

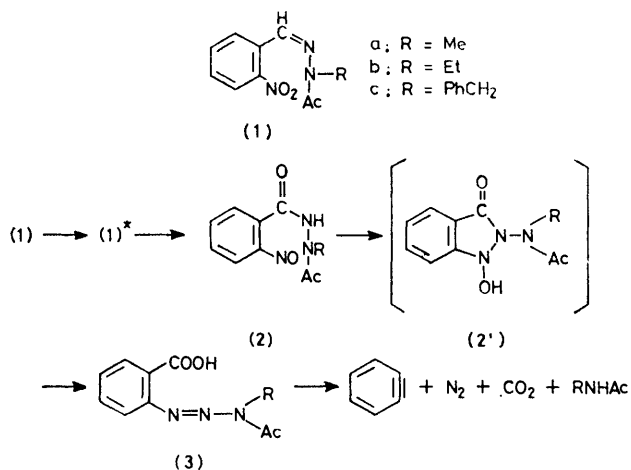
Photochemical Reactions. Part 20.¹ Photolysis of *o*-Nitrobenzaldehyde *N*-Acylhydrazones leading to Benzyne and 5-Nitrophthalazines²

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Irradiation of *o*-nitrobenzaldehyde *N*-acetyl-*N*-alkylhydrazones resulted in the generation of benzyne *via* decomposition of *o*-(*N*-acetyl-*N*-alkyltriazeno)benzoic acids derived from *o*-nitrosobenzoyl-*N*-acetyl-*N*-alkylhydrazides which are initially formed in an analogous fashion to the *o*-nitrobenzylideneaniline rearrangement. Photolysis of *o*-nitrobenzaldehyde *N*-acylhydrazones, however, resulted in photocyclisation leading to 1-substituted 5-nitrophthalazines, with benzyne generation only as a minor process.

A NUMBER of photochemical intramolecular rearrangements of nitroaromatic compounds are known in which the nitro group is reduced to a nitroso group while an oxygen atom is apparently transferred to an *ortho*-substituent.³ Our previous results on the photolysis of *N*-acyl-2-nitrodiphenylamines⁴ and benzylidene-*o*-nitroarylmethylhydrazines⁵ belong to this category.

In continuation of our photochemical studies on *o*-substituted nitroaromatic compounds, we have found that photolysis of *o*-nitrobenzaldehyde *N*-acetyl-*N*-alkylhydrazones (1) results in the generation of benzyne.



This type of photochemistry provides a novel example of benzyne generation. On the other hand, it was observed that photolysis of *o*-nitrobenzaldehyde acylhydrazones (4) results in photocyclisation leading to 1-substituted 5-nitrophthalazines (5) in preparative yields, and benzyne generation occurs only as a minor process. Thus, the photolysis of *o*-nitrobenzaldehyde hydrazones was proved to be significantly influenced by the nature of the nitrogen-substituents in the hydrazone moiety.

Photochemistry of *o*-Nitrobenzaldehyde *N*-Acetyl-*N*-alkylhydrazones (1).—Photodegradation of the *N*-methyl-*N*-acetylhydrazone (1a) in methanol was initiated with ease by irradiation by a high pressure mercury lamp under nitrogen through Pyrex. The reaction was followed by t.l.c. and n.m.r. spectroscopy. After long irradiation, g.l.c.–mass spectral analysis of the reaction mixture indicated the presence of *N*-methylacetamide

and a compound, *m/e* 228(*M*⁺) believed to be triphenylene.⁶ Irradiation of a mixture of (1a) and tetracyclone in methanol gave 1,2,3,4-tetraphenylnaphthalene in *ca.* 10% yield.

These experimental results indicate that the photolysis of (1a) ultimately generates benzyne.

Analogous results were obtained for the irradiation of *N*-ethyl- and *N*-benzyl-hydrazones (1b and c).

When the hydrazone(1a) in benzene was irradiated under similar conditions, the reaction mixture readily deposited *o*-nitrosobenzoyl-*N*-acetyl-*N*-methylhydrazone (2a) in 90% yield. The i.r. spectrum of (2a) showed bands at 3 230(NH), 1 680(CO), 1 530, and 1 340 cm⁻¹ (NH). The NH deformation bands were unequivocally assigned by a deuterium-labelling experiment. On the basis of the i.r. and mass spectral data, *m/e* 442 (*M*⁺), and also because it was colourless, the nitroso compound(2a) appears to exist as a dimer in the solid state. The nitroso compound (2a) in solution, however, appears to exist in the cyclic form(2'a), *i.e.*, the n.m.r. spectrum in [2H₆]DMSO showed a sharp singlet at τ - 1.18 assignable to NOH and the i.r. spectrum in [2H₄]methanol or [2H₆]DMSO exhibited an amide carbonyl band (1 725 cm⁻¹) characteristic of a five-membered lactam.

In the dark the nitroso compound (2a) in methanol was gradually converted into *o*-(*N*-acetyl-*N*-methyltriazeno)benzoic acid (3a) at room temperature. The structure of (3a) was fully supported by spectral data and microanalytical results. Mild alkaline treatment of (2a) followed by acidification also gave (3a) quantitatively.

Upon irradiation of the hydrazones (1b and c) in benzene, however, the irradiated solution deposited only a small amount of powdery products which were characterised as the corresponding nitroso compounds (2a and c) by conversion into the triazenobenzoic acids (3b and c) on warming in benzene. Thus, concentration of the irradiated solution on warming gave directly the triazenobenzoic acids (3b and c).

Independent irradiation of both the nitroso and triazeno compounds(2a) and (3a) showed that (3a) is much more photosensitive than (2a). These facts clearly indicate that the nitroso compound(2a) is thermally converted into the triazenobenzoic acid(3a), although the conversion can be accelerated to some extent by irradi-

ation, and (3a) easily undergoes photodegradation leading to benzyne.

The photolysis of (3a) in methanol in the presence of tetracyclone caused rapid decomposition resulting in the formation of *N*-methylacetamide(85%), 1,2,3,4-tetraphenylnaphthalene(15%), and undetermined products. Analogous irradiation of (3b and c) in the presence of tetracyclone also gave the tetraphenylnaphthalene in 10% yield.

The photolysis of (1a) was monitored by the n.m.r. spectroscopy using $[^2\text{H}_4]$ methanol as solvent (see Figure). The n.m.r. spectral changes of the *N*-methyl and acetyl methyl groups of (1a) during irradiation demonstrated that the photolysis proceeds cleanly *via* a detectable

subsequent reaction leading to the nitroso compound (2) appears to proceed in a similar fashion to the photorearrangement of *o*-nitrobenzylideneaniline to *o*-nitrosobenzanilide⁷ which involves an intramolecular photo-oxidation-reduction process typical of *o*-substituted nitroaromatic compounds.³ Further thermal rearrangement of (2) to the triazenobenzoic acid (3) could proceed *via* the cyclic intermediate (2'). An analogous cyclic intermediate has been proposed in the base-catalysed conversion of *o*-nitrosobenzanilide into azobenzene-2-carboxylic acid by Spence and Tennant.⁸ Photodegradation of the triazenobenzoic acid (3) could occur to generate benzyne with the simultaneous loss of nitrogen, carbon dioxide, and acetamide.

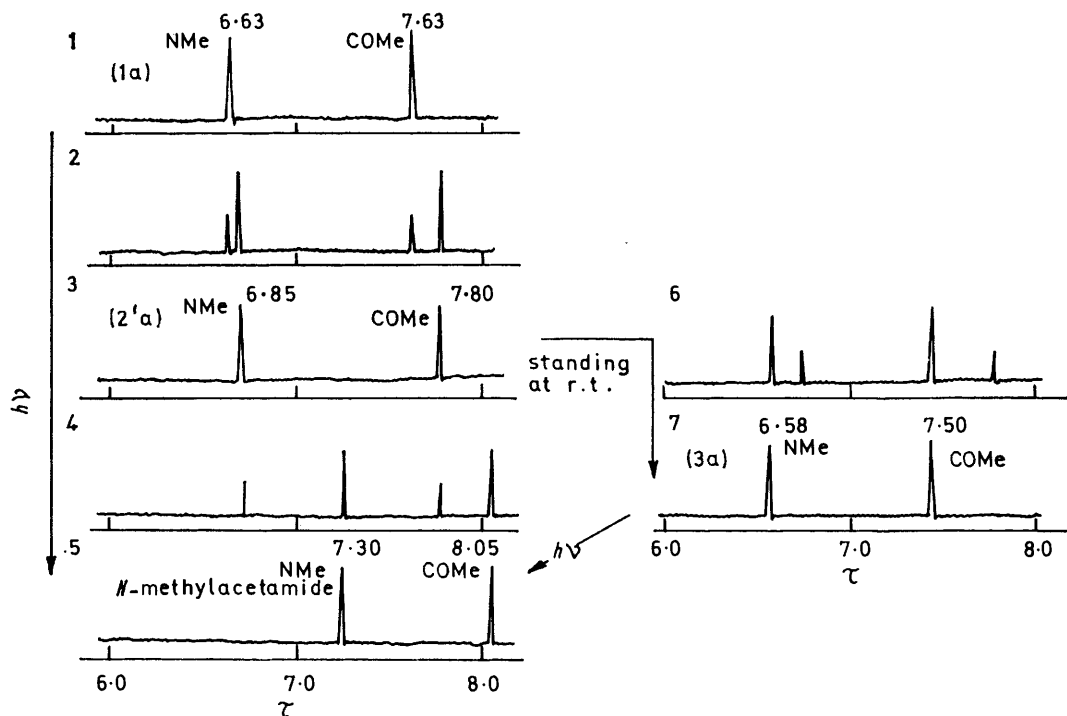


FIGURE Changes of *N*-methyl and acetyl methyl signals in the n.m.r. spectrum of *o*-nitrobenzaldehyde *N*-acetyl-*N*-methylhydrazone (1a) during irradiation in $[^2\text{H}_4]$ methanol. r.t. = room temperature

intermediate to give *N*-methylacetamide. Both the signals of the intermediate were consistent with those of the cyclic intermediate (2'a) which correspond to the n.m.r. signals of the nitroso intermediate (2a) in $[^2\text{H}_4]$ -methanol. On standing at room temperature, new signals arising from *o*-(*N*-acetyl-*N*-methyltriazeno)benzoic acid (3a) developed instead of the signals of (2'a). Upon irradiation, the signals of (3a) disappeared instantly and distinct signals of *N*-methylacetamide were finally observed. That no signals for (3a) were observed during continuous irradiation indicates the extreme photolability of (3a) formed thermally *via* the intermediate (2'a).

On the basis of these experiments, the reaction sequence is outlined as shown in Scheme 1.

The photoreaction can be initiated by excitation of the nitro group ($n-\pi^*$ triplet) of the hydrazone (1). The

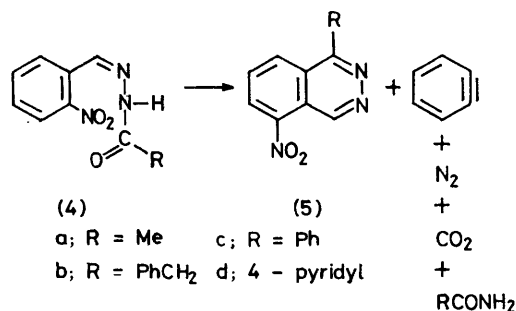
Photochemical generation of benzyne has been demonstrated in the photolysis of benzenediazonium *o*-carboxylate,^{9,10} *o*-iodophenylmercury(II) iodide,¹¹ phthaloyl peroxide,^{6,12} and benzothiadiazole 1,1-dioxide.¹³

Nakayama *et al.*¹⁴ have reported that thermolysis of *o*-dimethyltriazobenzoic acid produces benzyne. Thermolysis of the triazenobenzoic acids (3a-c) in monochlorobenzene generated benzyne which was trapped efficiently by tetracyclone.

Additionally, it should be noted that photolysis of *o*-nitrobenzaldehyde *NN*-dimethylhydrazone resulted in some undetermined photoreactions and no significant change was observed in the photolysis of *o*-nitrobenzaldehyde methylhydrazone.

Photochemistry of o-Nitrobenzaldehyde N-Acylhydrazones (4).—By analogy with the photochemistry of *o*-

nitrobenzaldehyde *N*-acetyl-*N*-alkylhydrazones (1a—c) we expected that *o*-nitrobenzaldehyde *N*-acylhydrazones (4a—d) should be photolysed to form benzyne. However, the photolysis of the hydrazones (4a—d) resulted in cyclisation to 1-substituted 5-nitrophthalazines accompanied by generation of benzyne only to a small extent.



SCHEME 2

o-Nitrobenzaldehyde *N*-acetylhydrazone (4a) in methanol reacted readily under nitrogen when irradiated by a high-pressure mercury lamp through a Pyrex filter. As the reaction proceeds, 1-methyl-5-nitrophthalazine (5a) is deposited. The presence of acetamide in the mother liquor was confirmed by g.l.c. and n.m.r. spectroscopy. Irradiation of the hydrazone (4a) in the presence of tetracyclone resulted in the formation of a small amount of 1,2,3,4-tetraphenylnaphthalene, indicating benzyne generation as in the case of the *N*-acetyl-*N*-alkylhydrazones (1). The product (5a) was identical in every respect with a sample prepared by nitration of 1-methylphthalazine.¹⁵

Analogously, phenylacetyl-, benzoyl-, and isonicotinylhydrazides (4b—d) gave the corresponding 5-nitrophthalazines (5b—d) as major products.

Photocyclisation of the six-electron system involving an amide function such as anilides¹⁶ and enamides¹⁷ have been well documented. Analogously, both the hydrazones (1) and (4) appear to undergo a photochemical six-electron electrocyclic reaction in competition with benzyne generation.

In the case of the *N*-acylhydrazone (4) the resulting cyclic intermediate (6; R¹ = H) can easily lose water thermally to give the phthalazine (5) in preparative yield. In the case of the *N*-acetyl-*N*-alkylhydrazone (1), however, the intermediate (6; R¹ = alkyl) can revert to the starting material because of the difficulty of the elimination of alcohols. Thus, the hydrazone (1) generates benzyne preferentially.

The present photochemical behaviour of the *o*-nitrobenzaldehyde isonicotinylhydrazone (4d) in solution is of interest in connection with its photothermochromism previously observed in the crystalline state.¹⁸

It is noteworthy that this type of photocyclisation is limited to *o*-nitrobenzaldehyde *N*-acylhydrazones (4), *i.e.*, the corresponding *N*-acylhydrazones of benzaldehyde and its *p*-nitro, *o*-methoxy, and *o*-cyano derivatives did not give phthalazines on similar irradiation. The

role of the *o*-nitro group is not clear at present and further studies are in progress.

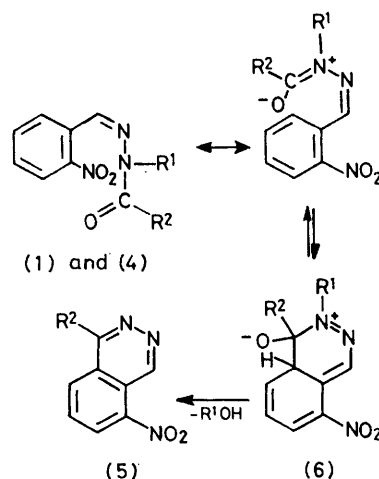
EXPERIMENTAL

I.r. spectra were recorded with a Hitachi 215 spectrometer for potassium bromide discs and ¹H n.m.r. spectra with a Hitachi R-20B 60 MHz spectrometer for solutions in [²H₄]methanol containing tetramethylsilane as internal standard. Mass spectra were measured at 75 eV with a JEOL JMS-01SG spectrometer. All irradiations were performed with a Rikosha 400W high pressure mercury lamp through a Pyrex filter under nitrogen at room temperature. Reagent grade benzene and methanol were redistilled prior to use as solvent. Column chromatography was performed on silica gel (Mallinckrodt; 100 mesh) with chloroform as eluant.

Preparation of o-Nitrobenzaldehyde N-Acetyl-N-alkylhydrazones (1a—c).—A solution of *o*-nitrobenzaldehyde *N*-methylhydrazone (1.8 g) in acetic anhydride (50 ml) was refluxed for 3 h. The solution was concentrated under reduced pressure to leave a solid mass, which was recrystallised from ethanol to give the *N*-acetylhydrazone (1a) (2.1 g, 95%) as yellow needles, m.p. 135° (Found: C, 54.1; H, 5.05; N, 19.25. C₁₀H₁₁N₃O₃ requires C, 54.3; H, 5.0; N, 19.0%). ν_{max} 1 680 cm⁻¹ (CO), τ 6.63 (3 H, s, NMe) and 7.63 (3 H, s, COMe).

A solution of *o*-nitrobenzaldehyde hydrazone (1.65 g) in acetic anhydride (50 ml) was stirred at room temperature for 2 h. The resulting precipitates were collected, dissolved in chloroform, and washed with 5% Na₂CO₃ solution and subsequently water. The organic layer was dried and concentrated. The residue was recrystallised from ethanol to give *o*-nitrobenzaldehyde *N*-acetylhydrazone (1.85 g, ca. 90%) as pale yellow needles, m.p. 173°.

To a solution of the *N*-acetylhydrazone (2.1 g) and sodium hydride (0.7 g; 50% oil dispersion) in dimethylformamide (50 ml) was added ethyl iodide (3.1 g) and the mixture was



SCHEME 3

stirred at room temperature for 2 h. The mixture was poured into water (50 ml) and extracted with chloroform and washed with water. The organic layer was dried and concentrated. The residue was recrystallised from ethanol to give the *N*-ethylhydrazone (1b) (1.65 g, 70%) as pale yellow needles, m.p. 78° (Found: C, 56.15; H, 5.55; N, 18.0. C₁₁H₁₃N₃O₃ requires C, 56.15; H, 5.55; N, 17.85%),

ν_{\max} 1 690 and 1 660 cm^{-1} (CO), τ 5.9 (2 H, q, J 7 Hz, CH_2), 8.8 (3 H, t, J 7 Hz, Me), and 7.6 (3 H, s, COMe).

Analogously, the *N*-benzylhydrazone (1c) was obtained from the *o*-nitrobenzaldehyde *N*-acetylhydrazone in 75% yield as pale yellow needles, m.p. 95° (Found: C, 64.75; H, 4.95; N, 14.3. $\text{C}_{16}\text{H}_{15}\text{N}_3\text{O}_3$ requires C, 64.65; H, 5.1; N, 14.15%), ν_{\max} 1 690 and 1 670 cm^{-1} (CO), τ 4.70 (2 H, s, CH_2) and 7.50 (3 H, s, COMe).

Photolysis of N-Acetyl-N-alkylhydrazones (1a—c).—(a) A solution of the hydrazone (1a) (1.1 g) in methanol (200 ml) was irradiated for 30 h. The mixture was concentrated under reduced pressure and the residue was chromatographed to isolate *N*-methylacetamide (85%) as an oil, which was identical in every respect with an authentic sample. G.l.c.—mass spectral analysis of the reaction mixture indicated the presence of *N*-methylacetamide and a compound, m/e 288 (M^+), assigned as triphenylene.

Analogous irradiation of the *N*-ethyl- and *N*-benzylhydrazones (1b and c) gave *N*-ethyl- and *N*-benzylacetamide accompanied by a detectable amount of triphenylene, respectively.

A mixture of the hydrazone (1a) (0.3 g) and tetracyclone (0.9 g) in methanol was irradiated for 15 h. Concentration of the irradiated solution followed by chromatographic

benzene. As in the case of (1b), the triazenobenzoic acid (3c) (80%) was obtained directly as pale yellow needles, m.p. 116° (Found: C, 64.8; H, 5.0; N, 14.35. $\text{C}_{16}\text{H}_{15}\text{N}_3\text{O}_3$ requires C, 64.65; H, 5.1; N, 14.15%), ν_{\max} 3 430 (OH) and 1 710 cm^{-1} (CO), τ 4.70 (2 H, s, CH_2) and 7.45 (3 H, s, COMe).

Conversion of o-Nitrosobenzoyl-N-methyl-N-acetylhydrazide (2a) into o-(N-Methyl-N-acetyltriazeno)benzoic Acid (3a).—A solution of the nitroso compound (2a) (1.1 g) in 3% NaOH (30 ml) was stirred for 30 min at room temperature. The dark brown solution was acidified to litmus with 5% HCl. The precipitated solid was collected, washed with water, dried, and recrystallised from *n*-hexane—ether (1 : 1) to give the triazenobenzoic acid (3a) (0.8 g, 73%) as needles, m.p. 155° (Found: C, 54.35; H, 5.05; N, 19.25. $\text{C}_{10}\text{H}_{11}\text{N}_3\text{O}_3$ requires C, 54.3; H, 5.0; N, 19.0%), ν_{\max} 3 400 (OH) and 1 720 cm^{-1} (CO), τ ($[\text{H}_6]$ DMSO) 2.0—2.7 (4 H, m, ArH), 6.67 (3 H, s, NMe), and 7.53 (3 H, s, COMe), τ ($[\text{H}_4]$ methanol) 6.58 (3 H, s, NMe) and 7.50 (3 H, s, COMe).

An analogous conversion was observed when the nitroso compound (2a) was left in methanol at room temperature (see text).

Thermolysis and Photolysis of o-(N-alkyl-N-acetyltriazeno)benzoic Acids (3a—d) in the Presence of Tetracyclone.—A

1-Substituted 5-nitrophthalazines (5a—d)

Compound (5a)	Reaction time (h)	M.p./°C (solvent)	Yield (%)	Found (%)		Formula	Required (%)			
				C	N		C	H	N	
(5a)	7.5	197 (decomp.) (MeOH)	50	57.25	3.8	22.1	$\text{C}_9\text{H}_7\text{N}_3\text{O}_2$	57.15	3.75	22.2
(5b)	8.0	233 (decomp.) (DMF—EtOH)	30	67.9	4.25	15.7	$\text{C}_{15}\text{H}_{11}\text{N}_3\text{O}_2$	67.9	4.2	15.85
(5c)	5.0	256 (decomp.) (DMF—EtOH)	55	67.0	3.65	16.9	$\text{C}_{14}\text{H}_9\text{N}_3\text{O}_2$	66.9	3.6	16.75
(5d)	5.0	276 (decomp.) (DMF—EtOH)	60	62.15	3.25	22.2	$\text{C}_{13}\text{H}_8\text{N}_4\text{O}_2$	61.9	3.2	22.2

purification isolated 1,2,3,4-tetraphenylnaphthalene (0.03 g) as needles, m.p. 204°, which is identical in every respect with an authentic sample.

(b) A solution of the hydrazone (1a) (1.1 g) in benzene (200 ml) was irradiated for 3 h. The precipitates were collected and dried to give *o*-nitrosobenzoyl-*N*-methyl-*N*-acetylhydrazide (2a) (1.1 g, 90%) as a powder, m.p. 150° (Found: C, 53.8; H, 5.05; N, 18.7. $\text{C}_{20}\text{H}_{22}\text{N}_6\text{O}_6$ requires C, 54.3; H, 5.0; N, 19.0%), ν_{\max} 3 230 (NH) and 1 680 cm^{-1} (CO), ν_{\max} ($[\text{H}_6]$ DMSO) 1 725 cm^{-1} (CO), ν_{\max} ($[\text{H}_4]$ methanol) 1 720 cm^{-1} , τ ($[\text{H}_6]$ DMSO) — 1.18 (1 H, s, OH), 1.95—2.65 (4 H, m, ArH), 6.93 (3 H, s, NMe), and 7.90 (3 H, s, COMe), τ ($[\text{H}_4]$ methanol) 6.85 (3 H, s, NMe) and 7.80 (5 H, s, COMe).

A solution of the hydrazone (1b) (1.2 g) in benzene (200 ml) was irradiated for 3 h. The mixture deposited only a small amount of powder which was characterised as the nitroso compound (2b) by conversion into the triazenobenzoic acid (3b) on warming in benzene. The mixture was concentrated without removal of the nitroso compound (2b) and the residue was purified by chromatography and recrystallisation from ether to obtain the triazenobenzoic acid (3b) (1.0 g, 85%) as pale yellow needles, m.p. 113° (Found: C, 56.3; H, 5.45; N, 17.7. $\text{C}_{11}\text{H}_{13}\text{N}_3\text{O}_3$ requires C, 56.15; H, 5.55; N, 17.85%), ν_{\max} 3 420 (OH), 1 710, and 1 730 cm^{-1} (CO), τ 5.85 (2 H, q, J 7 Hz, CH_2), 7.50 (3 H, s, COMe), and 8.90 (3 H, t, J 7 Hz, Me).

Irradiation of the hydrazone (1c) in benzene gave a small amount of the nitroso compound (2c) which was easily converted into the triazenobenzoic acid (3c) on warming in

mixture of the triazenobenzoic acid (3a) (0.05 g) and tetracyclone (0.2 g) in chlorobenzene (20 ml) was refluxed for 5 h and concentrated under reduced pressure. The residue was purified by chromatography and recrystallisation from *n*-hexane to give 1,2,3,4-tetraphenylnaphthalene (0.06 g, 61.4%) as needles, m.p. 204° (Found: C, 94.25; H, 5.65. Calc. for $\text{C}_{34}\text{H}_{24}$: C, 94.4; H, 5.6%).

Analogously, the tetraphenylnaphthalene was obtained from the thermolysis of the triazenobenzoic acids (3b and c) in the presence of tetracyclone.

A mixture of the triazenobenzoic acid (3a) (0.05 g) and tetracyclone (0.2 g) in methanol (20 ml) was irradiated for 3 h and concentrated under reduced pressure. The residue was purified by chromatography and recrystallisation from *n*-hexane to give 1,2,3,4-tetraphenylnaphthalene (0.015 g), m.p. 204°, identical with the sample obtained by thermolysis.

Analogously, the tetraphenylnaphthalene was obtained in the photolysis of the triazenobenzoic acids (3b and c) in the presence of tetracyclone.

Photochemical Formation of 1-Substituted 5-Nitrophthalazines (5a—d).—*o*-Nitrobenzaldehyde *N*-acylhydrazones (4a—d) (1 g) in methanol (200 ml) were irradiated. After irradiation for the time given in the Table, 5-nitrophthalazines (5a—d) precipitated, were collected by filtration, and recrystallised. The mother liquor deposited a further small amount of product after concentration.

In the irradiation of the *N*-acetylhydrazone (4a), the formation of acetamide was confirmed by n.m.r. spectroscopy, indicating generation of benzyne. Photolysis of the

N-acetylhydrazone (4a) in the presence of excess of tetracyclone gave a small amount of tetraphenylnaphthalene together with 1-methylphthalazine (5a).

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