The Aza-di-π-methane Rearrangement of 1-Aryl-4,4-dimethyl-6,6-diphenyl-2-azahexa-2,5-dienes. The Influence of Substituents on the *N*-Benzyl Group

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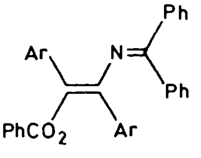
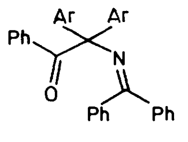
The acetophenone-sensitised irradiation of a series of 1-aryl-4,4-dimethyl-6,6-diphenyl-2-azahexa-2,5-dienes has been carried out. All undergo an aza-di-π-methane rearrangement to yield a cyclopropylimine. The determination of the quantum yields for the rearrangement showed a dependence on the nature of the substituents on the *N*-benzyl group and the reaction is most efficient with electron-withdrawing substituents. The linear relationship between log φ and σ^+ suggests that there is an homoconjugative interaction between the benzyl group and the nitrogen lone-pair.

The photoreactivity of β,γ-unsaturated systems has proved to be an interesting area of research.[1,2] During the past few years a good understanding of the reactions undergone by these compounds has been developed and our particular interest has focussed on the influence of nitrogen incorporation[3–7] into enone-like molecules. This often leads to dramatic changes in, for example, the photoreactivity of the azadienes (1) and the azaenones (2). The influence of nitrogen on the reactivity of the 1-aza-1,4-dienes (3) is also of particular interest. Within this framework we have demonstrated that the photochemical reaction in which imines from β,γ-unsaturated aldehydes rearrange *via* the aza-di-π-methane process to yield the cyclic imines (4) is influenced by the type of substituent attached to the nitrogen atom.[8,9] In this original group of compounds we observed that the greatest efficiency, in qualitative terms, was achieved with an *N*-benzyl or *N*-phenyl substituent. This feature of the reaction was thought to be the result of the involvement of the nitrogen lone pair of electrons in an intramolecular single electron transfer from the nitrogen to the alkene moiety. It thus seemed likely that among other energy-wasting steps the excited state of the imine could either proceed to the cyclic product (4) (path a) or else decay to the ground state *via* the radical cation/radical anion formed by the electron transfer (path b) (Scheme 1). A quantitative study of this effect using a series of substituted aryl derivatives (5) substantiated this proposal.[10] The influence of nitrogen substitution on the reaction has been investigated further in a study of the photochemical behaviour of the oxime acetate (6).[11] The present paper reports our results obtained from the study of the aza-di-π-methane reactivity of the substituted benzyl derivatives (7).



(1)



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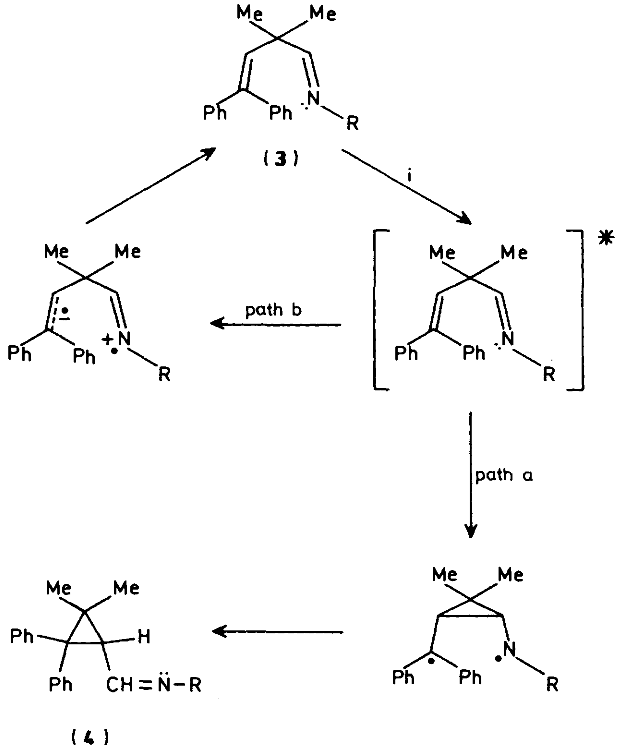
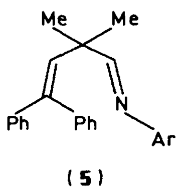


Scheme 1. *Conditions*: i, *h*ν, sensitiser.

Results and Discussion

The imines (7) required for the study were readily prepared in quantitative yield by the condensation of the aldehyde (8) with the appropriate amine and were readily identified by their spectroscopic characteristics. As with previous compounds of this type[10] the imines were susceptible to hydrolysis and also decomposed on attempted distillation. However, the imines were all stable when stored in anhydrous conditions under an atmosphere of nitrogen. Thus the imines were used as obtained



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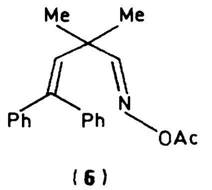

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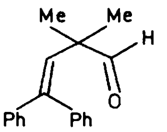
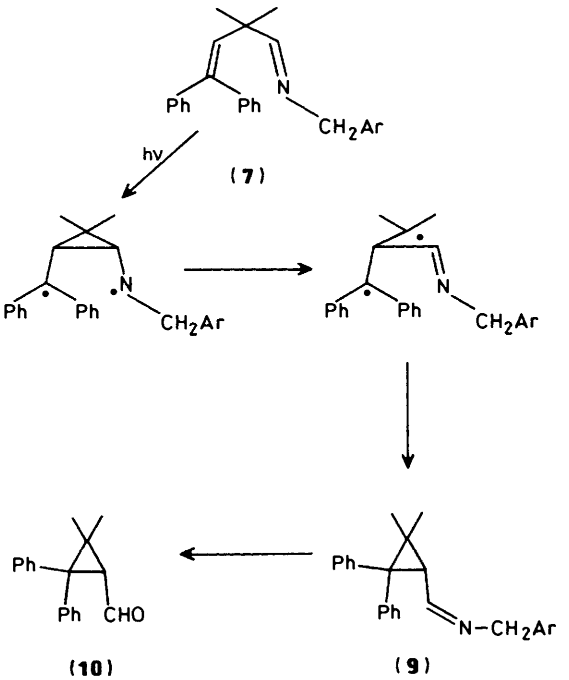


(8)

from the synthetic procedure since both the ^{1}H n.m.r. and the i.r. spectra of the crude reaction mixtures showed, in all the cases, the total disappearance of the starting aldehyde (**8**) and the only signals present in the ^{1}H n.m.r. spectra of the reaction mixture were those corresponding to the expected imine (**7**).

All of the imines (**7a–e**) are photochemically reactive and undergo an acetophenone-photosensitised aza-di-π-methane rearrangement to afford the non-isolated cyclopropylimines (**9a–e**) which were hydrolysed to the aldehyde (**10**) (Scheme 2). None of these experiments were optimised and all were run for 1 h thus providing a rough guide to the comparative efficiency of the reactions.



(7)(9)	Ar
a	Ph
b	p-MeC$_6$H$_4$
c	p-ClC$_6$H$_4$
d	m-FC$_6$H$_4$
e	p-CF$_3$C$_6$H$_4$

Scheme 2.

Table 1. Quantum yield (φ) for the cyclisation of imines (**7**).

Imine reactant	φ
(**7a**)	0.009 24
(**7b**)	0.006 56
(**7c**)	0.0111
(**7d**)	0.0144
(**7e**)	0.0167

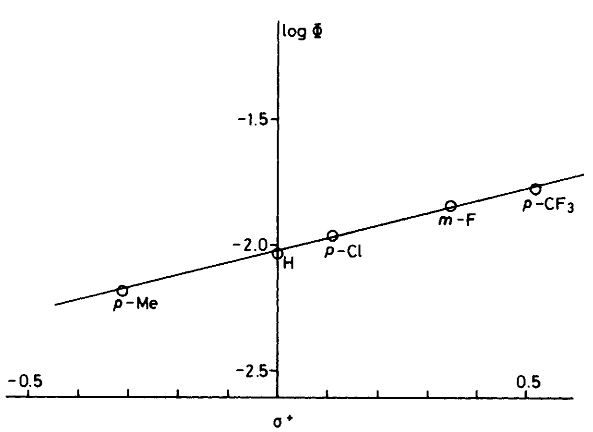


Figure. Plot of log φ *versus* σ^+. (Correlation coefficient = 0.998; $\rho = +0.50$; σ^+ values from refs. 14 and 15).

The quantum yield measurements for the photocyclisation of the imines (**7**) into the aldehyde (**10**) were made on conversions ranging between 1.3 and 10.6% and are based on a minimum of four measurements for each sample. The results were plotted and extrapolated to zero time to give the optimum quantum yield in each case. These values are shown in Table 1 and details are recorded in the Experimental section. During this study it was found that the parent imine (**7a**) was prone to decomposition and therefore it was felt necessary to redetermine the quantum yield for this compound. The value obtained in this study is considerably higher than that previously reported by us[9] clearly illustrating the problems with this imine.

In our previous study on the photochemistry of the imines (**5**) we observed[10] that the quantum yield for the rearrangement to the corresponding cyclic imine (**4**; R = Ar) was dependent on the nature of the substituent on the aryl ring. The cyclisation was more efficient when the substituents were electron withdrawing. This implies that there is reasonable overlap between the aryl ring and the nitrogen lone pair. Overlap of this sort has been suggested previously by Pratt[12] for simple *N*-phenylimines in which there was a preference for overlap between the aryl π-system and the lone pair rather than with the C–N double bond. The overlap will influence the ionisation potential and this potential will increase when the substituents are electron withdrawing. Thus if the nitrogen is less likely to undergo electron transfer then the excited state will be more likely to proceed to a cyclic product than to the energy-wasting electron transfer. A measure of the influence of the substituents can be obtained from the linear correlation between log φ and σ^+ values (slope = 1.058, coeff. = 0.997). These values were in good agreement with such a conjugative effect.

In the present study we have shown that there is a similar effect with the substituted benzyl derivatives (**7**) even though there are no literature precedents for benzyl participation in the all-carbon di-π-methane rearrangement.[1,13] The results from the quantitative sensitised irradiations of (**7**) also show a linear relationship between log φ and σ^+ with a ρ value of $+0.50$ and a correlation coefficient of 0.998 (Figure). This is a better correlation than that between log φ and σ (correlation coeff. = 0.985). The smaller ρ value from this set of experiments is to be expected because of the longer range effect between the benzyl group and the nitrogen lone-pair and is in accord with other Hammett correlations involving benzyl groups.[14]

Thus in the *N*-aryl and the *N*-benzyl derivatives there is a similar effect upon the quantum yield for formation of cyclic products. While direct conjugation was possible between the aryl group and the nitrogen lone-pair in compounds (**5**) this is not the case for the benzyl derivatives (**7**). The most likely interaction in this group of compounds is one of a homoconjugative type which is in accord with the results shown in the Figure. This interaction must also influence the ease with which the nitrogen can undergo electron transfer. Thus if the tendency for the excited state to undergo electron transfer, *i.e.* the formation of the energy wasting radical cation/radical anion, is minimised then the cyclisation step will become predominant (Scheme 1). This is the case when the substituents on the benzyl group are electron withdrawing.

It is of interest to note that the actual values of φ are greater for the benzyl (**7**) than for the aryl derivatives (**5**) described by us earlier.[10] The reason for this is not obvious since on first inspection it would seem that the direct conjugative overlap of the aryl group should have a greater effect. However, it is not certain how great the overlap is between the aryl π-system and the lone-pair. It may be that the angle of twist around the aryl C–N bond is such that the overlap is always small and consequently the effect on φ is smaller than might be expected. In the benzyl case the overlap with the lone pair can be greater and the consequent effect on φ would be larger. Thus far we have been unable to obtain other data in support of this postulate.

Table 2. Yields from the preparative photolyses[a].

Imine (7)	Mass of starting material/mg	Yield of (**8**)/mg %	Yield of (**10**)/mg %
(**a**)[b]	678	375 (75)	108 (21)
(**b**)	380	164 (61)	59 (22)
(**c**)	329	112 (51)	72 (33)
(**d**)	360	101 (41)	113 (45)
(**e**)	355	72 (33)	122 (56)

[a] Irradiation time 1 h. [b] Ref. 9.

The results obtained from the study of the benzyl derivatives show that there is a homoconjugative interaction between the benzyl group and the nitrogen lone pair. The effect is greater than expected and greater than the conjugative effect exhibited for the aryl compounds (**5**). This effect reduces the influence of the energy-wasting electron-transfer step and thus enhances the cyclisation to cyclopropyl imines.

Experimental

M.p.s were determined on a Buchi 510D apparatus in open capillaries and are uncorrected. I.r. spectra were recorded on a Perkin-Elmer 257 spectrophotometer. ^{1}H N.m.r. spectra were recorded on a Varian T-60A spectrometer with Me_4Si as internal standard.

Synthesis of Imines (**7**).—The imine (**7a**) was synthesised by the method described previously.[9] 2,2-Dimethyl-4,4-diphenylbut-3-enal (**8**) was synthesised by the method of Zimmerman and Pratt.[16] The imines (**7b**–**e**) were synthesised by reaction of (**8**) (1 g; 4 mmol) with an equimolar amount of the corresponding amine in toluene (50 cm^3). The mixtures were refluxed for 3 h during which time the water produced was removed in a Dean–Stark water separator. When the reaction was complete the solvent was removed under reduced pressure (*ca.* 15 mmHg). The i.r. and n.m.r. spectra of the crude product showed that the reaction was quantitative and had yielded the imine in each case.

4,4-*Dimethyl*-1-(p-*methylphenyl*)-6,6-*diphenyl*-2-*azahexa*-1,4-*diene* (**7b**).—$\nu_{max.}$(film) 1 670 cm^{-1} (C=N); δ_H(CDCl$_3$) 1.22 (6 H,

Table 3. Sensitised photolyses of imines (**7**).

Run No.	Starting imine/mmol	Light absorbed[a]	Conversion (%)	Product (**10**)/mmol	φ
	(**7a**)				
1	0.180	0.25	1.30	2.34×10^{-3}	9.18×10^{-3}
2	0.179	0.48	2.45	4.38×10^{-3}	9.11×10^{-3}
3	0.175	0.68	3.54	6.19×10^{-3}	9.06×10^{-3}
4	0.176	0.74	3.81	6.71×10^{-3}	9.05×10^{-3}
	(**7b**)				
5	0.201	3.45	10.65	2.10×10^{-2}	6.08×10^{-3}
6	0.199	1.63	5.20	1.04×10^{-2}	6.38×10^{-3}
7	0.212	1.43	4.30	9.13×10^{-3}	6.38×10^{-3}
8	0.212	0.57	1.98	3.70×10^{-3}	6.45×10^{-3}
	(**7c**)				
9	0.171	1.12	6.53	1.12×10^{-2}	9.94×10^{-3}
10	0.194	0.79	4.27	8.31×10^{-3}	1.05×10^{-2}
11	0.206	0.63	3.16	6.51×10^{-3}	1.04×10^{-2}
12	0.211	0.49	2.50	5.32×10^{-3}	1.08×10^{-2}
	(**7d**)				
13	0.205	0.68	4.54	9.37×10^{-3}	1.38×10^{-2}
14	0.221	0.56	3.53	7.82×10^{-3}	1.39×10^{-2}
15	0.212	0.41	2.71	5.78×10^{-3}	1.41×10^{-2}
16	0.194	0.37	2.66	5.17×10^{-3}	1.40×10^{-2}
	(**7e**)				
17	0.215	1.04	8.39	1.80×10^{-2}	1.70×10^{-2}
18	0.173	0.63	6.05	1.05×10^{-2}	1.67×10^{-2}
19	0.174	0.50	4.87	8.46×10^{-3}	1.70×10^{-2}
20	0.191	0.37	3.23	6.16×10^{-3}	1.68×10^{-2}

[a] Light absorbed is in millieinsteins; 1 einstein = 1 mole of photons.

s, 2 Me), 2.26 (3 H, s, Me), 3.97 (2 H, s, CH_2), 5.97 (1 H, s, vinyl), 6.86–7.13 (14 H, m, aryl), and 7.21 (1 H, s, CH=N).

1-(p-*Chlorophenyl*)-4,4-*dimethyl*-6,6-*diphenyl*-2-*azahexa*-1,4-*diene* (**7c**).—M.p. 44–47 °C; $\nu_{max.}$(film) 1 660 cm^{-1} (C=N); $\delta_H(CDCl_3)$ 1.23 (6 H, s, 2 Me), 3.98 (2 H, s, CH_2), 6.01 (1 H, s, vinyl), and 6.88–7.33 (15 H, m, aryl and CH=N).

1-(m-*Fluorophenyl*)-4,4-*dimethyl*-6,6-*diphenyl*-2-*azahexa*-1,4-*diene* (**7d**).—$\nu_{max.}$(film) 1 665 (C=N) and 1 250 cm^{-1} (C–F); $\delta_H(CDCl_3)$ 1.23 (6 H, s, 2 Me), 3.97 (2 H, s, CH_2), 5.97 (1 H, s, vinyl), 6.65–7.16 (14 H, m, aryl), and 7.24 (1 H, s, CH=N).

4,4-*Dimethyl*-6,6-*diphenyl*-1-(p-*trifluoromethylphenyl*)-2-*azahexa*-1,4-*diene* (**7e**).—$\nu_{max.}$(film) 1 660 (C=N) and 1 120 cm^{-1} (C–F); $\delta_H(CDCl_3)$ 1.22 (6 H, s, 2 Me), 3.98 (2 H, s, CH_2), 5.92 (1 H, s, vinyl), 6.91–7.16 (12 H, m, aryl), 7.23 (1 H, s, CH=N), and 7.33–7.43 (2 H, d, *J* 9 Hz, *o*-aryl).

Preparative Photolyses of the Imines (**7b–e**).—All of the photolyses were carried out in an immersion-well apparatus with a Pyrex filter and a 400 W medium-pressure Hg arc lamp. Solutions of the imines and acetophenone (1.40 g) in anhydrous benzene (320 cm^3) were purged for 1 h with nitrogen and irradiated under a positive pressure of nitrogen. Solvent was then removed under reduced pressure and the sensitiser was removed by distillation. The crude imine photolysates were hydrolysed using a mixture of aq. sulphuric acid (5 cm^3; 5%) in THF (30 cm^3). These mixtures were stirred at ambient temperatures for 1 h and were then extracted with ether. The organic layer was separated, washed with aq. $NaHCO_3$ (20 cm^3; 10%), dried ($MgSO_4$), filtered, and the solvent was removed under reduced pressure. The crude mixtures were chromatographed on silica gel using hexane–ether (95:5) as the eluant.

Quantum-yield Measurements for the Imines (**7a–e**).—Quantum-yield determinations were carried out using a 200 W high-pressure Hg arc lamp in conjunction with a Bausch and Lomb model 33-86-07 grating monochromator. Sensitised irradiations were carried out using acetophenone (0.53 mol dm^{-3}) as the sensitiser at 360 nm. Potassium ferrioxalate actinometry[17] was used to measure light output in all the experiments. Conversion into product was determined using g.l.c. of the crude hydrolysed photolysates with benzil as the internal standard. Solutions of the imine in benzene (30 cm^3, anhydrous) were irradiated in cylindrical quartz cells to 1.3–10.6% conversion under an atmosphere of nitrogen. The solutions were purged with nitrogen for 30 min prior to irradiation. The results obtained are presented in Table 3.

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References

1 S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, 1973, **73**, 531.
2 K. N. Houk, *Chem. Rev.*, 1976, **76**, 1.
3 D. Armesto, W. M. Horspool, R. Perez-Ossorio, and A. Ramos, *J. Chem. Soc., Perkin Trans. 1*, 1986, 96.
4 D. Armesto, M. J. Ortiz, R. Perez-Ossorio, and W. M. Horspool, *Tetrahedron Lett.*, 1983, **24**, 1197.
5 D. Armesto, W. M. Horspool, M. J. Ortiz, and R. Perez-Ossorio, *J. Chem. Soc., Perkin Trans. 1*, 1986, 623.
6 D. Armesto, W. M. Horspool, F. Langa, M. J. Ortiz, R. Perez-Ossorio, and S. Romano, *Tetrahedron Lett.*, 1985, **26**, 5213.
7 D. Armesto, M. G. Gallego, R. Perez-Ossorio, and W. M. Horspool, *Tetrahedron Lett.*, 1983, **24**, 1089; *J. Chem. Soc., Perkin Trans. 1*, 1986, 799.
8 D. Armesto, J. A. F. Martin, R. Perez-Ossorio, and W. M. Horspool, *Tetrahedron Lett.*, 1982, **23**, 2149.
9 D. Armesto, W. M. Horspool, J. A. F. Martin, and R. Perez-Ossorio, *J. Chem. Res. (S)*, 1986, 46; D. Armesto, F. Langa, J. A. F. Martin, R. Perez-Ossorio, and W. M. Horspool, *J. Chem. Soc., Perkin Trans. 1*, 1987, 743.
10 D. Armesto, W. M. Horspool, F. Langa, and R. Perez-Ossorio, *J. Chem. Soc., Perkin Trans. 2*, 1987, 1039.
11 D. Armesto, W. M. Horspool, and F. Langa, *J. Chem. Soc., Chem. Commun.*, 1987, 1874.
12 A. C. Pratt, *Chem. Soc. Rev.*, 1977, **6**, 63.
13 H. E. Zimmerman, *Org. Chem. Bull.*, 1980, **42**, 131.
14 C. D. Johnson, 'The Hammett Equation,' Cambridge University Press, Cambridge, 1973, p. 73.
15 C. D. Ritchie and W. F. Sager, *Prog. Phys. Org. Chem.*, 1964, **2**, 323.
16 H. E. Zimmerman and A. C. Pratt, *J. Am. Chem. Soc.*, 1970, **92**, 6259.
17 C. A. Parker and C. G. Hatchard, *Proc. R. Soc. London, Ser. A*, 1956, 235, 518.

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