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Reduction of Ag(I) by 1-Acyl-2-arylhydrazines: Mechanism of Photographic Infectious Development

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Abstract: The photographic process of 'infectious development' in which 1-acyl-2-arylhydrazines reduce Ag(I) has been studied using analogues. 1-Acyl-2-aryldiazenes, resulting from oxidation of 1-acyl-2-arylhydrazines, are hydrolysed to anions of aryldiazenes (ArN=NH), which undergo further oxidation with loss of nitrogen to yield aryl radicals. The aryl radicals cause 'feedback inhibition' which is prevented by the addition of benzhydrol.

The observation that photographic speed and contrast of silver halide photographic film may be increased during development by the addition of hydrazine derivatives was first observed 50 years ago.[1] Conventional development of photographic negatives converts those silver halide crystals, which have formed a stable cluster of Ag(I) atoms on absorption of photons of light (latent image), to Ag(0). During the onset of the development process, the hydrazine additives give localised formation of powerful reducing agents which 'infect' silver halide crystals in close proximity, irrespective of the exposure they have received. This process is called *'infectious development'*. Initially, the process could only be achieved at high pH (>12.5) which was impractical for general commercial use. The discovery that 1-aryl-2-formylhdrazines **1** functioned at a lower pH (11.5) facilitated the utilization of infectious development in photography. An even lower pH (10.5) can be used with hydrazine **2**, which has been patented and commercially exploited.[2,3] Used alone these hydrazines produce a high contrast in the *Density* versus *Log of Exposure* curve (Fig. 1) but the contrast falls off rapidly, indicating an inhibition process. The addition of benzhydrol overcomes the inhibition process (Fig. 1).

This paper describes our studies to elucidate the mechanisms involved in the process of infectious development with hydrazine **2** and benzhydrol. Preliminary results have been published.[2] Various studies have investigated the mechanism of infectious development but none have fully elucidated the process.[2-6]

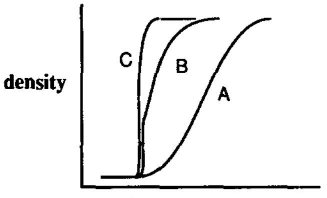
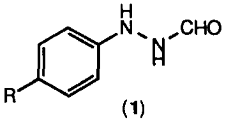
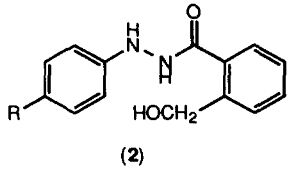


Figure 1
A normal development
B + acylhydrazine with feedback inhibition
C + acylhydrazine and contrast development agent

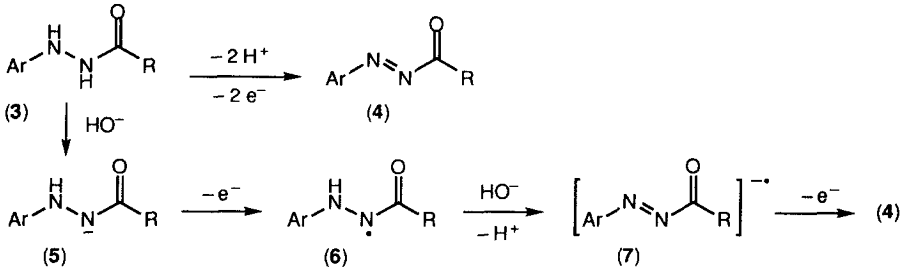


(1)



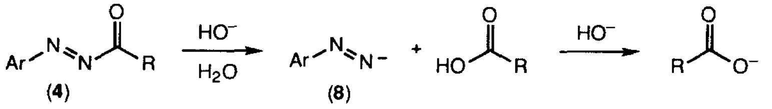
(2)

The radical and redox reactions of 1-acyl- and 1-sulfonyl- 2-aryldiazenes have been studied.[7,8,9] The first step in the photographic process is the oxidation of 1-acyl-2-arylhydrazines **3** to 1-acyl-2-aryldiazenes **4** (Scheme 1) which is well reported in the literature.[2-6,10] Either Ag(I) or quinone/semiquinone, resulting from photographic development, is responsible for the redox reaction. Our studies were concentrated on the reactions of the diazenes **4** because their formation by oxidation of the hydrazines **3** is well established. The intermediate radicals **6** and **7** have not been detected by EPR spectroscopy[6] which is not surprising because proton loss followed by electron loss should be rapid in the photographic development medium. In order to obtain evidence[11] for the intermediate radical anion **7** the radical anions of 1-benzoyl- and 1-acetyl-2-phenyldiazene were generated at low temperature by electron addition at 77 K in solid matrices of methyltetrahydrofuran and studied by EPR spectroscopy.[12] The spectra showed 2*N*, $A_{//}$ = *ca.* 19.5 and $A_{\perp}$ = *ca.* 0. Calculations using A_{iso} = *ca.* 6 which is observed for several diazenes in liquid phase give 2B = 13.5 G and a_p = 41% on each nitrogen. The unpaired electron is in a π^* molecular orbital and the spin density is roughly equivalent on each nitrogen atom but with little delocalised onto oxygen.



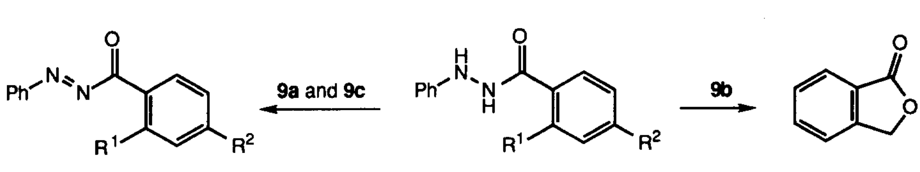
Scheme 1. Oxidation of 1-acyl-2-arylhydrazines to 1-acyl-2-aryldiazenes

After the formation of the 1-acyl-2-aryldiazenes **4**, their hydrolysis has been proposed as the next step (equation 1). Hydrolysis in the high pH aqueous NaOH solution is fast and aryldiazene anions **7** are good leaving groups. The pK$_a$ of phenyldiazene (PhN=NH) is *ca.* 18 and the anion has been shown to be present in aqueous NaOH solution.[13] The pK$_a$ of phenylhydrazine is *ca.* 40 and its anion is a poor leaving group which explains why the hydrazides are stable in the medium. The assumptions on the mechanism are supported by the rate of hydrolysis being a determining factor in infectious development. In a simple series, the faster the rate of hydrolysis the better the infectious development, *e.g.* for hydrazine **3**, the rate is formyl > benzoyl > acetyl as would be predicted.[2-6] The efficacy of the formyl group is also explained by a homolytic cleavage mechanism with loss of CO. On this basis, acyl groups such as trifluoroacetyl and *p*-nitrobenzoyl should show enhanced infectious development but are less effective than the formyl analogue.[2-4] The probable explanation is that there is a balance between rates of oxidation of the hydrazine anions **5** and the hydrolysis of the acyldiazenes **4**. Strong electron withdrawing groups favour hydrolysis but not the oxidation step.



(1)

The much improved infectious development from hydrazine **2** is because the rate of intramolecular attack on the acyl carbonyl is favoured by excellent orientation and proximity,[14] *i.e.* the rate of oxidation of the anion is similar to the the benzoyl derivative but the cleavage of the diazene-carbonyl bond is much faster. Infectious development with hydrazines **2** can be carried out at the low pH of 10.5.[2,3] We therefore sought to determine the relative rates of diazene-carbonyl bond cleavage for acyldiazenes **9a-c**. Acyldiazenes **9a** and **9c** were synthesised without difficulty by the normal procedure for converting acylhydrazines to acyldiazenes[2,8] and were stable under the conditions of the synthesis and work-up (Scheme 2). However, when **9b** was reacted



(10) (9) (11)

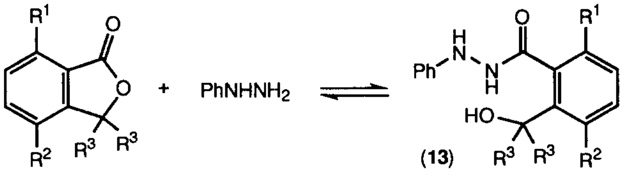
Scheme 2. **9 a**, $R^1 = R^2 = H$; **b**, $R^1 = CH_2OH$, $R^2 = H$; **c**, $R^1 = H$, $R^2 = CH_2OH$
NBS and pyridine in CH_2Cl_2, −78 °C

under the same conditions, none of the expected diazene **10b** was observed and only only phthalide **11** (55%) was isolated (Scheme 2). This result precluded rate studies, but indicated the importance of the fast rate of cyclisation and diazene-carbonyl bond cleavage when the hydroxymethyl group is in the *ortho*-position. Hydrazine **9b** gave excellent infectious development whereas **9a** and **9c** were much inferior.[2,3]

Further support for the importance of these steps was obtained from the NBS oxidation of 1-acetyl- and 1-formyl-2-phenylhydrazine. The formylhydrazine gave only decomposition, *i.e.* hydrolysis of the diazene-carbonyl bond in the reaction, whereas 1-acetyl-2-phenyldiazene was isolated in good yield. Other hydrazine derivatives capable of undergoing cyclisation and diazene-carbonyl bond cleavage, *e.g.* 1-[(2-aminophenyl)-acetyl]-, 1-[(2-hydroxymethylphenyl)acetyl]-, and 1-[(2-hydroxyphenyl)acetyl]-2-phenylhydrazine also gave similar infectious development.[3]

We sought to increase the rate of the cyclisation/ diazene-carbonyl bond cleavage by use of buttressing groups which are known to increase the rate of lactonisation of *o*-(hydroxymethyl)benzoic acids.[14] Reaction between phthalide and phenylhydrazine is used for the synthesis of 1-[(2-hydroxymethylphenyl)-2-phenylhydrazine and analogues. The reaction is reversible and gave only 27% of the desired hydrazine **9b** (equation 2). The equilibrium can be forced over and a higher yield obtained by precipitating out the more polar hydrazide. The required 3,3-dimethyl-, 7-methyl-, and 4-methyl-phthalides, **12 a**, $R^1 = R^2 = H$, $R^3 = Me$; **b**, $R^1 = Me$ $R^2 = H$, $R^3 = H$; **c**, $R^1 = H$, $R^2 = Me$, $R^3 = H$, respectively, were synthesised and reacted with phenylhydrazine under the same conditions. All three derivatives failed to give hydrazide products **13** and only starting materials were observed indicating that cyclisation is much faster than ring opening, *i.e.* the mechanistic parameter for improving the rate of cyclisation of the acyldiazenes precluded the synthesis of the required hydrazines.

(12)



(13) (2)

Hydrolysis/oxidation reactions of 1-benzoyl-2-phenyldiazene

1-Benzoyl-2-phenyldiazene was chosen as a suitable analogue because of the structural similarity to the diazene which would result from oxidation of the commercial hydrazine **2**. Cohen and Nicholson[8] have previously studied this compound but without Ag(I) and used methanol as the solvent. In order to avoid use of a solvent such as methanol that could act as a hydrogen-donor and because the photographic film consists of an aqueous emulsion, water was used as a medium even though the diazene is partly insoluble. Hydrolysis and oxidation reactions were carried out at room temperature under three general sets of conditions to determine the effect of Ag(I) and benzhydrol: *a.* no Ag(I) or benzhydrol, *b.* Ag(I) but no benzhydrol, and *c.* Ag(I) and benzhydrol. The results are presented in Table 1. The reactions were analysed by HPLC and products were isolated and characterised. The amount of Ag(I) reduced was measured by titration of the Ag(I) left at the end of reactions. The benzoic acid was measured by precipitation with acid at the end of the reaction and the yields

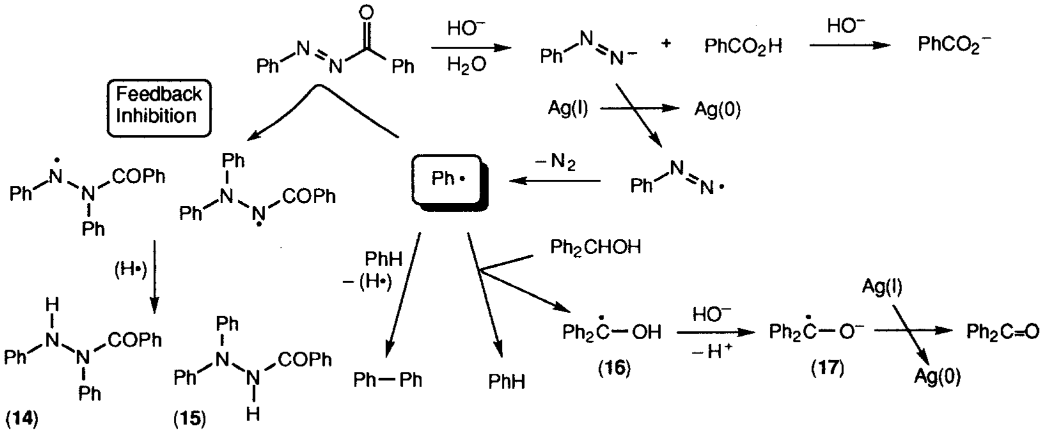
Table 1. Hydrolysis/oxidation reactions of 1-benzoyl-2-phenyldiazene

			% Yield						
[NaOH] M	reaction time (h)	reagents mmoles	unaltered diazene	**14**	**15**	benzene	biphenyl	$PhCO_2H$	Ph_2CO
0.01	18	3.5[a]	17	9	6	11	1	39	-
0.02	12	7.0[a]	14	12	7	37	1	35	-
0.02	36, 48	7.0[a]	4, 6	8, 17	4, 9	34, 43	2, 1	31, 33	-
1.00	3, 6	7.0[a]	10, 4	10, 9	9, 4	32, 28	1, 1	29, 32	-
0.02	3	7.0[b]	7, 2	7, 4	3, 3	52, 58	4, 4	28, 25	-
1.00	3	7.0[b]	10, 9	7, 8	4, 4	45, 40	4, 5	32, 29	-
0.02	3	14.0[b]	13, 10	8, 6	3, 5	56, 35	4, 4	25, 38	-
1.00	3	14.0[b]	13, 5	3, 5	2, 2	32, 43	4, 6	22, 27	-
1.00	2	7.0[c]	3, 2	4, 5	3, 4	81, 67	3, 3	41, 38	39, 58
1.00	2	14.0[c]	11	5	3	74	3	43	45
1.00	2	7.0[d]	1	2	2	41	8	30	35
1.00	3	14.0[e]	0, 0	0, 0	0, 0	78, 75	9, 11	-	90, 80
1.00	3	14.0[f]	0	0	0	75	14	-	100

[a] 1-benzoyl-2-phenyldiazene. [b] 1-benzoyl-2-phenyldiazene and Ag(I)NO_3. [c] 1-benzoyl-2-phenyldiazene, Ag(I)NO_3, and benzhydrol. [d] 1-benzoyl-2-phenyldiazene and benzhydrol (7.0 mmol), Ag(I)NO_3 (14.0 mmol). [e] 1-benzoyl-2-phenyldiazene and benzhydrol (14.0 mmol), Ag(I)NO_3 (49.0 mmol). [f] 1-benzoyl-2-phenyldiazene and benzhydrol (14.0 mmol), Ag(I)NO_3 (56.0 mmol).

are consistently low which is explained by complexing with Ag(I). The results are variable which is probably caused by solubility effects but were also observed by Cohen and Nicholson[7] in homogeneous solution.

Putative mechanisms to explain the results are shown in Scheme 3. In the absence of Ag(I) the hydrolysis and decomposition of the resulting phenyldiazene anion ($PhN{=}N^-$) was sluggish but was faster at higher concentrations of NaOH solution. Moderate amounts of benzene were formed with small amounts of biphenyl and two addition compounds, **14** and **15**, derived from phenyl radical addition to the starting diazene (Scheme 3). If the intermediate was phenyl anion, the predominant formation of **15** over **14** would be predicted from Michael addition. Phenyl radical is definitely an intermediate and has been identified by spin-trapping using EPR spectroscopic techniques.[4,10]



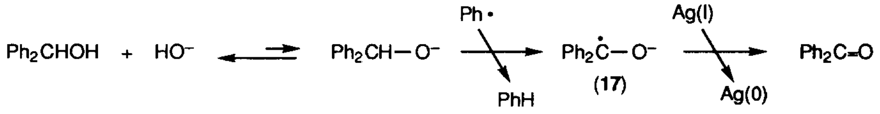
Scheme 3. Hydrolysis / Ag(I) oxidation reactions of 1-benzoyl-2-phenyldiazene

In the absence of Ag(I) the phenyldiazene anion will be in equilibrium with its conjugate acid, phenyldiazene (PhN=NH), which is well known to decompose via phenyl radicals.[13,15-17] The phenyl radical adds to the diazene or to benzene (to give biphenyl by homolytic aromatic substitution) or abstracts hydrogen to yield benzene. Other studies have reported similar results.[4,10,15] The addition of phenyl radical to the diazene provides a good explanation for the 'feed-back inhibition' observed in infectious development (see Fig. 1). The concentration of reagents did not appear to alter the course of the reaction, probably due to the heterogeneous mixture. Homolysis of 1-benzoyl-2-phenyldiazene has been proposed as a mechanism[10] but was ruled out because the diazene is indefinitely stable in the absence of base.

When Ag(I) (1 equiv.) was added the reaction was faster and the yield of benzene and biphenyl increased and **14** and **15** decreased. Addition of Fe(III) gave similar results.[8] The most obvious explanation is that Ag(I) is reduced to Ag(0) by electron transfer from the phenyldiazene anion to yield phenyldiazenyl (PhN=N•) which then undergoes loss of nitrogen to phenyl radical (Scheme 3). When Ag(I) (2 equiv.) was used there was 10% of unaltered diazene remained but 1.2 equivalents of Ag(I) was reduced indicating oxidation of species other than the diazene anion, *e.g.* oxidation of PhN=N• to PhN_2^+.

When benzhydrol (1 equiv.) was added the reaction was faster and there was a large increase in the amount of benzene formed (up to 80%) and a decrease in **14**, **15**, and unaltered diazene, indicating that phenyl radical was trapped by H-abstraction before addition to unreacted diazene, *i.e.* an explanation of the reduction of feedback inhibition by benzhydrol. Reactions with Ag(I) (2 equiv.) gave complete reduction of Ag(I). When Ag(I) was increased to 3.5 equiv. the most efficient reactions took place, *i.e.* high conversion of benzhydrol to benzophenone (80-100%) and phenyl radical to benzene and biphenyl, no addition products, **14** and **15**, and unreacted diazene, and reduction of 2.7 equivalents of Ag(I). In the photographic film the concentration of Ag(I) is high and therefore these latter experiments are most representative, clearly indicating the role of the benzhydrol in infectious development. The mechanisms in Scheme 3 only account for the reduction of two equivalents of Ag(I) and therefore other processes must be taking place to account for further reduction of Ag(I). When benzhydrol (2 equiv.) was used in a repeat of the last experiment, benzophenone (two equiv.) was formed. Interestingly, the increase in the amount of biphenyl indicates that phenyl radical addition to benzene is competitive under the trapping conditions.

Of central importance is the high reduction of Ag(I) and we propose that the radical **16**, formed after hydrogen-abstraction from benzhydrol, loses a proton to yield the radical anion of benzophenone **17** which reduces a second equivalent of Ag(I). The pK_{HA} of radical **16** is 9.2, *ca.* 10^6 times more acidic then benzhydrol,[18] and will rapidly deprotonate in the NaOH solution to give the radical anion of benzophenone **17**, which in turn will rapidly reduce Ag(I) to Ag(0). No benzopinacole was observed in any reactions. Reaction between the diazene and benzhydrol (2 equiv.) in the absence of Ag(I) gave a poor reaction: biphenyl (3%), **14** and **15** (20%), unaltered diazene 8%), benzene (43%), and benzophenone 60%), suggesting that electron-donation is more important than H-abstraction. Extensive studies[19] of the reaction between alcohols and aryl radicals indicates that H-abstraction from the radical anion is much faster than from the alcohol and therefore an alternative mechanism as shown in Scheme 4 is also possible. A small amount of benzhydrol (pK_{HA} = 15.3) will be ionized in NaOH solution.

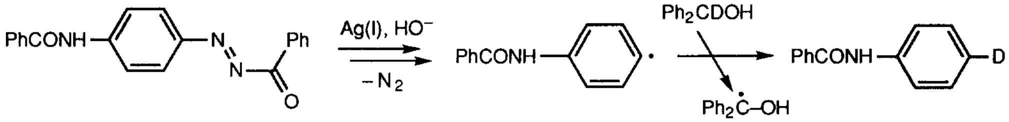


Scheme 4. Hydrogen abstraction from the anion of benzophenone

Hydrogen abstraction from benzhydrol by phenyl radical gives a benzylic- and α-hydroxy-stabilised radical **16**. On this basis, diphenylmethyl methyl ether (Ph_2CHOMe) and *N*-phenyl-1,1-diphenylmethylamine ($Ph_2CHNHPh$) were also studied because the rate of hydrogen abstraction should also be fast and intercept the phenyl radical and thereby prevent feedback inhibition. The reduction of only one equivalent of Ag(I) would be predicted. 1-Benzoyl-2-phenyldiazene, NaOH (1 M), Ph_2CHOMe (1 equiv.), and $AgNO_3$ (2 equivs.) were reacted to yield a mixture of products: unreacted Ph_2CHOMe (40%) and diazene (5%), benzene (50%), **14** (12%), **15** (7%), biphenyl (6%), phenyl benzoate (2%), and diphenylmethyl benzoate (6%), with the reduction of Ag(I) (1.2 equiv.). The reduction of feedback inhibition is poor and this result suggests that hydrogen abstraction is not the first and key reaction for trapping phenyl radical and that the mechanism in Scheme 4 may be relevant. *N*-Phenyl-1,1-diphenylmethylamine was reacted under the same conditions to give a poor reaction which yielded unreacted $Ph_2CHNHPh$ (90%), benzene (23%), and biphenyl (5%), with the reduction of Ag(I) (0.9 equiv.). *N*-(Diphenylmethylidene)aniline ($Ph_2C{=}NPh$) or benzophenone was not observed as products. Poor solubility may explain the sluggish reaction for both additives.

The hydrolysis/Ag(I) oxidation reaction was also carried out under optimum conditions with 9-hydroxyfluorene and 9-hydroxyxanthene, alcohols analogous to benzhydrol, to compare reactivity. Both the radicals and radical anions resulting from these compounds should be more stable than the analogous species from benzhydrol. The pK_{HA} of the 9-hydroxyfluoren-9-yl radical[18] is 6.3 and deprotonation will be fast. Similar results were obtained for 9-hydroxyfluorene and 9-hydroxyxanthene but gave cleaner reactions as compared to benzhydrol, with no phenyl-addition products, **14** or **15**, with similar reduction of Ag(I), but with lower formation of benzene, biphenyl, and respective ketones (fluorenone and xanthone). Their reactivity is possibly hindered by poor water solubility. The reaction with 9-hydroxyfluorene gave: unreacted 9-hydroxyfluorene (34%), benzene (40%), biphenyl (4%), fluorenone (66%), and Ag(I) reduction (2.3 equiv.). 9-Hydroxyxanthene gave: unreacted 9-hydroxyxanthene (24%), benzene (53%), biphenyl (6%), xanthone (76%), and Ag(I) reduction (2.5 equiv.).

We sought to provide further evidence for hydrogen-abstraction by phenyl radicals from benzhydrol and repeated the Ag(I) oxidation / hydrolysis studies with 1-benzoyl-2-phenyldiazene using optimum conditions with one equivalent of Ph_2CDOH. Difficulty was encountered isolating the benzene but the biphenyl which could be isolated only had 25% deuterium incorporation. In order to overcome the problems with the isolation of benzene, 1-(4-benzamidophenyl)-2-benzoyldiazene was studied (Scheme 5) because the predicted product, benzanilide, is crystalline. The required diazene was synthesized and reacted under the optimum conditions. Initial studies with benzhydrol gave benzanilide (64%) and benzophenone (74%) after separation. The reaction with deuteriobenzhydrol (Scheme 5) gave benzanilide (62%) and benzophenone (80%) by HPLC analysis and 52% and 64% yields respectively after separation, and 2.4 equivalents of Ag(I) were reduced. The two reactions were similar but only 17% deuterium incorporation was measured in the benzanilide.



Scheme 5. Ag(I) oxidation of 1-(4-benzamidophenyl)-2-benzoyldiazene in the presence of Ph_2CDOH

Conclusions regarding the poor deuterium incorporation are complicated by various factors. The isotope effect for deuterium abstraction relative to H-abstraction (normally k_H/k_D is between 4.5 and 9) may allow the intermediate aryl radical to abstract hydrogen from donors other than Ph_2CDOH. While the incorporation of deuterium provides further evidence for abstraction of hydrogen from benzhydrol by aryl radical intermediates and the results are comparable to reactions with 1-benzoyl-2-phenyldiazene, other mechanisms should also be

$$\mathrm{Ar{-}N{=}N^-} \xrightarrow{-\mathrm{N_2}} \mathrm{Ar^-} \xrightarrow{\mathrm{H_2O}} \mathrm{ArH} \qquad (3)$$

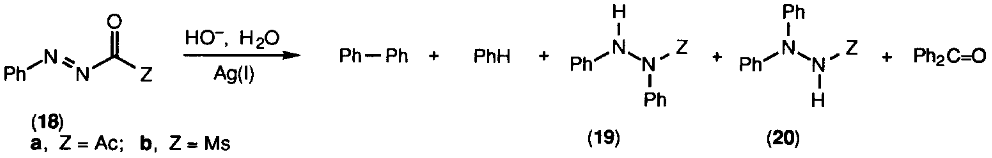
$$\mathrm{Ar{-}N{=}N^-} \rightleftharpoons \mathrm{Ar{-}N{=}NH} \longrightarrow \left[\mathrm{Ar{\bullet}\ N_2\ {\bullet}H}\right]_{\mathrm{cage}} \longrightarrow \left[\mathrm{ArH\ \ N_2}\right]_{\mathrm{cage}} \xrightarrow{-\mathrm{N_2}} \mathrm{ArH} \qquad (4)$$

$$\mathrm{Ar{-}N{=}N{\bullet}} + \mathrm{Ph_2CDOH} \longrightarrow \mathrm{Ar{-}N{=}ND} \rightleftharpoons \mathrm{Ar{-}N{=}N^-} \longrightarrow \mathrm{Ar^-} \longrightarrow \mathrm{ArH} \qquad (5)$$

considered, *e.g.* equations (3) - (5). Breakdown of benzenediazene anion ($PhN{=}N^-$) to phenyl anion [equation (3)] has been reported by several groups[7,15] and can partly explain the low deuterium incorporation. Bunnett has reported a wide variation in results for deuterium abstraction by Ph^- from MeOD in reactions proceeding via phenyl radicals and anions.[7] The homolysis shown in equation (4) has been reported to be unlikely and a number of alternative mechanisms have been considered.[13,16] Benzenediazenyl radicals [equation (5)] have a definite lifetime[20] and are reported[16] to lose nitrogen at a rate between 10^5 s^{-1} and 10^8 s^{-1} and may be able to abstract deuterium prior to breakdown. Most studies involving benzenediazene (PhN=NH) as an intermediate indicate that both phenyl radicals and anions are formed.[7,16,21] The known redox reactions involving benzenediazonium cations and benzenediazenyl radicals are a further complication.[13,16] Reduction of benzenediazonium cations to benzene-diazenyl radicals is well known and widely used, and has been recently reviewed.[16] Notwithstanding the complexity of possible mechanisms, Ag(I) is present at relatively high concentration and therefore the Ag(I) oxidation of $PhN{=}N^-$ is likely to be rapid and accounts for the high levels of Ag(I) reduction and the formation of benzophenone.

Hydrolysis/oxidation reactions of 1-acetyl- and 1-methanesulfonyl-2-phenyldiazene

1-Acetyl-2-phenyldiazene **18a** and 1-methanesulfonyl-2-phenyldiazene **18b** were also reacted with Ag(I) in sodium hydroxide solution using the general procedure to show the generality of the reactions with 1-benzoyl-2-phenyldiazene **9a** (Scheme 6). **18a** was reacted in NaOH solution (1 M), with Ag(I) (2 equiv.) (12 h), Ag(I) (2 equiv.) and benzhydrol (1 equiv.) (4 h), and Ag(I) (3.5 equiv.) and benzhydrol (1 equiv.) (3 h), respectively. The respective yields were: benzene (39, 52, and 71%), biphenyl (5, 7, and 11%), **19a** (2, 2, and 4%),and **20a** (4%, 3%, and 5%). The yield of benzophenone for the two latter reactions was 66% and 77% respectively. We propose that the reaction follows a similar pathway to that illustrated in Scheme 3 for 1-benzoyl-2-phenyldiazene. The phenyl-radical adducts, **19** and **20**, were formed in the same manner as for diazene **9a** but were not eliminated at high levels of benzophenone. In the last reaction, 2.6 equivalents of Ag(I) were reduced.



Scheme 6. Hydrolysis / Ag(I) oxidation of 1-acetyl- and 1-methanesulfonyl-2-phenyldiazene

1-Methanesulfonyl-2-phenyldiazene **18b** was reacted in NaOH solution (1 M), Ag(I) (2 equiv.) and benzhydrol (1 equiv.) (4 h), and Ag(I) (3.5 equiv.) and benzhydrol (1 equiv.) (3 h). The respective yields were: benzene (54 and 80%), biphenyl (5 and 7%), and **20b** (6 and 0%), and benzohenone (86 and 87%). No adduct **19b** was observed but small amounts of 1,2-diphenyldiazene (azobenzene) were isolated indicating either, elimination of methanesulfinic acid from **19b**, or methanesulfinyl ($MeSO_2\bullet$) from the radical intermediate. Attempts to synthesize **19b** by treatment of 1,2-diphenylhydrazine with methanesulfonyl chloride yielded only 1,2-diphenyldiazene. The analogous hydrazines of both **18a** and **18b** exhibited inferior infectious development, as compared to **9a**, which is predicted from their slower rates of hydrolysis.

Conclusions

Our results provide good evidence that the sequential abstraction of hydrogen by phenyl radical from benzhydrol and subsequent loss of an electron from the radical-anion of benzophenone is the central to the mechanism of infectious development. However, considerable study is yet required to fully understand all the mechanisms involved in infectious development.

Acknowledgements

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EXPERIMENTAL

General Procedures

Mass spectra were run on a Kratos MS80 spectrometer and are electron impact (EI) spectra unless otherwise stated. ^{1}H NMR spectra were run at 60 MHz using a Varian EM360A spectrometer and $CDCl_3$ was used as the NMR solvent with TMS as internal standard unless otherwise stated. IR spectra were determined as Nujol mulls using a Philips PU9500 spectrophotometer linked to an IBM IR data station unless otherwise stated. UV/visible spectra were determined on a Shimadzu UV160 spectrophotometer. Melting points were determined on a Kofler block and are uncorrected. Diethyl ether and light petroleum (b.p. 40-60 °C) were distilled from calcium chloride and dichloromethane was distilled from phosphorus pentoxide and stored. Pyridine and triethylamine were stored over potassium hydroxide pellets. HPLC analyses were carried out with a reverse phase microsorb C_{18} column using acetonitrile:water (60:40) as eluent at a flow rate of 1 cm^3/min. All HPLC analyses were carried out using calibration graphs of response versus concentration for each product. TLC was carried using silica gel as absorbent.

1-Acyl-2-arylhydrazines

(a) 1-Benzoyl-2-phenylhydrazine **9a**.[7] Benzoyl chloride (11.8 g, 84 mmol) was added dropwise with stirring to a solution of phenylhydrazine (10.0 g, 93 mmol) and triethylamine (9.4 g, 93 mmol) in diethyl ether (150 cm^3) at O °C. After stirring for 30 min the solution was filtered and the resulting colourless crystals of **9a** washed with water and recrystallised (14.1 g, 72 %); m.p. 171-172 °C (EtOH) (lit.[7] 168-169 °C); ν_{max} /cm^{-1} 3220 and 1640; δ_H 10.30 (1 H, s, NH), 7.20-8.00 (11 H, m).

(b)1-Formyl-2-phenylhydrazine.[22] Formic acid (13.6 g, 0.30 mol) was added slowly with stirring to phenylhydrazine (28.7 g, 0.27 mol). The reaction mixture was cooled in ice, and the colourless crystals filtered off, washed with diethyl ether and recrystallised (14.1 g, 70 %); m.p. 141-143 °C (EtOH) (lit.[22] 142-143 °C); ν_{max} /cm^{-1} 3300 and 1660; δ_H 9.50 (1 H, s, CHO), 6.60-8.10 (5 H, m).

(c) 1-(2-Hydroxymethylbenzoyl)-2-phenylhydrazine **9b**.[3] A mixture of phenylhydrazine (9.0 g, 83 mmol) and phthalide (11.1 g, 83 mmol) were heated at 70-80 °C for 5 h. The mixture was cooled to room temperature and the resulting solid suspended in diethyl ether, filtered, washed with diethyl ether and recrystallised to yield the hydrazine **9b** (5.5 g, 27 %); m.p. 160-161 °C (2-PrOH) (lit.[3] 159-160 °C); ν_{max}/cm^{-1} 3256, 1640, and 1040; δ_H 11.10 (1 H, s, NH), 6.50-7.60 (9 H, m), 4.62 (2 H, s, CH_2), and 3.20 (1 H, brs, OH). In a second procedure, phthalide (12.5 g, 93.4 mmol) was added to phenylhydrazine (10.1 g, 93.4 mmol) and heated at 80 °C. Hexane (30 cm^3) was slowly added and the hexane and reaction mixture refluxed overnight. The reaction mixture was cooled, and the solid material in the hexane layer filtered off and recrystallised. The solid material in the bottom layer was also recrystallised to give a combined yield of **9b** (10.6 g, 47 %).

(d) 1-(4-Hydroxymethylbenzoyl)-2-phenylhydrazine **9c**.[23] 4-Bromomethylbenzoic acid (10 g, 46.5 mmol) was refluxed in water (350 cm^3) until dissolved (2 h) and then for a further 2 h. The solution was cooled overnight in a refrigerator and the resulting white needles of 4-hydroxymethylbenzoic acid filtered off and dried (6.4 g, 91%); m.p. 183-185 °C (lit.[23] 181-183 °C); ν_{max} /cm^{-1} 3312 and 1686; δ_H 7.30-8.15 (9 H, q, Ar-H) and 4.71 (2 H, s, CH_2).

p-Hydroxymethylbenzoic acid (2.5 g, 16.5 mmol) was added with stirring to a mixture of phenylhydrazine (3.55 g, 33 mmol) and dicyclohexylcarbodiimide (3.74 g, 18.2 mmol) in CH_2Cl_2 (200 cm^3) and the reaction stirred for 2 h. The solution was filtered and the solvent evaporated to yield an oil which was dissolved in diethyl ether, filtered, and washed with dilute hydrochloric acid, and water. The ether solution was dried, evaporated, the resulting solid taken up in $CHCl_3$ and extracted with 2M NaOH (2 x 50 cm^3). The alkaline layer was acidified, extracted with $CHCl_3$ and the extracts dried and evaporated to give a solid which was recrystallised to give the the hydrazine **9c** (1.09 g, 28 %); m.p. 112-114 °C; (Found: C, 69.1; H, 5.7; N, 11.3. $C_{14}H_{14}N_2O_2$ requires for C, 69.40; H, 5.82; N,11.69%); ν_{max} /cm^{-1} 3500-3250 and 1680; δ_H 7.90-6.30 (11 H, m), 4.65 (2 H, s, CH_2), and 3.32 (1 H, brs, OH), *m/z* 242 [M^+ (15%) and 135.

(e) 2-Benzoyl-1,1-diphenylhydrazine **14** *and 2-benzoyl-1,1-diphenylhydrazine* **15** were synthesized using literature procedures. M.p.s and IR and ^{1}H NMR spectra corresponded with those reported.[7]

(f) 1-Methanesulfonyl-2-phenylhydrazine. Methanesulfonyl chloride (10.6 g, 92 mmol) was added dropwise to a solution of phenylhydrazine (10.0 g, 92 mmol) and triethylamine (9.4 g, 92 mmol) in diethyl ether (150 cm^3) at 0 °C. On completion of the addition the mixture was stirred for 30 min. The resulting solid was filtered, washed with diethyl ether, water, and recrystallized to give the 1-methanesulfonyl-2-phenylhydrazine (7.8 g, 45 %); m.p. 124-126 °C (EtOH); (Found: C, 45.2; H, 5.35; N, 15.6. $C_7H_{10}N_2SO_2$ requires for C, 45.2; H, 5.4; N 15.1%); ν_{max} /cm^{-1} 3370 and 1340; δ_H 7.90 (1 H, brs, NH), 6.80-7.40 (5 H, m), 6.62 (1 H, s, NH), and 2.93 (3 H, s, Me).

(g) 2-Acetyl-1,1-diphenylhydrazine **20a**. Acetyl chloride (1.61 g, 18.2 mmol) was added dropwise with stirring to a solution of 1,1-diphenylhydrazine hydrochloride (4.0 g, 18.2 mmol) and triethylamine (3.6 g, 36.4 mmol) in diethyl ether (150 cm^3) at 0 °C. The reaction was stirred for 1 h and the crystals filtered, washed with diethyl ether and water, and recrystallised (1.2 g, 29 %); m.p. 187-189 °C (EtOH); ν_{max} /cm^{-1} 3264 and 1670; δ_H (CDCl$_3$/DMSO(d$_6$)] 6.80-7.40 (11 H, m) and 2.23 (3 H, s, Me).

(h) 1-Acetyl-1,2-diphenylhydrazine **19a**. Procedure *(g)* gave **19a** (65 %); m.p. 161-163 °C (EtOH); ν_{max} /cm^{-1} 3248 and 1644; δ_H [CDCl$_3$/DMSO(d$_6$)] 8.50 (1 H, brs, NH), 6.60-7.70 (10 H, m), 2.25 (3 H, s, Me).

(i) 1,1-Diphenyl-2-methanesulfonylhydrazine **20b**. Methanesulfonyl chloride (1.6 g, 13.6 mmol) was added dropwise to a solution of 1,1-diphenylhydrazine hydrochloride (3.0 g, 13.6 mmol) and triethylamine (2.8 g, 27.2 mmol) in dry diethyl ether (100 cm^3). The solution was stirred for 1 h and evaporated to dryness. The resulting solid was washed with water and recrystallised (1.0 g, 28 %); m.p. 189-190 °C (EtOH), ν_{max} /cm^{-1} 3244 and 1264 ; δ_H [CDCl$_3$/DMSO(d$_6$)] 9.90 (1H, brs, NH), 6.90-7.40 (10 H, m), 2.72 (3 H, s, Me). 1,2-Diphenylhydrazine was reacted under the same conditions to yield only 1,2-diphenyldiazene and none of the required 1,2-diphenyl-2-methanesulfonylhydrazine.

1-Acyl-2-aryldiazenes

General procedure for the conversion of acylhydrazines to acyl-diazenes.

(a) 1-Benzoyl-2-phenyldiazene **10a**.[7] *N*-Bromosuccinimide (4.2 g, 23.6 mmol) was added over 10 min with stirring at low temperature (dry ice/acetone bath) to a solution of 1-benzoyl-2-phenylhydrazine **9a** (5.0 g, 23.6 mmol) and dry pyridine (2 g, 25.3 mmol) in CH_2Cl_2 (22 cm^3). The mixture was allowed to warm to room temperature and stirred for 30 min. The solution was filtered and the solvent evaporated to yield a solid which was triturated with diethyl ether, filtered, washed with dilute hydrochloric acid and then aqueous Na_2CO_3 solution, and dried. The ether solution was evaporated to dryness and the resulting solid recrystallised (3.7 g, 75 %); m.p. 27-28 °C (EtOH) (lit.[7] 32 °C); ν_{max} (neat)/cm^{-1} 1650 and 1495; δ_H 7.10-8.00 (m); λ_{max} (MeOH) 443.5 nm (ε 151).

(b) 1-Formyl-2-phenyldiazene. The general procedure was used with a solution of 1-formyl-2-phenylhydrazine. After work-up and analysis, none of the diazene was observed. TLC showed a complex mixture.

(c) 1-(2-Hydroxymethylbenzoyl)-2-phenyldiazene **10b**. *N*-Bromosuccinimide (0.74 g, 4.13 mmol) and 1-(2-hydroxymethylbenzoyl)-2-phenylhydrazine **9b** (1 g, 4.13 mmol) were reacted using the general procedure. After work-up no **10b** was observed, and the only isolated product was phthalide (0.3 g, 55 %), m.p. 73-75 °C (water). All data were identical with those of a commercial sample.

(d) 1-(4-Hydroxymethylbenzoyl)-2-phenyldiazene **10c**. *N*-Bromosuccinimide (0.36 g, 2.1 mmol) was was reacted with 1-(4-hydroxymethylbenzoyl)-2-phenylhydrazine **9c** (0.5 g, 2.1 mmol) using the general procedure to yield **10c** (0.32 g, 65 %); m.p. 55-57 °C (from EtOH); ν_{max} /cm^{-1} 3400, 1650, and 1420; δ_H 7.00-8.20 (9 H, m), 5.75 (2 H, s, CH_2), and 3.60 (1 H, brs, OH), λ_{max} (MeOH) 435 nm.

(e) 1-Acetyl-2-phenyldiazene. A commercial sample of 1-acetyl-2-phenylhydrazine (5 g) was converted to 1-acetyl-2-phenyldiazene using the general procedure. The product oil was purified by distillation (79%), b.p. (1 mmHg) 42-43 °C; ν_{max} (neat)/cm^{-1} 1746 and 1496; λ_{max} (MeOH) 433 nm (ε 302).

(f) 1-Methanesulfonyl-2-phenyldiazene. *N*-Bromosuccinimide (0.96 g, 5.4 mmol) and 1-methanesulfonyl-2-phenylhydrazine (1.0 g, 5.4 mmol) were reacted using the general procedure to yield the diazene **18b** (0.91 g, 91%); m.p. 71-73 °C (toluene/hexane) (lit.[9] 73-74.5 °C), ν_{max} (neat)/cm^{-1} 1454 and 1376; δ_H 7.30-8.00 (5 H, m) and 3.22 (3 H, s, Me); λ_{max} (MeOH) 423 nm (ε 165.1).

Synthesis and reactions of substituted phthalides

(a) 3,3-Dimethylphthalide (**12a**). 3,3-Dimethylphthalide was prepared by a literature procedure by reaction between di-*n*-butylphthalate and methylmagnesium iodide.[24] Phenylhydrazine (3 g, 27.8 mmol) and 3,3-dimethylphthalide (3 g, 18.5 mmol) were heated at 80 °C for 24 h. The mixture was cooled, suspended in diethyl ether, filtered and recrystallised. The only products obtained were 3,3-dimethylphthalide and phenylhydrazine. The same result was obtained after refluxing in toluene for 12 h.

(b) *7-Methylphthalide* (**12b**).[25] 7-Methylphthalide was prepared using a literature method[25] by NBS bromination of 2,6-dimethylbenzoylchloride (44 %). The Grignard reagent of 2-bromo-1,3-dimethylbenzene was treated with carbon dioxide to yield 2,6-dimethylbenzoic acid (79 %) which was converted to the acid chloride with thionyl chloride (86%). All data agreed with those reported.[25] 7-Methylphthalide (0.5 g, 3.4 mmol) and phenylhydrazine (0.73 g, 6.76 mmol) were heated in hexane at 80 °C for 24 h. After repeated reactions with varying conditions the only products obtained were 7-methylphthalide and phenylhydrazine.

(c) *4-Methylphthalide* (**12c**).[25] 4-Methylphthalide was prepared by the same general procedure as for 7-methylphthalide. 3-Bromo-1,2-dimethylbenzene was converted to 2,3-dimethylbenzoic acid (87%) which was treated to give the acid chloride (87%) which was converted with NBS to 4-methylphthalide (25%). All data agreed with those reported.[25] 4-Methylphthalide (0.5 g, 3.4 mmol) and phenylhydrazine (0.73 g, 6.76 mmol) were heated in hexane (2 cm^3) and again only starting materials were obtained.

General procedures for the hydrolyses of 1-acyl-2-aryldiazenes in aqueous NaOH solution

(a) In the absence of Ag(I). The aqueous solution of NaOH was de-oxygenated by bubbling nitrogen gas through for 30 min. The diazene under study was added and the solution allowed to stir for a fixed length of time. The reaction mixture was extracted with distilled CH_2Cl_2 and the extracts made up to 500 cm^3 in a volumetric flask, and 5 cm^3 aliquots removed for HPLC analysis. The concentration of the aqueous NaOH solution was 1 M unless otherwise stated. In a typical reaction, 2.5 mmol of diazene (*e.g.* 0.525 g for 1-benzoyl-2-phenyldiazene) was stirred as a suspension of aq. NaOH solution (1 M, 375 cm^3). The yield of benzoic acid was determined by acidification of the aqueous layer, extraction with $CHCl_3$, and evaporation of the $CHCl_3$ to give the benzoic acid.

(b) In the presence of $AgNO_3$ and/or benzhydrol. The same procedure and work-up were employed as described above, except that $AgNO_3$ was added first, followed by benzhydrol (or other hydrogen donors), and then the required diazene. Any other additives were added before addition of the diazene.

(c) *Procedure for the titration of excess Ag(I).* After separation from the organic layer, aqueous nitric acid (2 M, 10 cm^3) was added to the aqueous layer which was filtered and made up to 100 cm^3 in a volumetric flask with distilled water. An aliquot (20 cm^3) was removed by pipette and titrated using the Volhard method with aq. potassium thiocyanate solution (0.1 M) with Fe(III) ammonium sulfate as indicator; the end point being a colour change from colourless to red/brown. Each analysis was repeated twice.

Hydrolyses/Ag(I) oxidation reactions with 1-benzoyl-2-phenyldiazene

(a) Reactions with diphenylmethyl methyl ether. (i) Diphenylmethyl methyl ether. Sodium hydride (NaH) (4 g, 167 mmol) (80% in oil) was washed several times with light petroleum. Dry distilled THF (70 cm^3) was added and the mixture stirred under nitrogen. A solution of benzhydrol (5 g, 27 mmol) in THF (20 cm^3) was added slowly to the NaH, and the mixture stirred for 60 min and then quenched with methyl iodide MeI (4.25 g, 30 mmol) and left to stir for a further 2 h. Ice was added and the resulting solution extracted with diethyl ether. The diethyl ether extracts were dried and evaporated to give a yellow oil which was distilled under reduced pressure to give a colourless oil (4.2 g, 78 %), b.p. (5 mmHg) 125 °C [lit.[26] b.p (5 mmHg) 129 °C]; δ_H 7.00-7.50 (10 H, m), 5.23 (1 H, s, CH), 3.33 (3 H, s, Me).

(ii) Hydrolysis/Ag(I) oxidation. The general procedure for the hydrolysis/ Ag(I) oxidation was carried out using diphenylmethyl methyl ether (1 equiv.) and $AgNO_3$ (2 equiv.) with a 3 h reaction time. The reaction was worked up as normal and analysed by HPLC. The CH_2Cl_2 solution was evaporated to dryness and the residue analysed and products separated using preparative TLC [light petroleum:toluene (1:4)] to yield biphenyl (24 mg, 6 %), Ph_2CHOMe (0.4 g, 40 %), $PhCO_2Ph$ (10 mg), and $Ph_2CHOCOPh$ (42 mg). The latter

compound was characterised; m.p. 87-89 °C (EtOH) (lit.[27] 89 °C); (Found: C, 83.4; H, 5.6. $C_{20}H_{16}O_2$ requires for C, 83.3; H, 5.6%); ν_{max} /cm^{-1} 1710; δ_H 7.95-8.10 (2 H, dd), 7.10-7.50 (13 H, m), 7.05 (1 H, s, CH). Excess Ag(I) was titrated as previously described.

*(b) Reactions with N-phenyl-1,1-diphenylmethylamine. (i) N-Phenyl-1,1-diphenylmethylamine. N-*Benzylideneaniline was prepared by stirring benzaldehyde and aniline for 30 min and the resulting crystals filtered and recrystallised (84%). Phenyllithium (1 equiv.) was added by syringe through a septum to a solution of *N*-benzylideneaniline (4 g, 22.2 mmol) in dry, distilled THF (100 cm^3) under nitrogen. The solution was left to stir for 3 h, quenched with water (50 cm^3), and extracted with diethyl ether. The ether extracts were dried and evaporated to yield a brown oil (5.1 g). Column chromatography with alumina as absorbent and light petroleum:diethyl ether (7:3) as eluent was used to separate unaltered *N*-benzylideneaniline and *N*-phenyl-1,1-diphenylmethylamine (2.4 g, 42 %); m.p. 53-55 °C (hexane) (lit.[28] 53-54.5 °C); ν_{max} /cm^{-1} 3408, 3056, and 1600; δ_H 6.20-8.00 (15 H, m), 5.42 (1 H, s, CH), and 4.10 (1 H, s, NH); *m/z* 259 (21%) and 167 (100).

(ii) Hydrolysis/Ag(I) oxidation. The general procedure for the hydrolysis/Ag(I) oxidation was carried out using *N*-phenyl-1,1-diphenylmethylamine (1 equiv.) and $AgNO_3$ (2.0 equiv.) with a 3 h reaction time. Standard solutions of all the expected products from the reaction were prepared and analysed using HPLC.

(c) Hydrolysis/Ag(I) oxidation of 9-hydroxyfluorene and 9-hydroxyxanthene. The general procedure for the hydrolysis/Ag(I) oxidation, work-up, and analysis was carried out using 9-hydroxyfluorene (1 equiv.) and 9-hydroxyxanthene (1 equiv.) in separate reactions with $AgNO_3$ (3.5 equivalents) with a 3 h reaction time.

Deuterium abstraction studies

Deuteriobenzhydrol. Lithium aluminium deuteride (0.31 g, 7.5 mmol) was added to benzophenone (2.55 g, 14 mmol) in dry THF (50 cm^3) under anhydrous conditions and an atmosphere of nitrogen and stirred for 2 h. Water was added carefully and the mixture extracted with diethyl ether. The diethyl ether extracts were dried and evaporated to dryness to give a colourless solid (1.3 g, 51 %); m.p. 66-68 °C (from EtOH). The ^{1}H NMR spectrum did not show any non-deuteriated benzhydrol and the mass spectrum showed >95% deuterium incorporation.

The general procedure for the hydrolysis of 1-acyl-2-aryldiazenes in aqueous NaOH solution was used with 1-benzoyl-2-phenyldiazene, Ag(I) (3.5 equiv.), and Ph_2CDOH (1 equiv.). The crude product was analysed by HPLC and biphenyl was separated by preparative TLC.

1-(4-Benzamidophenyl)-2-benzoyldiazene. (a) 1-Benzoyl-2-(4-nitrophenyl)hydrazine. Benzoyl chloride (5.6 g, 40 mmol) was added dropwise with stirring to a solution of 4-nitrophenylhydrazine (6.0 g, 39.2 mmol) and triethylamine (4 g, 39.2 mmol) in EtOAc (250 cm^3). The mixture was left to stir for 2 h, the resulting yellow solid filtered off, washed with water, and recrystallised (4.2 g, 42 %); m.p. 198-200 °C (EtOH) (lit.[29] 194 °C), ν_{max} /cm^{-1} 3172, 1658, 1592, 1512, and 1344; δ_H 7.30-8.20; *m/z* 257 (M$^+$, 17%) and 105 (100). The hydrazine was also prepared by condensation of 4-nitrophenylhydrazine and benzoic acid using *N,N*-dicyclohexylcarbo-diimide in 33% yield.

(b) 1-(4-Aminophenyl)-2-benzoylhydrazine. Palladium on charcoal (10%) was added to a solution of 1-benzoyl-2-(4-nitrophenyl)hydrazine (5 g, 17.5 mmol) in dry EtOH (150 cm^3). The mixture was hydrogenated at room temperature under atmospheric pressure. After hydrogen uptake ceased (4 h) the catalyst was filtered off and the solvent removed to yield a colourless solid which was recrystallised (1.65 g, 93 %); m.p. 266-268 °C (EtOH), ν_{max} /cm^{-1} 3452 , 3264 , and 1664; δ_H [$CDCl_3$/DMSO (d_6)] 7.92 (2 H, s, NH_2), 7.85-6.90 (9 H, m), and 6.60-6.40 (2 H, m); *m/z* 227 (M$^+$, 9%).

(c) 1-(4-Benzamidophenyl)-2-benzoylhydrazine. Benzoyl chloride (1.36 g, 9.7 mmol) was added dropwise with stirring at O °C (ice bath) to a solution of 1-(4-aminophenyl)-2-benzoylhydrazine (2.2 g, 9.7 mmol) and triethylamine (0.98 g, 9.7 mmol) in CH_3CN (150 cm^3). The reaction was left to stir for 3 h and the resulting precipitate filtered off, washed with water and recrystallised to give colourless crystals of the hydrazine (2.7 g, 84 %); m.p. 248-250 °C (MeOH); (Found: C, 72.36; H, 5.13; N, 12.75. $C_{20}H_{17}N_3O_2$ requires C, 72.49; H, 5.17; N, 12.68%); ν_{max} /cm^{-1} 3292, 1660, and 1638; *m/z* 331 (M$^+$, 14%) and 105 (100).

*(d) 1-(4-Benzamidophenyl)-2-benzoyldiazene. N-*Bromosuccinimide (1.62 g, 9 mmol) was added with stirring to a solution of 1-(4-benzamidophenyl)-2-benzoylhydrazine (3 g, 9 mmol) in CH_2Cl_2 and pyridine

(150 cm^3, 1:1) at O °C. The reaction was stirred for 1 h and then allowed to warm to room temperature. Dilute hydrochloric acid was added to the reaction mixture and the organic layer separated, washed with dilute hydrochloric acid followed by water, and dried. The solvent was evaporated to dryness to yield orange crystals (2.38 g, 76 %); m.p. 194-196 °C (EtOH); (Found: C, 72.79, H, 4.56; N, 12.58%. $C_{20}H_{15}N_3O_2$ requires C, 72.94; H, 4.59; N, 12.75); ν_{max} /cm^{-1} 3384, 1692, 1674, and 1526; δ_H [$CDCl_3$/DMSO (d_6)] 10.5 (1 H, s, NH) and 7.40-8.30 (14 H, m), *m/z* 301 (4%), 224 (4), and 196 (9); λ_{max} (MeOH) 343 nm ($\varepsilon = 70$).

(e) Reaction with Ag(I). The general procedure for the hydrolysis of 1-acyl-2-aryldiazenes in aqueous NaOH solution was used with 1-(4-benzamidophenyl)-2-benzoyldiazene, Ag(I) (3.5 equiv.), and Ph_2CDOH (1 equiv.). The crude product was analysed by HPLC [benzanilide (62%) and benzophenone (80%)] and the products separated by preparative TLC (silica gel, light petroleum:diethyl ether, 6:4) to yield unaltered Ph_2CDOH (10%), benzanilide 52%), and benzophenone (64%). Titration showed that 2.4 equivalents of Ag(I) were reduced.

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