Mesoionic Oxazolones in Heterocyclic Syntheses. Reaction of 2,4-Diphenyloxazol-5(4*H*)-one with 1-Azabuta-1,3-dienes

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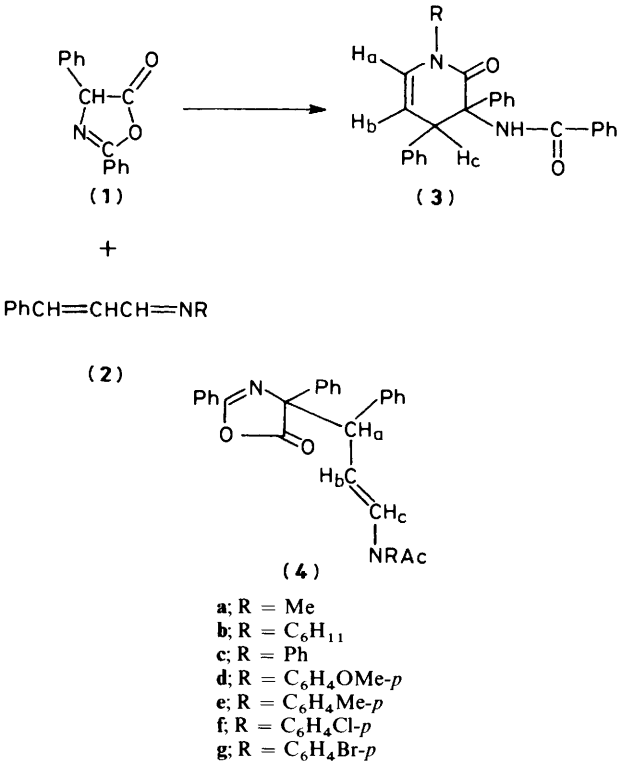
2,4-Diphenyloxazol-5(4*H*)-one reacted smoothly with 1-azabuta-1,3-dienes to afford the dihydro-α-pyridones (**3**) in good yields. The acetylated adducts (**4**) were isolated, allowing a mechanism for the formation of these products to be proposed.

Mesoionic compounds have greatly enhanced the development of heterocyclic syntheses and considerable work has been carried out towards an understanding of the mechanism of these reactions.[1] In recent years we have been studying the chemistry of 1-azabuta-1,3-dienes and have investigated their reactions with various acylic 1,3-dipoles, such as benzonitrile oxides,[2] nitrile imines,[3] and aziridines.[4] In these reactions the dipoles preferentially added to the carbon–nitrogen double bond and the carbon–carbon double bond was not involved. Azalactones are well known mesoionic compounds[5] and react with a variety of multiple bonds with the elimination of carbon dioxide to provide novel heterocycles,[5b,6] the most extensively studied system is 3-methyl-2,4-diphenyloxazolium-5-oxide (münchnone).[7] Huisgen described the reaction of münchnone with imines to give β-lactams in good yields. The β-lactam formation was assumed to take place *via* the ketene tautomer[8] and this postulate has been reasserted[9] although it was initially disputed.[10] During our studies on the cycloaddition reactions of 4-methyl-2-phenyloxazol-5(4*H*)-one we observed the formation of β-lactams[11] from the reaction of unconjugated imines and α-pyridones[12] with 1-azabuta-1,3-dienes. In analogy to Huisgen's proposed mechanism, we assumed the involvement of a ketene tautomer in these reactions. Now we describe the reaction of 2,4-diphenyloxazol-5(4*H*)-one (**1**) with 1-azabuta-1,3-dienes (**2**) from which we obtained the α-pyridones (**3**) when *N*-alkyl groups were used and the acetylated adducts† (**4**) when *N*-aryl analogues were used.



a; R = Me
b; R = C_6H_{11}
c; R = Ph
d; R = C_6H_4OMe-*p*
e; R = C_6H_4Me-*p*
f; R = C_6H_4Cl-*p*
g; R = C_6H_4Br-*p*

Scheme 1.

Results and Discussion

When equimolar quantities of the azalactone‡ (**1**) and the azadiene (**2a**) had been stirred at room temperature for 12 h under nitrogen (Scheme 1) (following the reaction by t.l.c.), removal of the solvent under reduced pressure gave a pasty material which could be purified by preparative t.l.c. to give a white crystalline solid, m.p. 142—143.5 °C in 60% yield. The assignment of structure (**3a**) to this product rests on elemental as well as spectral data. The i.r. spectrum (KBr) showed bands at 3 255, 1 660, and 1 645 cm^{-1} indicating the presence of NH and two amido carbonyl groups respectively. The 360 MHz ^1H n.m.r. spectra taken in $CDCl_3$ showed signals at δ 3.40 (s, 3 H), 5.18 (dd, *J* 8 Hz, 2.5 Hz, 1 H), 5.70 (unresolved t, 1 H), 6.25 (dd, *J* 8 Hz, 3.5 Hz, 1 H), 6.52 (br s, 1 H), 6.64 (m, 2 H), 6.77 (m, 2 H), 7.12—7.52 (m, 9 H), and 7.83 (m, 2 H). The double doublet at δ 5.18 was assigned to H_b, and was coupled with H_a (*J* 8 Hz) and H_c (*J* 2.5 Hz). The unresolved triplet at δ 5.70 was assigned H_c and its broadening appears to be due to benzylic coupling. The double doublet at δ 6.25 was assigned to H_a and coupled with H_b (*J* 8 Hz) and H_c (*J* 3.5 Hz). Presumably because of the dihedral angle, J_{c-b} was small and about the same as the allylic J_{c-a}. The couplings between H_a, H_b, and H_c were confirmed by spin–spin decoupling experiments. When H_c was decoupled by irradiation at δ 5.70, the double doublets at δ 6.25 and 5.18 collapsed to doublets. Similarly, H_b and H_a were decoupled by irradiation at δ 5.18 and 6.25 and the values of the coupling constants were confirmed. The assignment of δ 5.70 to the benzylic proton H_c was confirmed by recording ^{13}C satellites for this signal; this showed the $^1J_{CH}$ value to be about 132 Hz which was compatible with a carbon not substituted by any heteroatom.

The 90.52 MHz ^{13}C n.m.r. spectra of compound (**3a**) in

† The acetylated adducts (**4**) were only obtained when the azalactone (**1**), m.p. 90—92 °C (*i.e.* with acetic anhydride in the crystal lattice) was used.
‡ The azalactone (**1**), m.p. 90—92 °C (lit., [5b] m.p. 103.5—105.5 °C) was prepared following the method reported by Huisgen.[5b] Repeated crystallization from light petroleum did not raise the m.p. Interestingly, Cornforth[13] who first described the preparation of this compound also reported a lower m.p. (80—81 °C). The n.m.r. spectra of this compound showed the presence of acetic anhydride, presumably in the crystal lattice. Also it is noteworthy that azalactones have been used as dipoles by earlier workers by *in situ* generation without the removal of acetic anhydride.[14]

Table 1. Physical and analytical data of the α-pyridones (**3a—e**) and the acetylated adducts (**4c—g**)

Compound	Yield (%)	M.p. (°C)	Formula	Analyses (%) Found C	Found H	Found N	Required C	Required H	Required N
(**3a**)	60	142—143.5	$C_{25}H_{22}N_2O_2$	78.6	5.7	7.25	78.53	5.76	7.33
(**3b**)	60	189—190	$C_{30}H_{30}N_2O_2$	80.0	6.7	6.2	80.00	6.67	6.22
(**3c**)	14	197—198	$C_{30}H_{24}N_2O_2$	81.0	5.4	6.35	81.08	5.40	6.30
(**3d**)	20	189—190	$C_{31}H_{26}N_2O_3$	78.5	5.4	6.0	78.48	5.48	5.91
(**3e**)	15	195—196	$C_{31}H_{26}N_2O_2$	81.4	5.8	6.0	81.22	5.68	6.11
(**4c**)	50	163—164 (dec.)	$C_{32}H_{26}N_2O_2$	79.2	5.2	5.65	79.01	5.35	5.76
(**4d**)	46	170—171 (dec.)	$C_{33}H_{20}N_2O_4$	76.8	5.35	5.45	76.74	5.43	5.43
(**4e**)	48	152—153 (dec.)	$C_{33}H_{28}N_2O_3$	79.3	5.5	5.6	79.20	5.60	5.60
(**4f**)	51	172—173 (dec.)	$C_{32}H_{25}N_2O_3Cl$	74.0	4.7	5.4	73.85	4.81	5.38
(**4g**)	52	177—178 (dec.)	$C_{32}H_{25}N_2O_3Br$	67.9	4.4	5.0	67.96	4.42	4.95

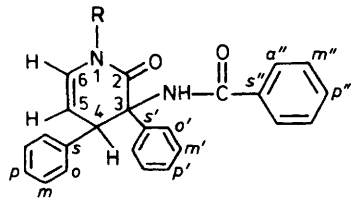
Table 2. Spectral data for the α-pyridones (**3a—e**) and the acetylated adducts (**4c—g**)

Compound	$\nu_{max.}$ (cm^{-1})	δ/p.p.m.	*m/z* (%)
(**3a**)	3 255, 1 660, 1 645	3.40 (s, 3 H), 5.18 (dd, *J* 8 Hz, 2.5 Hz, 1 H), 5.70 (unresolved t, 1 H), 6.25 (dd, *J* 8, 3.5 Hz, 1 H), 6.52 (br s, 1 H), 6.64 (m, 2 H), 6.77 (m, 2 H), 7.12—7.52 (m, 9 H), 7.83 (m, 2 H)	382(0.02), 261(80), 260(100), 146(60), 105(40)
(**3b**)	3 260, 1 662, 1 640	1.19—2.05 (m, 10 H), 4.70 (m, 1 H), 5.22 (dd, *J* 8, 2.5 Hz, 1 H), 5.65 (unresolved t, 1 H), 6.40 (dd, *J* 8 3.5 Hz, 1 H), 6.52 (br s, 1 H), 6.69 (m, 2 H), 6.75 (m, 2 H), 7.12—7.52 (m, 9 H), 7.84 (m, 2 H)	450(0.05), 329(70), 328(100), 214(60), 105(45)
(**3c**)	3 275, 1 670, 1 642	5.20 (dd, *J* 8, 2.5 Hz, 1 H), 5.67 (unresolved t, 1 H), 6.20 (dd, *J* 8, 3.0 Hz, 1 H), 6.50 (br s, 1 H), 6.70 (m, 2 H), 6.80 (m, 2 H), 7.12—7.54 (m, 14 H), 7.84 (m, 2 H)	444(0.1), 323(75), 322(100), 208(45), 105(60)
(**3d**)	3 270, 1 672, 1 645	3.83 (s, 3 H), 5.19 (dd, *J* 8, 2.5 Hz, 1 H), 5.70 (unresolved t, 1 H), 6.23 (dd, *J* 8, 3.0 Hz, 1 H), 6.51 (br s, 1 H), 6.72 (m, 2 H), 6.78 (m, 2 H), 7.10—7.54 (m, 13 H), 7.84 (m, 2 H)	474(0.15), 353(85), 352(100), 238(65), 105(48)
(**3e**)	3 274, 1 675, 1 642	2.37 (m, 3 H), 5.18 (dd, *J* 8, 2.5 Hz, 1 H), 5.65 (unresolved t, 1 H), 6.21 (dd, *J* 8, 3 Hz, 1 H), 6.48 (br s, 1 H), 6.71 (m, 2 H), 6.76 (m, 2 H), 7.12—7.54 (m, 13 H), 7.84 (m, 2 H)	458(0.2), 337(90), 336(100), 222(55), 105(50)
(**4c**)	1 826, 1 812, 1 775, 1 675, 1 648, 975	1.74 (s, 3 H), 4.30 (dd, *J* 10, 14 Hz, 1 H), 4.48 (d, *J* 10 Hz, 1 H), 6.93—8.02 (m, 21 H)	486(0.5), 443(3), 442(6), 399(71), 398(68), 321(37), 307(100), 295(38), 206(68), 193(75), 105(30)
(**4d**)	1 825, 1 814, 1 774, 1 675, 1 648, 980	1.74 (s, 3 H), 3.81 (s, 3 H), 4.30 (dd, *J* 10, 14 Hz, 1 H), 4.48 (d, *J* 10 Hz, 1 H), 6.90—8.00 (m, 20 H)	516(0.2), 473(3), 472(10), 429(70), 428(68), 321(40), 307(60), 236(70), 193(100), 105(40)
(**4e**)	1 825, 1 810, 1 775, 1 680, 1 650, 980	1.74 (s, 3 H), 2.36 (s, 3 H), 4.31 (dd, *J* 10, 14 Hz, 1 H), 4.47 (d, *J* 10 Hz, 1 H), 6.90—8.00 (m, 20 H)	500(0.3), 457(3), 456(12), 413(75), 412(70), 321(45), 220(77), 193(100), 105(45)
(**4f**)	1 823, 1 812, 1 780, 1 675, 1 645, 970	1.74 (s, 3 H), 4.30 (dd, *J* 10, 14 Hz, 1 H), 4.48 (d, *J* 10 Hz, 1 H), 6.93—8.00 (m, 20 H)	520(0.1), 477(2), 476(7), 433(70), 432(61), 355(30), 240(100), 193(70), 105(50)
(**4g**)	1 825, 1 812, 1 777, 1 677, 1 650, 970	1.74 (s, 3 H), 4.30 (dd, *J* 10, 14 Hz, 1 H), 4.48 (d, *J* 10 Hz, 1 H), 6.92—8.00 (m, 20 H)	566(0.2), 564(0.2), 523(3), 521(3), 479(11), 478(8), 477(11), 476(8), 308(41), 307(58), 306(41), 286(100), 284(100), 193(33), 173(46), 171(46), 105(80)

$CDCl_3$ showed signals due to NCH_3 and a benzylic carbon attached to H_c at 34.88 and 45.32 p.p.m. respectively. Signals at 109.63 and 130.25 p.p.m. were assigned to pyridone ring double-bonded carbons attached to H_b and H_c respectively. The two carbonyl groups present in compound (**3a**) showed absorptions at 168.57 and 168.80 p.p.m.; the electron impact mass spectrum showed a weak molecular ion peak at *m/z* (rel. int.) 382 (0.02%) with other major fragments at *m/z* 261 (80), 260 (100), 146 (60), and 105 (40). These peaks were in full agreement with the fragmentation pattern of an α-pyridone structure.[12b,c] Similarly when compound (**2b**) was employed in this reaction the α-pyridone (**3b**) was obtained in 60% yield, m.p. 189—190 °C. Microanalytical and spectral data of compound (**3b**) are given in Tables 1 and 2.

The reaction of the azalactone (**1**) with the azadiene (**2c**) under identical conditions gave on work-up the acetylated adduct (**4c**) (m.p. 163—164 °C, decomp.) in 50% yield. The i.r. (KBr) spectrum showed bands at 1 826, 1 812, 1 775, 1 675, 1 648, and 975 cm^{-1} indicating the presence of an oxazolone ring (characteristic absorptions at 1 826, 1 812, and 1 775 cm^{-1}) and a *trans*-enamine moiety (characteristic absorptions at 1 648 and 975 cm^{-1}). The 360 MHz ^1H n.m.r. spectra taken in $CDCl_3$ showed signals at δ 1.74 (s, 3 H, $COCH_3$), 4.30 (dd, J_{ab} 10 Hz, J_{bc} 14 Hz, 1 H, H_b), 4.48 (d, J_{ab} 10 Hz, 1 H, H_a), and 6.93—8.02 (m,

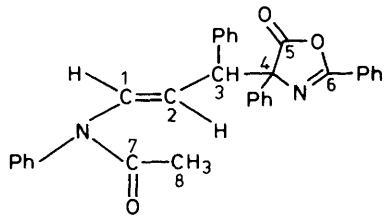
Table 3. ^{13}C N.m.r. chemical shifts and assignments for the α-pyridones (**3a**) and (**3b**) and the acetylated adduct (**4c**)*



(**3**)

a; R = $^{\alpha}CH_3$

b; R = α(β′ γ′ δ β γ)



(**4C**)

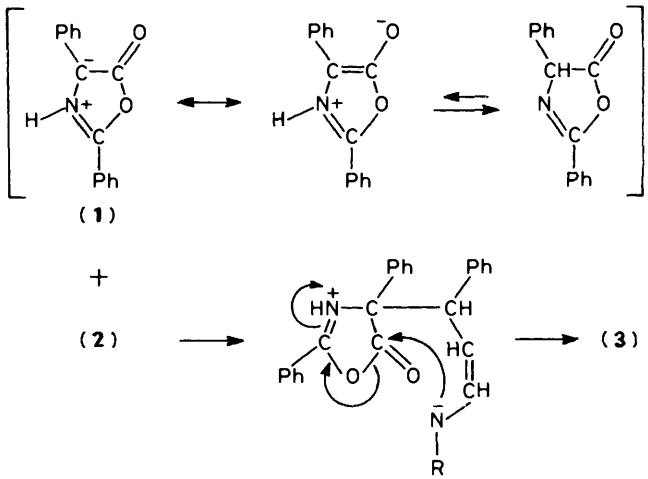
Compound	δ_c/p.p.m.
(**3a**)	168.80(C-2), 168.57(C-7), 138.47(*s*-C), 135.67(*s*′-C), 134.79(*s*″-C), 131.81(*p*″-C), 130.32(*o*-C), 130.25(C-6), 128.62(*m*″-C), 128.34(*p*,*p*′-C), 127.97(*m*-C), 127.46(*m*′-C), 127.15(*o*″,*p*′,*p*-C), 126.71(*o*′-C), 109.63(C-5), 67.89(C-3), 45.32(C-4), 34.88(α-C)
(**3b**)	168.61(C-7), 167.91(C-2), 138.67(*s*-C), 135.81(*s*′-C), 134.95(*s*″-C), 131.73(*p*″-C), 130.35(*o*-C), 128.60(*m*″-C), 128.23(*p*,*p*′-C), 127.90(*m*-C), 127.42(*m*′-C), 127.17(*o*″-C), 127.04(*p*′,*p*-C), 126.74(*o*′-C), 124.97(C-6), 109.89(C-5), 68.07(C-3), 52.99(α-C), 44.69(C-4), 31.81(β-C), 30.74(β′-C), 25.73 (γγ′-C), 25.51(δ-C)
(**4c**)	178.07(C-5), 168.40(C-7), 159.80(C-6), 139.42—125.78(aromatic C,C-1), 110.32(C-2), 79.11(C-4), 57.44(C-3), 23.01(C-8); $^1J_{C_2H_2}$ 156 Hz, $^1J_{C_3H_3}$ 131 Hz, $^1J_{C_8H_8}$ 129 Hz

* Values are in p.p.m. relative to Me_4Si, $CDCl_3$ as solvent.

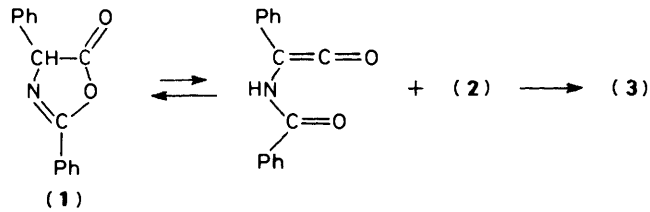
21 H, aromatic and H_c). The presence of a *trans*-CH=CH is clearly indicated by the J_{bc} value of 14 Hz.

The 90.52 MHz ^{13}C n.m.r. spectra of compound (**4c**) in $CDCl_3$ (Table 3) showed the signal for the methyl carbon of $COCH_3$ at 23.01 p.p.m. with a $^1J_{CH}$ value of 129 Hz. The signal at 57.44 p.p.m. ($^1J_{CH}$ 156 Hz) was assigned to the carbon atom attached to H_a. The signal at 110.32 p.p.m. with $^1J_{CH}$ 156 Hz was assigned to the carbon attached to H_b. Because of the large overlap of signals in the aromatic region, the carbon atom attached to H_c could not be assigned. The electron impact mass spectrum of compound (**4c**) showed the molecular ion at *m*/*z* (rel. int.) 486 (M^+, 0.5%), (M^+ − 43) at *m*/*z* 443 (3) due to the loss of $COCH_3$, and (M^+ − 44) at *m*/*z* 442 (6) due to the loss of carbon dioxide. Similarly, when the conjugated imines (**2d—g**) were allowed to react, the acetylated adducts (**4d—g**) were obtained. The characteristics of these compounds are recorded in Tables 1 and 2.

The isolation of acetylated adducts of the type (**4c—g**) clearly indicated that the reaction is initiated by attack of oxazolone at the C=C bond followed by *N*-acetylation. In the case of compounds (**2a**) and (**2b**) cyclized products (α-pyridones) were obtained; the most logical explanation is probably that the addition of oxazolone in its carbanion form to the C=C bond and attack of nucleophilic nitrogen is a completely concerted process (Scheme 2), leaving no time available for the attack of acetyl [the source of which appears to be the acetic anhydride in the crystal lattice of (**1**)] at nitrogen. In case of compounds (**4c—g**), the anion formed at the nitrogen atom is more stable and has a longer lifetime because of charge delocalisation into the aromatic ring, and the competing acetylation reaction is thus much faster than the intramolecular attack on the azalactone carbonyl carbon, giving the acetylated adduct as the sole isolable product.



Scheme 2.

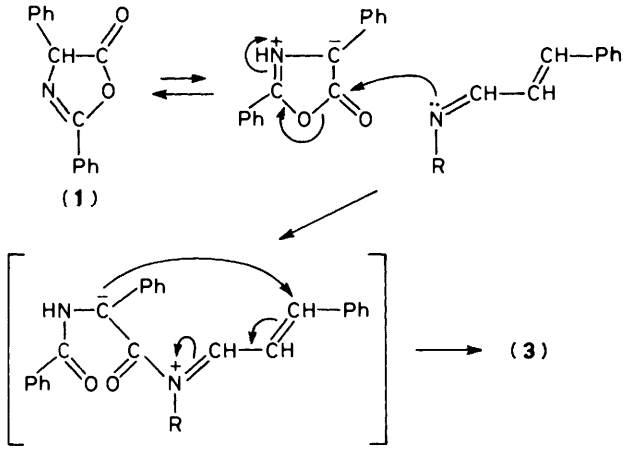


Scheme 3.

We were able to prepare the azalactone (**1**) free of acetic anhydride by passing the benzene solution of the residue left after acetic anhydride removal through a short column of active basic alumina, where all the acetic anhydride was trapped. The azalactone (**1**) thus obtained showed m.p. 103.5—105.5 °C (the same as that reported by Huisgen) and the n.m.r. spectra indicated the absence of any acetic anhydride. Acetic anhydride-free azalactone (**1**) reacted with the *N*-arylimines (**2c—e**) affording the α-pyridones (**3c—e**) in 14, 20, and 15% yields respectively. (The characteristics of these α-pyridones are recorded in Tables 1 and 2). However, its reaction with the *N*-alkylimines (**2a**) and (**2b**) yielded the α-pyridones (**3a**) and (**3b**) in comparable yields.

Mechanism for the Dihydro-α-pyridone Formation.—There are three possible mechanistic pathways for the formation of α-pyridones from conjugated imines and azalactones.

Firstly, the azalactones are known to undergo [4 + 2] cycloadditions involving the valence tautomeric ketene intermediate,[15] and α-pyridones may be formed analogously by a ketene imine reaction (Scheme 3). Secondly, the reaction may be



Scheme 4.

initiated by the attack of the imine at the carbonyl group of the azalactone and subsequent cyclization may yield the α-pyridone as shown in Scheme 4. This is analogous to the mechanism proposed by Knowles *et al.*[16] for the reaction between oxazolium perchlorate and Schiff bases.

Thirdly the reaction may be initiated by the attack of the azalactone in its carbanion form at the C=C bond of the 1-azadiene, and subsequent attack of nucleophilic nitrogen may yield the α-pyridone as shown in Scheme 2.

The isolation of the acetylated adducts (**4c**—**g**) indicates that the probable mechanism for this type of reaction is that shown in Scheme 2.

Experimental

M.p.s were determined in open capillary tubes on a Buchi apparatus and are uncorrected. The ^{1}H n.m.r. spectra were recorded on Bruker 360 MHz and 90 MHz spectrometers and chemical shift values are recorded in δ units (parts per million) relative to Me_4Si as internal standard. ^{13}C N.m.r. spectra were obtained with proton-noise decoupling and proton-coupling at 90.52 MHz with a Bruker 360 MHz instrument and chemical shifts are expressed relative to internal standard Me_4Si in $CDCl_3$. I.r. spectra were recorded on a Perkin-Elmer 237 B i.r. spectrometer in potassium bromide discs. Mass spectra were recorded on AEI MS 30 instrument by the electron impact method. 1-Azabuta-1,3-dienes were prepared by standard methods. Activated basic alumina was prepared by activating laboratory reagent grade basic alumina at 400 °C for 2 h.

2,4-*Diphenyloxazol*-5(4H)-*one* (**1**).—The azalactone (**1**) was prepared by cyclodehydration of *N*-benzoyl-*C*-phenylglycine following the literature method reported by Huisgen.[5b] This yielded a white crystalline solid (60%) which was recrystallized twice from light petroleum (b.p. 60—80 °C), m.p. 90—92 °C (lit. m.p. 103.5—105.5 °C).[5b] Further recrystallization from light petroleum did not raise the m.p., $\nu_{max.}$ 1 820, 1 780, and 1 635 cm^{-1}; δ($CDCl_3$) 2.33 (s, 3 H), 7.20—7.98 (m, 11 H); *m*/*z* (rel. int.) 237 (M^+, 100%), 209 (77), 193 (41), and 105 (80).

To prepare acetic anhydride-free azalactone (**1**), the residue left after acetic acid and acetic anhydride removal was dissolved in dry benzene and passed through a short column of activated basic alumina. The eluted solution was evaporated under reduced pressure and the residue was dissolved in the minimum amount of warm dry benzene and diluted with warm light petroleum (b.p. 60—80 °C) until slightly turbid. After scratching the solution was stored under nitrogen in the refrigerator for 12 h. The separated white crystalline solid (50%) was filtered and recrystallized from light petroleum, m.p. 103.5—105.5 °C (as reported by Huisgen); $\nu_{max.}$ 1 820, 1 785, 1 645 cm^{-1}; δ($CDCl_3$) 5.16 (s, 1 H), 7.20—7.35 (m, 8 H), 7.90 (m, 2 H); *m*/*z* (rel. int.) 237 (M^+, 87%), 209 (50), 193 (100), 165 (43), and 105 (75).

Reaction of the 1-*Substituted*-4-*phenyl*-1-*azabuta*-1,3-*dienes* (**2a**) *and* (**2b**) *with the Azalactone* (**1**). *General Procedure.*—To the stirred solution of the azadiene (**2a**) or (**2b**) (0.005 mol) in dry benzene (5 ml) was added the solution of the azalactone (**1**) (m.p. 90—92 °C) (0.005 mol) in dry benzene (5 ml) and the mixture was stirred at room temperature for a further 12 h under nitrogen. Benzene was removed under reduced pressure and the residue was purified by preparative t.l.c. (silica gel, benzene–ethyl acetate 19:1) to give the dihydro-α-pyridones (**3a**) and (**3b**) in 60% yields.

Reaction of the azadienes (**2a**) and (**2b**) with azalactone (**1**) (m.p. 103.5—105.5 °C) when carried out under similar conditions after purification by t.l.c. yielded the dihydro-α-pyridones (**3a**) and (**3b**) in 65% yields.

Reaction of the N-*Arylazadienes* (**2c**—**g**) *with the Azalactone* (**1**). *General Procedure.*—To the stirred solution of the azadiene (**2c**—**g**) (0.005 mol) in dry benzene (5 ml) under nitrogen was added a solution of the azalactone (**1**) (m.p. 90—92 °C) (0.005 mol) in dry benzene (5 ml) at room temperature. Stirring was continued for 12 h at room temperature under nitrogen. Benzene was then removed under reduced pressure and the residue left was purified on preparative t.l.c. (silica gel, benzene). This yielded the acetylated adducts (**4c**—**g**) as white crystalline solids in 46—52% yields.

The reactions of the azadienes (**2c**—**e**) with the azalactone (**1**) (m.p. 103.5—105.5 °C) were carried out in the same way. The residue left after benzene removal was purified by preparative t.l.c. (silica gel, benzene–ethyl acetate 20:1) to yield the dihydro-α-pyridones (**3c**—**e**) as white crystalline solids in 14—20% yields.

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