The Chemistry of 3-(α-Cyanobenzylidene)-1-phenyltriazenes and Their Conversion to Diarylmaleimides and Phenanthrene-9,10-dicarboximides

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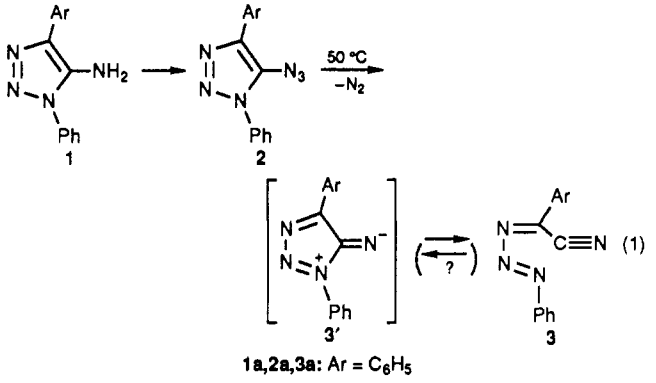
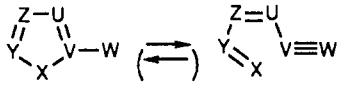
3-(α-Cyanobenzylidene)-1-phenyltriazine (**3a**), the product of thermolysis of 5-azido-1,4-diphenyl-1,2,3-triazole (**2**), is attacked by nucleophilic reagents at the azomethine carbon. Alcohols and phenol give rise to acetals of the *N*-phenylamidine of phenylglyoxylic acid (**4**), hydroxide produces 1-benzoyl-3-phenyltriazene, and piperidine produces an azoamidine, 3-(α-piperidinobenzylidene)-1-phenyltriazene (**9**). Compound **3a** is inert to acetic and trifluoroacetic acids, methyl iodide, styrene, and maleic anhydride, but anhydrous HCl cleaves it into benzenediazonium chloride and the hydrochloride of 2-imino-2-phenylacetonitrile (**10**). Hydrogen peroxide degrades **3a** to benzoic acid. Silver salts form adducts reversibly. Reduction by dithionite initially produces an open-chain dihydro derivative, which can be caused to cyclize to its isomer, 5-amino-1,4-diphenyl-1,2,3-triazole (**1**). The reactions of **3a** can be explained by the open-chain triazene structure without invoking the mesoionic, electronically stabilized nitrene structure, **3a′**. Variously substituted analogues of **3a** were prepared through the 5-amino-1,4-diaryltriazoles (**1**), which were converted to **3a** by direct oxidation or by way of the 5-azido compounds. The rates of fragmentation of the 5-azidotriazoles are much higher than those of phenyl azides and are little affected by substituents. Reaction of **3a** with phenylacetonitrile with basic catalysis gave rise to α-aryl-β-cyano-*N*-phenylcinnamiamidines (**19**), previously thought to be diarylmaleimidine derivatives **17**, to which they were easily isomerized by warm alcoholic alkali. Acid-catalyzed hydrolysis converted these cleanly to diarylmaleimides (**2**), which were further hydrolyzed by alkali to diarylmaleic anhydrides. Photolysis of **20** produced substituted phenanthrene-9,10-dicarboximides (**25**) and in some cases 9,10-dihydrophenanthrene-9,10-dicarboximides (**26**).

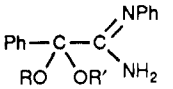
Some years ago, the preparation of 5-azido-1,4-diphenyl-1,2,3-triazole (**2a**) from the amine (**1a**), and its thermolysis, were reported;[2] a single product was formed, resulting from loss of two nitrogen atoms. At first, this substance was thought to be a singlet-state nitrene (**3a′**) stabilized by a high degree of electronic delocalization, but X-ray crystallography[3] of the 1-*p*-tolyl analogue showed an isomeric structure, 3-(α-cyanobenzylidene)-1-*p*-tolyltriazene (**3**), in the solid state.



Since then, much interest has been shown[4] in the type of ring–chain isomerism exemplified by eq 1, which appears to be a general process for azoles and analogues bearing a nitrenoid or carbenoid function at an α-position (eq 2). It has been shown in some cases to be reversible. The behavior of **3a** in certain reactions, and comparison to the analogous product from 5-azido-1,3,4-triphenylpyrazole, raised the question of whether **3a** equilibrates in solution with structure **3a′**. The first part of this paper addresses this question.



The previously reported[2] chemistry of **3a** consists of solvolysis in alcohols to form acetals of 2,*N*-diphenylglyoxylamidine (**4**), reaction with aniline to form phenylglyoxylonitrile anils or benzamidines, hydrolysis to benzoyl cyanide and benzenediazonium chloride, condensation with phenylacetonitrile to form supposed triphenylmaleimidines, and reduction by a variety of reagents to form **1**. In the first part of this paper, the chemistry of this representative of the little-known alkylidenetriazenes is expanded, to see if there might be any behavior not reasonably explained solely by structure **3**, and in the second part, an area of potential preparative usefulness of these compounds is explored.



Confirmation of Structure 3 by Reactivity

Preparation. The azide **2** can be prepared by the reaction of the corresponding diazonium salt with sodium azide, in the general preparative method for aryl azides, but **2** prepared in this way by previously published[2] procedures is usually contaminated with the 5-chlorotriazole, which is difficult to remove. We report a modified procedure that avoids this contaminant, which is formed by uncatalyzed Sandmeyer reaction of the diazonium salt. The triazene **3a** is formed from **2** by heating in petroleum ether. However, we have found that **3a** can be prepared more expeditiously directly from **1** by oxidation with *I,I*-

(1) From the doctoral dissertations of A. C. Watson and J. J. Friar. See also: Smith, P. A. S.; Mendenhall, G. D. *J. Org. Chem.*, following paper in this issue.

(2) Smith, P. A. S.; Krbechek, L. O.; Resemann, W. *J. Am. Chem. Soc.* **1964**, *86*, 2025.

(3) Schilling, J. W.; Nordman, C. E. *Acta Crystallogr., Sect. B* **1972**, 2177.

(4) (a) L'abbé, G.; Vanderdriessche, A.; Toppet, S. *Tetrahedron* **1988**, *44*, 3617. (b) Becher, J.; Broendum, K.; Krake, N.; Pluta, K.; Simonsen, O.; Molina, P.; Begtrup, M. *J. Chem. Soc., Chem. Commun.* **1988**, 541. (c) Gilchrist, T. L. *Adv. Heterocycl. Chem.* **1987**, *41*, 41 (review). (d) Molina, P.; Arguea, A.; Vinader, V.; Becher, J.; Brondum, K. *J. Org. Chem.* **1988**, *53*, 4654. (e) Moody, C. J.; Rees, C. W.; Tsoi, S. C. *J. Chem. Soc., Perkin Trans. 1* **1984**, 915. (f) Joucla, M. F.; Rees, C. W. *J. Chem. Soc., Chem. Commun.* **1984**, 374. (g) Baines, K. M.; Rourke, T. M.; Vaughn, K.; Hooper, D. L. *J. Org. Chem.* **1981**, *46*, 856. (h) Nakajima, M.; Hisada, R.; Anselme, J.-P. *J. Org. Chem.* **1978**, *43*, 2693. (i) Takimoto, H. H.; Denault, G. C. *Tetrahedron Lett.* **1966**, 5369. (j) Hall, J. H. *J. Am. Chem. Soc.* **1965**, *87*, 1147.

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diacetoxyiodobenzene. We also attempted a synthesis from open-chain precursors by treating benzoyl cyanide with the adduct of phenyl azide and triphenylphosphine (tetraphenylphosphazide) (eq 3). A small amount of **3a** was

$$PhCOCN + PhN{=}N{-}N{=}PPh_3 \rightarrow \mathbf{3a} + Ph_3PO \quad (3)$$

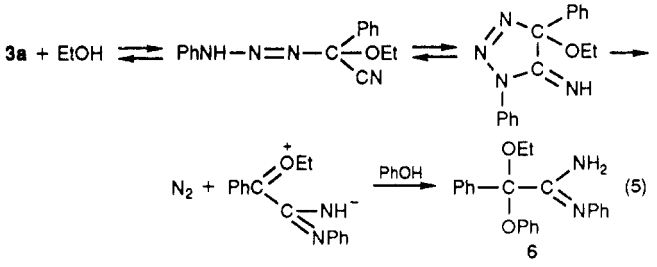
formed, identified by chromatography and conversion to 2,2-dimethoxy-2,*N*-diphenylacetamidine, but the reaction is not of preparative value because the reaction with benzoyl cyanide does not compete effectively with the rapid decomposition of the phosphazide reagent.

Solvolysis. When **3a** was treated with sodium hydroxide at room temperature, it was slowly converted to 1-benzoyl-3-phenyltriazene (**5**), identical with a sample prepared by the action of phenylmagnesium bromide on benzoyl azide.[5]

$$\mathbf{3a} + NaOH \rightarrow PhC(OH){=}N{-}\bar{N}Ph \rightarrow PhCON{=}N{-}NHPh + NaCN \quad (4)$$
$$\mathbf{5}$$

Solvolysis of **3a** with methanol, ethanol, propan-2-ol, and benzyl alcohol requires heating and/or the presence of the corresponding alkoxide, except in the case of methanol, which reacts spontaneously at room temperature.[2] We have obtained the cyclic acetal analogous to **4** by warming **3a** with ethylene glycol. However, we were unable to induce reaction with *tert*-butyl alcohol or pinacol, with or without the presence of the corresponding alkoxide.

Phenol would not react with **3a** in ether solution, even on long standing, but molten phenol containing some sodium phenoxide converted **3a** into the diphenyl acetal, 2,2-diphenoxy-2,*N*-diphenylacetamidine (**4**, R = Ph). When ethanol was added to the inert solution of **3a** and phenol in ether, reaction began immediately, and the mixed acetal, 2-ethoxy-2-phenoxy-2,*N*-diphenylacetamidine (**6**), was formed cleanly. Presumably the attack on **3a** is initiated by the more basic (or less hindered) oxygen of ethanol (eq 4). Methyl salicylate could not be induced to react with **3a** in the presence or absence of its sodium salt or of ethanol.



In order to see if an amine could be substituted for ethanol in eq 5, we treated **3a** with piperidine in the presence of phenol and sodium phenoxide; the red color of **3a** disappeared in seconds, and the main product obtained was 1-phenyl-3-(α-piperidinobenzylidene)triazene (**9**). Piperidine in the absence of phenol was found to give the same product and just as rapidly (eq 6). The triazene **9** is clearly the result of elimination of cyanide from an initial adduct analogous to **7**. These facts imply that loss

$$\mathbf{3a} + (CH_2)_5NH \rightarrow PhN{=}N{-}N{=}C(Ph)N(CH_2)_5 \quad (6)$$
$$\mathbf{9}$$

of cyanide from the analogue of **7** occurs faster than cyclization to the analogue of **8**, which would have led to a product incorporating phenol.

(5) Bertho, A. *J. Prakt. Chem.* **1927**, *116*, 101.

Sodium acetate in glacial acetic acid reacted only slowly with **3a**, even when heated, and only a low yield of acetanilide (15%) could be isolated. This surprising inertness led us to examine the reaction with isopropyl alcohol in acid. In the absence of acid or base, **3a** can be recrystallized from hot isopropyl alcohol without loss, and only in the presence of sodium isopropoxide has reaction to form the dialkoxy amidine (**4**) been reported. We found that reaction of **3a** with the alcohol was not initiated by acetic acid or even trifluoroacetic acid; **3a** was recovered unchanged.

Reaction with aqueous hydrochloric acid was originally[2] interpreted as proceeding by hydrolysis at the C=N bond to form benzoyl cyanide and phenyltriazene, which then underwent cleavage to ammonium and benzenediazonium chlorides. When we treated **3a** with anhydrous hydrogen chloride in ether, there was a slow discharge of color, with precipitation of a large amount of a yellow solid (79% calculated as **3a**·2HCl), without visible gas evolution. The hygroscopic product, which was completely soluble in water, reacted with 2-naphthol to form an azo dye and gave an immediate precipitate with silver nitrate. The IR spectrum showed bands inter alia at 2300, 1575, 1310, and 760 cm^{-1}, characteristic of benzenediazonium salts, as well as at 2280 cm^{-1} (—C≡N). Attempts to separate the product into components yielded an impure fraction with an IR spectrum consistent with 2-imino-2-phenylacetonitrile hydrochloride (**10**) free of absorption due to benzenediazonium chloride, but further efforts were abandoned because of violent explosions. Standing in water brought about hydrolysis to benzoic acid. We conclude the product to be a mixture of **10** and diazonium salt, arising from protonation of the imine nitrogen of **3a** and cleavage of the N–N bond without hydrolysis.

$$\mathbf{3a} \rightarrow [PhN{=}N{-}NH{=}C(Ph)CN] \rightarrow PhN_2^+Cl^- + PhC(=NH)CN{\cdot}HCl \quad (7)$$
$$\mathbf{10}$$

Potassium cyanide was without action on **3a**. This fact suggests that if reaction analogous to eq 5 (CN in place of EtO) takes place as far as the analogue of **8**, the reaction cannot go on to the next stage, owing to the high energy of the carbocation that would result from ring opening.

Reducing Agents. Reduction of **3a** to **1** under a variety of conditions was one of the more convincing pieces of evidence[2] for the structure **3a′**. We have found that even potassium iodide in glacial acetic acid brings about this transformation (74% yield). However, careful and rapid handling of the reduction with sodium dithionite, which discharged the red color of **3a** in 10 s, gave rise to an intermediate yellow compound (**11**) (70% yield), quite distinct from **1** in melting point and IR spectrum. It readily underwent conversion to **1**, especially in the presence of strong base, but the yield was low (33%), owing to the ease with which **11** lost gas. On the strength of its formation, transformation, and IR spectrum, **11** is deduced to have the structure shown (or a tautomer). This reduction and isomerization are parallel to those observed with the analogue of **3a** obtained from the pyrazole analogue of **2**. The original argument for structure **3′** thus loses its force.

$$\mathbf{3a} + Na_2S_2O_4 \rightarrow PhNHNHN{=}C(Ph)CN \rightarrow \mathbf{1}$$
$$\mathbf{11}$$

Oxidation. When **3a** was treated with 30% hydrogen peroxide, the red color slowly faded. The only product that could be isolated was benzoic acid.

Heat. Solutions of **3a** in xylene decomposed very slowly at the boiling point to give a red solution somewhat paler

Table I. Comparison of UV Spectra of Benzophenone Phenylglyoxylonitrile Azine (14) and 3

	azine (14)		3	
solvent[a]	λ_{max}, nm	$\epsilon \times 10^{-4}$	λ_{max}, nm	$\epsilon \times 10^{-4}$
heptane	337	2.24	343	2.28
dimethylformamide	343	1.98	350	2.00
methylene chloride	342	1.56	352	2.8

[a] Concentration 5×10^{-5} M.

Table II. Comparison of IR Spectra of Benzophenone Phenylglyoxylonitrile Azine (14) and 3[a]

azine (14), cm^{-1}	3, cm^{-1}	azine (14), cm^{-1}	3, cm^{-1}
3060 (w), 2225 (w)	3010–3070 (w)	1475 (s)	1475 (s)
2225 (w)	2230 (w)	1450 (s)	1450 (s)
1605 (w)	1600 (w)	1390 (m)	1390 (m)
1590 (m)	1590 (m)	1317 (m)	1317 (m)
1560 (s)	1560 (s)	1295 (m)	1305 (m)
1495 (m)	1490 (w)		

[a] Nujol mull.

than at the start. At least 9 h was required for disappearance of the spot due to **3a** in TLC. Most of the resulting mixture did not travel in chromatography; small amounts of diphenylfumaronitrile (**12**), 2-phenyl-2-phenyliminoacetonitrile (**13**), and benzoic acid (formed by hydrolysis during chromatography) were the only products that could be characterized. This result differs from the previously reported thermolysis in pyridine by the formation of **12** along with **13**, but in other respects the reactions are similar.

Other Reagents. Both silver tetrafluoroborate and silver nitrate formed bright orange adducts with **3a**. These compounds were easily decomposed into their components, even by extraction with water, and they turned black on prolonged exposure to light.

Methyl iodide, maleic anhydride, and styrene (in glacial acetic acid) each were without action on **3a**, even on extended exposure.

Spectra. The unsymmetrical azine, phenylglyoxylonitrile (diphenylmethylene)hydrazone (**14**) (prepared from the diphenyldiazomethane–triphenylphosphine adduct and phenylglyoxylonitrile) has the same bond system as **3**, with replacement of PhN= by Ph_2C=. However, the terminal group Ph_2C= of **14** has no unshared electron pair, and therefore cannot equilibrate with a structure analogous to **3′**. The UV spectrum of **14** would be expected to resemble

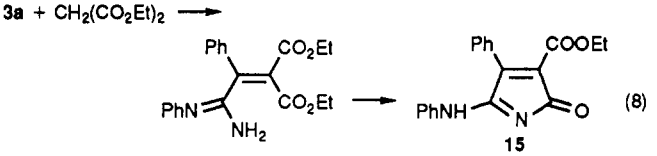
$$Ph_2C{=}N{-}N{=}C(Ph)CN$$
14

that of **3a** if the structure in solution is **3**, but not if it is **3a′**. The spectra of **3a** and **14** were compared in three solvents: heptane, dimethylformamide, and methylene chloride (Table I). Each compound had three maxima, those of **3a** coming at 7 nm longer wavelength than those of **14**, with similar overall shape. Owing to limited solubility, it was not practical to compare IR spectra in solution, but in the solid state (Nujol mulls), the spectra were nearly superimposable above 1300 cm^{-1} and closely alike below that (Table II). With both compounds, the nitrile absorption at 2225–2230 cm^{-1} was very weak and only discernible with thick samples. Unlike **3a**, **14** was inert to methanol even in the presence of sodium methoxide.

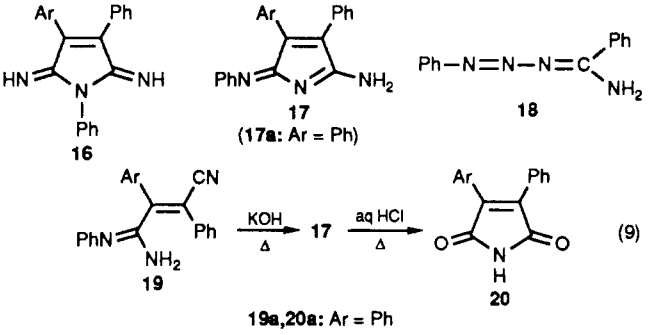
From the foregoing observations, **3a** emerges as a fairly strong electrophile, sensitive to bulk in the attacking nucleophile, with the site of its reactivity at the azomethine carbon. It shows only feeble nucleophilic or basic character, contrary to the expectation for structure **3′**. Its properties and principal reactions are explicable in terms of the open-chain triazene structure **3**, and none requires the involvement of **3′**.

Preparative Utilization of 3

The reactivity of **3a** toward nucleophiles suggested that treatment with carbanions could lead to preparatively useful results if a reaction analogous to eq 5 could be achieved, replacing ethanol with, for example, active methylene compounds. Diethyl malonate reacted readily with **3a** in ether in the presence of sodium phenoxide, but isolation of a pure product was accompanied by large losses, owing to further changes and formation of mixtures; in repeated experiments, the only characterizable product was a maleimide derivative (18%) of the apparent structure of **15**. Attention was therefore diverted to arylacetonitriles.



Phenylacetonitrile was previously found[2] to react with **3a** in the presence of sodium with loss of nitrogen to form in low yield a pair of products deduced to be *N*-phenyldiphenylmaleimidines (**16** and **17**) from their IR spectra (absorption characteristic of amidines and none corresponding to nitrile stretching). We have reexamined this reaction, and now report an improved procedure, using potassium *tert*-butoxide, which gives better yields (22–68%) and leads initially to a single product, the *N*-phenylamidine of α-phenyl-β-cyanocinnamic acid (**19**), previously thought to be **16**. Brief heating with alcoholic alkali isomerized **19** cleanly to **17**; boiling **17** in aqueous HCl hydrolyzed it in good yield to diphenylmaleimide (**20**).



Use of sodamide as the base led to preferential attack by amide ion rather than the carbanion, with formation of 1-phenyl-3-(α-aminobenzylidene)triazene (**18**). An analogous condensation of phenylglyoxylanilide with ethyl phenylacetate, leading to *N*-phenylmaleimides, has been reported by Scudi and Dingwall,[6] but they concluded that it had no preparative value owing to its extreme slowness. It is the greater electrophilic reactivity of **3** that makes the condensation reaction with it of practical value. Phenylglyoxylonitrile (benzoyl cyanide) is an even closer analogue of **3**, but the reported[5] reactions of carbanion reagents with it produce mainly ketones and tertiary alcohols with concomitant loss of cyanide.

The foregoing reactions were carried out with a variety of 1-amino-1-phenyl-4-aryl-1,2,3-triazoles, prepared in good yields from phenyl azide and arylacetonitriles[8] (available from the corresponding benzyl alcohols or benzyl halides (Table III)). They were converted to the triazenes (**3**) either by oxidation with *I,I*-diacetoxyiodobenzene or by conversion to the 5-azidotriazoles (**2**) (Table IV) followed

Table III. 5-Amino-1,4-diaryl-1,2,3-triazoles (1)

	4-Ar	1-Ar	yield, %	mp,[a] °C	mp,[b] °C
1b	p-$CH_3OC_6H_4$	C_6H_5	53	162–164	162–164
1c	m-$CH_3OC_6H_4$	C_6H_5	42	108–109	110–111
1d	p-ClC_6H_4	C_6H_5	99	188–190	189
1e	p-ClC_6H_4	p-ClC_6H_4	72	184	184
1f	m-ClC_6H_4	C_6H_5	95	152–155	162–164
1g	p-BrC_6H_4	C_6H_5	69	189–190	190–191
1h	p-FC_6H_4	C_6H_5	37	177–179	191–192
1i	3,5-$(CH_3)_2C_6H_3$	C_6H_5	59	129–131	132–133
1j	1-$C_{10}H_7$	C_6H_5	52	94–95	95–96
1k	p-$O_2NC_6H_4$	C_6H_5	89	207	207
1l	p-$O_2NC_6H_4$	p-$O_2NC_6H_4$	66	180	183

[a] Melting point of product for which yield is given. [b] Melting point of analytical sample.

Table IV. 5-Azido-1,4-diaryl-1,2,3-triazoles (2) and Rate of Decomposition

	substituents on 4-Ar	substituents on 1-Ar	yield, %	mp,[a] °C	$k \times 10^4$, s^{-1} (52 °C)
2a	H	H			3.2
2b	p-CH_3O	H	79–90	82–83 dec	9.0
2d	pCl	H	92	78–80 dec	4.3
2e	pCl	p-Cl	61	153–154 dec	4.5
2g	p-Br[b]	H	83	89 dec	
2h	p-F	H	~80	96–97 dec	
2k	p-O_2N	H	65	160–162 dec	1.7
2l	p-O_2N	p-O_2N	71	189 dec	
2m	H	p-CH_3O	41	dec <100	4.0

[a] Dependent on rate of heating. [b] Not analyzed.

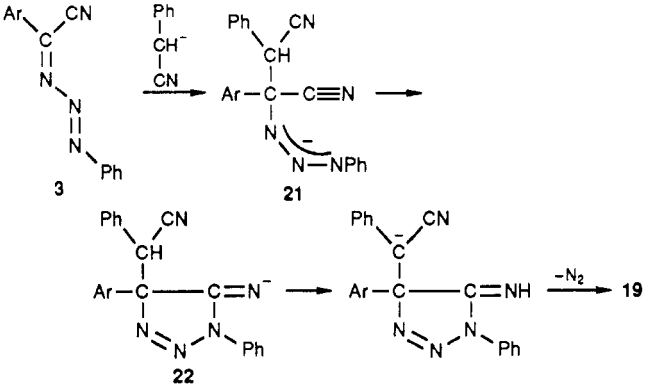
by thermolysis (Table V). Three representatives were treated with methanol, with which they reacted as expected with loss of nitrogen and formation of α,α-dimethoxyarylacetamidines (Table VI).

The azides **2** are more sensitive to heat than are phenyl azides, and easily measurable decomposition takes place as low as 40 °C, a fact that makes purification by recrystallization difficult. We have made rough measurements of the rates of decomposition of six of them by following the appearance of **3a** by UV spectroscopy at 325 K. The rates (Table IV) were, as expected, first-order, and the effects of substituents on the phenyl groups were small (k = (2.7–9.0) × 10^{-4} s^{-1}). The rates are nearly 10 times faster at 325 K than phenyl azide at 414 K (4.23 × 10^{-5} s^{-1}),[6] and faster even than those phenyl azides having unsaturated groups, such as nitro, in the ortho position (*o*-nitrophenyl azide, k = 3.97 × 10^{-5} s^{-1} at 345 K).[9] The difficulties in purification of some of the azidotriazoles appear to be a result of differences in solubility and rate of solution, resulting in some cases in longer exposure to warm solvent.

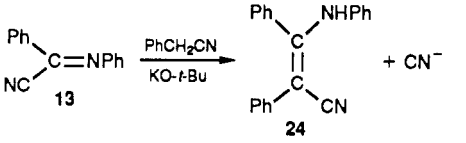
Condensation with phenylacetonitrile and the subsequent conversions of eq 9 were carried out on seven of the new triazenes (**3b–d,f–i**), (Tables VII–IX). Yields were in general satisfactory to good, except for the condensation reaction with halogen-bearing substrates. Attempts with **3** bearing nitro groups failed, evidently due to reduction of the nitro group under the reaction conditions.

Both **17a** and **19a** have a single maximum in the near ultraviolet, the former at 303 nm, the latter at 294 nm; **19a** is colorless, because the absorption falls off sharply at longer wavelengths, whereas **19a** is yellow, owing to tailing of the maximum into the edge of the visible. With other compounds of structure **19**, the tail possesses a slight shoulder at about 355 nm.

In compounds of type **19** in which Ar ≠ Ph, spectroscopy does not unequivocally establish the relative positions of Ar and Ph. The structures were assigned as shown because their formation is analogous to other reactions of **3** in which the *N*-phenyl group is transferred to the cyano carbon of **3**, presumably through an intermediate triazoline and subsequent loss of nitrogen (cf. **22** and **23** in the formation of **19**). However, formation of the position isomer (Ar and Ph interchanged), which would involve a six-membered triazine intermediate, is also a possibility. Attempts to resolve the amibiguity by ozonolysis failed, but X-ray crystallography[10] of the β-(*p*-fluorophenyl) compound established both the structure and the geometry shown. An attempt to make **19a** from diphenylfumaro-



nitrile through its mono (imino ester) derivative and reaction with aniline failed. Although the imino ester appeared to have been formed, aniline brought about reversion to the dinitrile. An attempt was also made to prepare **17a** by another route, the reaction of 2-phenyl-2-(phenylimino)acetonitrile (**13**) with phenylacetonitrile. The product obtained, however, was β-anilino-α-phenylcinnamonitrile, (**24**), resulting from loss of cyanide, or a mixture with the tautomeric imine structure. Three of



the maleimides were selected for further hydrolysis with potassium hydroxide; mild acidification of the hydrolysate precipitated the corresponding maleic anhydrides and not the acids (Table X).

The availability of a general route to diarylmaleimides prompted a brief examination of their potential as sources of phenanthrene derivatives. Eight diarylmaleimides were photolyzed through a Pyrex filter (without a filter, tarry products were obtained), following Sargent and Timmons.[11] With free access of air and in the presence of a catalytic amount of iodine, modest yields (24–53%) of phenanthrene-9,10-dicarboximides (**25**) were produced, accompanied by the corresponding 9,10-dihydrophenanthrene-9,10-dicarboximides (**26**) in two instances (**20**, Ar = *m*-chlorophenyl and Ar = *m*-bromophenyl).

(6) Scudi, J. V.; Dingwall, H. G. *J. Am. Chem. Soc.* **1935**, *57*, 2302.
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(10) We are much indebted to Dr. William Butler for carrying out this determination.
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Table V. 1-Aryl-3-(α-cyanobenzylidene)triazenes (3), Ar'N=N—N=C(CN)Ar

	Ar	Ar'	procedure	yield, %	mp,[a] °C	mp,[b] °C	IR, cm^{-1}
3b	*p*-$CH_3OC_6H_4$	C_6H_5	B	75	142	142	
			A	91–95			
3c	*m*-$CH_3OC_6H_4$	C_6H_5	B	75	85–86	86–87	2215, 1610, 1605, 1585, 1030
3d	*p*-ClC_6H_4	C_6H_5	A	77	132–133	135	2215, 1590
			B	89			1551, 1405
3e	*p*-ClC_6H_4	*p*-ClC_6H_4	A	61	174	174	
3f	*m*-ClC_6H_4	C_6H_5	B	66	100–102	101–102	2230, 1575, 1550, 1290
3g	*p*-BrC_6H_4	C_6H_5	A	67[c]	134–136		2225, 1585
			B	89	139–142	142	1575, 1545
3h	*p*-FC_6H_4	C_6H_5	A	58[c]	173–175	174–175	
3i	3,5-$(CH_3)_2C_6H_3$	C_6H_5	B	74	105–107	106–107	1550, 1325, 1200, 1150
3j	1-$C_{10}H_7$	C_6H_5	B	76	127–129	128–129	2210, 1570, 1545, 1510
3k	*p*-$O_2NC_6H_4$	C_6H_5	A	88	161	164–165	
			B	93			
3l	*p*-$O_2NC_6H_4$	*p*-$O_2NC_6H_4$	A	92	189	192	

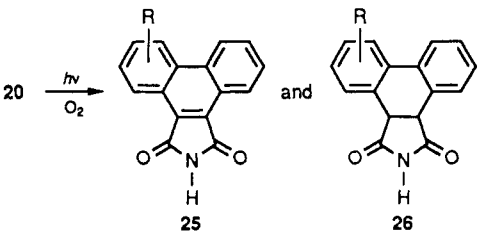
[a] Melting point of product for which yield is given. [b] Melting point of analytical sample. [c] Based on the 5-aminotriazole.

Table VI. *N*-Phenyl-α,α-dimethoxy-α-arylacetamidines (4)

Ar	yield, %	mp,[a] °C	mp,[b] °C
p-$CH_0OC_6H_4$	54	94–95	94–95
p-ClC_6H_4	56	109–110	110–111
p-FC_6H_4	61	93–95	95

[a] Melting point of product for which yield is given. [b] Melting point of analytical sample.

With a meta substituent on Ar of **20**, both the correspondind 2- and 4-substituted isomers of **25** are possible products. However, only the least hindered (the 2-substituted isomers) were obtained (in addition to spectroscopic evidence, the 2-methoxy isomer was hydrolyzed to the known 2-methoxyphenanthrene-9,10-dicarboxylic anhydride).



25 **26**

Table VII. α-Cyano-β-aryl-*N*-phenylcinnamamidines (19)

	Ar'	Ar	yield, %	mp,[a] °C	mp,[b] °C	IR, cm^{-1}
19b	*p*-CH_3O	H	61	170–171	171–172	
19d	*p*-Cl	H	30	192–196	204–205	3400, 3250, 2215, 1625, 1585
19c	*m*-CH_3O	H	62	195–196	195–196	
19f	*m*-Cl	H	22	177–180	179–181	3450, 3260, 2220, 1635, 1600
19g	*p*-Br	H	29	208–211	211–212	3400, 3240, 2205, 1635, 1590
19h	*p*-F	H	32	184–187	186–187	3240, 3230, 2210, 1635, 1590
19i	3,5-Me_2	H	68	205–207	206–207	3420, 3240, 2210, 1624, 1590
19n	*p*-CH_3	*p*-Cl	67	193–195	195–196	3400, 2210, 1630, 1590

[a] Melting point of product for which yield is given. [b] Melting point of analytical sample.

Table VIII. 5-Amino-3,4-diaryl-*N*-phenyl-2*H*-pyrrol-2-imines (17)

	substituent on					
	3-Ph	4-Ph	yield, %	mp,[a] °C	mp,[b] °C	IR, cm^{-1}
17b	*p*-CH_3O	H	70	206–208	208	
17c	*m*-CH_3	H	66	217–218	217–218	3420, 3300, 1650, 1635, 1050
17d	*p*-Cl	H	51	249–251	250–251	3415, 1675, 1630, 1590
17f	*m*-Cl[c]	H	90	200–202	200–202	3420, 3350, 1675, 1635
17g	*p*-Br[d]	H	74	234–235		
17h	*p*-F	H	43[e]	245–246	245–246	3410, 3280, 1675, 1635, 1590
17i	3,5-$(CH_3)_2$	H	80	240–242	243–244	3400, 3280, 1675, 1635, 1590
17n	*p*-CH_3	*p*-Cl	72	203–207	220–221	3405, 3290, 1675, 1630, 1590, 1035

[a] Melting point of product for which yield is given. [b] Melting point of analytical sample. [c] Mass spectrum *m/e* 357. [d] Not obtained pure but carried directly to **8g**. [e] Recrystallized twice.

Table IX. Diarylmaleimides (20)

	substituent on					
	Ar	Ar'	yield, %	mp,[a] °C	mp,[b] °C	IR, cm^{-1}
20b	*p*-CH_3O	H	86	207–211	222–223	1515, 1250, 1175, 1020
20c	*m*-CH_3O[c]	H	93	184–185	184–185	3170, 1775, 1575, 1025
20d	*p*-Cl	H	78	173–175	175–176	3180, 1770, 1715, 1590, 1100
20f	*m*-Cl	H	67	149–154	153–154	3150, 1770, 1715, 1340, 1150
20g	*p*-Br	H	99	189–190	189–190	3170, 1770, 1700, 1020
20h	*p*-F	H	81	186–187	190–191	3150, 1775, 1710, 1520
20i	3,5-$(CH_3)_2$	H	74	157–159	159–160	3200, 1760, 1710, 1340
20n	*p*-CH_3	*p*-Cl	99	174–176	179–180	3160, 1765, 1705, 1600, 1515, 1015

[a] Melting point of product for which yield is given. [b] Melting point of analytical sample. [c] NMR ($CDCl_3$) δ 7.32 (s, 9 H), 6.84 (s, 1 H), 3.38 (s, 3 H).

Table X. Diarylmaleic Anhydrides

substituent	mp, °C	yield, %	IR,[a] cm^{-1}
p-CH_3O	128–130	50	1825, 1769, 1610, 1520, 1185, 1025, 930
m-CH_3O	69–70	69	1840, 1775, 1590, 1305, 1250, 1050
p-CH_3O, p'-Cl	183–181	89	1825, 1760, 1600, 1515, 1275, 1175, 1025

[a] Selected peaks.

Table XI. Photolysis of Diarylmaleimides (20) in the Presence of O_2. Phenanthrene-9,10-dicarboximides (25) and 9,10-Dihydrophenanthrene-9,10-dicarboximides (26)

		yield, %	
substrate	substituent on **25** or **26**	**25**	**26**
20b	3-CH_3O	24	none
20c	2-CH_3O	24	none
20d	3-Cl	34	none
20f	2-Cl	26[a]	none
20g	3-Br	44	11.2
20h	3-F	53	none
20i	2,4-$(CH_3)_2$	50 (99)[b]	none
20m	3-CH_3O-6-Cl	38	none

[a] Mixture with phenanthrene-9,10-dicarboximide. [b] Crude.

In two instances, some dehalogenation took place during photolysis, as has been noted in some other examples of photolysis of stilbene derivatives.[12] With Ar = *p*-bromophenyl, **20** gave the expected 3-bromo derivative of **25**, accompanied by a 1:3 mixture of 3-bromo derivative of **26** and unsubstituted **26**, the identity of which was established by TLC, elemental analysis, mass spectrometry (which showed parent peaks at *m/e* 329 and 327 for the 3-bromo compound and at *m/e* 249 for **26**), and precipitation of silver bromide by reaction of the HBr formed in the reaction mixture. The example of **20** with Ar = *m*-chlorophenyl gave a 7:1 mixture of the 2-chloro derivative of **25** and unsubstituted **25**, on the basis of similar evidence.

With careful exclusion of oxygen, photolysis was less satisfactory. Three examples of **20** produced mostly or entirely **26**, two produced no phenanthrenes at all, and one (Ar = *p*-methoxyphenyl) curiously produced only **25**. Evidence has been presented that the initial products are the 4a,4b-dihydro isomers, which isomerized first to the 1,4-dihydro isomers, which in turn isomerize to 9,10-dihydrophenanthrene-9,10-dicarboximides, **26**, and that oxidation to **25** is a competing reaction. However, Srinivasan and Hsu have shown with an analogous example that the 9,10-dihydro may arise by a radical-chain process, involving hydrogen from the medium rather than isomerization of an initially formed 4a,4b-dihydro compound. The results of all the photolyses are given in Tables XI and XII.

Experimental Section

Melting points are uncorrected. Infrared spectra were obtained as Nujol mulls in the case of solid samples or as thin films in the case of liquids and oils, unless otherwise stated, on a Perkin-Elmer grating spectrophotometer, Model 237B. Ultraviolet spectra were obtained either on a Cary spectrometer, Model 11, or on a Perkin-Elmer, Model 202, spectrophotometer, and NMR spectra were obtained on Varian A-60, T-60, or HR-100 instruments. Vapor-phase chromatographic analyses were performed with a Perkin-Elmer Model 810 gas chromatograph or F and M Scientific Corporation, Model 500, programmed temperature gas chromatograph. Thin-layer chromatography (TLC) was effected with Eastman Chromatogram Sheet, Type 6060 (silica gel with fluorescent indicator) or Type 6062 (alumina). Analyses were performed by Spang Microanalytical Laboratory, Eagle Harbor, MI.

Table XII. Photolysis of Diarylmaleimides in the Absence of O_2

		yield, %	
substrate	substituent on **25** or **26**	**25**	**26**
20b	3-CH_3O	23	none
20c	2-CH_3O	10	11
20f	2-Cl	tar	
20h	3-F	none	41
20i	2,4-$(CH_3)_2$	none	84
20m	3-CH_3O-6-Cl	no reaction	

Dimethyl sulfoxide (Crown Zellerbach Corp.) was purified by the method of Caine[15] (distillation after storage over calcium hydride) or by the method of Smith, Fainberg, and Winstein[16] (storage over Linde 4A molecular sieves, followed by distillation). The following compounds were made as starting materials: 4-methoxybenzyl chloride, by the method of Muller,[17] and 4-fluorobenzyl and 4-bromobenzyl bromides, by the method of Weizman;[18] they were converted to the corresponding nitriles by a recommended method.[19] *I,I*-Diacetoxyiodobenzene was made by the method of Pausacker.[20] Phenyl azide was made by the method of Lindsey and Allen.[21]

5-Azido-1,4-diphenyl-1,2,3-triazole (2a) and 3-(α-Cyanobenzylidene)-1-phenyltriazene (3a). (A) Via 5-Azido-1,4-diphenyltriazole. The following procedure differs slightly from the previously published one and thereby produces a chlorine-free product.

A mixture of 10 g (42.4 mmol) of 5-amino-1,4-diphenyl-1,2,3-triazole[5] (**1a**) and 300 mL of concentrated hydrochloric acid was cooled to 0 °C (ice was *not* added directly to the mixture). A solution of 5.0 g (72.4 mmol) of sodium nitrite in 20 mL of water was added dropwise with stirring, and the stirring was continued at 0 °C for 1 h. The mixture was filtered directly into a solution of 6.0 g (90 mmol) of sodium azide in 30 mL of water, and the residue was washed with concentrated hydrochloric acid only. A white precipitate which formed in the filtrate was discarded. The clear yellow solution was diluted with water to give a lemon-yellow precipitate of **2**. This was decomposed without further purification in refluxing petroleum ether (bp 60–75 °C). The product (**3**) that separated on cooling was recrystallized from isopropyl alcohol; 8.5 g (86%); mp 110–113 °C (lit.[2] mp 115–116 °C corrected).

(B) By Oxidation of 5-Amino-1,4-diphenyl-1,2,3-triazole (1a). A solution of 16.1 g (44.7 mmol) of *I,I*-diacetoxyiodobenzene in 150 mL of methylene chloride was added dropwise to a stirred suspension of 11.8 g (50.0 mmol) of **1a** in 100 mL of methylene chloride cooled in an ice bath. The ice bath was removed, the mixture was stirred for 1 h at room temperature, and the red solution was then evaporated. Crystallization was effected with isopropyl alcohol; 9.4 g (80%) of **3a** was obtained; mp 112–114 °C.

5-Chloro-1,4-diphenyl-1,2,3-triazole. A stirred mixture of 0.5 g (2.12 mmol) of **1a**, 15 mL of concentrated hydrochloric acid, and 30 mL of water was brought to −5 °C by means of an ice–salt bath. A solution of 0.25 g (3.62 mmol) of sodium nitrite in 2 mL of water was added to the white suspension, which immediately became bright yellow. After 15 min, a yellow precipitate (0.16 g) was collected; wt 0.16 g. More of the same precipitated as the filtrate came to room temperature; wt 0.33 g (total yield 90%); mp 134–136 °C (lit.[22] mp 137–138 °C). A mixture mp with material prepared[22] from 5-hydroxy-1,4-diphenyltriazole was un-

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depressed; the IR spectrum was the same for each (3070, 1605, 1555, 770, 740, and 705 cm^{-1} among others), as was the NMR spectrum ($CDCl_3$), δ 7.18–7.66 (m, 8 H) and 7.93–8.18 (uns q, 2 H).

1-Benzoyl-3-phenyltriazene (5) from 3a. One drop of 50% aqueous NaOH was added to 1.00 g (4.28 mmol) of **3a** in a stirred two-phase system consisting of approximately 150 mL of a mixture of petroleum ether, ethyl ether, and acetone and 75 mL of water. After 10 min, the aqueous phase was yellow, but the organic phase was still red after 5 h. Addition of 5 mL of 10% NaOH solution resulted in both phases becoming yellow after 2 h. The organic solvents were evaporated, the mixture was filtered, and the filtrate was saturated with sodium chloride and extracted with ethyl ether and chloroform. The combined yellow extracts were dried ($MgSO_4$) and evaporated, leaving a yellow oil, which was caused to solidify only with considerable difficulty. Two recrystallizations from petroleum ether and one from lighter petroleum ether gave 0.40 g (42%) of yellow crystals of 1-benzoyl-3-phenyltriazene; IR (Nujol mull) 3230 (NH), 1680 (C=O), 1520 (amide II), 1480, 1470, 1255, 1130, 770, 695 cm^{-1} and weaker absorption elsewhere; NMR ($CDCl_3$) δ 7.24–7.68 (m, ca. 8 H), 7.88–8.06 (q, ca. 2 H). The UV in basic solution had λ_{max} 341 (ε, 21 900), 233 nm (ε, 13 800); in acidic solution, λ_{max} 302 nm (ε, 20 900), 233 nm (ε, 13 800).

An authentic sample[23] prepared from phenylmagnesium bromide and benzoyl azide had an identical IR spectrum; mp 80–81 °C, mixture mp 79–80 °C.

2,*N*-Diphenyl-2,2-(ethylenedioxy)acetamidine (4, R and R′ = CH_2CH_2). A mixture of 1 g (4.27 mmol) of **3a**, 2.6 mL (4.69 mmol) of ethylene glycol, and 30 mL of acetone was refluxed for 3 h. The pale orange solution was evaporated, and the resultant yellow oil was dissolved in 50 mL of benzene. This solution was washed with dilute sodium chloride solution, dried ($MgSO_4$), and evaporated. The dark yellow solid was recrystallized from a small volume of isopropyl alcohol: 0.66 g (58%); mp 143–146 °C); IR (Nujol mull) 3500 (NH), 3395 (NH), 1670 (C=N), 1595, and 1575 (possibly C=N), 1245 (doublet, possibly acetal), 1010 with two shoulders at 1000 and 985 (possibly acetal), and 720 cm^{-1}; NMR ($CDCl_3$) δ 4.15 (s, 4 H), 6.9–7.5 (m, 9–10 H), 7.60–7.88 (m, 2 H). A loss of 1–2 protons from the multiplet at 6.9–7.5 occurred on treatment with D_2O. An analytical sample (from isopropyl alcohol) was pale yellow; mp 145–147 °C. Anal. Calcd for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 6.01; N, 10.44. Found: C, 71.69; H, 5.90; N, 10.53.

Attempted Reaction of 3a with *tert*-Butyl Alcohol and with Pinacol. A mixture of 0.5 g (2.14 mmol) of **3a** and 50 mL of *tert*-butyl alcohol in which a little sodium had been dissolved was stirred for 1 h at room temperature and then boiled for 4 h. A little potassium *tert*-butoxide was added, and boiling was continued for 19 h. TLC (silica gel) and the persistent red color of the solution indicated that **3** was unchanged.

A mixture of 1 g (4.27 mmol) of **3a**, 0.55 g (4.69 mmol) of pinacol in which a little sodium had been dissolved, and 30 mL of dimethyl sulfoxide was stirred at room temperature for 24 h. TLC and the red color of the solution indicated that **3a** was unchanged.

2,*N*-Diphenyl-2,2-diphenoxyacetamidine (4, R = R′ = Ph). To a mixture of 9.65 g (0.103 mol) of phenol and 1 g (8.6 mmol) of sodium phenoxide at approximately 60 °C was added 1.0 g (4.27 mmol) of **3a** with stirring. The original red color changed hue. After 3.5 h, the dark red mixture was partitioned between ice-cold 5% NaOH solution and ethyl ether. The brown aqueous layer was discarded, and the ether layer was washed, dried ($MgSO_4$), and evaporated, leaving a yellow solid. Recrystallization from aqueous ethanol gave 0.68 g (40%) of **4**: mp 185–187 °C; IR (Nujol mull) 3450 (NH), 3255 (NH), 1640 (C=N), 1595 (C=N), 1575, 1480, 1230 (doublet), 1210 (possibly acetal), 1030 (triplet), 1015, 995 (possibly acetal), 755, 710, and 700 cm^{-1}. In chloroform, the spectrum was simpler and several peaks were shifted to higher frequency, notably: 3545 (NH), 3430 (NH), 1670 (C=N), and 1595 cm^{-1} (C=N); NMR ($CDCl_3$) δ 6.50–7.93 (m). Two recrystallizations from ethanol/water gave an analytical sample: yellow needles; mp 185–186 °C. Anal. Calcd for $C_{28}H_{22}O_2N_2$: C, 79.16; H, 5.62; N, 7.10. Found: C, 79.15; H, 5.51; N, 7.14.

2,*N*-Diphenyl-2-ethoxy-2-phenoxyacetamidine (4, R = Et, R′ = Ph). A mixture of 4 g (0.87 mmol) of absolute ethanol and 80 mL of anhydrous ethyl ether was added cautiously at room temperature to a stirred solution of 10 g (0.106 mol) of phenol, 0.5 g (4.32 mmol) of sodium phenoxide, 100 mL of anhydrous ethyl ether, and 9.4 g (0.040 mol) of **3a**. Vigorous gas evolution accompanied the addition. Stirring was continued for 1 h, whereupon the pale red solution containing yellow solid was diluted with ethyl ether, washed with 5% sodium hydroxide solution, washed with water, dried ($MgSO_4$), and evaporated, leaving an orange solid. Trituration with petroleum ether (bp 30–60 °C) and recrystallization from cyclohexane gave a yield of 9.7 g (70%): mp 126–128 °C; IR (Nujol mull) 3460 (NH), 3270 (NH), 1645 (C=N), 1600, 1575, 1495, 1225 (possible acetal), 1045 (possible acetal), 995, 760, and 710 cm^{-1} (in chloroform solution, there were some differences, such as 3520 (NH), 3410 (NH), 1670 (C=N), 1600 and 1495); NMR ($CDCl_3$) δ 1.16–1.36 (t, 3 H), 3.42–3.78 (m, 2 H), 7.00–7.68 (m, 15 H), 7.68–8.00 (m, 2 H). A mixture mp with 2,*N*-diphenyl-2,2-diphenoxyacetamidine was depressed (120–183 °C); TLC on silica gel gave different R_f values for the two amidines. An analytical sample recrystallized from aqueous isopropyl alcohol and twice from aqueous methanol pale yellow needles: mp 127–129 °C. Anal. Calcd for $C_{22}H_{22}O_2N_2$: C, 76.27; H, 6.40; N, 8.09. Found: C, 76.37; H, 6.46; N, 8.14.

In an experiment using a USP grade of ethyl ether, the same product was obtained without adding ethanol, owing to the ethanol present in the solvent.

Attempted Reaction of 3a with Phenol Alone. A solution of 0.5 g (2.14 mmol) of **3a** in 5.0 g (0.53 mmol) of phenol and 40 mL of anhydrous ethyl ether was stirred at room temperature for 2 weeks and allowed to stand at room temperature for 3 more weeks. TLC and the persistent red color indicated that no reaction had occurred. Addition of ethanol to this system produced no observable result until sodium phenoxide was added, whereupon a steady evolution of gas was observed and the solution became yellow in 5 min. Working up as before gave 0.59 g (80%) of the ethoxy phenoxy amidine; mp 115–121 °C.

Attempted Reaction of Methyl Salicylate with 3a. A suspension of 0.5 g (2.14 mmol) of **3a** and 0.8 g (4.32 mmol) of the sodium salt of methyl salicylate (prepared from sodium methoxide and methyl salicylate in methanol and subsequent removal of the methanol) in 15.6 g (0.103 mol) of redistilled methyl salicylate (bp 113–114 °C at 42 mm) and 40 mL of anhydrous ethyl ether was stirred, and 1 mL (16.9 mmol) of absolute ethanol was added. Ten minutes later, a further 1 mL of absolute ethanol was added, and the mixture was stirred for 70 min and filtered. TLC on the red filtrate showed only a spot corresponding to **3a**. Addition of methanol to the filtrate produced a slow gas evolution and discharge of the red color.

In another experiment in which the reactants were refluxed in benzene, the results were identical.

Reaction of 3a with Diethyl Malonate. A solution of 0.7 g (4.83 mmol) of diethyl malonate in anhydrous ethyl ether was added to a stirred solution of 0.5 g (2.14 mmol) of **3a** and 0.25 g (2.16 mmol) of sodium phenoxide in 9.65 g (0.103 mol) of phenol and 40 mL of anhydrous ethyl ether. There was an immediate vigorous gas evolution, and the color changed from red to dark yellow. The solution was washed with ice-cold 5% sodium hydroxide solution, washed with water, dried ($MgSO_4$), and evaporated, leaving a yellow oil, which solidified on standing. Recrystallization from aqueous isopropyl alcohol, once more from aqueous methanol, and once from petroleum ether (bp 60–75 °C), gave pale yellow crystals: wt 0.12 g (18%) of **7**; mp 85–87 °C; IR (Nujol mull) 3245 (NH), 1745 and 1715 (C=O), 1655 (C=N), 1495 cm^{-1} and much at lower frequencies; NMR ($CDCl_3$) δ 1.12–1.38 (t, 3 H, J = 7 Hz), 4.14-4.49 (q, 2 H, J = 7 Hz), 7.44–7.52 (d, ca. 11 H). An analytical sample from petroleum ether (bp 40–60 °C) after recrystallization from aqueous methanol was obtained as pale yellow crystals; mp 87–88 °C. Anal. Calcd for $C_{19}H_{16}O_3N_3$: C, 71.24; H, 5.03; N, 8.75. Found: C, 71.32; H, 4.98; N, 8.75.

Reaction of Piperidine with 3a: 1-Phenyl-3-(α-piperidinobenzylidene)triazene (9). A solution of 0.2 g (2.4 mmol) of piperidine in anhydrous ether was added quickly with stirring to 0.50 g (2.1 mmol) of **3a** in 40 mL of ether. The mixture became yellow after 30 s but was stirred for 1 h. The solution was washed with 5% aqueous NaOH, washed with water, dried (Na_2SO_4), and evaporated, leaving a pale orange solid. Trituration with petroleum ether containing a small amount of ethyl acetate

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gave 0.273 g (44%) of deep yellow **9**: mp 170–172 °C; IR (Nujol mull) 1560, 1420, 1280, and at lower frequencies, but transparent between 1600 and 2900 cm^{-1}; NMR ($CDCl_3$) δ 1.50–1.83 (m, 6 H), 6.97–7946 (m, 10 H), 2.8–4.2 (broad m) (N-CH_2); analytical sample, mp 170–172 °C, from cyclohexane. Anal. Calcd for $C_{18}H_{20}N_4$: C, 73.94; H, 6.90; N, 19.16. Found: C, 73.85; H, 6.91; N, 19.00.

In another experiment, 5 g (0.53 mmol) of phenol and 0.25 g (2.16 mmol) of sodium phenoxide were also introduced into the reaction mixture. Almost the same changes occurred, but slow gas evolution was also observed. In this instance, 0.35 g (57%) of 8 was isolated by filtration from the washed and dried ether solution after the latter had been evaporated to a small volume.

Effect of Nonaqueous Acids on 3a. A mixture of 0.1 g (0.43 mmol) of **3a**, two drops of trifluoroacetic acid, and 20 mL of isopropyl alcohol was refluxed for 45 min; the color remained unchanged, and no gas was evolved.

A mixture of 0.1 g (0.43 mmol) of **3a**, 10 mL of glacial acetic acid, and 10 mL of isopropyl alcohol was heated on a steam bath for 45 min; the color remained unchanged, and no gas was evolved.

Reduction of 3a with Potassium Iodide. A heterogeneous mixture of 0.50 g (2.24 mmol) of **3a**, 8.0 g (48.2 mmol) of potassium iodide, 20 mL of glacial acetic acid, and 20 mL of benzene was stirred for 14 h, 20 mL of acetone was added, and stirring was continued for 6 h, at which time TLC no longer detected **3a**. The more volatile solvents were evaporated, and the residue was diluted with water. The yellow precipitate was filtered from the red solution and was washed with water: wt 0.37 g (74%); mp 174–176 °C dec (reported[2] mp for 5-amino-1,4-diphenyl-1,2,3-triazole (1) 170–171 °C); IR identical with an authentic sample of 1.

Reduction of 3a with Sodium Dithionite: 1-Phenyl-3-(α-cyanobenzyl)triazene (11). A saturated solution of sodium dithionite in water (20 mL) was added quickly to a stirred solution of 1.0 g (4.28 mmol) of **3a** in 50 mL of acetone at room temperature. The red color was discharged in 10 s, and a solid precipitated. The reaction mixture was immediately poured onto 50 g of cracked ice, and the yellow solid (11) was collected and washed with water: wt 0.71 g (70%); mp 143–144 °C (gas evolution, red melt); IR (Nujol mull) 3230 (NH), 3120, 3030, 2265 (C≡N), 1610, 1530, 1500, 1470, 1260, and at lower frequencies. The compound was not analyzed owing to its low stability.

A small amount of sodium methoxide was added with stirring to a suspension of 0.24 g (1.017 mmol) of 11 in 40 mL of anhydrous methanol. There was a slow but distinct evolution of gas, and after 10 min, the solid had dissolved and the solution was pale yellow. Evaporation left a pale yellow solid, which was dissolved in methylene chloride. The solution was washed with water, dried ($MgSO_4$), and evaporated, leaving a pale yellow solid; trituration with petroleum ether left 0.08 g (33%) of pale yellow crystals: mp 169–173 °C; mixture mp with 1 172–174 °C; IR identical with that of 1.

The conversion of 11 to 1 was also brought about by use of KCN in place of sodium methoxide.

Thermolysis of 3a in Xylene. A solution of 2.0 g (8.36 mmol) of **3a** in 40 mL of xylene (bp 138.5–139.5 °C) was refluxed. The color became paler, reaching a limiting condition in 7 h. TLC showed tht 3 had disappeared in 9 h in one experiment, but lasted for 19 h in another. The solvent was evaporated by codistillation with benzene, leaving a red oil: IR (neat) 3260, 3010, 2920, 2860, 2220, 2130, 1610, 1575, 1520, 1495, 1455, 800, 780, and 700 cm^{-1}.

From chromatography on silica gel, a colorless oil was first eluted with 4% benzene in petroleum ether: TLC showed but one spot; IR (neat) 3050–2860, 1620, 770, and 705 cm^{-1}, among others. The IR spectrum was different from those of xylene and biphenyl, but no further identification was made.

A yellow oil was eluted next with 60% petroleum ether/40% benzene. The oil partially solidified after standing for several days and was crystallized from isopropyl alcohol and water. The yellow solid weighed 20 mg (1.1%): mp 57–59 °C; IR 2220 (C≡N), 1605, 1575, 1490, 1455 cm^{-1}, among others. The IR spectrum was almost identical with that of 2-phenyl-2-phenyliminoacetonitrile (13), an authentic sample of which had mp 71–73 °C; mixture mp 68–72 °C. Identification of the product as impure 13 was confirmed by GLC over 1% SE 30 stationary phase on gas-chrom Q, a support deactivated with dimethyldichlorosilane; the identity of retention times was established by peak enhancement with authentic 13 at 150 °C and at 125 °C; two volatile impurities, one with short retention time and one very close to that of 13, were detected.

The third fraction from column chromatography, a yellow, oily solid eluted with 40% petroleum ether/60% benzene, became white on trituration with petroleum ether (bp 40–60 °C): wt 63 mg (3%); mp 155–160 °C (reported[24] mp for diphenylfumaronitrile (12), 161 °C); IR (Nujol mull) 2225 (C≡N), 2240, 1585, 1450, 1255, 925, 760, and 695 cm^{-1}, among others; NMR ($CDCl_3$) δ 7.22–8.0 (m).

The last elutable substance from the column, obtained using ether, was an orange oil, from which impure benzoic acid was isolated by extraction with petroleum ether: wt 16 mg; IR identical with that of an authentic sample.

Thermolysis under nitrogen and in *p*-xylene (bp 138 °C) gave the same qualitative results but with lower yield (<1% for 12).

Action of Anhydrous Hydrogen Chloride on 3a. Hydrogen chloride gas was bubbled rapidly into a vigorously stirred solution of 1.0 g (4.28 mmol) of **3a** in 200 mL of anhydrous ether. The red color was slowly discharged and a solid precipitated. After 5 min, the solution was brought to a volume of 300 mL with more ether, and the mixture was transferred to a nitrogen tent, where it was filtered and washed liberally with ether. The pale yellow residue weighed 2.04 g (79% assuming it to be **3a** + 2HCl): mp 92–95 °C (vigorous gas evolution, deep red melt); IR (Nujol mull and Fluorolube) 3370, 3140, 3040, 2300, 2280, 1765, 1575, 1570, 1410, 1310, 1175, 1080, 775, 760, 730, and 675 cm^{-1}. It was stable for a least 4 days in a desiccator, but was hygroscopic and unstable in the presence of moisture. The material was completely soluble in water and in methanol and ethanol (yellow solution), and gave an immediate precipitate with silver nitrate. When the solid itself or a cooled aqueous solution of it was mixed with a cold alkaline solution of β-naphthol, a heavy bright orange precipitate of azo dye formed almost immediately.

The product from an analogous reaction of hydrogen chloride with **3a** was dissolved immediately while still in the nitrogen tent in 20 mL of anhydrous methanol, and the solution was poured into approximately 150 mL of anhydrous ether, whereupon a white solid formed that no longer showed the bonds at 2300, 1575, and 1310 cm^{-1} characteristic of benzenediazonium salts but retained the other absorptions of the original reaction mixture (notably including that at 2280 cm^{-1}) that are consistent with the structure 2-imino-2-phenylacetonitrile hydrochloride (10).

Further attempts to achieve separation of the components by crystallization from ether/alcohol mixtures resulted in destructively violent explosion.

Hydrolysis. A solution of 0.7 g of "**3a·2HCl**" in 50 mL of distilled water was stirred at room temperature for 3 h and then extracted with ether. Evaporation of the dried extract gave a pale red oil, which solidified on standing. The solid was partitioned between ether and sodium bicarbonate solution. Acidification of the aqueous phase precipitated 0.05 g (21%) of crude benzoic acid: mp 116–119 °C, mixture mp 117–121 °C; IR identical with that of an authentic sample.

Attempted Reaction of 3a with Iodomethane. A solution of 1.0 g of compound **3a** and 3.0 g of methyl iodide in 200 mL of anhydrous ethyl ether was still deep red after 24 h. Evaporation left a solid residue with an IR spectrum identical with that of **3a**; recrystallization from i-PrOH gave 0.78 g (78%) of pure **3a**, mp 114–116 °C.

Reaction of 3a with Sodium Acetate and Acetic Acid. A solution of 0.50 g (2.14 mmol) of **3a** and 0.50 g (7.14 mmol) of sodium acetate in 40 mL of glacial acetic acid was subjected to the combined conditions of 90 h at room temperature and 15 h on a steam bath. TLC indicated that **3a** was no longer present. The mixture was neutralized with saturated sodium carbonate solution and extracted with ethyl ether. The brown ether solution was washed with saturated aqueous sodium bicarbonate solution and with water, dried ($MgSO_4$), and filtered to give a deep yellow solution. Evaporation left a brown oil, which was chromatographed on alumina. A yellow oily solid was eluted with 2% ether/98% benzene; recrystallization from CCl_4 gave 42 mg (15%) of acetanilide: mp 108–110 °C; IR and NMR identical with that of an authentic sample.

(24) Coe, D. G.; Gale, M. M.; Linstead, R. P.; Timmons, C. J. *J. Chem. Soc.* **1957**, 123.

Oxidation of 3a with Hydrogen Peroxide. With vigorous stirring, 10 mL of 30% hydrogen peroxide was added to a solution of 0.75 g (6.42 mmol) of **a** in 10 mL of methylene chloride cooled in an ice bath. The ice bath was removed, and after 34 h the yellow methylene chloride layer was separated, washed with water, dried ($MgSO_4$), and evaporated, leaving a brown solid. Extraction with petroleum ether and evaporation of the extract left a pale yellow solid, which was dissolved in 5% sodium hydroxide and reprecipitated with aqueous HCl: 0.10 g (26%); mp 119–122 °C; IR superimposable on that of benzoic acid.

Reaction of Silver Salts with 3a. (A) With Silver Fluoroborate. A solution of 0.85 g (4.36 mmol) of silver fluoroborate in 5 mL of absolute ethanol was added with swirling to a solution of 0.5 g (2.14 mmol) of **3a** in 40 mL of anhydrous ether at room temperature. The bright orange solid that immediately precipitated was filtered and washed: wt 0.52 g; mp 122 °C (vigorous gas evolution, green to black melt); IR (Nujol mull) 2230 (C≡N), 1540, 1170, 1050 (B—F), 780, 775, and 680 cm^{-1} (distinct from, although similar to, that of **3**). In a control experiment, **3a** remained completely soluble. The orange addition product was insoluble in carbon tetrachloride and sparingly soluble in benzene under conditions in which **3a** was completely soluble. The product slowly darkened when exposed to light. Addition of water to a solution of 0.1 g of the product in absolute ethanol caused immediate precipitation. The collected material weighed 0.04 g: mp 110–113 °C; IR identical with that of **3a**. The filtrate gave an immediate white, ammonia-soluble precipitate of silver chloride when mixed with sodium chloride. Recrystallization of the addition product was not attempted because of its ease of dissociation.

(B) With Silver Nitrate. A solution of 0.7 g (4.12 mmol) of silver nitrate in 10 mL of 50% aqueous ethanol added to a solution of 0.5 g (2.14 mmol) of **3a** in 40 mL of ether gave an analogous adduct: 0.81 g; mp 129 °C (vigorous dec); IR similar to the foregoing fluoroborate adduct, except for bands attributable to nitrate.

Spectroscopic Comparison of 3a and the Unsymmetrical Azine of Benzophenone and Phenylglyoxylonitrile (14). Benzophenone phenylglyoxylonitrile azine (**14**) was synthesized from diphenyldiazomethane–triphenylphosphine adduct and phenylglyoxylonitrile as reported:[7] mp 112–113 °C (reported[25] mp 110–110.5 °C). The IR spectral data of **3a** and the azine are shown in Table I and the UV spectral data in Table II.

Attempted Reaction of Benzophenone Phenylglyoxylonitrile Azine (14) with Methanol and Sodium Methoxide. A solution of 0.50 g (1.62 mmol) of **14** in 40 mL of methanol was refluxed for 24 h; TLC showed no changes in composition. A small amount of sodium methoxide was added, and refluxing was continued for 26 h; TLC showed starting material as the only significant solute. Evaporation left a yellow oil, which was dissolved in ether; the solution was washed with water, dried ($MgSO_4$), and evaporated to an oily solid, which solidified on trituration with petroleum ether: mp 108–110 °C; IR identical with that of **14**.

Synthesis of 3a from Phenyl Azide and Phenylglyoxylonitrile. A solution of 2.2 g (8.4 mmol) of triphenylphosphine in 20 mL of methylene chloride was cooled by means of an acetone–dry ice bath and poured with swirling onto 1 g (8.4 mmol) of phenyl azide at the same temperature. A suspension of 1.1 g (8.4 mmol) of phenylglyoxylonitrile in 10 mL of methylene chloride at the same temperature was added to the yellow mixture with stirring. After 15 min, the acetone–dry ice bath was replaced with an ice–salt bath, and the temperature was maintained at ca. −10 °C. The solution had already started to turn red before the temperature had risen to −10 °C and after 7 h was deep red. The solution was allowed to come to room temperature, whereupon the methylene chloride was evaporated, leaving a deep red oil. Chromatography on silica gel produced only impure oils.

In another experiment, the red oil was extracted with petroleum ether and the extract was evaporated; TLC of the residue with benzene and with chloroform as eluent gave red spots with an R_f value matching that of **3a**. The red color of the oil was discharged by the addition of methanol, and TLC of the resulting solution showed a spot with an R_f value matching that of 2,2-dimethoxy-2,*N*-diphenylacetamidine (**4**, R = R^1 = CH_3).

5-Amino-1,4-diaryl-1,2,3-triazoles. 5-Amino-4-(3,5-dimethylphenyl)-1-phenyl-1,2,3-triazole (1i). 3,5-Dimethylphenylacetonitrile (31.0 g, 0.215 mol) in 10 mL of methanol was added to a solution of 4.93 g (0.215 mol) of sodium and 26.0 g (0.215 mol) of phenyl azide in 120 mL of absolute ethanol. The mixture was heated on the steam bath for 1.25 h; solid material began to appear after 45 min. The mixture was cooled in ice for 1 h, and 25 mL of water was added; the resulting tan precipitate was filtered off and washed with water. Trituration of the dried solid with 200 mL of hot ethanol gave 33.6 g (59%) of light tan **2i**, mp 129–131 °C. An analytical sample, colorless crystals from benzene, had the following properties: mp 132–133 °C; IR 3250 (NH_2), 3400 (NH_2), 1600, 1515, 1320, 1290, 850, and 770 cm^{-1}.

Other 5-amino-1,4-diaryltriazoles were obtained similarly; details are given in Table III. Each had IR absorption at 3350–3425 an d3250–3350 (NH_2), 1620–1650, 1580–1605, and 1510–1525 cm^{-1} (triazole ring).[26] The 1-*p*-methoxyphenyl derivative (used to prepare azide **2m**) was prepared by the published method.[26]

5-Azido-1,4-diaryl-1,2,3-triazoles (2). 5-Azido-1-phenyl-4-(*p*-fluorophenyl)-1,2,3-triazole (2h). A mixture of 20.4 g (0.0805 mol) of 5-amino-1-phenyl-4-(*p*-fluorophenyl)-1,2,3-triazole (**1h**) in 560 mL of warm glacial acetic acid was stirred for 1.5 h, dissolving most of the triazole. Adding 100 mL of concentrated hydrochloric acid dissolved the remaining solid. After cooling to 2 °C, a mixture of 5.9 g (0.0855 mol) of sodium nitrite in 12 mL of water was added dropwise, followed by a mixture of 10.4 g (0.16 mol) of sodium azide in 40 mL of water added dropwise, and the solution was stirred for an additional 25 min. Upon adding 350 mL of ice and water, pale yellow **2h** precipitated. After 1 g of product was set aside for analytical purposes, the balance of the crude azide was used directly (without complete drying) to make 1-phenyl-3-(α-cyano-*p*-fluorobenzylidene)triazene (**3h**). An analytical sample from acetone and water formed cream-colored crystals: mp 96–97 °C; IR 2140 (N_3), 1600, 1570, 1510, 1310, 1230, 1170, 850, and 775 cm^{-1}.

The 5-azidotriazoles prepared by this procedure are listed in Table IV.

1-Aryl-3-(α-cyanobenzylidene)triazenes (1). Procedure A. 1-Phenyl-3-(α-cyano-*p*-fluorobenzylidene)triazene (3, Ar = *p*-FC_6H_4). The foregoing azide **2h** was added to 200 mL of petroleum ether (bp 90–100 °C), and the mixture was refluxed for 1.5 h, producing deep red crystals. The filtrate was evaporated to 10 mL, and additional precipitate was obtained. Trituration of the combined solids with benzene gave 11.7 g (0.0465 mol, 58% from aminotriazole) of 1-phenyl-3-(α-cyano-*p*-fluorobenzylidene)triazene (**1h**): mp 173–175 °C; IR 2200 (CN), 1600, 1555, 1175, and 865 cm^{-1}. Analytical sample (deep red crystals from benzene) had mp 174–175 °C.

Procedure B. 1-Phenyl-3-(α-cyano-*p*-methoxybenzylidene)triazene (3b). A solution of 30.0 g (0.012 mol) of *I,I*-diacetoxyiodobenzene in 165 mL of dichloromethane was added dropwise to a suspension of 28 g (0.102 mol) of 5-amino-4-*p*-anisyl-1-phenyl-1,2,3-triazole in CH_2Cl_2, which had been cooled to 3 °C. The solvent was evaporated, and the residue was triturated with isopropyl alcohol, leaving 14.3 g (53.1%) of deep red crystals: mp 138–140 °C.

By the foregoing procedures, other examples of **3** were prepared, as summarized in Table V. The yields given were obtained after one recrystallization, unless otherwise stated.

***N*-Phenyl-α,α-dimethoxy-α-arylacetamidines (4).** The following representative procedure was used. A solution of 0.30 g (1.1 mmol) of 1-phenyl-3-(α-cyano-*p*-chlorobenzylidene)triazene (**3g**) in 8.0 mL of methanol was stirred; within 15 s it began to bubble. After 5 min, the methanol was distilled off and the residue was recrystallized from petroleum ether (bp 60–90 °C), yielding 0.9 g (55.6%) of *N*-phenyl-α,α-dimethoxy-α-*p*-chlorophenyl)-acetamidine. The data are collected in Table VI. The IR spectra were similar, having inter alia absorption at 3440, 3240–3259, 1635–1640, and 1590 cm^{-1}.

(25) Ciganek, E. *J. Org. Chem.* **1965**, *30*, 4198.

(26) Lieber, E.; Chao, T. S.; Rao, C. N. R. *J. Org. Chem.* **1957**, *22*, 656.
(27) Pinner, A. *Ber. Dtsch. Chem. Ges.* **1889**, *22*, 1609.

Table XIII. Phenanthrene-9,10-dicarboximides (25)

substituent	mp, °C	UV[b] λ_{max}, nm	UV[b] $\epsilon \times 10^{-3}$	NMR, δ (Me_2SO-d_6)	IR,[c] cm^{-1}
2-CH_3O	285–286	230, 290	40, 17		3200, 1170, 1715, 1625, 1600, 1300, 1225, 1020
3-CH_3O	299–301	390, 245, 270, 300	4.7, 38, 14,[a] 9.0		
3-Cl	330–331	213, 239, 254, 279, 291, 380	33, 55, 40,[a] 27,[a] 12, 6.3	3.68 (s), 7.83 (m)	3180, 1765, 1725, 1610, 1115, 1015, 780
3-Br	324–325	247, 267, 275, 283, 295, 375	51, 28,[a] 21,[a] 15,[a] 7.1, 7.9		3215, 1760, 1720, 1585, 1110, 1010, 830, 800
3-F	346–348	237, 245, 273, 281, 291, 380	45, 34,[a] 20,[a] 17, 14, 7.6		3150, 1780, 1690, 1350, 1180, 1170, 750
2,4-$(CH_3)_2$	279–280	204, 240, 285, 385	47, 84, 35, 12		3380, 1760, 1700, 130, 1120, 770
3-CH_3O-6-Cl	309–310	208, 252, 298, 390	38, 49, 13,[a] 7.1		

[a] Inflection. [b] 10^{-5} M in 95% ethanol. [c] Selected peaks.

Table XIV. 9,10-Dihydrophenanthrene-9,10-dicarboximides (26)

substituent	mp, °C	UV[b] λ_{max}, nm	UV[b] $\epsilon \times 10^{-3}$	NMR, δ (Me_2SO-d_6)	IR,[c] cm^{-1}
2-CH_3O	188–189	207, 270, 312	39, 12, 6.2[a]	3.28 (s, 3 H), 4.40 (s, 2 H), 7.35 (m, 3 H), 11.33 (s, 1 H)	3160, 1775, 1705, 1590, 1330, 1120, 1080
3-Cl	251–252	243, 278, 300, 312	12, 18, 3.5, 3.2	3.65 (s), 4.22 (s), 4.50 (s), 7.75 (m)	3160, 1760, 1700, 1176, 1150, 775
3-F	262–263	241, 276, 289, 295	7.8, 13, 8.0,[a] 6.1	3.30 (s, 1 H), 4.55 (s, 1 H), 4.70 (s, 1 H), 7.60 (m, 7 H)	3160, 1760, 1690, 1610, 1160, 1130
2,4-$(CH_3)_2$	182–183	218, 276	33, 19	2.30 (s, 3 H), 3.22 (br s, 1 H), 4.1 (s, 3 H), 4.4 (d, 1 H), 4.5 (d, 1 H), 7.4 (m, 6 H)	3150, 1780, 1690, 1350, 1180, 1170, 750

[a] Inflection. [b] 10^{-5} M in 95% ethanol. [c] Selected peaks.

α-Phenyl-β-cyano-*N*-phenylcinnamamidine (19). (A) To a solution of 0.50 g (2.2 mmol) of **3a** in 6 mL of phenylacetonitrile was added 0.075 g (0.7 mmol) of potassium *tert*-butoxide. Bubbling began at once. After warming for 5 min on the steam bath and then cooling, pale yellow crystals formed. Recrystallization from a 1:1 benzene–petroleum ether mixture (bp 90–100 °C) gave 0.138 g (20.0%) of cream-colored crystals of α-phenyl-β-cyano-*N*-phenylcinnamamidine (**19a**): mp 191 °C (lit.[2] mp 191 °C); IR (KBr disk) 3450 and 3300 (NH), 3100, 2240 (CN), 1640, 1600, 1500, 1460, 1400, 1260, and 840 cm^{-1}.

By the same procedure, **3b** gave **19b** in 38% yield: mp 170 °C; IR similar to **19a**; UV (95% ethanol) λ_{max} 323 nm (ε 16 500).

(B) To a solution of 0.60 g (2.6 mmol) of **3a** in a mixture of 50 mL of dimethyl sulfoxide and 2.0 g (017.1 mml) of phenylacetonitrile was added 0.050 g (0.4 mmol) of potassium *tert*-butoxide. Bubbling began at once. After 30 min, 150 g of ice and water was added, producing a yellow precipitate, which was washed with water and dried. Recrystallization from benzene gave 0.480 g (58.0%) of colorless α-phenyl-β-cyano-*N*-phenylcinnamamidine, mp 190 °C. The results of Procedure B with other examples of **3** are given in Table VII.

Reaction of 3, *p*-Methoxyphenylacetonitrile, and Sodamide in Dimethyl Sulfoxide: 1-Phenyl-3-(α-aminobenzylidene)triazene (18). To a solution of 0.30 g (1.28 mmol) of **3** in 25 mL of dried dimethyl sulfoxide was added 1.0 g (6.8 mmol) of *p*-methoxyphenylacetonitrile. To this was added 0.100 g (2.56 mmol) of sodium amide last. After 5 min, 50 g of ice and water was added, producing a red-brown precipitate.

Recrystallization from benzene gave 0.101 g (35%) of a yellow solid, 1-phenyl-3-(α-aminobenzylidene)triazene (**18**): mp 181 °C (lit.[17] mp 181 °C; IR 3420 and 300 (NH_2), 1590, 1580, 1525, 1300, 1135, 1040, and 765 cm^{-1}, among others; ^1H NMR ($CDCl_3$) δ 6.3 (broad, 2 H) and 7.5–8.2 (m, 10 H).

5-Amino-3,4-diaryl-2-(phenylimino)-2*H*-pyrrole (17). The preparation of 5-amino-3-(*p*-methoxyphenyl)-4-phenyl-2-(phenylimino)-2*H*-pyrrole (**17b**) provides a representative example.

To a solution of 6.0 g of potassium hydroxide in a mixture of 15 mL of water and 15 mL of ethanol was added 0.180 g (0.51 mmol) of **19b**. Upon heating for 30 min, a yellow precipitate formed and was washed with water and dried. Recrystallization from benzene gave 0.125 g (69.5%) of **5**: mp 206–208 °C; IR (Nujol mull and KBr disk) 3400 (w) (NH), 3280 (vw) (NH), 1630 (s,b), 1590 (s), 1250 (s), 1175 (s), and 840 (m) cm^{-1}; UV (95% ethanol) λ_{max} 298 nm (ε 10 900); NMR δ 2.3–3.7 (s, 3 H), 6.7–7.7 (m, 3 H), and 7.8 (broad, 2 H). An analytical sample, yellow crystals from benzene, had mp 208 °C.

Diarylmaleimides. 2-(*p*-Methoxyphenyl)-3-phenylmaleimide (20b). The following procedure for **20b** is representative of the group.

A solution of 2.38 g (6.7 mmol) of **17b** in 20 mL of concentrated hydrochloric acid was refluxed for 5.5 h, producing a somewhat gummy precipitate, which was collected, washed with water, and dried. Recrystallization from benzene gave 1.6 g (5.8 mmol, 85.5%) of chartreuse crystals of **20b**: mp 207–21 °C; IR 3190 (m) (NH), 1760 (s), 1710 (s), 1600 (s), 2560 (m), 1515 (s), 1250 (s), 1175 (s), and 1020 (s) cm^{-1}; UV (95%) ethanol λ_{max} 247, 293 (inflec) μm (ε 6000, 2000). An analytical sample from benzene had mp 222–223 °C. The data on the examples of **20** are collected in Table IX.

Diarylmaleic Anhydrides. 2-(*p*-Methoxyphenyl)-3-phenylmaleic Anhydride. A solution of 0.195 g (0.70 mmol) of 2-(*p*-methoxyphenyl)-3-phenylmaleimide (**20b**) in a mixture of 6.0 g of potassium hydroxide in 24 mL of 50% ethanol was boiled for 30 min. Careful acidification with hydrochloric acid gave a precipitate of 2-(*p*-methoxyphenyl)-3-phenylmaleic anhydride, which was collected, washed with water, and dried. Recrystallization from acetone and water gave 0.101 g (0.35 mmol, 50%) of pale yellow crystals: mp 124–126 °C (128–130 °C after another recrystallization). The compounds obtained by this method are listed in Table X.

Attempted Preparation of 19a from Diphenylfumaronitrile. To a solution of 1.0 g (4.34 mmol) of diphenylfumaronitrile in 30 mL of benzene was added 0.250 g (5.43 mmol) of absolute ethanol. Then 26.08 mL of 0.25 M hydrogen chloride (6.52 mmol) in benzene was added slowly, and the solution was stirred for 1 h and allowed to stand for 48 h. The addition of 0.434 g (4.77 mmol) of aniline precipitated 0.153 g of aniline hydrochloride. An additional 0.434 g (4.77 mmol) of aniline was added, and the solvent was evaporated to a volume of 5 mL; 0.181 g of dark red material, mp 145–148 °C, identified as starting material, separated. After filtering, the filtrate was added to aqueous potassium carbonate solution and extracted promptly into chloroform, but only a further amount of starting material was obtained.

Photolysis of Diarylmaleimides. The following several examples illustrate the procedures and results. Owing to the very low solubility of most of the products, purification was difficult, and good spectra could not be obtained in all cases (hence the absence of integration in some of the NMR spectra). The results are compared in Tables XI and XII; the properties of the products are listed in Tables XIII and XIV.

2,4-Dimethylphenanthrene-9,10-dicarboximide (25, R = 2,4-Me_2). A solution of 1.018 g (3.73 mmol) of 2-(3,5-dimethyl-

phenyl)-3-phenylmaleimide (**20i**) and 0.0254 g of iodine (0.1 mmol) in 290 mL of absolute ethanol was irradiated by a 450-W Hanovia lamp (Pyrex filter) for 7.0 h. A yellow precipitate that appeared in the course of the irradiation was filtered off. After 7.0 h of further irradiation and stripping to 40 mL and cooling, a further quantityof yellow precipitate was obtained; total weight, 0.515 g. Complete stripping gave an additional 0.489 g of gummy, yellow-orange material; total crude weight, 1.004 g (98.6%).

The 0.515-g crop was recrystallized from benzene, producing 0.500 g (1.85 mmol, 49.5%) of bright yellow 2,4-dimethylphenanthrene-9,10-dicarboximide, mp 278–279 °C (mp 279–280 °C after recrystallization from benzene.

2-Methoxyphenanthrene-9,10-dicarboximide (25, R = 2-MeO). A solution of 0.585 g (2.11 mmol) of 2-(*m*-methoxyphenyl)-3-phenylmaleimide (**20c**) in 290 mL of absolute ethanol was irradiated with a 450-W Hanovia lamp (Pyrex filter) for 9 h. Stripping the solution down to 40 mL gave 0.136 g (4.9 mmol, 23.5%) of yellow 2-methoxyphenanthrene-9,10-dicarboximide: mp 284–285 °C; IR 3200 (NH), 1770, 1715, 1625, 1600, 1300, 1225, and 1020 cm^{-1}; UV λ_{max} 230, 290, 390 (tail) nm (ϵ 40 000, 17 000, 4700); NMR (Me_2SO-d_6) δ 3.32 (s, 1 H), 3.98 (s, 3 H), 7.3–7.7 (m, 4 H), 8.42 (d, 1 H), 9.34 (q, 1 H).

An analytical sample, bright yellow from ethanol, had mp 285–286 °C.

A 0.190-g (0.7-mmol) sample of the foregoing imide was boiled 10 min with a mixture of 6 g of potassium hydroxide in 24 mL of 50% ethanol. Upon acidification with concentrated hydrochloric acid, a gummy yellow precipitate of 2-methoxyphenanthrene-9,10-dicarboxylic anhydride formed. Recrystallization from glacial acetic acid gave a yellow product, mp 274–275 °C, cor (lit.[28] mp 274–275 °C). (The mp of 1-methoxyphenanthrene-9,10-dicarboxylic anhydride[19] is 235.5–236 °C, cor, and the mp of 3-methoxyphenanthrene-9,10-dicarboxylic anhydride[28] is 221.5–222 °C, cor.

3-Bromophenanthrene-9,10-dicarboximide (25, R = 3-Br) and 3-Bromo-9,10-dihydrophenanthrene-*cis*-9,10-dicarboximide (26, R = 3-Br). A solution of 0.500 g (1.51 mmol) of 2-(*p*-bromophenyl)-3-phenylmaleimide (20g) in 290 mL of absolute ethanol was irradiated for 12.0 h by a 450-W Hanovia lamp (Pyrex filter). Some yellow product was obtained at this point, and evaporation of the solvent to a volume of 20 mL gave additional yellow material for a total of 0.221 g (0.67 mmol, 44.2%) of 3-bromophenanthrene-9,10-dicarboximide, mp 322–324 °C (324–325 °C after trituration with ethanol). After the solution had stood overnight, 0.056 g (0.17 mmol, 11.2%) of white product, mp 221 °C, was deposited.

An analytical sample of this supposed 3-bromo-9,10-dihydrophenanthrene-*cis*-9,10-dicarboximide was obtained with difficulty as colorless crystals by recrystallization from ethanol: mp 228–229 °C; IR 3165 (NH), 1765, 1700, 1160, and 750 cm^{-1}; UV (95% ethanol) λ_{max} 275, 287 (infl), 307 nm (ϵ 21 000, 16 000, 1400); NMR (Me_2SO-d_6) δ 4.42 (s, 2 H), 7.74 (m, 8 H); MS *m/e* 329 and 327, 249. TLC with prolonged chloroform development showed two spots, the one with higher R_f being identical with that of 9,10-dihydrophenanthrene-9,10-dicarboximide. The filtrate from the photolysis gave an immediate pale yellow precipitate (AgBr) with silver nitrate. Anal. Calcd for $C_{16}H_{10}NO_2Br$: C, 58.55; H, 3.07; N, 4.27. Calcd for the unsubstituted analogue, $C_{16}H_{11}NO_2$: C, 77.10; H, 4.45; N, 5.62. Calcd for 25.2% $C_{16}H_{10}NO_2Br$ + 74.8% $C_{16}H_{11}NO_2$: C, 72.09; H, 4.19; N, 5.24. Found: C, 72.08; H, 4.23; N, 5.15.

3-Chlorophenanthrene-9,10-dicarboximide (25, R = 3-Cl) and 3-Chloro-9,10-dihydrophenanthrene-*cis*-9,10-dicarboximide (26, R = 3-Cl). A solution of 0.490 g (0.17 mmol) of 2-(*p*-chlorophenyl)-3-phenylmaleimide (**20d**) in 290 mL of absolute ethanol was irradiated with a 450-W Hanovia lamp (Pyrex filter) for 11 h, which produced 0.164 g (0.58 mmol, 33.6%) of 3-chlorophenanthrene-9,10-dicarboximide: bright yellow; mp 327–329 °C (320–331 °C after recrystallization from ethanol).

The filtrate was evaporated to a volume of 12 mL, and 0.179 g (0.62 mol, 36.6%) of 3-chloro-9,10-dihydrophenanthrene-*cis*-9,10-dicarboximide was obtained: cream-colored powder; mp 249–251 °C, mp 249–251 °C (after recrystallization from ethanol, colorless crystals, mp 251–252 °C).

2-Chlorophenanthrene-9,10-dicarboximide (25, R = 2-Cl). A solution of 0.381 g (1.34 mmol) of 2-(*m*-chlorophenyl)-3-phenylmaleimide (20F) in 275 mL of absolute ethanol was irradiated by a 450-W Hanovia lamp (Pyrex filter) for 7.75 h, producing 0.070 g (0.25 mmol, 19.6%) of a yellow solid: mp 296–297 °C; IR 3175 (NH), 1765, 1715, 1565, 1115, and 770 cm^{-1}.

An analytical sample, bright yellow crystals from ethanol, had mp 297–298 °C. Anal. Calcd for $C_{16}H_8NO_2Cl$: C, 68.22; H, 2.87; N, 4.97. Calcd for $C_{16}H_9NO_2$: C, 77.72; H, 3.67; N, 5.66. Found: C, 69.40; H, 3.13; N, 5.13.

The analysis corresponds to a mixture of 86% 2-chlorophenanthrene-9,10-carboximide and 14% phenanthrene-9,10-dicarboximide: C, 69.55; H, 2.98; N, 5.07. Prolonged development with benzene on silica TLC plates gave two spots. The mass spectrum gave the expected *m/e* 283 and 281 parent peaks for 2-chlorophenanthrenene-9,10-dicarboximide, as well as a strong peak at *m/e* 247 (loss of chlorine and gain of hydrogen).

3-Fluorophenanthrene-9,10-dicarboximide (25, R = 3-F). Air was bubbled through a solution of 0.500 g (1.9 mmol) of 2-(*p*-fluorophenyl)-3-phenylmaleimide (**20h**) in 285 mL of absolute ethanol containing 0.0254 g (0.1 mmol) of iodine for 30 min, after which the solution was irradiated with a 450-W Hanovia lamp (Pyrex filter) for 9.25 h. Evaporation to a volume of 12 mL precipitated 0.265 g (53.1%) of bright yellow crystals of 3-fluorophenanthrene-9,10-dicarboximide: mp 345–374 °C (346–348 °C after recrystallization from benzene).

2,4-Dimethyl-9,10-dihydrophenanthrene-*cis*-9,10-dicarboximide (26, R = 2,4-Me_2). A solution of 0.0780 g (2.8 mmol) of 2-(3,5-dimethylphenyl)-3-phenylmaleimide (**20i**) in 290 mL of absolute ethanol was irradiated under prepurified nitrogen by a 450-W Hanovia lamp (Pyrex filter) for 12 h. Nitrogen had been passed through the system for 3.5 h before irradiation began. Concentration to a volume of 12 mL gave a white precipitate; recrystallization from ethanol gave 0.650 g (2.34 mmol, 83.5%) of 2,4-dimethyl-9,10-dihydrophenanthrene-*cis*-9,10-dicarboximide: mp 180–182 °C (mp 182–183 °C after recrystallization from ethanol). The UV spectrum is similar to that reported[11] for 9,10-dihydrophenanthrene-*cis*-9,10-dicarboximide.

Reaction of Phenylacetonitrile with 13. To a solution of 0.600 g (2.91 mmol) of **13**[29] and 3.0 g (25.6 mmol) of phenylacetonitrile in 100 mL of Me_2SO was added 0.090 g (0.8 mmol) of potassium *tert*-butoxide; the solution immediately darkened. After 15 min, 100 g of ice and water was added, producing 0.718 g (78.5%) of presumed β-anilino-α-phenylcinnamonitrile, mp 192–194 °C; an analytical sample (white crystals) from benzene had the following properties: mp 206 °C; IR 3250 (NH), 3150, 2210, 1605, 1595, 1500 cm^{-1}; NMR ($CDCl_3$) δ 6.55 (s, 1 H), 7.3 (m, 15 H); UV (10^{-5} M in 95% ethanol) λ_{max} 258 (ϵ 17 100) and 353 nm (ϵ 9800). A purer sample could not be obtained. Anal. Calcd for $C_{21}H_{16}N_2$: C, 85.11; H, 5.44; N, 9.45; *m/e* 296.1314. Found: C, 84.35; H, 5.45; N, 9.08; *m/e* 296.1317.

Rate Measurements on 5-Azidotriazoles (2). Solutions of the substrates in 1,2-dichloroethane at controlled temperature were monitored at timed intervals by following the UV extinction of quickly quenched aliquots at the wavelength of the characteristic maximum of the product (**3**) (340–360 nm), compared to the extinction on samples carried to completion. Where necessary, a correction was made for absorption by the substrate at the wavelength used. The first-order rate constants were determined graphically, and the results are given in Table II. For two substrates (**2a** and **2d**), measurements were made at 40.0 °C, 52.0 °C, and 64.4 °C. The activation energies were calculated to be 25.4 and 26.0 kcal/mol, respectively (these figures should be regarded as only approximate, since they are derived from single determinations and are subject to unknown error).

Registry No. **1a**, 29704-63-0; **1b**, 126158-47-2; **1c**, 126158-48-3; **1d**, 118946-58-0; **1e**, 126158-49-4; **1f**, 126158-50-7; **1g**, 126158-51-8; **1h**, 126158-52-9; **1i**, 126158-53-0; **1j**, 126158-54-1; **1k**, 118946-59-1; **1l**, 126189-12-6; **1m**, 126159-19-1; **2a**, 32364-53-7; **2b**, 126158-55-2; **2d**, 118946-70-6; **2e**, 126158-56-3; **2g**, 126158-57-4; **2h**, 126158-58-5; **2k**, 118946-71-7; **2l**, 126158-59-6; **2m**, 126158-60-9; **3a**, 95980-52-2;

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3b, 126158-61-0; **3c**, 126158-62-1; **3d**, 118946-84-2; **3e**, 126158-63-2; **3f**, 126158-64-3; **3g**, 126158-65-4; **3h**, 126158-66-5; **3i**, 126158-67-6; **3j**, 126158-68-7; **3k**, 118946-85-3; **3l**, 126158-69-8; **3n**, 126159-21-5; **4** (Ar = *p*-MeC_6H_4, R = R′ = Me), 126158-70-1; **4** (Ar = *p*-ClC_6H_4, R = R′ = Me), 118946-86-4; **4** (Ar = *p*-FC_6H_4, R = R′ = Me), 126158-71-2; **4** (R, R′ = CH_2CH_2), 126159-12-4; **4** (R = R′ = Ph), 126159-13-5; **4** (R = R′ = Me), 94572-63-1; **5**, 29411-28-7; **6**, 126159-14-6; **7**, 126159-15-7; **9**, 126159-16-8; **10**, 126159-18-0; **11**, 126159-17-9; **12**, 2450-55-7; **13**, 4686-14-0; **14**, 6080-60-0; **17b**, 126158-80-3; **17c**, 126158-81-4; **17d**, 126158-82-5; **17f**, 126158-83-6; **17g**, 126158-84-7; **17h**, 126158-85-8; **17i**, 126158-86-9; **17n**, 126158-87-0; **18**, 125879-46-1; **19a**, 126159-20-4; **19b**, 126158-72-3; **19c**, 126158-74-5; **19d**, 126158-73-4; **19f**, 126158-75-6; **19g**, 126158-76-7; **19h**, 126158-77-8; **19i**, 126158-78-9; **19n**, 126158-79-0; **20b**, 126158-88-1; **20c**, 126158-89-2; **20d**, 126158-90-5; **20f**, 126158-91-6; **20g**, 126158-92-7; **20h**, 126158-93-8; **20i**, 126158-94-9; **20n**, 126158-95-0; **25** (R = 3-OMe), 126158-98-3; **25** (R = 2-OMe), 126158-99-4; **25** (R = 3-Cl), 126159-00-0; **25** (R = 2-Cl), 126159-01-1; **25** (R = 3-Br), 126159-02-2; **25** (R = 3-F), 126159-03-3; **25** (R = 2,4-Me_2), 126159-04-4; **25** (R = 3-OMe, 6-Cl), 126159-05-5; **25** (R = H), 2510-61-4; **26** (R = 3-Br), 126159-06-6; **26** (R = 2-OMe), 126159-07-7; **26** (R = 3-Cl), 126159-08-8; **26** (R = 3-F), 126159-09-9; **26** (R = 2,4-Me_2), 126159-10-2; **26** (R = H), 2510-69-2; *t*-BuOH, 75-65-0; *o*-$HOC_6H_4CO_2Me$, 119-36-8; $EtO_2CCH_2CO_2Et$, 105-53-3; $PhCO_2H$, 65-85-0; PhN_3, 622-37-7; PhCOCN, 613-90-1; *p*-$MeOC_6H_4CN$, 874-90-8; *m*-$MeOC_6H_4CN$, 1527-89-5; *p*-ClC_6H_4CN, 623-03-0; *m*-ClC_6H_4CN, 766-84-7; *p*-BrC_6H_4CN, 623-00-7; *p*-FC_6H_4CN, 1194-02-1; *p*-$NO_2C_6H_4CN$, 619-72-7; PhN_3, 622-37-7; *p*-$ClC_6H_4N_3$, 3296-05-7; *p*-$NO_2C_6H_4N_3$, 1516-60-5; $PhCH_2NH_2$, 140-29-4; *p*-$MeOC_6H_4CH_2CN$, 104-47-2; *p*-$H_2NC_6H_4C(Ph)=C(Ph)CN$, 126159-22-6; 3-(4-methoxyphenyl)-4-phenylmaleic anhydride, 104594-83-4; 3-(3-methoxyphenyl)-4-phenylmaleic anydride, 126158-96-1; 3-(4-methylphenyl)-4-(4-chlorophenyl)maleic anhydride, 126158-97-2; 5-chloro-1,4-diphenyl-1,2,3-triazole, 126159-11-3; pinacol, 76-09-5; piperidine, 110-89-4; 3,5-dimethylbenzonitrile, 22445-42-7; 1-naphthalenecarbonitrile, 86-53-3; 2-methoxyphenanthrene-9,10-dicarboxylic anhydride, 109036-17-1.

Supplementary Material Available: Analytical data for the new compounds listed in Tables III–X, XIII, and XIV and details of the crystal-structure determination of compound **19h** (12 pages); structure factors of compound **19h** (8 pages). Ordering information is given on any current masthead page.

Notes

Reaction of an α-Cyanobenzylidenetriazene with Amines and Related Bases[1]

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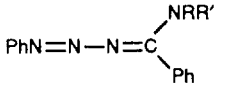
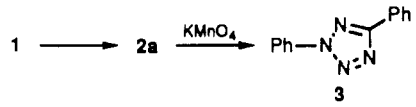
3-(α-Cyanobenzylidene)-1-phenyltriazene[2] (**1**) shows pronounced electrophilic character at the benzylidene carbon and reacts with piperidine to form an (α-aminobenzylidene)triazene (**2e**) with loss of cyanide, whereas with aniline it forms an imine of phenylglyoxylic acid, with loss of nitrogen.[3] An analogous difference has been observed between sodium hydroxide, which converts **1** to 1-benzoyl-3-phenyltriazene with loss of cyanide, and alkoxides and phenoxide, which convert **1** to ketals of phenylglyoxylamidine with loss of nitrogen.[3] We report here a brief comparison of other nitrogen bases with the respective reactions of piperidine and aniline.



2a: R = R′ = H
b: R = CH_3, R′ = H
c: R = R′ = CH_3
d: R = Ph; R′ = CH_3
e: RR′ = $(CH_2)_5$

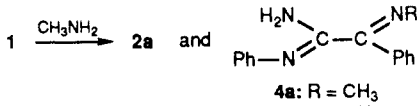
The reactions of **1** with amines were generally spontaneous and mildly exothermic, accompanied in some cases by visible evolution of gas. Ammonia reacted in the same way as piperidine and converted **1** to **2a** (or a tautomer). Support for the structure was obtained by oxidation with permanganate to form 2,5-diphenyl-(2*H*)-tetrazole (**3**) (eq 1).



(1)

3

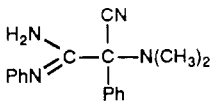
Methylamine gave two products, one corresponding to that formed by ammonia, piperidine, and hydroxide, the other (**4a**) related to that formed by alkoxide and phenoxide and aniline (eq 2).



(2)

4a: R = CH_3
b: R = NH_2
c: R = OH

Dimethylamine also gave two products, in a ratio of ca. 2.5:1: a yellow triazene (**2c**) and a colorless, new type of compound, **5**, which had acquired the elements of HCN.



5

In an experiment conducted in the presence of an excess of added HCN, the ratio was about 1:2. The HCN required for forming **5** in the first experiment may have come from that released in the formation of **2**. Hydrolysis of **5** was accomplished with alcoholic alkali; aniline and benzoic acid were produced.

N-Methylaniline reacted incompletely and only with heating and converted **1** to **2d**. In contrast, hydrazine

(1) From the Senior Honors thesis of G.D.M.
(2) Smith, P. A. S.; Krbechek, L. O.; Resemann, W. *J. Am. Chem. Soc.* **1964**, *86*, 2025.
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