AZIRIDINATION AND 1,3-DIPOLAR CYCLOADDITION OF 2,6-DIBENZYLIDENECYCLOHEXANONE

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Abstract - 2,6-Dibenzylidenecyclohexanone (**1**), 5-benzylidene-1-(2-alkyl-3,4-dihydro-4-oxoquinazolin-3-yl)-4-oxo-2-phenyl-1-azaspiro[2,5]octane (**3**) and 7-benzylidene-1,3,4-triphenyl-6-oxo-1,2-diazaspiro[4,5]decane (**10**) were aziridinated using 3-acetoxyamino-2-alkylquinazolin-4(3*H*)-ones (**2a-c**) to form 1,6-di-(2-alkyl-3,4-dihydro-4-oxoquinazolin-3-yl)-4-oxo-2,7-diphenyl-1,6-diazadispiro[2,1,2,3]decane (**4a-c**) and 8-(2-alkyl-3,4-dihydro-4-oxoquinazolin-3-yl)-1,3,4,9-tetraphenyl-6-oxo-1,2,8-triazadispiro[2,1,4,3]dodecane derivatives (**9a**) and (**9b**) as single stereoisomers. The stereostructures of **3a** and **9a** were confirmed by X-Ray crystallography.

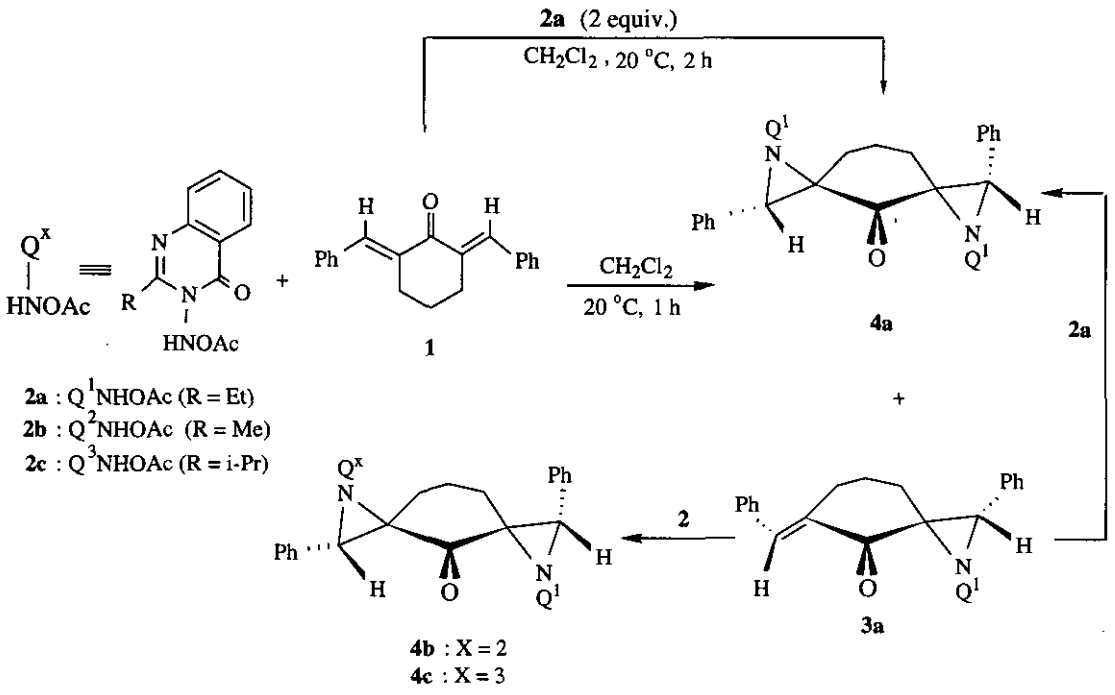
3-Acetoxyaminoquinazolinones (**2a,c**) are efficient aziridination agents for alkenes of widely differing electron availability ranging from silyl ketene acetals to α,β-unsaturated esters and ketones.[1] Efficient aziridination of α,β-unsaturated esters and α,β-unsaturated ketones requires s-*trans* conformations[2] of these substrates and thus 5-, 6-membered ring α,β-unsaturated lactones or ketones are not reactive. Since 2-arylidenecyclohexanones are conformationally locked in the s-*cis* conformation, they would be expected to be efficiently aziridinated by **2a-c** which we find to be the case with compound (**1**). When the 2-position of cyclohexanone is chiral and spiro-substituted, as in compounds (**3**) and (**10**), aziridination is highly diastereoselective.

3-Acetoxyaminoquinazolinone [Q[1]NHOAc] (**2a**) was prepared by the reaction of lead tetraacetate (LTA) with the corresponding 3-aminoquinazolinone at -20 °C as previously described.[1]

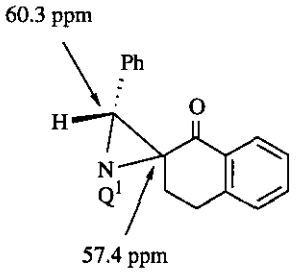
This aziridinating agent (**2a**) (1 equiv.) converted 2,6-dibenzylidenecyclohexanone (**1**) (1 equiv.) into a mixture of 5-benzylidene-1-(2-alkyl-3,4-dihydro-4-oxoquinazolin-3-yl)-4-oxo-2-phenyl-1-azaspiro[2,5]-octane (**3**), and 1,6-di-(2-alkyl -3,4-dihydro-4-oxoquinazolin-3-yl)-4-oxo-2,7-diphenyl-1,6-diazadispiro-[2,1,2,3]decane (**4a**) in a ratio of 7 : 3 (Scheme 1).

Since aziridinations using Q^1NHOAc (**2a**) are stereospecific with retention of the alkene configuration in the product, the relative configuration at the two chiral centres in **3a** is as shown and is confirmed by X-Ray crystallography (Figure 1).

The ^{13}C NMR spectrum of *mono*-aziridine (**3a**) showed signals for the C-H and *spiro* carbons in the aziridine ring at δ 62.45 and 58.14 ppm respectively and these chemical shifts correspond to those of the respective nuclei in the ^{13}C spectra of 1-tetralone-2-spiro-2'-[1'-(2-ethyl-3,4-dihydro-4-oxoquinazolin-3-yl)-3'-phenyl]aziridine (**5**) and 1-indanone-2-spiro-2'-[1'-(2-ethyl-3,4-dihydro-4-oxoquinazolin-3-yl)-3'-phenyl]aziridine (**6**).



Scheme 1



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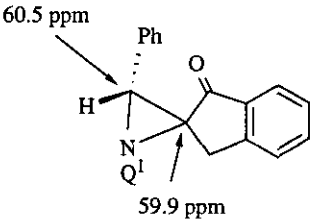

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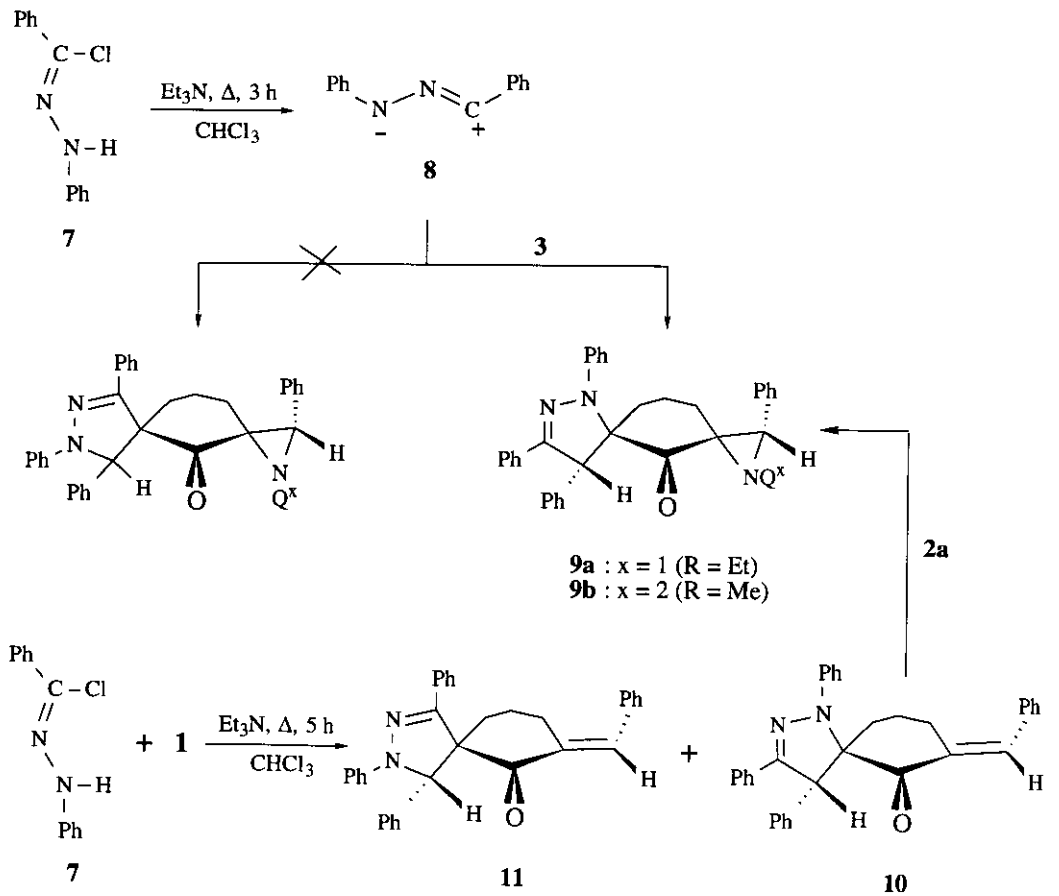
These compounds (**5**) and (**6**) were prepared by aziridination of 2-benzylidene-1-tetralone and 2-benzylidene-1-indanone respectively in good yield using Q^1NHOAc (**2a**) by the same method used to prepare compound (**3**).

Bisaziridine (**4a**) was formed as a single diastereoisomer. As expected, further aziridination of the *mono*-aziridinated compound (**3a**) with Q^1NHOAc (**2a**) gave the diastereoisomer (**4a**) in good yield and also, the aziridination of **3a** with **2b** and **2c** [Q^XNHOAc, x = 2, 3] gives diastereoisomer products (**4b**) and (**4c**), respectively. The diastereoisomer (**4a**) was also prepared by the aziridination of **1** (1 equiv.) with Q^1NHOAc (**2a**) (2 equiv.) (Scheme 1). The ^{1}H NMR spectrum of **4a** showed one characteristic singlet at δ 4.02 ppm (2H) assignable to the isochronous aziridine ring protons.

The unreacted double bond in the *mono*aziridines (**3a**) and (**3b**) underwent the regiospecific and completely stereoselective 1,3-dipolar cycloaddition with in *situ* generated benzonitrilium *N*-phenylimide (**8**) to produce 8-(2-alkyl-3,4-dihydro-4-oxoquinazolin-3-yl)-1,3,4,9-tetraphenyl-6-oxo-1,2,8-triazadispiro[2,1,4,3]-dodecane derivatives (**9a**) and (**9b**), the stereostructure of **9a** being confirmed by an X-Ray crystal structure determination (Figure 2).



Scheme 2

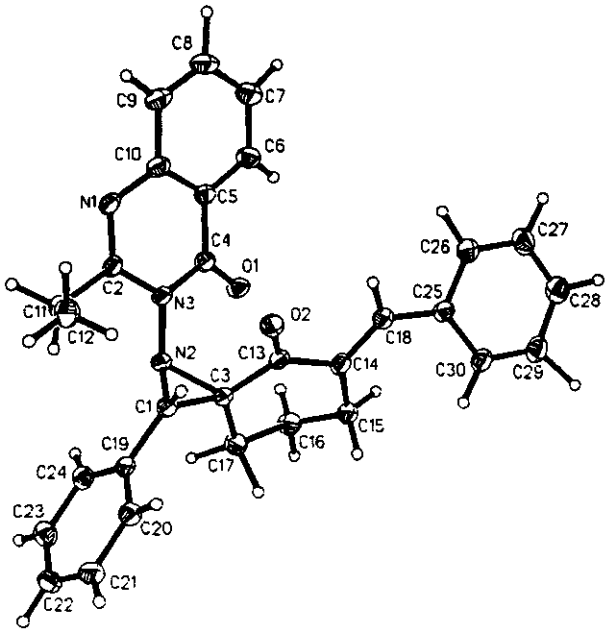


Figure 1. X-Ray structure of 3a

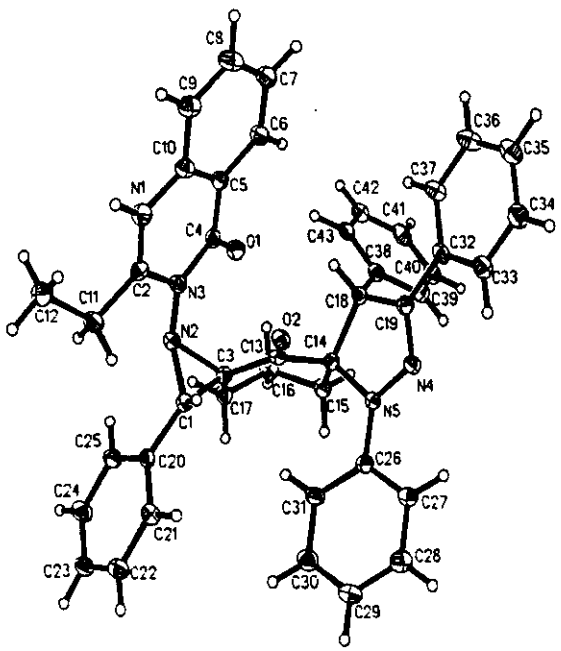


Figure 2. X-Ray structure of 9a

The same diastereoisomer (**9a**) was obtained by aziridination of the unreacted double bond in the major cycloadduct (**10**) formed by a 1,3-dipolar cycloaddition to 2,6-dibenzylidenecyclohexanone (**1**) by comparing ^{1}H, ^{13}C NMR, and mixed melting point of the product (**9a**) from the two methods. The stereochemistry of the diastereoisomer (**9**) corresponds to the 1,3-dipolar addition at the diastereoface opposite to the aziridine nitrogen atom of the dibenzylidenecyclohexanone.

It appears that the presence of the aziridine ring dictates not only the face of the double bond remaining in compound (**3**) which is attacked by the 1,3-dipole but also affects its regioselectivity of the cycloaddition since reaction of 2,6-dibenzylidenecyclohexanone (**1**) with *C,N*-diphenylhydrazonoyl chloride (**7**) gives two regioisomers (**10**) and (**11**) in the ratio of 7 : 3 (Scheme 2). It is known that the cycloaddition of nitrilimide (**8**) to α,β-unsaturated ketones (including benzalacetone[3]) leads normally to a mixture of two regioisomeric 4,5-dihydropyrazoles.[4]

The facial selectivity of the 1,3-dipolar cycloaddition to the diastereoisomer (**3**), i.e. attack on the double bond anti to the NQ residue of the aziridine as revealed by the crystal structure of **9a**, suggests that the relative configuration of the two aziridines in **4** is probably also trans.

EXPERIMENTAL

All melting points are uncorrected. Infrared spectra (KBr) were measured on a Perkin-Elmer 298 spectrophotometer or on a Nicolet Magna 520 FT-IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were obtained in deuteriochloroform on a Varian DPX-400 FT-NMR spectrometer using tetramethylsilane as internal reference. Microanalyses were performed on a 2400 Perkin Elmer Series 2 CHNS analyser in King Abdulaziz university, Jeddah. Standard MS were recorded on either a Micromass 16B spectrometer or a Kratos 'concept' 1H. Accurate mass measurements were made on the latter at Leicester University. The the 3-amino-2-alkylquinazolin-4(3*H*)-one derivatives (**2**) and *C,N*-diphenylhydrazonoyl chloride (**7**) were prepared as previously described.[5]

Preparation of 5-benzylidene-1-(2-alkyl-3,4-dihydro-4-oxoquinazolin-3-yl)-4-oxo-2-phenyl-1-azaspiro[2, 5]octane. General method - To a solution of 2,6-dibenzylidenecyclohexanone (**1**) (1.37 g, 5 mmol) in dry CH_2Cl_2 (10 mL) was added the appropriate 3-acetoxyamino-2-alkylquinazolin-4(3*H*)-one derivative (**2**) (6 mmol) for 20 min at -20 °C [prepared by the reaction of LTA (6.5 mmol) in CH_2Cl_2 (10 mL) with 3-amino-2-alkylquinazolin-4(3*H*)-one (**2**) (6 mmol) at -20 °C for 20 min]. Then the reaction mixture left stirring for 1 h at r t. The TLC [using pet. ether : ethyl acetate (8 : 2 v/v) as eluant] indicated that the reaction mixture contained only two products (R_f 0.71 for the *mono*aziridine and R_f 0.61 for the bisaziridine). After ordinary working up, the ^{1}H NMR spectrum for the residue showed that these two products found in ratio of 7 : 3. The residue was then triturated with small amount of ethyl acetate where upon it solidified. The crude solid was collected and double recrystallization from ethyl acetate gave the corresponding *mono*aziridine (**3**) as the major product. The minor product bisaziridine (**4**) was found in the

filtrate. The filtrate was then evaporated and the residue was recrystalized from ethyl acetate to give diastereoisomer (**4**) or purify by column chromatography using pet. ether : ethyl acetate (8 : 2 v/v) as eluant. Compound (**3a**) had mp 196-197 °C, 57 %; ^{1}H NMR : δ ($CDCl_3$) 1.26 (t, J = 7 Hz, 3H, CH_3), 1.55 (m, 1H), 1.86 (m, 1H), 2.26 (m, 1H), 2.53 (m, 1H), 2.73 (q, J = 7 Hz, 2H, CH_2), 3.11 (m, 2H), 4.59 (s, 1H, C-H anisochronous proton), 7.24-7.86 (m, 14H, Ar-H) and 8.13 (d, J = 6 Hz, 1H, H-5 in the quinazolinone) ppm; ^{13}C NMR : δ ($CDCl_3$) 188.7 (C=O), 159.9 (NC=O), 62.4 (anisochronous carbon), 58.1 (*spiro* centre), 28.0 (CH_2), 11.5 (CH_3) and 28.9, 27.0, 21.1 ppm for the three CH_2 in the cyclohexanone; MS (EI) (%) : 461 (M^+, 07), 287 (100), 260 (12), 298 (10), 173 (55), 157 (11), 129 (18), 118 (19), 105 (38), 91 (16), 77 (13), 51 (09); MS (FAB) (%) : 462 (M^++1, 38), 288 (48), 260 (08). Anal. Calcd for $C_{30}H_{27}N_3O_2$: C, 78.07; H, 5.90; N, 9.10. Found : C, 77.83; H, 6.09; N, 8.83.

Compound (**3b**) had mp 188 °C, 63 %; ^{1}H NMR : δ ($CDCl_3$) 1.54 (m, 1H), 1.71 (m, 1H), 2.21 (m, 1H), 2.48 (m, 1H), 2.63 (s, 3H, CH_3), 3.07 (m, 2H), 4.54 (s, 1H, C-H anisochronous proton), 7.21-7.83 (m, 14H, Ar-H) and 8.11 (d, J = 6 Hz, 1H, H-5 in the quinazolinone) ppm; ^{13}C NMR : δ ($CDCl_3$) 188.9 (C=O), 159.7 (NC=O), 62.0 (anisochronous carbon), 58.4 (*spiro* centre), 23.7 (CH_3) and 28.9, 27.1, 21.0 ppm for the three CH_2 in the cyclohexanone.

Synthesis of 1,6-di-(2-alkyl-3,4-dihydro-4-oxoquinazolin-3-yl)-4-oxo-2,7-diphenyl-1,6-diazadispiro-[2,1,2,3]decane (4a-c) . The *mono*aziridine (**3a**) was aziridinated by the above general procedure, using the appropriate 3-acetoxyamino-2-alkylquinazolin-4(3*H*)-one derivative (**2**). The residue was triturated with small amount of ethyl acetate where upon it solidified. The crude solid was collected and recrystallisation from ethyl acetate gave the corresponding bisaziridines (**4a-c**).

Compound (**4a**) had mp 183-184 °C, 83 %; IR : υ (KBr) 1710 (C = O) cm^{-1}; ^{1}H NMR : δ ($CDCl_3$) 1.17 (t, J = 7 Hz, 6H, $2CH_3$), 1.52 (m, 3H), 1.98 (m, 1H), 2.19 (m, 2H), 2.76 (q, J = 7 Hz, 4H, $2CH_2$), 4.02 (s, 2H, 2C-H anisochronous protons), 7.17-7.70 (m, 16H, Ar-H) and 8.16 (d, J = 6 Hz, 2H, 2H-5 in the quinazolinone) ppm; ^{13}C NMR : δ ($CDCl_3$) 186.8 (C=O), 158.4 and 158.2 (2NC=O), 61.5 & 60.1 (anisochronous carbons), 55.5 and 55.4 (two *spiro* centres), 27.6 and 27.5 ($2CH_2$), 10.5 and 10.3 ($2CH_3$) and 26.4, 26.2, 17.5 ppm for the three CH_2 in the cyclohexanone; MS (FAB) (%) : 650 (M^++1, 100), 610 (06), 593 (04), 576 (03), 649 (07), 460 (04), 391 (02), 289 (08), 175 (07). Anal. Calcd for $C_{40}H_{36}N_6O_3$: C, 74.06; H, 5.59; N, 12.95. Found : C, 74.23; H, 5.71; N, 13.19.

Compound (**4b**) had 77 %; IR : υ (KBr) 1709 (C = O) cm^{-1}; ^{1}H NMR : δ ($CDCl_3$) 1.24 (t, J = 7 Hz, 3H, CH_3), 1.51 (m, 3H), 1.96 (m, 1H), 2.21 (m, 2H), 2.63 (s, J = 7 Hz, 3H, CH_3), 2.70 (q, J = 7 Hz, 2H, CH_2), 3.93 (s, 2H, 2C-H anisochronous protons), 7.15-7.71 (m, 16H, Ar-H) and 8.13 (d, J = 6 Hz, 2H, 2H-5 in the quinazolinone) ppm.

Compound (**4c**) had mp 194-195 °C, 57%; IR : υ (KBr) 1710 (C = O) cm^{-1}; H NMR : δ ($CDCl_3$) 1.17 (t, J = 7 Hz, 3H, CH_3), 1.25 (d, J = 7 Hz, 3H, CH_3), 1.33 (d, J = 7 Hz, 3H, CH_3), 1.52 (m, 3H), 1.98 (m, 1H), 2.19 (m,2H), 2.60 (m, 1H, C<u>H</u>Me_2), 2.76 (q, J = 7 Hz, 2H, CH_2), 3.97 (s, 2H, 2C-H anisochronous proton),

7.17-7.70 (m, 16H, Ar-H) and 8.16 (d, J = 6 Hz, 2H, 2H-5 in the quinazolinone)ppm; ^{13}C NMR : δ ($CDCl_3$) 186.5 (C=O), 158.2 and 158.1 (2NC=O), 61.4 and 60.3 (anisochronous carbons), 55.6 and 55.3 (two *spiro* centres), 26.6 (CH_2), 9.4 (CH_3), 29.0 ($\underline{C}HMe_2$), 20.5 and 18.7 ($CH\underline{Me}_2$) and 26.2, 26.1, 17.0 ppm for the three CH_2 in the cyclohexanone. Anal. Calcd for $C_{41}H_{38}N_6O_3$: C, 74.30; H, 5.78; N, 12.67. Found : C, 73.99; H, 5.68; N, 12.46.

Alternate synthesis for bisaziridine (4a). To a solution of 3-acetoxyamino-2-ethylquinazolin-4(3*H*)-one (**2a**) (2.47 g, 10 mmol) in CH_2Cl_2 (20 mL) was added 2,6-dibenzylidenecyclohexanone (**1**) (1.37 g, 5 mmol) at -20 °C. The reaction mixture was left stirring for 2 h at r t. The residue was triturated with small amount of ethyl acetate where upon it solidified. The crude solid was collected and recrystallised from ethyl acetate. The product was found identical in all respects (mix. mp, spectra) with the bisaziridine (**4a**).

Synthesis of 1-tetralone-2-spiro-2'-[1'-(2-ethyl-3,4-dihydro-4-oxoquinazolin-3-yl)-3'-phenyl]aziridine (5) and 1-indanone-2-spiro-2'-[1'-(2-ethyl-3,4-dihydro-4-oxoquinazolin-3-yl)-3'-phenyl]aziridine (6). Each of the 2-benzylidene-1-tetralone and 2-beznylidene-1-indanone was aziridinated by the above general method. The crude solid was recrystallised from ethanol to give aziridines (**5**) and (**6**).
Compound (**5**) had 181°C, 83 %; ^{1}H NMR : δ ($CDCl_3$) 1.29 (t, J = 7 Hz, 3H, CH_3), 1.88 (m, 1H), 2.26 (m, 1H), 2.53 (m, 1H), 2.70 (m, 1H), 2.86 (q, J = 7 Hz, 2H, CH_2), 4.52 (s, 1H, C-H anisochronous proton), 7.14-7.62 (m, 11H, Ar-H), 7.78 (d, J = 6 Hz, 1H) and 8.03 (d, J = 6 Hz, 1H, H-5 in the quinazolinone)ppm; ^{13}C NMR : δ ($CDCl_3$) 188.0 (C=O), 160.1 (NC=O), 60.3 (anisochronous carbon), 57.4 (*spiro* centre), 26.8 (CH_2), 11.4 (CH_3) and 28.1 and 26.7 ppm for the two CH_2 in the tetralone; MS (%) : 421 (M^+, 53), 318 (47), 302 (23), 248 (100), 173 (21), 157 (12), 130 (31), 115 (38), 90 (31), 77 (28), 63 (12).
Compound (**6**) had mp 201 °C, 73 %; ^{1}H NMR : δ ($CDCl_3$) 1.32 (t, J = 7 Hz, 3H, CH_3), 2.88 (q, J = 7 Hz, 2H, CH_2), 3.07 (d, J = 8 Hz, 1H), 3.80 (d, J = 8 Hz, 1H), 4.26 (s, 1H, C-H anisochronous proton), 7.21-7.80 (m, 12H, Ar-H) and 8.05 (d, J = 6 Hz, 1H, H-5 in the quinazolinone) ppm; ^{13}C NMR : δ ($CDCl_3$) 194.2 (C=O), 159.7 (NC=O), 60.5 (anisochronous carbon), 59.9 (*spiro* centre), 27.7 (CH_2), 10.7 (CH_3) and 31.1 ppm for the CH_2 in the indanone; MS (%) : 407 (M^+, 16), 378 (09), 234 (100), 219 (26), 191 (13), 173 (27), 157 (13), 130 (29), 102 (14), 76 (18), 63 (07). Anal. Calcd for $C_{26}H_{21}N_3O_2$: C, 76.64; H, 5.20; N, 10.31. Found : C, 76.93; H, 5.28; N, 10.13.

Synthesis of 7-benzylidene-1,3,4-triphenyl-6-oxo-1,2-diazaspiro[4,5]decane (10). To a solution of 2,6-dibenzylidenecyclohexaone (**1**) (5.48 g, 0.02 mol) and *C,N*-diphenylhydrazonoyl chloride (**7**) (4.61 g, 0.02 mol) in dry $CHCl_3$ (30 mL) was added triethylamine (2.22 g, 0.022 mol) at r t. The mixture was refluxed for 4 h. The solvent was then evaporated. The ^{1}H NMR spectrum for the residue showed that the two cycloadducts (**10**) and (**11**) were formed in ratio 7 : 3 . The residue was triturated with a small amount of methanol where upon it solidified. The curde solid was collected and recrystallisation from ethanol gave

the corresponding cycloadduct (**10**), mp 111-112 °C; yield 76%; ^{1}H NMR : δ ($CDCl_3$) 1.14-2.27 (m, 6H, $3CH_2$), 4.93 (s, 1H, 4-H pyrazole), 6.78-7.67 (m, 21H, Ar-H) ppm ; ^{13}C NMR : δ ($CDCl_3$) 198.3 (C = O), 148.4 (C = N in the pyrazole ring), 81.8 (*spiro* centre), 63.1 (4-CH in the pyrazole ring), 29.9, 28.7, 19.8 ppm for the three CH_2 in the cyclohexanone MS (%) : 468 (M^+, 17), 412 (06), 323 (15), 287 (100), 246 (10), 173 (19), 128 (38), 105 (53), 77 (51), 55 (22). Anal. Calcd for $C_{33}H_{28}N_2O$: C, 84.59; H, 6.02; N, 5.98. Found : C, 84.96; H, 6.24; N, 5.82.

Synthesis of 8-(2-alkyl-3,4-dihydro-4-oxoquinazolin-3-yl)-1,3,4,9-tetraphenyl-6-oxo-1,2,8-triazadispiro[2,1,4,3]dodecane derivatives (9a) and (9b). To a solution of the appropriate *mono*aziridine (**3**) (5 mmol) and *C,N*-diphenylhydrazonoyl chloride (**7**) (1.15 g, 5 mmol) in dry $CHCl_3$ (30 mL) was added triethylamine (0.61 g, 6 mmol) . The mixture was refluxed with stirring for 5 h. The solvent was then evaporated and the residue was triturated with a small amount of methanol where upon it solidified. The curde solid was collected and recrystallization from ethanol gave diastereoisomer (**9**).

Compound (**9a**) : mp : 190-191 °C, yield 79%, R_f 0.53 [Pet. ether : ethyl acetate (8 : 2 v/v)], ^{1}H NMR, δ ($CDCl_3$) 1.14 (t, J = 7 Hz, 3H, CH_3), 1.17-2.37 (m, 6H, $3CH_2$), 2.68 (q, J = 7 Hz, 2H, CH_2), 4.15 (s, 1H, anisochronous proton), 5.47 (s, 1H, CH in the pyrazole), 6.74-7.63 (m, 23H, Ar-H) and 8.04 (d, J = 6 Hz, 1H, H-5 in the quinazolinone) ppm ^{13}C NMR : δ ($CDCl_3$) 202.0 (C=O), 159.3 (NC=O), 62.9 (anisochronous carbon), 62.6 (C-H in the pyrazole ring), 55.9 (*spiro* centre of the aziridine ring), 75.6 (*spiro* centre of the pyrazole ring), 26.4 (CH_2), 10.0 (CH_3) and 27.0, 26.4, 17.8 ppm for the three CH_2 in the cyclohexanone; MS (FAB) (%) : 656 (M^++1, 19), 454 (17), 401 (23), 355 (28), 327 (29), 281 (83), 221 (53), 147 (100) 231 (55).

Compound (**9b**) had mp 195°C; 79 %, ^{1}H NMR, δ ($CDCl_3$) 1.13-2.28 (m, 6H, $3CH_2$), 2.52 (s, 3H, CH_3), 4.20 (s, 1H, anisochronous proton), 5.51 (s, 1H, CH in the pyrazole), 6.75-7.67 (m, 23H, Ar-H) and 8.05 (d, J = 6 Hz, 1H, H-5 in the quinazolinone) ppm; ^{13}C NMR : δ ($CDCl_3$) 203.4 (C=O), 159.6 (NC=O), 63.8 (anisochronous carbon), 64.0 (C-H in the pyrazole ring), 57.6 (spiro centre of the aziridine ring), 77.2 (*spiro* centre of the pyrazole ring), 23.3 (CH_3) and 28.4, 27.8, 19.1 ppm for the three CH_2 in the cyclohexanone; MS FAB (%) : 642 (M^++1, 36), 454 (39), 376 (12), 483 (23), 466 (25), 454 (42), 376 (13), 349 (33), 323 (74), 132 (79); Calcd 641.742, $C_{42}H_{35}N_5O_2$, Found: 641.27883.

Aziridination of cycloadduct (10). To a solution of 3-acetoxyamino-2-ethylquinazolin-4(3*H*)-one (**2a**) (1.24 g, 5 mmol) in dry CH_2Cl_2 (15 mL) was added the cycloadduct (**10**) (2.34 g, 5 mmol) for 30 min at -20 °C. The reaction mixture was left stirring for 2 h at r t. The TLC for the reaction mixture showed that a new spot appeared R_f 0.53 [pet. ether : ethyl acetate (8 : 2 v/v)]. After normal working up. The residue left was triturated with ethyl acetate where upon it solidified. The crude solid was collected and recrystallised twice from ethyl acetate. The product (yield 17%) was found identical in all respects (mix. mp, spectra) with the diastereomer (**9a**)..

Crystal data - Unit cell parameters for **3a** and **9a** were determined by least squares refinement of the optimised setting angles of respectively 37 and 27 reflections in the range $4.5 < q < 12.5^{o}$. Intensity data were measured on a Siemens P4 diffractometer at 190 K using as ω scan method and the data were corrected for Lorentz and polarisation effects. The structures were solved by direct methods using the program SHELXTL-PC[6] and refined by full-matrix least squares on F[7] using the program SHELX-93[7]. All hydrogen atoms were included in calculated positions C-H = 0.96 Ao. All nonhydrogen atoms were refined with anisotropic displacement parameters.

For **3a** : $C_{30}H_{27}N_3O_2$, M = 461.44, Triclinic, space group P1, a = 8.601(2), b = 9.639(2), c = 14.662(2) Å, α = 84.07(2), β = 77.53(2), γ = 82.80(2)°, V = 1173.9(4)Å^3, Z = 2, D_C = 1.306 Mg m^{-3}, F(000) = 488, μ = 0.083 mm^{-1}, λ (Mo-K_α) = 0.7107 Å. The crystal used for data collection was a colourless block with the approximate dimensions 0.59 x 0.35 x 0.17 mm. Intensity data for 4011 reflections were measured with 3253 independent reflections (R_{int} = 0.0352). Final cycles of refinement gave R1 = 0.071, wR_2 = 0.219 for all data with 316 variables, $R1 = \sum || Fo | - | Fc || \setminus \sum | Fo |$, $wR\,2 = [\sum w (Fo^2 - Fc^2)^2 \setminus \sum w (Fo^2)^2]^{0.5}$, $w = 1 \setminus [\sigma^2 (Fo^2) + 0.0925\,P)^2 + 1.59\,P]$ and $P = [\max (Fo^2, 0) + 2\,F\,c^2] / 3$. and $P = [\max (Fo^2, 0) + 2f\,c^2] / 3$. The maximum and minimum electron densities in the final ΔF map were 0.57 and -0.27 e Å^{-3} respectively.

For **9a** : $C_{43}H_{37}N_5O_2$, M = 655.78, Triclinic, space group P1, a = 9.938(4), b = 13.152(5), c = 13.507 (5) Å, α = 82.43(2), β = 85.69(2), γ = 72.48(2)°, V = 1667.7(4)Å^3, Z = 2, D_C = 1.306 Mg m^{-3}, F(000) = 692, μ = 0.082 mm^{-1}, λ (Mo-K_α) = 0.7107 Å. The crystal used for data collection was a colourless plate with the approximate dimensions 0.39 x 0.36 x 0.08 mm. Intensity data for 5246 reflections were meas ured with 4341 independent reflections (R_{int} = 0.0275). Final cycles of refinement gave R1 = 0.046, wR_2 = 0.114 for all data with 451 variables, $R1 = \sum || Fo | - | Fc || \setminus \sum | Fo |$, $wR\,2 = [\sum w (Fo^2 - Fc^2)^2 \setminus \sum w (Fo^2)^2]^{0.5}$, $w = 1 \setminus [\sigma^2 (Fo^2) + 0.0490\,P)^2 + 0.09\,P]$ and $P = [\max (Fo^2, 0) + 2\,F\,c^2] / 3$. The max imum and minimum electron densities in the final ΔF map were 0.16 and -0.19 e Å^{-3} respectively.

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