New Heterospiro-ring Systems by Condensation of Some Heterocyclic *o*-Dicarboxylates with 1,3-Diphenylguanidine

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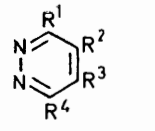
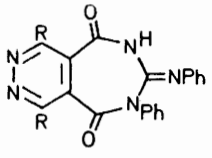
The behaviour of some heterocyclic *o*-dicarboxylates towards 1,3-diphenylguanidine and sodium hydride was investigated. Whereas the pyridine and isothiazole derivatives (11) and (22) gave the amides (12) and (13), and (23), respectively, as the main products, the pyrimidine and isoxazole esters (17) and (24) afforded, through a spiro-cyclization reaction, the heterospiro-compounds (20) and (26). The structures of these new ring systems were established on the basis of chemical and spectroscopic data.

RECENT studies in our laboratory [1,2] pointed out a feature, hitherto unknown, in the chemistry of pyridazine derivatives. When the esters (1)—(3) were allowed to react with 1,3-diphenylguanidine (DPG) in the presence of sodium hydride, the expected pyridazinodiazepines (5)—(7) were not obtained, but we isolated the tetra-azaspirodecadienes (8)—(10) in high yields.

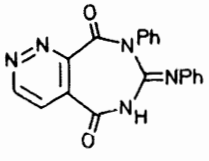
The presence of a strongly electron-withdrawing group at the 3- or 5-position was shown to play a determinant role for the spiro-cyclization, which could also be carried out with carbon 1,3-binucleophiles.[1] In order to ascertain the potential and the limits of this new reaction as a route for the synthesis of heterospiro-ring systems, we investigated the behaviour towards DPG of some



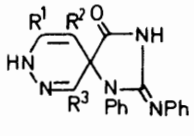
(1) $R^1 = R^4 = H$, $R^2 = R^3 = CO_2Et$
(2) $R^1 = R^4 = Me$, $R^2 = R^3 = CO_2Et$
(3) $R^1 = R^2 = CO_2Et$, $R^3 = R^4 = H$
(4) $R^1 = R^4 = Me$, $R^2 = CO_2Et$, $R^3 = CO{-}NH{-}C(=NPh){-}NHPh$



(5) R = H
(6) R = Me



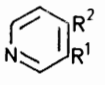
(7)



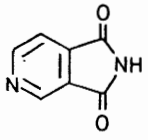
(8) $R^1 = R^3 = H$, $R^2 = CO_2Et$
(9) $R^1 = R^3 = Me$, $R^2 = CO_2Et$
(10) $R^1 = R^2 = H$, $R^3 = CO_2Et$

SCHEME 1

azaheterocyclic *o*-dicarboxylates with a CO_2R group *para* to the ring nitrogen. Several attempts to obtain spiro-compounds from diethyl pyridine-3,4-dicarboxylate (11) and DPG under different conditions were unsuccessful; the reaction always afforded a mixture of the pyridine derivatives (12)—(14), *O*-ethyl-*NN'*-diphenylisourea (15), and *NN'*-diphenylurea (16), which were separated by a careful column chromatography and identified by spectral evidence or by comparison with authentic samples (see Table and Experimental section).



(11) $R^1 = R^2 = CO_2Et$
(12) $R^1 = CO_2Et$, $R^2 = CO{-}NH{-}C(=NPh){-}NHPh$
(13) $R^1 = CO{-}NH{-}C(=NPh){-}NHPh$, $R^2 = CO_2Et$



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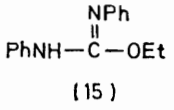

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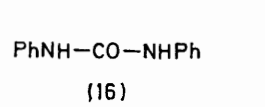

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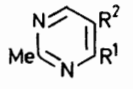
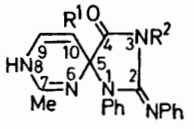


(17) $R^1 = R^2 = CO_2Et$
(18) $R^1 = CO_2Et$, $R^2 = H$
(19) $R^1 = CO{-}NH{-}C(=NPh){-}NHPh$, $R^2 = H$



(20) $R^1 = CO_2Et$, $R^2 = H$
(21) $R^1 = CO_2Et$, $R^2 = Me$

SCHEME 2

Conversely diethyl 2-methylpyrimidine-4,5-dicarboxylate (17) condensed smoothly with DPG and sodium hydride in anhydrous tetrahydrofuran at room temperature to give ethyl 4-oxo-7-methyl-1-phenyl-2-(phenylimino)-1,3,6,8-tetra-azaspiro[4.5]deca-6,9-diene-10-carboxylate (20), whose structure followed from spectral evidence. The amidic and the conjugated ester CO groups give rise to a strong band at about 1 700 cm^{-1} in the i.r. spectrum, which closely resembled those of compounds (8) and (10). Although the H-9 signal was masked in the ^1H n.m.r. spectrum by the pattern of the phenyl and NH protons both in $CDCl_3$ and $(CD_3)_2SO$ solutions, the dihydropyrimidine moiety was strongly supported by the remarkable upfield shift of the 7-Me

TABLE

^{1}H N.m.r. spectra [90 MHz, δ values (*J*/Hz), from internal $SiMe_4$ as reference], in $CDCl_3$ unless stated otherwise

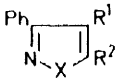
Compound	δ	Assignment
(12)	1.30 (t) } (7)	*Me*–CH_2–O
	4.31 (q) }	Me–*CH_2*–O
	7.15—7.45 (m)	Ph, 5-H, and NH
	8.54 (d)	6-H
	9.16 (s)	2-H
	9.6 (br s) [a]	NH
(13)	1.32 (t) } (7)	*Me*–CH_2–O
	4.29 (q) }	Me–*CH_2*–O
	7.2—7.5 (m)	Ph and NH
	7.67 (d) } (5)	5-H
	8.68 (d) }	6-H
	8.83 (s)	2-H
	9.33 (br s) [a]	NH
(15)	1.31 (t) } (7)	*Me*–CH_2–O
	4.34 (q) }	Me–*CH_2*–O
	5.45 (br s) [a]	NH
	6.8—7.3 (m)	Ph
(17)	1.41 (m)	2 × *Me*–CH_2–O
	2.83 (s)	2-Me
	4.46 (m)	2 × Me–*CH_2*–O
	9.18 (s)	6-H
(18)	1.41 (t) } (7)	*Me*–CH_2–O
	2.83 (s) }	2-Me
	4.40 (q) (7)	Me–*CH_2*–O
	7.77 (d) } (5)	5-H
	8.83 (d) }	6-H
(19)	2.52 (s)	2-Me
	6.9—7.8 (m)	2 × Ph
	7.85 (d) } (5)	5-H
	8.85 (d) }	6-H
	9.85 (br s) [a]	NH
	10.40 (br s) [a]	NH
(20)	1.19 (t) (7)	*Me*–CH_2–O
	1.94 (s)	7-Me
	4.13 (q) (7)	Me–*CH_2*–O
	7.0—7.55 (m)	2 × Ph, 9-H, and 2 × NH
(20) [b]	1.15 (t) (7)	*Me*–CH_2–O
	1.94 (s)	7-Me
	4.05 (q) (7)	Me–*CH_2*–O
	6.9—7.6 (m)	2 × Ph, 9-H, and NH
	9.85 (br s) [a]	NH
(21)	1.24 (t) (7)	*Me*–CH_2–O
	1.91 (s)	7-Me
	3.21 (s)	3-NMe
	4.16 (q) (7)	Me–*CH_2*–O
	6.45—7.0 (m)	2 × Ph
	7.24 (s)	9-H
	8.60 (br s) [a]	8-NH
(22) [b]	3.88 (s)	CO_2Me
	3.93 (s)	CO_2Me
	7.46—7.80 (m)	Ph
(23) [b]	3.73 (s)	CO_2Me
	7.2—7.75 (m)	3 × Ph and NH
	10.22 (br s) [a]	NH
(24)	3.86 (s)	CO_2Me
	3.95 (s)	CO_2Me
	7.35—7.53 (m)	Ph (3 H)
	7.6—7.78 (m)	Ph (2 H)
(25)	3.45 (s)	2-NMe
	3.68 (s)	CO_2Me
	7.35—7.65 (m)	Ph
(26) [b]	3.15 (s)	CO_2Me
	7.0—7.7 (m)	3 × Ph and 2 × NH
(27)	2.90 (s)	2-NMe
	3.22 (s)	8-NMe
	3.30 (s)	CO_2Me
	6.5—7.5 (m)	3 × Ph
(28)	3.08 (s)	2-NMe
	3.31 (s)	CO_2Me
	3.98 (s)	9-OMe
	6.4—7.0 (m)	2 × NPh
	7.36 (s)	3-Ph

[a] Signal disappears on deuteriation. [b] In $(CD_3)_2SO$.

resonance with respect to those of same group of compounds (17)—(19) (Table). On the other hand the spectrum of the *N*-methyl derivative (21), easily obtained from (20) with ethereal diazomethane, clearly showed a singlet at δ 7.24 attributable to a dihydropyrimidine ring proton. The spiro-structure (20) was unambiguously confirmed by the proton-coupled ^{13}C n.m.r. spectrum in $(CD_3)_2SO$, characterized by two singlets at δ 79.7 and 96.7, which were assigned to the quaternary carbons at the 5- and 10-position respectively.

The stability of the 1,4-dihydropyridazine spiro-compounds in solution largely depended both on the nature of the solvent and the position of the substituents.[1,2] For example the dimethyl derivative (9) exists almost exclusively in a spiro-structure in $(CD_3)_2SO$ solution,[1] but it gives rise to a ring–chain tautomerism between the structures (9) and (4) when it is dissolved in $CDCl_3$. Besides two singlets at δ 2.06 and 2.08 for the methyl groups of (9) (80—82%), the ^{1}H n.m.r. spectrum exhibits two signals at δ 2.65 and 2.70 attributable to the same groups of the form (4) (18—20%).

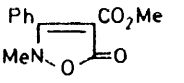
The lack of any resonance between δ 8.5 and 9.5 in the spectra of (20) (Table) indicated that this compound



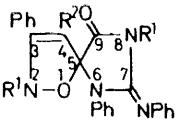
(22) X = S, R^1 = R^2 = CO_2Me

(23) X = S, R^1 = CO_2Me, R^2 = CO–NH–C(=NPh)–NHPh

(24) X = O, R^1 = R^2 = CO_2Me

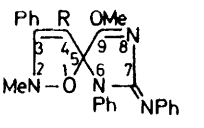


(25)



(26) R^1 = H, R^2 = CO_2Me

(27) R^1 = Me, R^2 = CO_2Me



(28) R = CO_2Me

fully exists in the spiro-form both in $(CD_3)_2SO$ and $CDCl_3$ solutions.

As reported for ethyl pyridazine-4-carboxylate,[1] the spiro-cyclization did not occur when the mono-ester (18) was treated with DPG and sodium hydride even in refluxing tetrahydrofuran, but the reaction afforded the amide (19) which was identified on the basis of its n.m.r. spectrum (Table).

As for the five-membered dicarboxylates (22) and (24), their reactivity was dramatically influenced by the nature of the X heteroatom. Whilst dimethyl 3-phenylisothiazole-4,5-dicarboxylate (22) reacted with DPG and sodium hydride to yield, even under drastic conditions, only the isothiazole (23), treatment of the ester (24) with the same reagents at room temperature afforded methyl 9-oxo-3,6-diphenyl-7-(phenylimino)-1-oxa-2,6,8-triazaspiro[4.4]non-3-ene-4-carboxylate (26) in high yield. The i.r. absorption frequencies of the ester CO group of (23) (1 725 cm^{-1}) and (26) (1 700 cm^{-1})

were identical to those of compounds (22) and (25) respectively. The chemical shifts of the CO_2Me protons (Table) were strictly comparable for the isothiazoles (22) and (23), whereas the spiro-compound (26) displayed, likewise the isoxazolone (25), a diagnostic upfield shift for the same group attributable to the $>N-C=C-CO_2Me$ conjugation. The most important evidence against a spiro-structure for (23) came from its ^{13}C n.m.r. spectrum in $(CD_3)_2SO$, which showed in the region of saturated carbons only a signal at δ 52.6 for the methyl group. On the contrary the proton-coupled spectrum of compound (26) in the same solvent displays, besides a quartet at δ 50.3 for the CO_2Me group, two singlets at δ 91.6 and 93.2 which, on the basis of the chemical shift (δ 89.5) of the C-4 carbon of the ester (25), could be tentatively assigned to the C-4 and C-5 quaternary carbon atoms.

The spiro-compound (26) reacted with ethereal diazomethane to give a mixture of the dimethyl derivatives (27) and (28), which were separated by column chromatography and identified on the basis of their ^1H and ^{13}C n.m.r. spectra. The assignment of the methyl resonances (Table) was accomplished by mutual comparison of the spectra and on the basis of the chemical shift of the N–Me group of compound (21). The 8-NMe and 9-OMe groups give rise to two quartets at δ 38.2 and 58.2 in the proton-coupled ^{13}C n.m.r. spectra in $CDCl_3$ of compounds (27) and (28) respectively; the presence in the same spectra of two singlets at δ 92.0 and 97.4, and at δ 89.2 and 91.2, respectively, strongly supported the spiro-structures.

The results of this work clearly show that the spirocyclization reaction of heterocyclic *o*-dicarboxylates with 1,3-binucleophiles is not confined to the pyridazine ring system, but it can be also advantageously carried out both with pyrimidine and isoxazole derivatives. Conversely, the reaction cannot be generalized since it appears to be critically influenced both by the degree of heteroaromaticity of the starting material and the stability of the dihydro-structures which characterize the heterospiro-compounds.

EXPERIMENTAL

Unless otherwise stated, i.r. spectra were measured for dispersions in potassium bromide with a Perkin-Elmer 457 spectrometer, and u.v. spectra for solutions in methanol with a Cary 14 recording spectrophotometer. ^1H N.m.r. spectra were recorded on a Perkin-Elmer R32 instrument and ^{13}C n.m.r. spectra were obtained by the Fourier-transform technique with a Varian CFT-20 spectrometer; chemical shifts are reported in p.p.m. downfield from internal $SiMe_4$, coupling constants in Hz. Silica gel plates (Merck F_{254}) and silica gel 60 (Merck; 230—400 mesh) were used for analytical and preparative t.l.c., and for column chromatography, respectively. Sodium hydride refers to an 80% dispersion in oil (Merck–Schuchardt), and light petroleum to the fraction of b.p. 30—50 °C. Extracts were dried over sodium sulphate, and solvents were removed under reduced pressure.

Reactions of Esters with 1,3-*Diphenylguanidine* (DPG).—Except where further details are reported, the reaction conditions and the proportions of reagents were as indicated in the following general procedure.

DPG (5—10 mmol) and sodium hydride (10—20 mmol) were stirred in anhydrous tetrahydrofuran (20—40 ml) until evolution of gas ceased; a solution of the ester (5—10 mmol) in the same solvent (10—20 ml) was added dropwise and the mixture was stirred at room temperature for 10—20 h. After removal of the solvent, the residue was treated with ice-cold water (20—50 ml) and the solution (or suspension) was neutralized or made weakly acidic with concentrated hydrochloric acid; the solid which separated was filtered off and dried.

(*i*) Diethyl pyridine-3,4-dicarboxylate (11) [3] (2 g) afforded a solid (2.2 g) which was resolved into five components by column chromatography with chloroform–ethyl acetate (3 : 1 v/v) as eluant. The fastest-running band gave *O-ethyl-NN′-diphenylisourea* (15) (0.35—0.4 g), b.p. 112 °C at 0.1 mmHg (lit.,[4] 200 °C at 20 mmHg), with a Raman spectrum identical to that reported in the literature; [5] $\nu_{max.}$ (film) 3 400, 1 655, 1 600, and 1 587 cm^{-1}. The second band yielded a small amount of *NN′-diphenylurea* (16), identical (m.p., i.r., and n.m.r. spectra) with an authentic sample. The third band afforded *ethyl* 4(3)-[(*NN′-diphenylamidino*)*carbamoyl*]*pyridine*-3(4)-*carboxylate* (12) (0.15—0.2 g), m.p. 152—153 °C (from ethyl acetate) (Found: C, 67.8; H, 5.1; N, 14.1. $C_{22}H_{20}N_4O_3$ requires C, 68.0; H, 5.2; N, 14.4%); $\nu_{max.}$ 3 600—2 800br, 1 730, 1 610, 1 585, 1 525, and 1 360 cm^{-1}; $\lambda_{max.}$ 284 nm (log ε 4.29). The fourth band gave *ethyl* 3(4)-[(*NN′-diphenylamidino*)*carbamoyl*]*pyridine*-4(3)-*carboxylate* (13) (0.2—0.25 g), m.p. 173—174 °C (from ethyl acetate) (Found: C, 68.3; H, 5.2; N, 14.3. $C_{22}H_{20}N_4O_3$ requires C, 68.0; H, 5.2; N, 14.4%); $\nu_{max.}$ 3 500—2 700br, 1 725, 1 600, 1 570, and 1 370 cm^{-1}; $\lambda_{max.}$ 272 nm (log ε 4.26). The slowest-running band afforded a small amount (*ca.* 0.1 g) of *pyridine-3,4-dicarboximide* (14), identical (m.p., i.r., and n.m.r. spectra) with an authentic sample.[6] When the reaction was carried out at reflux for 8 h, a crude product (2.2 g) was obtained, almost identical (t.l.c. and n.m.r. spectrum) with the foregoing material.

(*ii*) Diethyl 2-methylpyrimidine-4,5-dicarboxylate (17) [7] (1.5 g) gave a solid which was washed with ether to yield *ethyl* 4-*oxo*-7-*methyl*-1-*phenyl*-2-(*phenylimino*)-1,3,6,8-*tetraazaspiro*[4.5]*deca*-6,9-*diene*-10-*carboxylate* (20) (0.6 g). The aqueous mother-liquors were extracted with chloroform (3 × 30 ml); evaporation to dryness of the extracts left a yellow residue which was treated with ether to give a second crop (1.65 g, overall yield 88.5%) of compound (20). An analytical sample was obtained by preparative layer chromatography with ethyl acetate–methanol (4 : 1 v/v) as eluant; the product was extracted with methanol at room temperature and the extracts were evaporated to dryness. The residue was dissolved at room temperature in the minimum amount of ethyl acetate and the solution was cooled to give an ivory-coloured solid, m.p. 141—143 °C (Found: C, 65.3; H, 5.4; N, 17.1. $C_{22}H_{21}N_5O_3$ requires C, 65.5; H, 5.25; N, 17.4%); $\nu_{max.}$ 3 600—2 600br, 1 700, 1 605, 1 570, and 1 500 cm^{-1}; $\lambda_{max.}$ 250 and 300(sh) nm (log ε 4.35 and 3.76).

(*iii*) Ethyl 2-methylpyrimidine-4-carboxylate (18) (1 g) afforded a yellow solid which was washed with ether to yield 4-[(*NN′-diphenylamidino*)*carbamoyl*]-2-*methylpyrimidine* (19) (1.1 g), m.p. 174—176 °C after two crystallizations from ethyl acetate (Found: C, 69.1; H, 5.1; N, 21.0. $C_{19}H_{17}N_5O$ requires C, 68.9; H, 5.2; N, 21.1%); $\nu_{max.}$

3 310, 3 280, 1 700, and 1 655 cm^{-1}; $\lambda_{max.}$ 252 nm (log ε 4.25). The aqueous mother-liquors were extracted with chloroform (3 × 30 ml) and the extracts evaporated to dryness. The residue was treated with ether to give a further 0.3 g (overall yield 70%) of (19). When the reaction was carried out at reflux for 6 h, a solid (1.42 g, 71%) was obtained, identical (i.r., and n.m.r. spectra) with the material reported above.

(*iv*) Dimethyl 3-phenylisothiazole-4,5-dicarboxylate (22) [8] (1.5 g) gave *methyl* 5-[(NN′-*diphenylamidino*)*carbamoyl*]-3-*phenylisothiazole*-4-*carboxylate* (23) (2.3 g, 93%), m.p. 143—145 °C after two crystallizations from methanol (Found: C, 66.0; H, 4.5; N, 12.1. $C_{25}H_{20}N_4O_3S$ requires C, 65.8; H, 4.4; N, 12.3%); $\nu_{max.}$ 3 360, 1 730, 1 615, and 1 580 cm^{-1}; $\lambda_{max.}$ 240 and 282 nm (log ε 4.53 and 4.44). When the reaction was carried out at reflux for 6 h, a solid (2.4 g, 97%) was obtained, identical (m.p., i.r., and n.m.r. spectra) with the product just described.

(*v*) Following the general method reported above, dimethyl 3-phenylisoxazole-4,5-dicarboxylate (24) [9] (1 g) was reacted with DPG (0.81 g) and sodium hydride (0.23 g) in anhydrous tetrahydrofuran (50 ml) at room temperature for 15 h. Removal of the solvent left a residue which was treated with ice-cold water (100 ml) and extracted with ether (50 ml). The aqueous solution was then cautiously acidified (pH 6) with concentrated hydrochloric acid and extracted again with ether (30 ml). Further acidification of the solution (pH 2) precipitated *methyl* 9-*oxo*-3,6-*diphenyl*-7-(*phenylimino*)-1-*oxa*-2,6,8-*triazaspiro*[4.4]*non*-3-*ene*-4-*carboxylate* (26) (1.4 g; 83.3%), as a pale yellow solid which changed very quickly into a pink-orange product, which gradually decomposed above 120 °C (Found: C, 66.9; H, 4.5; N, 12.6. $C_{25}H_{20}N_4O_4$ requires C, 68.1; H, 4.6; N, 12.7%); $\nu_{max.}$ 3 400—2 300br, 1 775, and 1 700 cm^{-1}. Purification of (26) by dissolution in aqueous sodium hydroxide, filtration, and re-precipitation with hydrochloric acid did not improve the analytical results.

Ethyl 2-*Methylpyrimidine*-4-*carboxylate* (18).—This compound was prepared according to the method of Reiner and Eugster,[10] by condensation of ethyl ethoxymethylenepyruvate with acetamidine; the reaction afforded the ester (18) as a colourless oil, b.p. 66—67 °C at 0.07 mmHg, which rapidly turned yellow on standing.

Methyl 2,5-*Dihydro*-5-*oxo*-2-*methyl*-3-*phenylisoxazole*-4-*carboxylate* (25).—A suspension of 2,5-dihydro-5-oxo-2-methyl-3-phenylisoxazole-4-carboxylic acid [11] (1 g) in ether (100 ml) was treated with an excess of ethereal diazomethane and set aside overnight. The solid (0.9 g) formed was separated by filtration and consisted mainly (t.l.c. and n.m.r. spectrum) of the ester (25) with a small amount of the starting material. The product was dissolved in methylene chloride and washed with aqueous sodium hydrogen carbonate; evaporation of the solvent left white crystals, m.p. 159—160 °C (from ethyl acetate) (Found: C, 62.1; H, 4.9; N, 5.95. $C_{12}H_{14}NO_4$ requires C, 61.8; H, 4.75; N, 6.0%); $\nu_{max.}$ 1 765, 1 700, 1 525, and 1 200 cm^{-1}; $\lambda_{max.}$ 221 and 278 nm (log ε 4.17 and 4.09).

Methylation of the Spiro-compounds (20) *and* (26) *with Diazomethane.*—(*i*) A solution of compound (20) (0.55 g) in ether (30 ml) and methanol (20 ml) was allowed to react overnight with an excess of ethereal diazomethane. Removal of the solvent left a sticky residue which was treated with light petroleum–ether to give a yellow solid (0.57 g) which consisted mainly (t.l.c. and n.m.r. spectrum) of *ethyl* 4-*oxo*-3,7-*dimethyl*-1-*phenyl*-2-(*phenylimino*)-1,3,6,8-*tetra*-*azaspiro*[4.5]*deca*-6,9-*diene*-10-*carboxylate* (21). An analytical sample, obtained by two crystallizations from ethyl acetate, after melting at about 190 °C, resolidified at higher temperature and then re-melted at 208—209 °C (Found: C, 66.5; H, 5.6; N, 16.6. $C_{23}H_{23}N_5O_3$ requires C, 66.2; H, 5.55; N, 16.8%); $\nu_{max.}$ 3 400—2 600br, 1 755, 1 705, 1 660, and 1 620 cm^{-1}; $\lambda_{max.}$ 250 and 277 nm (log ε 4.05 and 4.04).

(*ii*) A suspension of the spiro-compound (26) (1 g) in ether (100 ml) was treated with an excess of diazomethane as reported above. The reaction mixture was filtered and the filtrate was evaporated to dryness to give a residue (0.95 g) mainly containing two products (t.l.c.) which were separated by column chromatography with light petroleum–ether (2 : 1 v/v) as eluant. The first band afforded *methyl* 9-*methoxy*-2-*methyl*-3,6-*diphenyl*-7-(*phenylimino*)-1-*oxa*-2,6,8-*triazaspiro*[4.4]*nona*-3,8-*diene*-4-*carboxylate* (28) (0.2 g), m.p. 164—165 °C (from ether) (Found: C, 68.9; H, 5.0; N, 11.7. $C_{27}H_{24}N_4O_4$ requires C, 69.2; H, 5.2; N, 12.0%); $\nu_{max.}$ 1 760, 1 670, 1 625, 1 590, 1 490, 1 440, and 1 415 cm^{-1}; $\lambda_{max.}$ 233 and 270(sh) nm (log ε 4.75 and 4.29).

The second band gave *methyl* 9-*oxo*-2,8-*dimethyl*-3,6-*diphenyl*-7-(*phenylimino*)-1-*oxa*-2,6,8-*triazaspiro*[4.4]*non*-3-*ene*-4-*carboxylate* (27) (0.25 g), m.p. 183—184 °C (from ether) (Found: C, 69.5; H, 5.2; N, 12.0. $C_{27}H_{24}N_4O_4$ requires C, 69.2; H, 5.2; N, 12.0%); $\nu_{max.}$ 1 745, 1 670, 1 625, 1 590, 1 500, 1 440, and 1 360 cm^{-1}; $\lambda_{max.}$ 215 and 277 nm (log ε 4.36 and 4.25).

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