130	$C_{12}H_{17}N_3O_2$	235.1320	235.1321	11.95(1H, s) 6.67–8.10(4H, m) 4.33(2H, q) 3.70(2H, t) 1.55–1.99(2H, m) 1.35(3H, t) 0.99(3H, t)	NH aromatic O—CH$_2$ N—CH$_2$ C·CH$_2$·C O·C·Me C·Me	"
d	Cyclohexyl	Et	86	35–36‡	—	$C_{15}H_{21}N_3O_2$	275.1633	275.1634	11.87(1H, s) 6.70–8.06(4H, m) 4.30(2H, q) 3.5(1H, m, broad) 1.0–2.1(10H, m) 1.30(3H, t)	NH aromatic O—CH$_2$ N—CH methylenes O·C·Me	"
e	PhCH$_2$	Et	80	28–29‡	—	$C_{16}H_{17}N_3O_2$	283.1319	283.1321	12.02(1H, s) 6.67–8.00(9H, m) 4.83(2H, s) 4.25(2H, q) 1.25(3H, t)	NH aromatic N—CH$_2$ O—CH$_2$ O·C·Me	"
f	Et	Me	40	26–27§	—	$C_{10}H_{13}N_3O_2$	207.1002	207.1008	11.88(1H, s) 6.72–8.05(4H, m) 3.83(3H, s) 3.70(2H, q) 1.28(3H, t)	NH aromatic O—Me N—CH$_2$ O·C·Me	"
g	Me	Me	67	33–34§	—	$C_9H_{11}N_3O_2$	193.0849	193.0851			"

*Due to the unstable nature of these compounds, satisfactory elemental analyses could not be obtained.
†From aqueous ethanol.
‡From ethanol.
§Decompose upon recrystallization.
‖A satisfactory n.m.r. spectrum could not be obtained due to rapid decomposition in solution.

[1]



(Ar = o-R′O$_2$C·C$_6$H$_4$—)

The i.r. spectra of all the triazenes (**3**a–g) display N—H absorption at 3300 cm^{-1}, carbonyl absorption at 1690 cm^{-1}, and a strong band at 1495 cm^{-1}, assigned to the azo group, N=N, stretching vibration. The N=N stretching frequency of 1-aryl-3,3-dialkyl triazenes (**4**) has been identified with absorption at 1410–1415 cm^{-1} in the i.r. (7); absorption in the region 1400–1420 cm^{-1} is either very weak or non-existent in the i.r. spectra of the triazenes (**3**). The high frequency of N=N absorption in the triazenes (**3**) suggests non-conjugation of the azo and phenyl groups, indicating a preference for tautomer **3***ii* over **3***i*. The n.m.r. chemical shifts and splitting patterns are consistent with the assigned structures (**3**), and also favor tautomer *ii*. The amino (NH) proton signal is broad in the range 11.87–12.02 p.p.m., compared with 10.95 p.p.m. for compounds of the type ArNH·N=C< (8). Molecular formulae are supported by high resolution molecular ion mass measurement.

The chemical properties of the triazenes (**3**) are also in accord with the assigned structures. Thus, refluxing the triazenes (**3***a*, *e* and *g*) in aqueous ethanol gave the corresponding 3-alkyltriazinones (**1***a* or *e*) in 65–92% yields. Similar treatment of the *n*-propyltriazene (**3***c*) gave a mixture of the *n*-propyltriazinone (**1***c*) and ethyl anthranilate, and of triazenes (**3***b* and *d*) gave only ethyl anthranilate. The formation of the triazines in these reactions compares with analogous cyclizations of 1-aryl-3-(*o*-carbalkoxyphenyl)-triazenes (**3**, R = aryl, R′ = alkyl) (3), but the formation of ethyl anthranilate has not been observed in the reactions of the aryl series. The overall yield of alkyltriazinone (**1**) in these reactions, based on alkyl anthranilate as starting material, is as high as 60%, and is raised to over 80% when the alumina-catalyzed method of cyclization, described below, is employed, representing a substantial improvement over the 20–30% yields reported previously (4). Alkaline hydrolysis of the methyltriazene (**3***a*) gave a high yield of anthranilic acid (**2**, R′ = H), whereas the major product of acid hydrolysis is ethyl anthranilate, with a minor yield of the methyltriazinone (**1***a*).

The formation of anthranilate esters in the degradation reactions of the triazenes (**3**) is best described as an example of general acid–base catalysis. In the case of acid catalysis, either mineral or very weak acid such as water or ethanol, the reaction probably proceeds by protonation of tautomer *ii*, followed by a fragmentation similar to that observed in the diazoamino → aminoazobenzene rearrangement (7) eq. 1.

In the case of alkaline hydrolysis, the equilibrium $i \rightleftharpoons ii$ may be facilitated to the right, leading eventually to exclusive formation of anthranilic acid (**2**, R′ = H), after hydrolysis of the ester group. An alternative route to anthranilic acid in an alkaline medium involves nucleophilic displacement at the azo-nitrogen atom in tautomer *ii*, resulting in replacement of the arylamino group by hydroxide ion eq. 2. There is no evidence in the literature to support

[2]

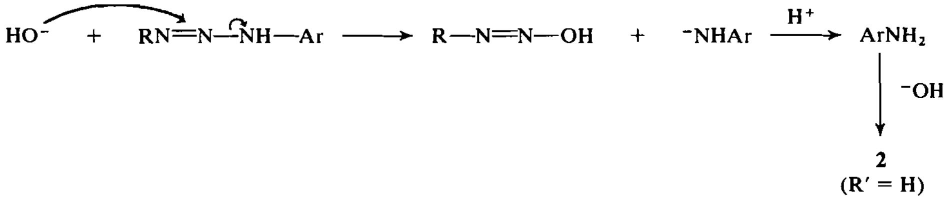


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TABLE 2. Product distribution in the alumina-catalyzed decomposition of 1-methyl-3-(*o*-carbethoxyphenyl)-triazene (**3***a*)

Type of alumina	Activity	Bake-out temperature* (°C)	Reaction time (min)	Yield (%) Ethyl anthranilate	Yield (%) Triazine (**1***a*)
Basic	I	—	35	41	38
Neutral	I	—	35	54	24
Acid	I	—	35	62	8
Basic	I	120	35	—	100
Neutral	I	120	35	23	73
Acid	I	120	35	64	36
Basic	I	300	35	11	81
Neutral	I	300	35	51	36
Acid	I	300	35	61	16
Basic	I	600	35	33	64
Acid	I	600	35	79	10
Basic	II†	—	35	—	91
Basic	V†	—	12 (h)	—	100
Neutral	V†	—	12 (h)	—	100
Acid	V†	—	12 (h)	—	100

*Activity I alumina was baked out at the given temperature for an overnight period immediately prior to use.

†Activity II and V alumina were obtained from the commercial activity I alumina by addition of the quantity of water specified by the manufacturer.

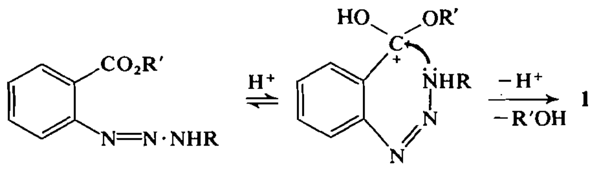
this latter postulation, although van Heyningen (4) made a similar proposal to account for reformation of anthranilate ester in the coupling reaction described previously.

The observation that the triazenes (**3**) undergo cyclization to the triazinones (**1**) under acidic conditions, frequently accompanied by fragmentation to anthranilate ester, suggests that protonation at the carbonyl-oxygen competes successfully with protonation at the amino-nitrogen, catalyzing the cyclization reaction, thus [3].

The alumina-catalyzed decomposition of 1-methyl-3-(*o*-carbethoxyphenyl)-triazene (**3***a*) in anhydrous benzene has been extensively studied. Two modes of reaction are evident: (*a*) cyclization to the methyltriazinone (**1***a*); (*b*) triazene cleavage to ethyl anthranilate, with concomitant evolution of nitrogen gas. The proportion of the two products varies a great deal with the nature of the alumina, and the product distributions obtained with various types of alumina are shown in Table 2.

The compositions of mixtures of ester and triazinone obtained in these reactions, and also in the acid hydrolysis of **3***a*, have been determined by a quantitative i.r. method, which permits rapid analysis and does not require separation of the components. The method thus eliminates any inaccuracies that might be introduced if the mixtures were separated by distillation or chromatography. The method derives from the fact that ethyl anthranilate absorbs strongly at 3500 cm^{-1} (NH stretch) in the i.r., whereas the triazinone (**1***a*) is essentially transparent above 3000 cm^{-1}, but absorbs strongly at 960 cm^{-1} (assigned to N—N stretch). Ethyl anthranilate is almost transparent between 900 and 1000 cm^{-1}. Measurement of the relative intensities of the 3500 and

[3]



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960 cm^{-1} peaks in the i.r. spectrum of an unknown mixture, and comparison with a series of mixtures of known composition, allowed determination of the composition of the unknown without separation.

Several general trends are evident from the data in Table 2. The yield of triazinone increases as the activity of the alumina is lowered, and is quantitative for activity V alumina, whether acid, neutral, or basic. (This reaction represents the most efficient way of synthesizing the methyltriazinone (**1***a*) from the triazene.) For a particular activity, the ratio of the yields, triazinone:ester, is greatest for basic alumina, least for acid alumina, and intermediate for neutral alumina. The yield of triazinone is also increased markedly by baking out the alumina at 120° prior to reaction, but this effect is lessened somewhat by baking out at higher temperatures.

The product distributions in the acid alumina-catalyzed reactions are almost identical to the distribution of products obtained in the reaction of the triazene (**3***a*) with mineral acid. The acidic sites on the surface of alumina can be either Bronsted or Lewis acid sites, the latter probably being due to the exposure of Al^{3+} ions at the surface (9, 10), so it seems likely that the acid alumina-catalyzed reaction proceeds according to eqs. 1 and 3, or by similar routes involving Al^{3+} ion instead of H^+. The action of acid alumina is completely changed by addition of a small amount of water (activity V), triazinone formation taking over completely, suggesting that adsorbed water molecules cover the previously exposed Lewis acid sites.

The reaction of the triazene (**3***a*) with basic alumina, giving triazinone formation almost exclusively, is very different from the reaction with aqueous alkali. The mechanisms represented by eqs. 1 and 2 are seemingly not applicable in this instance. An alternative course for triazinone formation, involving base catalysis, is proton abstraction from the amino nitrogen, followed by nucleophilic addition at the ester carbonyl group (eq. 4). There does not appear to be a reasonable explanation for the fact that cyclization does not take place in aqueous alkali.

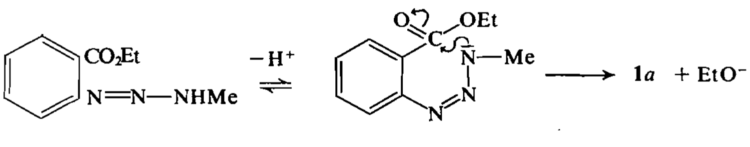
The effect of baking out the alumina before use is more pronounced for basic than for acid alumina, resulting in preference for triazinone formation. de Boer (11) has shown that surface water in alumina is removed easily at 120°, exposing a greater number of active sites. In the case of basic alumina, this might result in a greater facility to catalyze the cyclization by a mechanism such as [4]. At higher temperatures, adjacent ^-OH groups are expelled as water molecules, leaving behind exposed Al^{3+} ions and thus increasing the proportion of acid sites on the surface (10). The observation that the triazinone yield drops in favor of anthranilate formation if the alumina is baked out at a higher temperature, 300 or 600°, is in accordance with these postulations.

Conclusion

The results presented in this paper provide an explanation for the fact that previous workers did not isolate the intermediate triazenes (**3**). The use of a sodium acetate buffer in the coupling reaction is very common, but the present work shows that the 1-alkyl-3-aryltriazenes cannot be isolated when the coupling reaction is buffered. This is in contrast to the reaction of diazonium salts with aromatic primary amines, in which case the yield of diazoamino compound is increased by the use of a buffer (2, 3). van Heyningen (4) used a direct coupling reaction with the aliphatic amine without a buffer, but yet did not isolate the intermediates. Indeed, the conditions of reaction in the present work are virtually identical with those employed by van Heyningen; the difference must be in the method of work-up.

van Heyningen purified his products by distillation under reduced pressure, obtaining low yields of triazinone (**1**) and a high recovery of the starting material, alkyl anthranilate. We have shown here that the coupling reaction of diazonium salts with aliphatic primary amines

[4]



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sometimes affords a mixture of the intermediate triazene and *regenerated* alkyl anthranilate, that the intermediates are extremely unstable, resisting all attempts at separation from mixtures, and further that the decomposition of the triazenes (**3**) frequently gives rise to a mixture of triazinone and alkyl anthranilate. Thus, it seems very likely that van Heyningen did in fact isolate the triazenes, either pure or as mixtures with anthranilate, but also equally likely that they decomposed on distillation. Therefore, there is little contradiction between the present work and previously reported results; simply a slight modification of conditions and work-up that results in the isolation of previously unobserved reaction intermediates.

Experimental

Melting points were obtained on a Fisher–Johns apparatus and are corrected. The i.r. spectra were recorded with liquid paraffin mulls on a Perkin–Elmer Infracord spectrophotometer. N.m.r. spectra were obtained with a Varian A-60A spectrometer using tetramethylsilane as the internal standard, and mass spectra with a Dupont/C.E.C. model 21-110B high resolution spectrometer. Molecular ion mass measurements were done by the peak-matching method using electrical detection. Merck grade alumina was obtained from Brinkmann Instruments (Canada) Limited.

1-Alkyl-3-(o-carbalkoxyphenyl)-triazenes (3a–g)

Methyl or ethyl anthranilate (0.006 mol) was added to 2 *M* hydrochloric acid (9.0 ml) and diluted with water (20 ml) to dissolve the precipitated salt. The resulting solution was cooled to 0°, diazotized with sodium nitrite (0.45 g) in a minimum volume of water, and stirred at 0° until a clear solution was obtained (up to 1 h). An aqueous solution of the appropriate amine (0.036 mol) was added to the cold diazonium salt solution in one portion, and the solid which separated was isolated immediately by filtration and crystallized from ethanol or aqueous ethanol to afford the *1-alkyl-3-(o-carbalkoxyphenyl)-triazenes* (**3**) as colorless or pale yellow prisms (Table 1). Some of the products separated from the reaction mixture as oils; these were isolated by extraction with ether and evaporation of the washed and dried (Na_2SO_4) ether extract. Attempted purification of the oils by distillation or chromatography resulted in decomposition.

In the reaction of diazotized ethyl anthranilate with ethylamine, affording the triazene (**3***b*), the aqueous mother liquor gave a precipitate on standing, identified as 3-ethyl-1,2,3-benzotriazin-4-one (**1***b*) (11%), m.p. 68.5–70° (lit. (4) 70–71°), ν_{max} 1675 cm^{-1}.

The reaction of diazotized methyl anthranilate with *n*-butylamine or *iso*-butylamine resulted in quantitative recovery of methyl anthranilate.

3-Methyl-1,2,3-benzotriazin-4-one (1a)

(*a*) 1-Methyl-3-(*o*-carbethoxyphenyl)-triazene (**3***a*) (1.0 g) was refluxed in 70% aqueous ethanol (30 ml) for 4 h. The solution was concentrated *in vacuo* and the precipitated solid was filtered to yield 3-methyl-1,2,3-benzotriazin-4-one (**1***a*) (0.5 g, 65%), m.p. 121–122 °C (ethanol), ν_{max} 1670 cm^{-1} (C=O), which was identical with an authentic sample (i.r. spectrum and mixed m.p. 122–122.5 °C) prepared by diazotization of *N*-methylanthranilamide (**5**, R = Me) (12).

Similar treatment of 1-methyl-3-(*o*-carbomethoxyphenyl)-triazene (**3***g*) gave an identical product (yield 92%).

(*b*) A cold solution of ethyl anthranilate (1.0 g) in concentrated hydrochloric acid (1.75 ml) and water (30 ml) was diazotized with aqueous sodium nitrite (0.45 g in a minimum volume of water). The resulting diazonium salt solution was treated with 40% aqueous methylamine dropwise with constant agitation, at such a rate that the temperature did not rise above 0 °C, until the solution was strongly alkaline (p*H* > 11). A precipitate appeared at this stage, but was not separated. The mixture was allowed to warm to room temperature slowly with stirring, and after stirring overnight the precipitate was collected to yield the methyltriazinone (**1***a*) (0.8 g, 82%), m.p. 120 °C, identical with a sample prepared above.

(*c*) Ethyl anthranilate (1.0 g) was dissolved in 2 *M* hydrochloric acid (9 ml) and water (20 ml) and the solution cooled to 0 °C. The cold solution was diazotized with sodium nitrite to starch–iodide end-point and then made neutral by the addition of a solution of sodium acetate (17.2 g) in water. 40% aqueous methylamine (3.5 ml) was added quickly in one portion, forming a yellow precipitate which was filtered immediately to yield the methyltriazinone (**1***a*) (0.8 g, 82%), identical with a sample prepared above.

(*d*) 1-Methyl-3-(*o*-carbethoxyphenyl)-triazene (**3***a*) (0.5 g) was dissolved in anhydrous benzene (50 ml) and activity V alumina (6.0 g) was added. The resulting slurry was stirred for 12 h at room temperature and filtered. The residual alumina was washed several times with aliquots (10 ml) of anhydrous benzene and the combined filtrate and washings evaporated to dryness *in vacuo* to yield the methyltriazinone (**1***a*) (yield quantitative) identical with a sample prepared above.

3-Benzyl-1,2,3-benzotriazin-4-one (1e)

Refluxing 1-benzyl-3-(*o*-carbethoxyphenyl)-triazene (**3***e*) in aqueous ethanol, as under procedure *a* above, gave the benzyltriazinone (**1***e*), in 70% yield, m.p. 120–121.5 °C (lit. (5) 122–123 °C), ν_{max} 1670 cm^{-1}.

3-(n-Propyl)-1,2,3-benzotriazin-4 one (1c)

1-(*n*-Propyl)-3-(*o*-carbethoxyphenyl)-triazene (**3***c*) (0.5 g) was refluxed in 70% aqueous ethanol (15 ml) for 2 h. The solution was concentrated *in vacuo* to remove ethanol and the aqueous residue was extracted with chloroform. Evaporation of the dried (Na_2SO_4) extract yielded a yellow oil which partly solidified on standing. Filtration of the mixture yielded, from the solid phase, the *n*-propyltriazinone (**1***c*) (0.11 g, 27.5%), m.p. 56–56.5 °C (aqueous ethanol) (lit. (13) 61–62°), ν_{max} 1675 cm^{-1}. The oily filtrate was identified as ethyl anthranilate (0.23 g, 66%) by comparison with an authentic sample (Eastman).

Similar treatment of 1-ethyl-3-(*o*-carbethoxyphenyl)-triazene (**3***b*) or of 1-cyclohexyl-3-(*o*-carbethoxyphenyl)-triazene (**3***d*) gave only ethyl anthranilate (yields 78 and 67% respectively).

3-(i-Propyl)-1,2,3-benzotriazin-4-one (1d)

A solution of methyl anthranilate (1.0 g) in 2 *M* hydrochloric acid (9.9 ml) and water (20 ml) was cooled below 5 °C and diazotized with sodium nitrite (0.45 g) in water. 40% aqueous *iso*-propylamine (6.4 ml) was added slowly, giving a strongly alkaline solution (no precipitate was evident at this stage), which was stirred at room temperature for 5 days. The precipitated solid was filtered to afford the *iso*-propyltriazinone (**1***d*) (1.0 g, 80%), m.p. 55.5–56.0° (lit. (5) 60–61°), ν_{max} 1680 cm^{-1}.

Alkaline Hydrolysis of 1-Methyl-3-(o-carbethoxyphenyl)-triazene (3a)

1-Methyl-3-(*o*-carbethoxyphenyl)-triazene (0.75 g) was refluxed in 2 *M* sodium hydroxide (25 ml) for 1 h. The resulting yellow solution was cooled, acidified to p*H* 5.5 by the addition of glacial acetic acid (6.8 ml) and extracted with chloroform. Evaporation of the dried (Na_2SO_4) chloroform extracts afforded anthranilic acid (0.45 g, 90%), identical (m.p. and mixed m.p. 143–144°, i.r. spectrum) with an authentic sample (Eastman).

Acidic Hydrolysis of 1-Methyl-3-(o-carbethoxyphenyl)-triazene (3a)

The triazene (**3***a*) (0.5 g) was added to cold 1 *M* sulfuric acid (10 ml), whereupon a vigorous effervescence took place and a clear pink solution resulted immediately. The solution was basified at once with concentrated ammonia (2.0 ml) and extracted with chloroform, yielding an orange oil (0.35 g). Analysis of the residue by quantitative i.r. measurements showed that it was a mixture of ethyl anthranilate (75% yield) and 3-methyl-1,2,3-benzotriazin-4-one (**1***a*) (14% yield).

Alumina-catalyzed Decomposition of 1-Methyl-3-(o-carbethoxyphenyl)-triazene (3a)

General Procedure

The triazene (**3***a*) (1.0 g) was dissolved in anhydrous benzene (100 ml) and alumina (12 g) was added in one portion. The slurry was stirred at room temperature for 35 min or 12 h, dependent on the activity of the alumina (see Table 1). The alumina was removed by filtration and washed with 5 × 10 ml aliquots of anhydrous benzene; in some cases Soxhlet extraction was necessary to desorb all organic material from the catalyst. The combined benzene washings and extracts were evaporated to dryness *in vacuo*. At this stage, the residue was either a solid or an oil. In the former case, the solid was invariably identified as 3-methyl-1,2,3-benzotriazin-4-one (**1***a*) by comparison (m.p., mixed m.p., and i.r. spectrum) with an authentic sample (12). The oils were shown to be mixtures of the triazine (**1***a*) and ethyl anthranilate, and the composition was determined by quantitative i.r. measurements of the relative intensities of the absorption peaks at 3500 (NH stretch, anthranilate) and 960 cm^{-1} (N—N stretch, triazine) (see Discussion). The results of this analysis for reactions with various types of alumina are shown in Table 2.

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