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Tandem [4+2] cycloaddition versus electrocyclisation reactions of 1-aryl-2-phenyl-5-alkyl/aryl-1,3-diazapenta-1,3,4-trienes in aza-Wittig reactions of *N*′-aryl-*N*-(triphenylphosphoranlidene) benzenecarboximidamides with ketenes†

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Abstract—1-Aryl-2-phenyl-5-alkyl/aryl-1,3-diazapenta-1,3,4-triene **3** generated in situ aza-Wittig reactions of *N*′-aryl-*N*-(triphenylphosphoranylidene)carboximidamides **1** which are shown to undergo selective [4+2] cycloaddition and electrocyclisation reactions leading to the formation of novel pyrimidinone derivatives **5** and quinazoline derivatives **7** with monosubstituted ketenes and diphenylketene, respectively.

The utility of iminophosphoranes in synthesis of azadienes and heterocumulene-associated azadienes has been well demonstrated.[1] The azadienes in turn have proved to be promising building blocks in hetero Diels–Alder reactions and in construction of numerous azaheterocyclic and substituted open chain systems.[2] The compounds containing a heterocumulene attached to a vinylic group have exhibited rich chemistry and continue to be the subject of intense investigations.[1,3] However, the compounds containing a heterocumulene attached to a carbon–nitrogen double bond remain unexplored.[4] Rossi et al.[5] have observed that the 1,3-diazabuta-1,3-dienes formed in aza-Wittig reactions of *N*′-aryl-*N*-(triphenylphosphoranylidene)carboximidamides **1** with aldehydes undergo a facile electrocyclic ring closure to yield quinazoline and dihydroquinazoline derivatives. It was felt that a similar aza-Wittig reaction of *N*-imidoyl iminophosphoranes with heterocumulenes viz. ketenes, isocyanates and isothiocyanates may lead to an efficient and convenient route to *N*-imidoyl heterocumulenes. As part of our studies on 1,3-diazabuta-1,3-diene-ketene cycloaddition reactions,[6] we report herein, tandem [4+2] cycloaddition/electrocyclic ring closure of 1-aryl-2-phenyl-5-alkyl/aryl-1,3-diazapenta-1,3,4-trienes **3** formed in aza-Wittig reactions of *N*-imidoyl iminophosphoranes **1** with ketenes.

Thus the treatment the of *N*′-aryl-*N*-(triphenylphosphoranylidene)benzenecarboximidamide **1** with 3 equivalents of chloro-, methyl- and phenylketenes, generated in situ from the corresponding acid chloride in presence of triethylamine, resulted in good yields of products which were characterised as pyrimidinones **5** on the basis of spectral and analytical data.[7] The probable mechanistic pathway that best explains the formation of these pyrimidinones **5** is depicted in Scheme 1. In this mechanism it is assumed that an initial aza-Wittig reaction of *N*′-aryl-*N*-(triphenylphosphoranylidene) benzenecarboximidamide **1** with ketene leads to 1-aryl-5-alkyl/aryl-2-phenyl-1,3-diazapenta-1,3,4-triene **3**. The [4+2] cycloaddition reaction of this intermediate with another molecule of ketene, involving either a stepwise or the recently proposed concerted Diels–Alder type mechanism,[8] leads to the formation of pyrimidinone **4** which finally isomerises to the stable pyrimidinone **5**. It is surprising to note the absence of an electrocyclisation route to the quinazoline derivatives in these reactions as observed by Rossi et al.[5] in similar reactions of *N*-imidoyliminophosphoranes **1** with aldehydes. It may be mentioned that the reactions of **1** with 1.5 equivalents of ketene did not show the complete disappearance of starting material (tlc) while the formation of the pyrimidinone **5** was indicated.

However, similar reactions of *N*-imidoyl iminophosphoranes **1** with diphenylketene did not form pyrimidinone **5** and resulted in good yields of quinazoline derivatives **7**. The quinazolines **7** are presumably the

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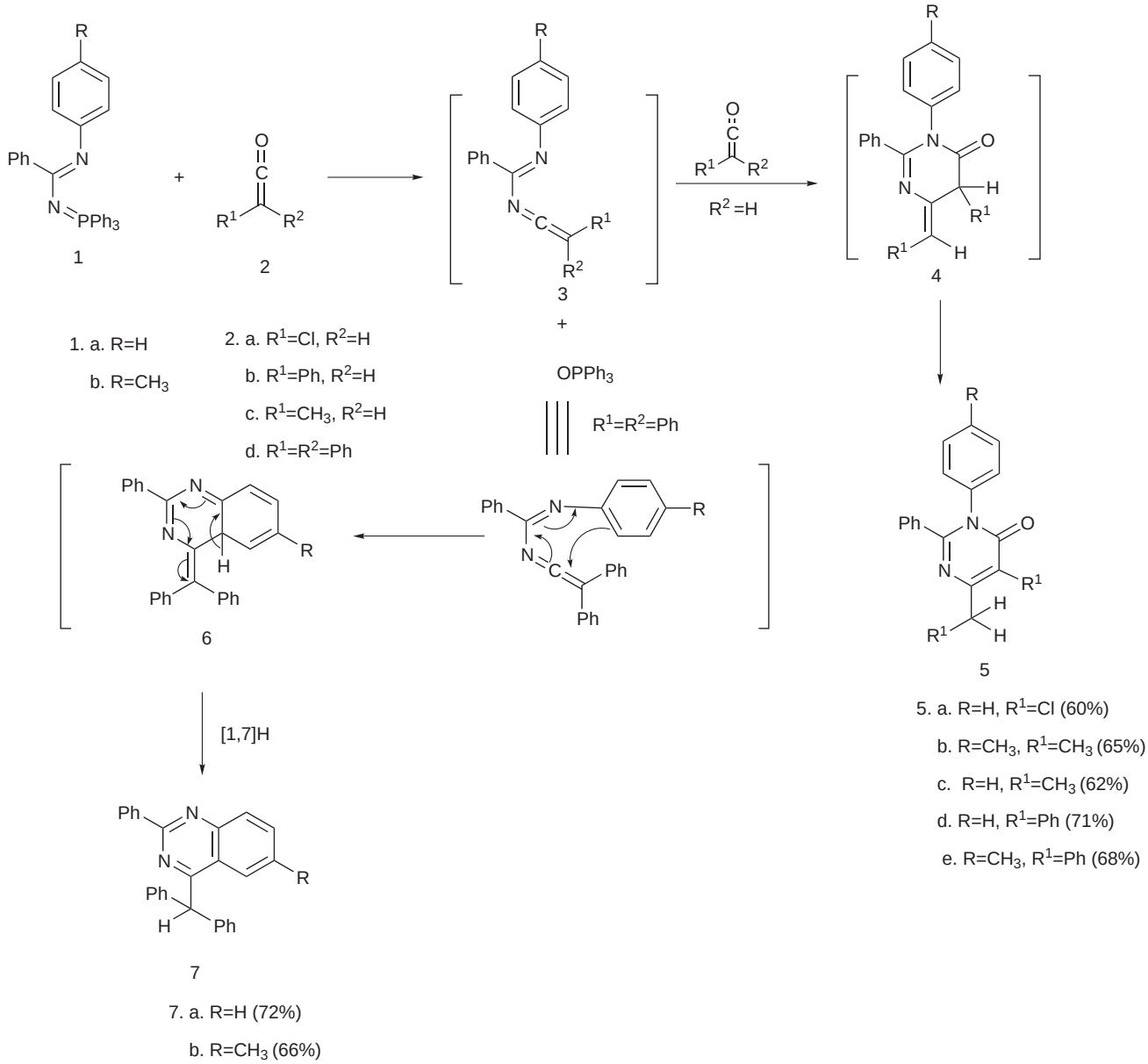

Scheme 1.

result of the electrocyclic ring closure of the intermediate 1-aryl-2-phenyl-5-diphenyl-1,3-diazapenta-1,3,4-triene **3** to yield another intermediate **6** which undergoes a [1,7]H shift to finally yield the aromatic quinazolines **7**. A number of attempts were made to intercept the intermediate **3** in a [4+2] cycloaddition reaction with diphenylketene but such attempts, even with an excess of diphenylketene, resulted invariably in the isolation of quinazoline **7**. It is likely that the geminal diphenyls in the intermediate triene **3** lie orthogonal to the rest of the molecular plane and then the approach of another diphenylketene molecule to this intermediate from either face of the molecular plane is sterically hindered. Therefore, 1,3-diaza-1,3,4-triene **3** is less likely to undergo [4+2] cycloaddition reaction with diphenylketene and the alternative electrocyclic ring closure route to quinazoline **7** is favoured.

In conclusion the previously unknown 1,3-diazapenta-1,3,4-trienes **3** can be easily obtained by the aza-Wittig reactions of *N*-imidoyl iminophosphoranes **1** with monosubstituted/disubstituted ketenes and selectively utilised in intermolecular [4+2] cycloaddition/electrocyclic ring closure reactions for the formation of pyrimidinone **5** and quinazoline **7** derivatives.

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7. **6-Ethyl-5-methyl-3-(*p*-tolyl)-2-phenyl pyrimidine-4-one 5b:** yield: (65%); mp: 158–160°C. Anal. calcd for $C_{20}H_{20}N_2O$: C, 78.92; H, 6.62, N, 9.20; observed: C, 78.90; H, 6.64, N, 9.18. IR (KBr $\nu_{max}cm^{-1}$) 1661, 1551, 1385, 1253. δ_H (200 MHz): 1.08 (t, $J=7.3$, 3H, $-CH_3$); 2.08 (s, 3H, $-CH_3$); 2.29 (q, $J=7.3$, 2H, $-CH_2$); 2.38 (s, 3H, $-CH_3$), 7.03 (d, $J=8.1$, 2H, ArH), 7.16–7.41 (m, 5H, ArH), 7.49–7.55 (m, 2H, ArH). δ_C (50.4 MHz): 11.06 ($-CH_3$), 13.27 ($-CH_3$), 21.12 ($-CH_3$), 226.72 ($-CH_2$), 118.29 (C-5), 127.47, 127.87, 128.58, 128.94, 130.27, 134.71, 138.68, 138.77 (ArC), 157.61 (C-6), 158.51 (C-2), 163.80 (C-4). m/z: 305(M^{+1}), 304(M^+).
2-Phenyl-4-diphenylmethyl-6-methyl quinazoline 7b: yield: (66%); mp: 153–155°C. Anal. calcd for $C_{28}H_{22}N_2$; C, 87.01; H, 5.74; N, 7.25; observed: C, 87.15; H, 5.72; N, 7.26. IR (KBr $\nu_{max}cm^{-1}$) 1559, 1336. δ_H (200 MHz): 2.52 (s, 3H, CH_3); 6.34 (s, 1H, $CHPh_2$); 7.15–7.50 (m, 13H, ArH); 7.63 (d, $J=8.6$, 1H, ArH); 7.87 (s, 1H, ArH); 7.95 (d, $J=8.6$, 1H, ArH); 8.42 (m, 2H, ArH). δ_C (50.4 MHz): 22.1 (CH_3); 54.5 (CH); 122.7, 123.2, 126.7, 128.3, 128.5, 128.6, 135.6, 137.2, 141.6, 150.2, 159.8, 169.2. m/z: 386 (M^+).
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