Spirocyclisation Reactions of Diethyl Pyridazine-4,5-dicarboxylate with 1,3-Binucleophiles

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Treatment of diethyl pyridazine-4,5-dicarboxylate (1) and diethyl 3,6-dimethylpyridazine-4,5-dicarboxylate (2) with 1,3-diphenylguanidine in the presence of sodium hydride, gave ethyl 4-oxo-1-phenyl-2-(phenylimino)-1,3,7,8-tetra-azaspiro[4,5]deca-6,9-diene-10-carboxylate (11) and its 6,9-dimethyl derivative (13), respectively. The influence of the nature of the substituents on the spirocyclisation reaction was investigated by studying the reactivity of the esters (3)—(6) towards the same reagents. The ester (1) condensed with diethyl succinate to yield a small amount of diethyl 5,8-dihydroxyphthalazine-6,7-dicarboxylate (18), but reacted with diethyl glutarate and diethyl acetonedicarboxylate to give the diazaspirodecadienes (19) and (20), respectively.

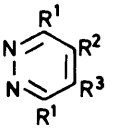
We have recently reported that pyridazine-4,5-dicarboxylates condense with *o*-phenylenediamine in the presence of sodium hydride to give pyridazino[4,5-*c*]-[1,6]benzodiazocines.[1]

In the hope of extending this procedure to the synthesis of seven-membered condensed pyridazines, we studied the reactivity of the ester (1) towards 1,3-binucleophiles. However, when it was treated with 1,3-diphenylguanidine (DPG) and sodium hydride in anhydrous tetrahydrofuran at room temperature, the expected cyclisation to the pyridazinodiazepine (10) did not occur; instead a product $C_{21}H_{19}N_5O_3$ was obtained in high yield. Spectral evidence led us to formulate this compound as ethyl 4-oxo-1-phenyl-2-(phenylimino)-1,3,7,8-tetra-azaspiro[4,5]deca-6,9-diene-10-carboxylate (11). The i.r. spectrum showed a broad pattern between 3 500 and 2 700 cm^{-1} (NH) and two bands at 1 725 and 1 695 cm^{-1} attributable to the stretching vibrations of the amidic and conjugated ester CO groups, respectively. Apart from a difference in intensity for the maximum at lower

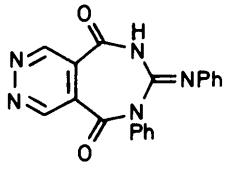
[1] G. Adembri, S. Chimichi, F. De Sio, R. Nesi, and M. Scotton, *J.C.S. Perkin I*, 1974, 1022.

wavelength, the u.v. spectrum (see Experimental section) closely resembles those of compounds (15) [2] and (16).[3] The resonances of the dihydropyridazine ring protons at positions 6 and 9 were easily recognized in the ^1H n.m.r. spectrum (Table) as a singlet and a doublet at δ 6.9 and 7.56, respectively. The off-resonance-decoupled ^{13}C n.m.r. spectrum exhibits a singlet at δ 66.1 attributable to the spiro-carbon atom.

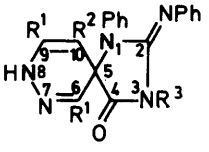
(1) R^1 = H, R^2 = R^3 = CO_2Et
(2) R^1 = Me, R^2 = R^3 = CO_2Et
(3) R^1 = H, R^2 = CN, R^3 = CO_2Me
(4) R^1 = R^2 = H, R^3 = CO_2Et
(5) R^1 = H, R^2 = CO·NEt_2, R^3 = CO_2Me



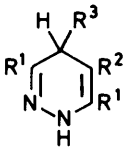
(6) R^1 = H, R^2 = NH_2, R^3 = CO_2Et
(7) R^1 = R^2 = H, R^3 = CO·NH·C(:NPh)·NHPh
(8) R^1 = H, R^2 = CO·NEt_2, R^3 = CO·NH·C(:NPh)·NHPh
(9) R^1 = H, R^2 = R^3 = CO·NHPh



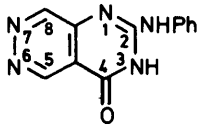
(10)



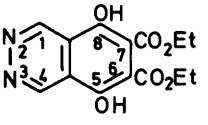
(11) R^1 = R^3 = H, R^2 = CO_2Et
(12) R^1 = H, R^2 = CO_2Et, R^3 = Me
(13) R^1 = Me, R^2 = CO_2Et, R^3 = H
(14) R^1 = R^3 = H, R^2 = CN



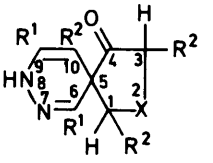
(15) R^1 = Me, R^2 = R^3 = CO_2Et
(16) R^1 = Me, R^2 = CO_2Et, R^3 = CH_2·OH



(17)

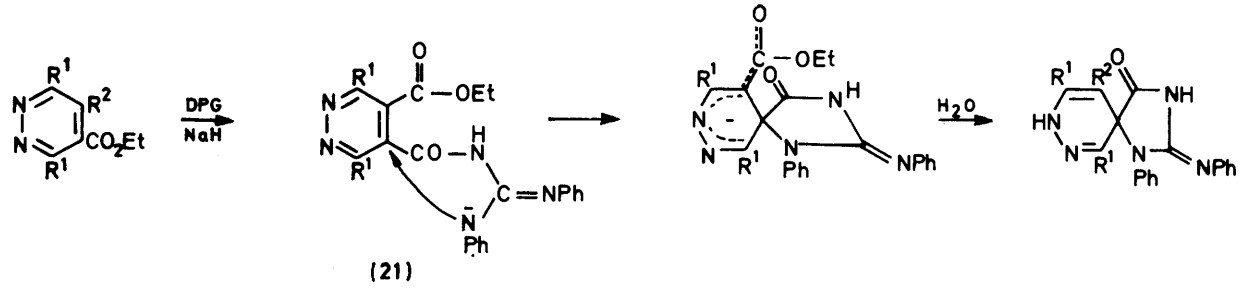


(18)



(19) R^1 = H, R^2 = CO_2Et, X = CH_2
(20) R^1 = H, R^2 = CO_2Et, X = CO

SCHEME 1



(21)

SCHEME 2

Diethyl 3,6-dimethylpyridazine-4,5-dicarboxylate (2) reacted with the same reagents to give the spiran (13), identified on the basis of its spectroscopic properties.

In particular the chemical shifts of the ring methyl groups (Table) were similar to those of the dihydropyridazine (16) in the same solvent (δ 2.0 and 2.13).

The formation of the spiro-compounds (11) and (13) can be rationalized in terms of nucleophilic attack at the 4-position by the terminal nitrogen of the anionic intermediate (21).

In order to establish the influence of the nature of the substituent R^2 on the reaction, the behaviour of the esters (3)—(6) was investigated. Methyl 5-cyanopyridazine-4-carboxylate (3) condensed smoothly with DPG in the presence of sodium hydride at room temperature to yield the spiran (14), but compound (4), bearing only one ester function, and compound (5), containing one ester and one diethylcarbamoyl group, afforded only the amides (7) and (8), respectively, even under more drastic conditions. On the other hand,

[2] W. L. Mosby, *J. Chem. Soc.*, 1957, 3997.
[3] G. Adembri, F. De Sio, R. Nesi, and M. Scotton, *J. Heterocyclic Chem.*, 1975, **12**, 95.
[4] P. F. Zanazzi, personal communication.

ethyl 5-aminopyridazine-4-carboxylate (6) did not react with DPG and sodium hydride at room temperature, whereas it was cyclised to 2-anilinopyrimido[4,5-*d*]pyridazin-4(3*H*)-one (17) on treatment with the same reagents in refluxing tetrahydrofuran. The structures of compounds (7), (8), (14), and (17) were determined on the basis of spectroscopic data (see Table and Experimental section). As expected for an enamino-nitrile,[5] the CN stretching vibration of (14) showed a marked lowering of frequency (*ca.* 33 cm^{-1}) in comparison with the cyano-derivative (3).

N.m.r. spectra (90 MHz; δ values; *J* in Hz; internal tetramethylsilane as reference)

Compd.	Solvent	Proton resonance	Assignment
(7)	$(CD_3)_2SO$	7.1—7.6(m)	2 × Ph
		7.97(dd) } $J_{5,6}$ 5.3	5-H
		9.38(dd) } $J_{3,6}$ 1.3	6-H
		9.54(dd) } $J_{3,5}$ 2	3-H
		10.5(s) [a]	2 × NH
(8)	$(CD_3)_2SO$	0.93(t), 1.12(t) } *J* 7	2 × CH_3·CH_2·N
		2.88(q), 3.40(q) } *J* 7	2 × CH_3·CH_2·N
		7.1—7.5(m)	2 × Ph
		9.2(d) } *J* 1.2	3-, 6-H
		9.6(d) } *J* 1.2	
		10.35(s) [a]	2 × NH
(9)	$(CD_3)_2SO$	7.0—7.85(m)	2 × Ph
		9.65(s)	3-, 6-H
		10.80(s) [a]	2 × NH
(11)	$(CD_3)_2SO$	1.15(t) } *J* 7	CH_3·CH_2·O
		4.06(q) } *J* 7	CH_3·CH_2·O
		6.9(s)	6-H
		7.0—7.6(m)	2 × Ph
		7.56(d) [b] *J* 4	9-H
		9.28br(s) [a]	N(3)H
		10.29(d) [a] *J* 4	N(8)H
(12)	$CDCl_3$	1.22(t) *J* 7	CH_3·CH_2·O
		3.27(s)	NMe
		4.13(q) *J* 7	CH_3·CH_2·O
		6.5—7.0(m)	2 × Ph and 6-H
		7.45(d) [b] } *J* 4.1	9-H
		8.95(d) [a] } *J* 4.1	N(8)H
(13)	$(CD_3)_2SO$	1.12(t) *J* 7	CH_3·CH_2·O
		1.94(s), 2.0(s)	6-, 9-Me
		4.0(m)	CH_3·CH_2·O
		6.9—7.8(m)	2 × Ph
		9.28br(s) [a]	N(3)H
		10.48(s) [a]	N(8)H
(14)	$(CD_3)_2SO$	6.97(s)	6-H
		7.0—7.8(m)	2 × Ph
		7.68(s) [c]	9-H
		9.5br(s) [a]	N(3)H
		11.0br(s) [a]	N(8)H
(17)	$(CD_3)_2SO$ [d]	7.2—7.9(m)	Ph
		8.5br(s) [a]	2 × NH
		9.22(d) } *J* 1	5-, 8-H
		9.32(d) } *J* 1	
(18)	$CDCl_3$	1.39(t) } *J* 7	2 × CH_3·CH_2·O
		4.45(q) } *J* 7	2 × CH_3·CH_2·O
		8.62br(s) [a]	2 × OH
		9.97(s)	1-, 4-H
(19)	$CDCl_3$	1.1—1.4(m)	3 × CH_3·CH_2·O
		2.25—2.95(m)	2-CH_2
		3.37(m)	1-H
		3.77(m)	3-H
		4.0—4.4(m)	3 × CH_3·CH_2·O
		6.44(s)	6-H
		7.52(d) [b] } *J* 4.5	9-H
		8.24(d) [a] } *J* 4.5	N(8)H
(20)	$CDCl_3$	1.1—1.5(m)	3 × CH_3·CH_2·O
		3.9—4.6(m)	3 × CH_3·CH_2·O and 1- or 3-H
		6.4(s)	6-H
		7.62(d) [b] } *J* 4	9-H
		8.87(d) [a] } *J* 4	N(8)H
		11.35br(s) [a]	OH

[a] Signal disappears on deuteriation. [b] Signal collapses to a singlet on deuteriation. [c] The lack of coupling for H-9 is probably due to rapid exchange of the adjacent NH proton. [d] Spectrum recorded at 130 °C. [e] Compound (20), for which five tautomeric structures could be taken into consideration, exists predominantly in a keto-enol form in this solvent.

The foregoing reactions of compounds (3)—(6) appear to show that the presence of a strongly electron-withdrawing group at position 5 plays a determining role in inducing spirocyclisation.

Attempts to prepare spiro-compounds from the ester (1) and *NN'*-diphenylurea have so far been unsuccessful: pyridazine-4,5-dicarboxanilide (9) and ethyl phenylcarbamate have been isolated as main products.

Diethyl pyridazine-4,5-dicarboxylate (1) condensed with diethyl succinate in the presence of sodium hydride, under various conditions, to give diethyl 5,8-dihydroxyphthalazine-6,7-dicarboxylate (18) in low yield; in contrast, when the diester (1) was treated with carbon 1,3-binucleophiles, spirocyclisation was again observed. Treatment with diethyl glutarate and diethyl acetonedicarboxylate in the presence of sodium hydride or sodium ethoxide, afforded triethyl 4-oxo-7,8-diazaspiro-[4,5]deca-6,9-diene-1,3,10-tricarboxylate (19) and triethyl 2,4-dioxo-7,8-diazaspiro[4,5]deca-6,9-diene-1,3,10-tricarboxylate (20), respectively. Comparison of their n.m.r. spectra with that of compound (12) (Table) strongly supported the assigned spirodihydropyridazine structures.

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 with a Perkin-Elmer R 32 instrument and the ^{13}C n.m.r. spectrum of compound (11) was obtained for a solution in $(CD_3)_2SO$ by the Fourier transform technique with a Bruker WH-90 spectrometer (deuterium lock; tetramethylsilane as internal standard). Silica gel plates (Merck F_{254}) were used for analytical and preparative t.l.c. Sodium hydride refers to an 80% dispersion in oil (Merck-Schuchardt). Extracts were dried over sodium sulphate, and solvents were removed under reduced pressure.

Reactions of the Esters (1)—(5) *with* 1,3-*Diphenylguanidine* (*DPG*).—Except where further details are given, the proportions of reagents and the reaction conditions were as indicated in the following general method.

DPG (5 mmol) and sodium hydride (10 mmol) were stirred in anhydrous tetrahydrofuran (15 ml) until evolution of hydrogen ceased; a solution of the ester (5 mmol) in the same solvent (5—10 ml) was then added dropwise and the mixture was stirred at room temperature for 18 h. The residue left after removal of the solvent was treated with ice-cold water (15—40 ml) and the solution (or suspension) was neutralised with concentrated hydrochloric acid; the solid which separated was filtered off, dried, and washed with ether.

(i) Diethyl pyridazine-4,5-dicarboxylate (1) (1.12 g) gave *ethyl* 4-*oxo*-1-*phenyl*-2-(*phenylimino*)-1,3,7,8-*tetra-azaspiro*-[4,5]*deca*-6,9-*diene*-10-*carboxylate* (11) (1.68 g, 86.4%), m.p. 200—202° (after two crystallisations from methanol)

[5] S. Baldwin, *J. Org. Chem.*, 1961, **26**, 3288.

(Found: C, 64.7; H, 5.1; N, 17.8. $C_{21}H_{19}N_5O_3$ requires C, 64.8; H, 4.9; N, 18.0%); $\lambda_{max.}$ 244 and 315 nm (log ε 4.37 and 3.77).

(ii) Diethyl 3,6-dimethylpyridazine-4,5-dicarboxylate (2) (1.26 g) gave *ethyl 4-oxo-6,9-dimethyl-1-phenyl-2-(phenylimino)-1,3,7,8-tetra-azaspiro*[4,5]*deca-6,9-diene-10-carboxylate* (13) (1.67 g, 77%) as a pale yellow product which was purified by preparative layer chromatography with ethyl acetate as developer; the product was extracted with methanol at room temperature and crystallised from water. Compound (13), as its monohydrate, gradually darkened above 190° and melted at 225—230° (decomp.) (the m.p. is sensitive to the rate of heating) (Found: C, 63.7; H, 5.7; N, 16.3. $C_{23}H_{23}N_5O_3,H_2O$ requires C, 63.4; H, 5.8; N, 16.1%); $\nu_{max.}$ 3 600—2 700br, 1 700, and 1 670 cm^{-1}; $\lambda_{max.}$ (Me_2SO) 259 and 317 nm (log ε 4.39 and 3.83).

(iii) Methyl 5-cyanopyridazine-4-carboxylate (3) [6] (0.815 g) afforded *4-oxo-1-phenyl-2-(phenylimino)-1,3,7,8-tetra-azaspiro*[4,5]*deca-6,9-diene-10-carbonitrile* (14) (1.36 g, 79.4%). A sample obtained by several crystallisations from dimethyl sulphoxide–water gradually darkened with wrinkling above 150°, and melted at about 200° (decomp.) (m.p. varies with rate of heating) (Found: C, 66.4; H, 4.1; N, 24.3. $C_{19}H_{14}N_6O$ requires C, 66.7; H, 4.1; N, 24.55%); $\nu_{max.}$ 3 500—2 600br, 2 205, and 1 700 cm^{-1}; $\lambda_{max.}$ 260 and 305sh nm (log ε 4.39 and 3.75).

(iv) Ethyl pyridazine-4-carboxylate (4) [7] (0.76 g) yielded *N-(diphenylamidino)pyridazine-4-carboxamide* (7) (1.37 g, 86.3%), m.p. 170—171° (from ethyl acetate) (Found: C, 68.4; H, 4.9; N, 22.1. $C_{18}H_{15}N_5O$ requires C, 68.1; H, 4.8; N, 22.1%); $\nu_{max.}$ 3 400—2 500br and 1 610 cm^{-1}; $\lambda_{max.}$ 220sh and 295 nm (log ε 4.3 and 4.15). When the reaction was carried out at reflux for 15 h, a solid (1.37 g, 86.3%) was obtained, identical (i.r. and n.m.r. spectra) with the material just described.

(v) Methyl 5-(diethylcarbamoyl)pyridazine-4-carboxylate (5) [6] (1.185 g) gave *N-(diphenylamidino)-5-(diethylcarbamoyl)-pyridazine-4-carboxamide* (8) (1.66 g, 79.7%), m.p. 198—199° (after purification by preparative layer chromatography with ethyl acetate as developer) (Found: C, 66.6; H, 6.0; N, 19.9. $C_{23}H_{24}N_6O_2$ requires C, 66.3; H, 5.8; N, 20.2%); $\nu_{max.}$ 3 400—2 800br, 1 640, and 1 615 cm^{-1}; $\lambda_{max.}$ 235sh, 277, and 298 nm (log ε 4.2, 4.05, and 4.06). When the reaction was carried out at reflux for 15 h, a product (1.6 g) was obtained, identical (i.r. and n.m.r. spectra) with the material just described.

Reactions of Ethyl 5-Aminopyridazine-4-carboxylate (6) *with DPG.*—(*a*) DPG (0.63 g) and sodium hydride (0.18 g) were stirred in anhydrous tetrahydrofuran (30 ml) until evolution of hydrogen subsided; the ester (6) [8] (0.5 g) was added and the mixture was stirred at room temperature for 18 h. The residue left after removal of the solvent was treated with ice-cold water (20 ml), neutralised with concentrated hydrochloric acid, and extracted with chloroform (2 × 50 ml). The extracts were evaporated to dryness and the residue was treated with ether to give a solid (0.5 g), which largely consisted of unchanged compound (6) (t.l.c. and i.r. and n.m.r. spectra).

(*b*) The reaction was carried out under the same conditions but at reflux for 18 h. Evaporation of the mixture to dryness left a yellow-brown residue which was treated with ice-cold water (20 ml) to yield a pale yellow solid; this was filtered off, dried, washed with ether (3 × 20 ml), and dissolved in aqueous ammonium hydroxide. Acidification with acetic acid precipitated *2-anilinopyrimido*[4,5-d]*-pyridazin-4(3H)-one* (17) (0.2 g), m.p. >330° (from dimethyl sulphoxide). Neutralisation of the original alkaline mother liquors afforded a second crop (0.18 g) of (17) (Found: C, 60.1; H, 3.7; N, 29.5. $C_{12}H_9N_5O$ requires C, 60.25; H, 3.8; N, 29.3%); $\nu_{max.}$ 3 400—2 500br and 1 715 cm^{-1}; $\lambda_{max.}$ 238sh and 295 nm (log ε 3.96 and 4.28).

Methylation of Compound (11) *with Diazomethane.*—A suspension of compound (11) (0.3 g) in ether (15 ml) and methanol (15 ml) was treated with an excess of ethereal diazomethane and set aside overnight. The pale yellow solid (0.31 g) left after removal of the solvent was crystallised from ethyl acetate to give *ethyl 4-oxo-3-methyl-1-phenyl-2-(phenylimino)-1,3,7,8-tetra-azaspiro*[4,5]*deca-6,9-diene-10-carboxylate* (12) as white needles, m.p. 213—215° (Found: C, 65.7; H, 5.3; N, 17.55. $C_{22}H_{21}N_5O_3$ requires C, 65.5; H, 5.25; N, 17.4%); $\nu_{max.}$ (CCl_4) 3 470, 1 750, and 1 700 cm^{-1}; $\lambda_{max.}$ 207, 265sh, and 305 nm (log ε 4.52, 4.0, and 3.92).

Reaction of Compound (1) *with* NN'*-Diphenylurea.*—By the general method described above, the ester (1) (1 g) was treated with *NN'*-diphenylurea (0.95 g) and sodium hydride (0.27 g) in anhydrous tetrahydrofuran (50 ml). Removal of the solvent left a residue which was treated with ice-cold water (25 ml); after neutralisation with concentrated hydrochloric acid, the mixture was extracted with ether (60 ml) and then with chloroform (5 × 70 ml). Evaporation of the chloroform extracts afforded a solid which was washed with ether to give *pyridazine-4,5-dicarboxanilide* (9) (0.45 g), m.p. 227—228° (after several crystallisations from ethyl acetate) (Found: C, 68.2; H, 4.5; N, 17.9. $C_8H_{14}N_4O_2$ requires C, 67.9; H, 4.4; N, 17.6%); $\nu_{max.}$ 3 320, 3 270, 1 680, and 1 660 cm^{-1}; $\lambda_{max.}$ 232 and 293 nm (log ε 4.33 and 3.85).

Concentration of the ethereal extract caused separation of a mixture (*ca.* 0.1 g) of compound (9) and *NN'*-diphenylurea (i.r. spectrum), which was filtered off. The filtrate was evaporated to dryness to yield an oil (0.55 g), which was purified by preparative layer chromatography with chloroform as developer. The fastest running band afforded ethyl phenylcarbamate, identical (i.r. and n.m.r. spectra) with an authentic sample.

Diethyl 5,8-Dihydroxyphthalazine-6,7-dicarboxylate (18).—To a stirred suspension of sodium hydride (0.27 g) in anhydrous tetrahydrofuran (20 ml) were added simultaneously (dropwise) solutions of diethyl pyridazine-4,5-dicarboxylate (1) (1 g) and diethyl succinate (0.78 g) in the same solvent (3 ml), and the mixture was gently refluxed with stirring for 6 h. Removal of the solvent left a brown solid which was dissolved in ice-cold water (30 ml); the solution was neutralised with concentrated hydrochloric acid and extracted with chloroform (5 × 50 ml). Evaporation of the extracts to dryness gave a sticky residue, which was treated with a minimal amount of methanol; the yellow brown solid which separated was filtered off and washed with ether to give *compound* (18) (0.12 g). A sample obtained by several crystallisations from methanol gradually darkened above 145° and melted at 151—153° (decomp.) (Found: C, 54.8; H, 4.6; N, 9.1. $C_{14}H_{14}N_2O_6$ requires C, 54.9; H, 4.6; N, 9.15%); $\nu_{max.}$ 3 300—2 200br, 1 745, and 1 670 cm^{-1}; $\lambda_{max.}$ 209, 246, 325sh, and 374 nm (log ε 4.5, 4.25, 3.46, and 3.85).

[6] Unpublished results from this laboratory.

[7] W. J. Leanza, H. J. Becker, and E. F. Rogers, *J. Amer. Chem. Soc.*, 1953, **75**, 4086.

[8] J. Kinoshita and R. N. Castle, *J. Heterocyclic Chem.*, 1968, **5**, 845.

Triethyl 4-Oxo-7,8-diazaspiro[4,5]*deca-6,9-diene-1,3,10-tricarboxylate* (19).—The ester (1) (1 g) was condensed with diethyl glutarate (0.84 g) in the presence of sodium hydride (0.27 g) in anhydrous tetrahydrofuran as described for (18). The mixture was evaporated to dryness and the residue was treated with ice-cold water (10 ml); after neutralisation with concentrated hydrochloric acid, the pale yellow solid was filtered off, dried, and washed with ether to yield *compound* (19) (0.7 g), m.p. 113—115° (from ether). Concentration of the ethereal washing afforded a further 0.03 g of (19) (44.6%) (Found: C, 55.8; H, 6.1; N, 7.65. $C_{17}H_{22}N_2O_7$ requires C, 55.7; H, 6.05; N, 7.65%); $\nu_{max.}$ (CCl_4) 3 460, 1 755, 1 735, and 1 680 cm^{-1}; $\lambda_{max.}$ 225sh, 298sh, 308, and 337 nm (log ε 3.88, 3.61, 3.66, and 3.39).

Triethyl 2,4-Dioxo-7,8-diazaspiro[4,5]*deca-6,9-diene-1,3,10-tricarboxylate* (20).—To a stirred suspension of sodium ethoxide (0.61 g) in anhydrous toluene (10 ml) were added simultaneously (dropwise) the ester (1) (2 g) and diethyl acetonedicarboxylate (1.8 g) in the same solvent (2 ml). The mixture was gently refluxed with stirring for 1 h, during which much solid was deposited. After cooling, water (20 ml) was added, and the aqueous layer was separated, neutralised with concentrated hydrochloric acid, and washed with chloroform (2 × 50 ml). The aqueous solution was then acidified and extracted with chloroform (4 × 100 ml); the residue left after evaporation of the extracts to dryness was treated with the minimum amount of ether to yield a solid (1.35 g) which largely consisted (t.l.c. and n.m.r. spectrum) of the *ester* (20), m.p. 154—156° (after several crystallisations from ether) (Found: C, 53.9; H, 5.4; N, 7.4. $C_{17}H_{20}N_2O_8$ requires C, 53.7; H, 5.3; N, 7.4%); $\nu_{max.}$ (CCl_4) 3 460, 1 735, 1 690, and 1 655 cm^{-1}; $\lambda_{max.}$ 244 and 332 nm (log ε 4.04 and 3.3).

[6/1798 *Received, 24th September,* 1976]