Aroylation of Carbanions Derived from *N*-(Diphenylmethyl)arylmethanimines. A Synthesis of 4-Aroyloxy-2-azabuta-1,3-dienes

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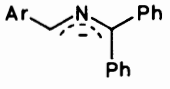
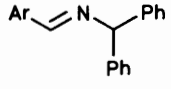
The acylation of carbanions derived from *N*-(diphenylmethyl)arylmethanimines using aroyl chlorides, allows the preparation of a new type of substituted 2-azabuta-1,3-dienes in which the imino group is conjugated with an enol ester. The reaction is quite general and facilitates the preparation of a wide range of 2-azadienes with electron-donating and electron-withdrawing groups on the phenyl rings. The site selectivity for the attack of the electrophile on the aza-allyl anion can be controlled by the substituents on the carbanion and on the hardness of the electrophile.

The generation and reactivity of carbanions have been the subject of extensive studies.[1] However, there are comparatively few reports on carbanions derived from imines in which the nitrogen atom is central in the resultant allyl anion. Kauffman[2] has described the generation of some 2-aza-allyl carbanions using LDA as the base in THF. The trapping of the anion by electrophiles, *e.g.* alkyl halides,[3] ketones,[4] aldehydes,[5] imines,[6] and azo compounds[6] allows the preparation of heterocycles and 2-azadienes among other products. Surprisingly, acylation of these carbanions has not been reported.

We wish to report the generation of carbanions (**1**) derived from *N*-(diphenylmethyl)arylmethanimines (**2**) and their trapping using *p*-substituted benzoyl chlorides (**3**). The influence of electronic and steric factors in the carbanion on the site selectivity of the reaction and the influence of the hardness of the electrophile have been studied. The electronic effects of typical electron-donating and electron-withdrawing groups, such as methoxy and nitro, have been compared with hydrogen.



(**1**)

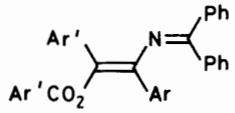


(**2**)

ArCOCl

(**3**)

a; Ar = Ph
b; Ar = *p*-$NO_2C_6H_4$
c; Ar = *p*-$MeOC_6H_4$



(**4**)

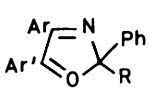
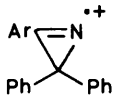
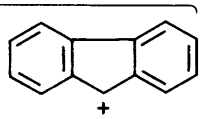
a; Ar = Ph; Ar′ = Ph
b; Ar = Ph; Ar′ = *p*-$MeOC_6H_4$
c; Ar = *p*-$NO_2C_6H_4$; Ar′ = Ph
d; Ar = *p*-$NO_2C_6H_4$; Ar′ = *p*-$NO_2C_6H_4$
e; Ar = *p*-$NO_2C_6H_4$; Ar′ = *p*-$MeOC_6H_4$
f; Ar = *p*-$MeOC_6H_4$; Ar′ = Ph
g; Ar = *p*-$MeOC_6H_4$; Ar′ = *p*-$MeOC_6H_4$

Results and Discussion

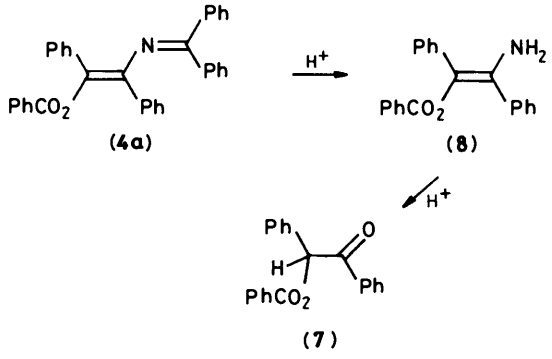
The carbanions (**1**) were generated from the corresponding imines (**2**) using NaH as the base in hexamethylphosphoramide (HMPA)–THF, at room temperature. The highly coloured solutions of (**1**) were quenched by dropwise addition of the acyl chlorides (**3**) in THF at O °C. The reactions afford, in yields ranging from fair to good, highly coloured products that were identified as 4-aroyloxy-2-azabuta-1,3-dienes (**4**) from their spectroscopic properties and from chemical evidence. The ^{13}C n.m.r. spectra show that all the new azadienes are obtained as one isomer. The stereochemistry of this single isomer was deduced to be *trans* on the basis of earlier work by Alcaide *et al.*[7] who observed that monoimines of 1,2-dicarbonyl compounds adopt the *anti* configuration during reduction. This configuration is, therefore, probable for anion (**11**), the intermediate in the synthesis of compound (**4**) and effectively fixes the substituent on the double bond in the *trans* arrangement. The i.r. spectra of these compounds show strong absorptions *ca.* 1 730 cm^{-1} which are consistent with the presence of enol ester groups.[8] Bands at *ca.* 1 590 cm^{-1} in the i.r. spectrum are assigned to the conjugated imino groups in accord with the data reported by Kauffman.[4a] The ^{13}C n.m.r. spectra of compound (**4**) exhibit resonances around 170 and 160 p.p.m. (Table) as well as a complicated pattern for the aryl carbons. The signals at higher field have been assigned to an ester group,[9] while those at lower field are broadly in agreement with the values reported by Ripoll *et al.*[10] for the imino group of simple 2-azabuta-1,3-dienes. Furthermore, the difference between the ester and imino resonances was clearly established by comparison of the ^{13}C n.m.r. spectra of compound (**4a**) and (**5**) obtained by acylation of the carbanion from the imine (**6**). The ^{13}C n.m.r. spectrum of compound (**5**) shows an upfield shift of 2.2 p.p.m. for the imino resonance due to the replacement of phenyl by a methyl group. The mass spectra of compound (**4**) shows the consecutive loss of two ArCO radicals follows by fragmentation to ArCN and the fluorenyl cation, except in the case of compound (**5**) (Table). The ^1H n.m.r. spectra only show aryl absortions and were in good agreement with the proposed structure. Further evidence was obtained by acid hydrolysis of (**4a**) using H_2SO_4 in THF. The isolated products were identified as benzoin benzoate (**7**) and benzophenone by comparison with authentic samples. The formation of benzoin benzoate is readily explained by hydrolysis of the imino group in (**4a**) *via* the enamine (**8**).

The syntheses of acyclic 2-aza-1,3-dienes reported in the literature consist mainly of the thermal fragmentation of 1-azetines,[11] 2*H*-azirines,[12] oxazolones,[13] and Diels–Alder adducts.[14] Other routes to azadienes include the reaction of carbonyl compounds with 1-amino phosphonates[15] and *N*,*N*-

Table. Relevant spectroscopic data for compounds (**4a**—**g**) and (**5**)

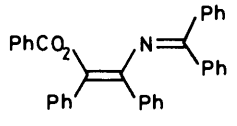
	Mass spectra[c]				^{13}C n.m.r.[a]		I.r.[b]
Compd	M^+		 (Me)		C=N	O ‖ CO	O ‖ CO
(**4a**)	479 (26)	374 (100)	269 (44)	165 (57)	170.3	165.4	1 725
(**4b**)	539 (18)	404 (100)	269 (20)	165 (39)	170.6	165.4	1 720
(**4c**)	524 (12)	419 (66)		165 (56)	171.7	165.1	1 730
(**4d**)	614 (10)	464 (100)	314 (45)	165 (75)	173.2	163.4	1 750
(**4e**)	584 (1)	449 (18)		165 (17)	170.4	165.3	1 730
(**4f**)	509 (15)	404 (100)	299 (24)	165 (49)	173.6	165.3	1 725
(**4g**)	569 (16)	434 (100)		165 (36)	170.4	165.3	1 725
(**5**)	417 (33)	312 (100)	207 (15)		168.1	165.9	1 730

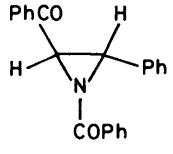
[a] In $CDCl_3$ with chemical shift in p.p.m. *vs.* internal Me_4Si. [b] In KBr, cm^{-1}. [c] % Abundance shown in parentheses.



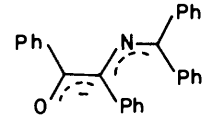
Scheme 1.

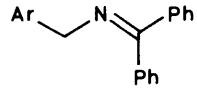
bis(silyl) enamines,[16] the isomerization of enamines[17] or allylimines,[18] the rearrangement of azetidines,[19] and the reaction of 1*H*-azirines with carbenes.[20] Photochemical routes have also been reported and involve the intramolecular cycloaddition of alkynes with nitriles[21] or the ring opening of 2*H*-azirines.[22] None of the above afford compounds of the type synthesized by us. However, Padwa *et al.*[23] have reported the formation of compound (**9**) from the thermal rearrangement of the aziridine (**10**). As far as we are aware this is the only reference to such compounds.

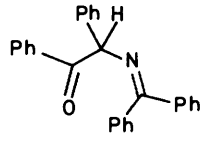

(**9**)

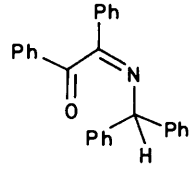

(**10**)

The formation of the azadiene (**4**) in the reaction described by us can be interpreted as involving a second acylation of the putative monoacylated carbanion (**11**). Unsuccessful attempts were made to isolate the monoacylated product (**13**) by adding the carbanion (**1**), after removal of the excess NaH, to a large excess of benzoyl chloride, in an attempt to avoid the equilibration between the carbanions (**1**) and (**11**). Under these conditions the only isolated products were the corresponding 2-azadienes (**4**) in very low yield and a mixture of the starting imine (**2**) and its isomer (**12**). However, the formation of (**13**) in the reaction medium is indisputable since the 2-azadiene (**4a**) was obtained by acylation of the carbanion (**11**) generated from the benzyl monoimine (**14**) under the same experimental conditions.[24] The second acylation occurs at the oxygen as predicted by electronic and steric factors.[25]


(**11**)


(**12**)

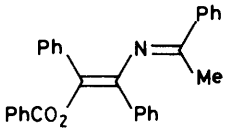

(**13**)


(**14**)

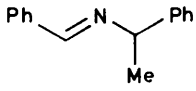
The generation of the carbanion (**1**) can also be made using imines such as (**12**) (**12a**; Ar = Ph; **b**; Ar = *p*-$MeOC_6H_4$) with less acidic hydrogens. The formation and trapping of these carbanions by benzoyl chloride under experimental conditions the same as those used with the imines (**2**), gave the corresponding azadienes (**4a**) and (**4f**) in similar yield (60 and 62% respectively). However, from a synthetic point of view it is preferable to use the route *via* the imines (**2**) since they are in general more readily available.

The study of the imine (**6**) is of interest since in this case there exists the possibility of equilibration between the two carbanions (**15**) and (**16**). The generation followed by trapping of the carbanion(s) under the experimental conditions mentioned previously permits the isolation of the 2-azadienes (**5**) in moderate yield. This conforms that the alkyl substituted imine (**6**) can be used to yield carbanion (**15**) in our synthetic sequence.

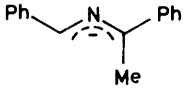
The Site-selectivity in the Acylation of Aza-allyl Carbanions.—Murphy *et al.*[26] have found that the reaction between 1,1,3-triphenylprop-2-enyl anion (**17**), an all carbon system analogous to (**1a**) and alkyl halides, gives exclusively alkylation at the secondary carbon. They concluded that the principle of least motion is not applicable in this case and that steric factors



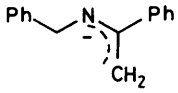
(5)



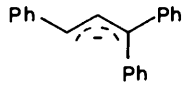
(6)



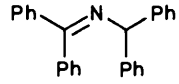
(15)



(16)



(17)



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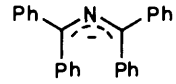

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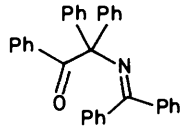

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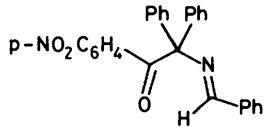

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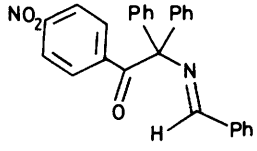

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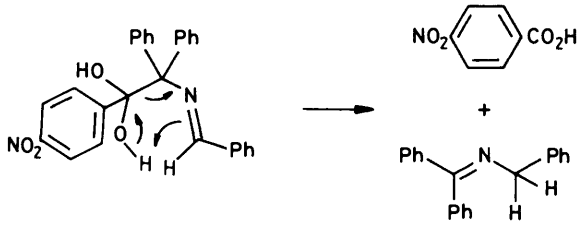

Scheme 2.

direct the course of the reaction. Also, Hullot *et al.*,[3] described the alkylation of (**1a**) using benzyl chloride to give the product resulting from the attack at the less hindered position. However, studies on the influence of substituents in the phenyl rings on the site-selectivity in the capture of these carbanions by electrophiles have not been reported.

In order to determine the scope of the acylation and, at the same time, the influence of electron-donating and electron-withdrawing groups on the site-selectivity of the reaction, the acylation was carried out using imines differently substituted in the *para*-position. The influence of the hardness of the electrophile was also studied using *para*-substituted benzoyl chlorides.

When relatively soft electrophiles such as benzoyl chloride (**3a**) and *p*-methoxybenzoyl chloride (**3c**) are used, the only observed products were those resulting from the attack at the second site, in good agreement with the data reported for the alkylation of (**1a**)[3] and (**17**).[26] A similar situation is observed with the carbanion (**1c**). The capture of (**1c**) using (**3a** and **c**) give the corresponding 2-azadienes showing that the electrophilic attack takes place at the secondary carbon. This site selectivity can be explained as a consequence of steric factors as postulated by Murphy in the alkylation of (**17**).[26]

The 2-azadiene is not formed in the reactions between (**1a** or **c**) and *p*-nitrobenzoyl chloride (**3b**). In these cases the only isolated products after column chromatography on silica gel were *p*-nitrobenzoic acid, benzophenone, benzaldehyde (or *p*-methoxybenzaldehyde), the starting imine, and the isomeric imine (**12**). The presence of benzophenone and benzaldehyde in fractions that do not correspond to their usual retention times show that they arise from the decomposition of other products during chromatography. In these carbanions (**1a** and **c**) the higher electron density should be located at the more hindered position and, at the same time, the electrophile is the hardest. Both factors should favour the attack at the tertiary carbon. A possible explanation of the observed reactivity could be that the attack does not occur due to steric hindrance. There is no doubt, however, that some reaction between compound (**3b**) and the carbanion is taking place since the colour of the anion disappears on the addition of the acyl chloride. Furthermore, the carbanion (**19**) from the imine (**18**) reacts with benzoyl chloride to give the acylated product (**20**), showing that steric factors do not prevent the reaction.

A more sensible explanation could be that the attack of the electrophile takes place at the tertiary site to give the ketone (**21**) which during isolation decomposes to the observed products by the route shown in Scheme 2. This fragmentation is analogous to one reported by us.[27]

It now seems clear, in the reaction of the aza-allyl carbanions (**1a** and **c**) with soft electrophiles such as alkyl halides or even moderately hard electrophiles such as benzoyl chloride (**3a**) and *p*-methoxybenzoyl chloride (**3c**), that the reagent attacks at the less hindered position instead of at the site of the higher electron density. These results are in good agreement with the site selectivity observed by Murphy[26] in the reaction between 1,3,3-triphenylprop-2-enyl-sodium and alkyl halides. It appears, therefore, that steric factors are directing the course of the reaction.

The reaction between (**1a** and **c**) and *p*-nitrobenzoyl chloride (**3b**) are consistent with attack at the tertiary site. A possible explanation could be that, because of the hardness of the electrophile, the hard–hard interaction between the electrophile and the position with the higher electron density should be so strongly favoured that steric hindrance is overcome.

In the reaction between (**1b**) and (**3b**) the effect of the nitro group in (**1b**) should increase the electron density at the secondary carbon. Thus, in these cases both electronic and steric factors favour the attack at this site.

Experimental

Melting points were determined with a Buchi 510D apparatus in open capillaries and are uncorrected. I.r. and u.v./visible spectra were recorded on Perkin-Elmer 257 and Perkin-Elmer I 24 spectrophotometers respectively. N.m.r. spectra were recorded on Varian T-60A (for ^1H) and Varian FT-80A (for ^{13}C) spectrometers. The samples were dissolved in $CDCl_3$ and the chemical shifts are expressed in p.p.m. downfield from Me_4Si. Mass spectra were determined on a Varian MAT-711 spectrometer. Elemental analyses were performed by the Consejo Superior de Investigaciones Científicas, Madrid.

HMPA (Aldrich) was purified by reflux and distillation from

NaH under nitrogen. THF was dried by being refluxed over and distilled from $LiAlH_4$ and stored under nitrogen. All the aroyl chlorides were distilled under nitrogen prior to use.

General Procedure for the Preparation of Imines.—The imines (**2**) were prepared by a minor modification of the procedures described for the synthesis of benzyl monoimines.[28] A mixture of diphenylmethanamine (2.93 g, 16 mmol), the corresponding aldehyde (16 mmol) and zinc chloride (*ca.* 50 mg) as catalyst in toluene (150 ml) was refluxed for 30 min. The water generated during the condensation was removed azeotropically using a Dean and Stark trap. The mixture was then cooled and the catalyst was removed by filtration. The solution was concentrated under reduced pressure to yield the imine as a colourless solid in quantitative yield. All the imines were crystallized from ethanol. Isolated yields after crystallization are indicated.

The imines (**2**) have previously been synthesized by a different procedure.[29] Compounds prepared by our route have identical melting points and spectral properties with those reported in the literature.[29]

N-(*Diphenylmethyl*)*phenylmethanimine* (**2a**): 3.16 g, 73% as white crystals; m.p. 100—101 °C; δ_H 5.66 (1 H, s, CH), 7.30—7.86 (15 H, m, ArH), and 8.35 (1 H, s, CH=N); $\nu_{max.}$(KBr) 3 060, 1 630, 1 590, 1 440, 1 370, 1 270, 1 020, 750, 730, and 690 cm^{-1} (Found: C, 88.8; H, 6.35; N, 5.35. $C_{20}H_{17}N$ requires C, 88.56; H, 6.27; N, 5.16%).

N-(*Diphenylmethyl*)-p-*nitrophenylmethanimine* (**2b**): 4.85 g, 96% as slightly yellow crystals; m.p. 134—135 °C; δ_H 5.50 (1 H, s, CH), 6.95—8.07 (14 H, m, ArH), and 8.20 (1 H, s, CH=N); $\nu_{max.}$(KBr) 3 020, 1 640, 1 600, 1 520, 1 490, 1 450, 1 350, 865, 750, and 700 cm^{-1} (Found: C, 75.8; H, 5.0; N, 8.9. $C_{20}H_{16}N_2O_2$ requires C, 75.95; H, 5.06; N, 8.86%).

N-(*Diphenylmethyl*)-p-*methoxyphenylmethanimine* (**2c**): 4.33 g, 90% as white crystals; m.p. 108—109 °C; δ_H 3.63 (3 H, s, MeO), 5.57 (1 H, s, CH), 6.80 (2 H, m, ArH), 7.20 (10 H, m, ArH), 7.70 (2 H, m, ArH), and 8.23 (1 H, s, CH=N); $\nu_{max.}$(KBr) 3 060, 1 600, 1 585, 1 510, 1 440, 1 305, 1 250, 1 170, 1 130, 835, 740, and 700 cm^{-1} (Found: C, 83.6; H, 6.35; N, 4.55. $C_{21}H_{19}NO$ requires C, 83.85; H, 6.30; N, 4.64%).

N-(*Diphenylmethyl*)*diphenylmethanimine* (**18**): The method for the preparation of the imines (**2**) was generally followed except that the reaction was refluxed for 320 h. Recrystallization from ethanol gave the imine (**18**) (5.27 g, 95%, as white crystals); m.p. 150—151 °C; δ_H 5.50 (1 H, s, CH) and 7.15—7.68 (20 H, m, ArH); $\nu_{max.}$(KBr) 3 040, 1 620, 1 590, 1 570, 1 480, 1 440, 1 310, 1 270, 1 020, 770, 740, 720, and 695 cm^{-1} (Found: C, 89.8; H, 3.05; N, 4.1. $C_{26}H_{21}N$ requires C, 89.91; H, 3.17; N, 4.03%).

N-*Benzyl*(*diphenyl*)*methanimine* (**12a**): This material was prepared by standard procedure for the preparation of imines. The reaction time in this case was 135 h. Recrystallization from ethanol gave the imine (**12a**) (2.64 g, 61%, as colourless crystals); m.p. 54—56 °C; δ_H 4.50 (2 H, s, CH_2) and 7.20—7.70 (15 H, m, ArH); $\nu_{max.}$(KBr) 3 060, 1 615, 1 590, 1 485, 1 440, 1 310, 1 280, 1 175, 1 150, 1 070, 1 010, 780, 770, 710, and 700 cm^{-1} (Found: C, 88.7; H, 6.3; N, 5.4. $C_{20}H_{17}N$ requires C, 88.60; H, 6.27; N, 5.20%).

N-(p-*Methoxybenzyl*)*diphenylmethanimine* (**12b**): The reaction time in this case was 160 h, (3.46 g, 72%); m.p. 76 °C; δ_H 3.63 (3 H, s, MeO), 4.67 (2 H, s, CH_2), and 6.67—7.70 (14 H, m, ArH); $\nu_{max.}$(KBr) 3 060, 1 620, 1 600, 1 585, 1 510, 1 450, 1 440, 1 305, 1 260, 1 120, 740, and 705 cm^{-1} (Found: C, 83.75; H, 6.2; N, 4.5. $C_{21}H_{19}NO$ requires C, 83.85; H, 6.30; N, 4.64%).

N-(1-*Phenylethyl*)*phenylmethanimine* (**6**): 2.51 g, 75% as a coloured oil; b.p. 130—133 °C/0.7 mmHg; δ_H 1.5 (3 H, d, Me); 4.42 (1 H, q, CH), 7.06—7.80 (10 H, m, ArH); 8.16 (1 H, s, CH=N); $\nu_{max.}$(film) 3 045, 1 645, 1 605, 1 585, 1 495, 1 450, 1 380, 1 295, 1 120, 980, 910, 760, and 700 cm^{-1} (Found: C, 86.0; H, 7.0; N, 6.5. $C_{15}H_{15}N$ requires C, 86.12; H, 7.17; N, 6.69%).

General Procedure for the Acylation of 2-Aza-allyl Carbanions.—A dispersion of NaH (930 mg, 31 mmol; 80% Fluka) in anhydrous HMPA (60 ml), was placed under an atmosphere of nitrogen in a dried 250 ml three necked round-bottomed flask containing a magnetic stirring bar. Subsequently, a solution of the corresponding imine (9 mmol) in anhydrous THF (6 ml) was added at room temperature. The highly-coloured reaction mixture was stirred at ambient temperature for 15 min after which it was cooled to 0 °C using an ice bath. A solution (5 ml) of the acid chloride (4.5M) in THF was introduced in a dropwise fashion. After the addition of approximately an equimolar amount of the aroyl chloride (*ca.* 2 ml, 9 mmol) the colour of the carbanion disappeared. The solution was warmed to 50 °C and stirred for 20—30 min after which a colour reappeared. The reaction mixture was then cooled to 0 °C and the addition of the acid chloride (*ca.* 1 ml, 4.5 mmol) was resumed until the intense colour had been discharged. The process was repeated up to five times until the colour did not redevelop after stirring for 1 h at 50 °C. A total amount of 20.2 mmol of the acid chloride had been added. The reaction mixture was poured into ether (200 ml) and ice, to avoid partial hydrolysis of the azadiene by local concentration of base. The ether layer was separated and the aqueous solution was extracted five times with 50 ml portions of water and dried ($MgSO_4$). Ether was removed by rotary evaporation to yield orange oils. The product mixtures were separated by column chromatography on silica gel. The azadienes were separated using a 3 × 100 cm slurry packed silica gel column eluted with 10% ether in hexane, except for the azadienes (**4e** and **d**) in which 20% hexane in benzene was used. All the azadienes were crystallized from ethanol. Isolated yields after crystallization are indicated.

4-(*Benzoyloxy*)-1,1,3,4-*tetraphenyl*-2-*azabuta*-1,3-*diene* (**4a**): 2.59 g, 60% as yellow crystals; m.p. 156 °C; δ_H 6.83—7.70 (m, ArH); δ_C 170.3 (C=N), 165.4 (C=O), 140.3, 138.2, 135.3, 133.0, and 129.9—127.1; $\nu_{max.}$(KBr) 3 020, 1 725, 1 600, 1 590, 1 580, 1 550, 1 440, 1 310, 1 270, 1 240, 1 180, 1 010, 770, and 700 cm^{-1}; *m/z* 479 (M^+, 26%), 374 (100), 269 (44), 166 (27), 165 (57), 105 (55), and 77 (12); $\lambda_{max.}(CH_2Cl_2)$ 254 (ε 21 500 dm^3 mol^{-1} cm^{-1}) and 270 (10 000) nm (Found: C, 85.3; H, 5.1; N, 2.9. $C_{34}H_{25}NO_2$ requires C, 85.17; H, 5.21; N, 2.92%).

4-(p-*Methoxybenzoyloxy*)-4-(p-*methoxyphenyl*)-1,1,3-*triphenyl*-2-*azabuta*-1,3-*diene* (**4b**): 3.54g, 73% as yellow crystals; m.p. 178—180 °C; δ_H 3.76 (3 H, s, MeO), 3.83 (3 H, s, MeO), and 6.76—7.96 (23 H, m, ArH); δ_C 170.6 (C=H), 165.4 (C=O), 163.8, 159.0, 139.0—113.7, and 55.2 (MeO); $\nu_{max.}$(KBr) 3 030, 2 820, 1 720, 1 600, 1 510, 1 440, 1 320, 1 250, 1 170, 1 100, 1 030, 830, 770, and 700 cm^{-1}; *m/z* 539 (M^+, 18%), 405 (43), 404 (100), 269 (20), 166 (15), 165 (39), 135 (58), 105 (20), and 77 (9); $\lambda_{max.}(CH_2Cl_2)$ 260 (ε 42 444), 285 (25 655), and 370 (4 000) nm (Found: C, 80.25; H, 5.4; N, 2.7. $C_{36}H_{29}NO_4$ requires C, 80.14; H, 5.38; N, 2.59%).

4-(*Benzoyloxy*)-3-(p-*nitrophenyl*)-1,1,4-*triphenyl*-2-*azabuta*-1,3-*diene* (**4c**): 2.78 g, 59% as yellow crystals; m.p. 214—215 °C; δ_H 6.60—8.80 (m, ArH); δ_C 171.7 (C=N), 165.1 (C=O), 146.6, 145.1, and 138.4—122.8; $\nu_{max.}$(KBr) 3 030, 1 730, 1 630, 1 590, 1 515, 1 345, 1 240, 1 090, 870, 760, and 700 cm^{-1}; *m/z* 524 (M^+, 12%), 420 (22), 419 (66), 404 (21), 403 (64), 373 (20), 166 (21), 165 (56), 105 (100), and 77 (31); $\lambda_{max.}(CH_2Cl_2)$ 234 (ε 55 033), 258 (52 349), 276 (48 322) and 371 (20 134) nm (Found: C, 77.7; H, 4.8; N, 5.35. $C_{34}H_{24}N_2O_4$ requires C, 77.86; H, 4.58; N, 5.34%).

4-(p-*Methoxybenzoyloxy*)-4-(p-*methoxyphenyl*)-3-(p-*nitrophenyl*)-1,1-*diphenyl*-2-*azabuta*-1,3-*diene* (**4e**): 2.73 g, 52% as

orange crystals; m.p. 180 °C; δ_H 3.73 (3 H, s, MeO), 3.80 (3 H, s, MeO), and 6.70—7.93 (22 H, m, ArH); δ_C 170.4 (C=N), 165.3 (C=O), 163.5, 158.5, 158.2, 139.1—112.9, 55.4 (MeO), and 55.2 (MeO); $\nu_{max.}$(KBr) 3 070, 2 820, 1 730, 1 605, 1 590, 1 510, 1 440, 1 340, 1 250, 1 160, 1 100, 765, 700, and 690 cm^{-1}; $\lambda_{max.}(CH_2Cl_2)$ 268 (ε 37 630) and 384 (9 756) nm; *m/z* 584 (1%), 449 (18), 434 (26), 433 (100), 166 (6), 165 (17), and 135 (98) (Found: C, 74.1; H, 4.95; N, 4.95. $C_{36}H_{28}N_2O_6$ requires C, 73.97; H, 4.95; N, 4.80%).

4-(p-*Nitrobenzoyloxy*)-3,4-*di*(p-*nitrophenyl*)-1,1-*diphenyl*-2-*azabuta*-1,3-*diene* (**4d**): 4.81 g, 87% as yellow crystals; m.p. 225 °C; δ_H 7.10—8.23 (m, ArH); δ_C 173.2 (C=N), 163.4 (C=O), 151.3, 147.0—123.1; $\nu_{max.}$(KBr) 3 090, 1 750, 1 630, 1 595, 1 530, 1 510, 1 340, 1 100, 870, 710, and 700 cm^{-1}; $\lambda_{max.}(CH_2Cl_2)$ 267 (ε 29 142) and 376 (13 725) nm; *m/z* 614 (10%), 465 (35), 464 (100), 314 (45), 166 (30), 165 (75), 150 (35), 105 (30), and 77 (15) (Found: C, 66.6; H, 3.55; N, 9.0. $C_{34}H_{22}N_4O_8$ requires C, 66.45; H, 3.60; N, 9.12%).

4-*Benzoyloxy*-3-(p-*methoxyphenyl*)-1,4,4-*triphenyl*-2-*azabuta*-1,3-*diene* (**4f**): 3.11 g, 68% as yellow crystals; m.p. 150—152 °C; δ_H 3.63 (3 H, s, MeO), and 6.5—8.0 (24 H, m, ArH); δ_C 169.8 (C=N), 165.0 (C=O), 160.0, 135.5—113.3, and 55.1 (MeO); $\nu_{max.}$(KBr) 3 030, 1 725, 1 610, 1 595, 1 510, 1 450, 1 270, 1 245, 1 180, 1 120, 770, 720, and 700 cm^{-1}; $\lambda_{max.}(CH_2Cl_2)$ 255 (ε 35 606), 258 (33 333), 282 (28 788), and 386 (3 788) nm; *m/z* 509 (16%), 405 (13), 404 (100), 299 (24), 166 (18), 165 (49), 105 (27), 77 (11) (Found: C, 82.5; H, 5.35; N, 2.75. $C_{35}H_{27}NO_3$ requires C, 82.5; H, 5.3; N, 2.75%).

4-p-*Methoxybenzoyloxy*-3,4-*di*(p-*methoxyphenyl*)-1,1-*diphenyl*-2-*azabuta*-1,3-*diene* (**4g**): 3.74 g, 74% as yellow crystals; m.p. 195 °C; δ_H 3.66 (3 H, s, MeO), 3.73 (3 H, s, MeO), 3.83 (3 H, s, MeO), and 6.43—7.96 (22 H, m, ArH); δ_C 170.4 (C=N), 165.3 (C=O), 163.5, 158.2, 139.1—112.9, 55.4 (MeO), 55.2 (MeO), 55.0 (MeO); $\nu_{max.}$(KBr) 3 030, 2 820, 1 725, 1 620, 1605, 1 594, 1 580, 1 510, 1 445, 1 255, 1 175, 1 100, 1 030, 840, and 700 cm^{-1}; $\lambda_{max.}(CH_2Cl_2)$ 261 (ε 56 910), 293 (26 829), and 379 (4 878) nm; *m/z* 569 (16%), 436 (9), 435 (44), 434 (100), 166 (14), 165 (36), 135 (60), and 77 (12) (Found: C, 78.1; H, 5.6; N, 2.6. $C_{37}H_{31}NO_5$ requires C, 78.03; H, 5.44; N, 2.46%).

1-*Benzoyloxy*-1,2,4-*triphenyl*-3-*azapenta*-1,3-*diene* (**5**): 2.06 g, 55% as yellow crystals; m.p. 192—193 °C; δ_H 2.2 (3 H, s, Me) and 7.0—8.0 (20 H, m, ArH); δ_C 168.1 (C=N), 165.8 (C=O), 127.1—139.1, and 18.7 (Me); $\nu_{max.}$(KBr) 3 030, 1 730, 1 625, 1 600, 1 580, 1 500, 1 450, 1 370, 1 240, 1 120, 1 040, 770, and 700 cm^{-1}; $\lambda_{max.}(CH_2Cl_2)$ 237 (ε 23 413) and 283 (11 508) nm; *m/z* 417 (33%), 312 (100), 207 (15), 105 (45), and 77 (16) (Found: C, 83.7; H, 5.6; N, 3.35. $C_{29}H_{23}NO_2$ requires C, 83.45; H, 5.51; N, 3.35%).

1,2,2,4,4-*Pentaphenyl*-3-*azabut*-3-*en*-1-*one* (**20**): The standard procedure for the acylation of carbanions was used yielding the *enone* (**20**) (2.59 g, 64% as colourless crystals, m.p. 158 °C; δ_H 6.13—6.26 (2 H, m, ArH) and 6.66—7.83 (23 H, m, ArH); $\nu_{max.}$(KBr) 3 040, 1 685, 1 675, 1 615, 1 590, 1 570, 1 440, 1 220, 1 045, 840, 775, and 700 cm^{-1}; $\lambda_{max.}$(EtOH) 222 (ε 13 117) and 252 (13 229) nm; *m/z* 346 (100%), 165 (31) (Found: C, 87.5; H, 5.45; N, 3.1. $C_{33}H_{25}NO$ requires C, 87.80; H, 5.54; N, 3.10%).

Reaction of the Carbanion (**1a**) *with* p-*Nitrobenzoyl Chloride*.—The standard procedure for the preparation of 2-azadienes was followed. An equimolar amount of *p*-nitrobenzoyl chloride as a 4.5M solution in THF was added dropwise at 0 °C to a solution of the carbanion [prepared from (**2a**) (500 mg, 1.8 mmol)]. The reaction was quenched in ether–ice and the product was isolated as described in the general procedure for acylations. After the removal of solvent under reduced pressure, the remaining oil (740 mg) was triturated with ethanol and the solid residue was removed by filtration to yield a mixture (140 mg) of the starting imine (**2a**) and the imine (**12a**) as demonstrated by ^1H n.m.r. spectroscopy. The residue obtained from the concentration of the filtrate amounting to 593 mg was chromatographed on a slurry packed column of silica gel (3 × 50 cm). Elution with ether–hexane (7:93) gave benzophenone and benzaldehyde (355 mg) followed by a mixture (70 mg) of the imines (**2a**) and (**12a**). Final elution with ethanol gave *p*-nitrobenzoic acid (130 mg). The total mass balance was 695 mg, (95%).

Reaction of the Carbanion (**1c**) *with* p-*Nitrobenzoyl Chloride*.—The standard procedure for the preparation of 2-azadienes was followed. An equimolar amount of *p*-nitrobenzoyl chloride (as a 4.5M solution in THF) was added dropwise at 0 °C to a solution of the carbanion [prepared from compound (**2c**) (500 mg, 1.66 mmol)]. The reaction was quenched in ether–ice and the product was isolated as described in the general procedure. After the removal of solvent under reduced pressure the residual oil (800 mg) was chromatographed on a slurry packed column of silica gel (3 × 50 cm). Elution with ether–hexane (3:97) gave benzophenone (100 mg), a mixture (280 mg) of the imines (**2c**) and (**12c**), and *p*-methoxybenzaldehyde (190 mg). Final elution with ethanol gave *p*-nitrobenzoic acid (140 mg). The total mass balance was 710 mg (89%).

Hydrolysis of 4-*Benzoyloxy*-1,1,3,4-*tetraphenyl*-2-*azabuta*-1,3-*diene* (**4a**).—A solution of H_2SO_4 in water (60 ml, 15%) was added dropwise at room temperature to a magnetically stirred solution of the azadiene (**4a**) (1 g, 2.1 mmol). The mixture was stirred for 2 h. After the reaction was complete the yellow colour of the azadiene had disappeared. The reaction mixture was then extracted with ether. The extract was dried over Na_2SO_4, filtered, and the solvent removed under reduced pressure. The oily residue was chromatographed on silica gel (3 × 100 cm). Ether–hexane (3:97) eluted benzophenone (378 mg, 97%). Ether alone eluted benzoin benzoate (560 mg, 85%) identified by comparison with an authentic sample.

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