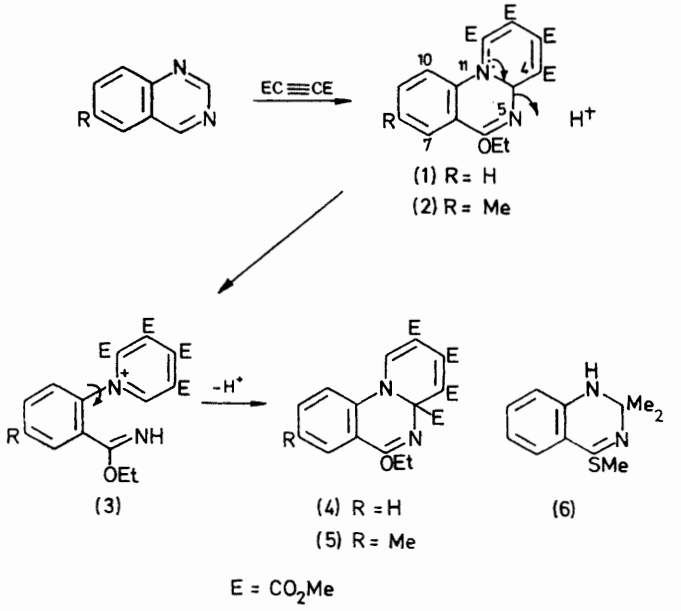
Addition Reactions of Heterocyclic Compounds. Part LXII.[1] A New Rearrangement in the Quinazoline Series

By Patrick J. Abbott, R. Morrin Acheson,* Mikhail Y. Kornilov, and J. K. Stubbs, Department of Biochemistry, South Parks Road, Oxford OX1 3QU

Dimethyl acetylenedicarboxylate with 4-ethoxyquinazoline and its 6-methyl derivative give tetramethyl 6-ethoxy-4a*H*-pyrido[1,2-*a*]quinazoline-1,2,3,4-tetracarboxylates, which by an acid catalysed ring-opening–ring-closure process isomerise to the corresponding 2,3,4,4a-tetracarboxylates. The structures of these compounds have been deduced from ^{1}H and ^{13}C n.m.r. spectra, and their interactions with lanthanide shift reagents have been examined.

THE products from the reactions of dimethyl acetylenedicarboxylate with quinazoline and some alkyl derivatives,[2] and with 2-methoxypyridine,[3] where the heterocyclic ring can be opened, have been examined previously; the investigation has now been extended to the products formed from 4-ethoxyquinazolines.

4-Ethoxyquinazoline and its 6-methyl derivative, but not the 8-methyl analogue (which does not react), combine with dimethyl acetylenedicarboxylate in refluxing calcium hydride-dried acetonitrile to give 1 : 2 molar



adducts [(1) and (2)] in high yield. The ^{1}H n.m.r. spectra (Table 1) of these adducts show that the protons of the carbocyclic ring are essentially similar to those of the starting materials, and that the low-field singlet corresponding to the 2-H of the original quinazoline has been replaced by a singlet (τ *ca.* 4.2) at too high a field for –N=CH–.[4] The ^{13}C n.m.r. spectrum of (1) also shows a resonance at 67.4 p.p.m. due to an sp^3 carbon atom bearing one proton. Few model compounds for this type of structure are available, but C-2 of the dihydroquinazoline[5] (6) resonates at 70.37 p.p.m. and C-4 of tetramethyl 7,9-dimethyl-4*H*-quinolizine-1,2,3,4-tetracarboxylate at 65.5 p.p.m.[6] This is consistent with the idea of a new ring being built up across the 1- and 2-positions of the quinazoline ring in the usual way,[7] and with the fact that 4-ethoxy-8-methylquinazoline does not react with the acetylenic ester significantly, because of steric hindrance by the methyl group to electrophilic attack at N-1. It excludes the possibility of ring formation across the 3- and 4-positions or of benzodiazannulene formation through, for example, breakage of the 4a,11-bond in (1).

The adducts (1) and (2) undergo a rapid rearrangement in the presence of even traces of strong acid (*e.g.* trifluoroacetic acid) to give the isomers (4) and (5). The rearrangement may be followed in an n.m.r. sample tube after adding a drop of trifluoroacetic acid to a solution of (1) in [^{2}H]chloroform. If the acetonitrile used for the original preparation of (1) and (2) is dried over phosphorus pentaoxide and redistilled it contains sufficient acid to promote the rearrangement. The u.v. spectra of compounds (4) and (5) (Table 3) have a pronounced peak at 208—210 nm which may be interpreted as due to the isolated methoxycarbonyl group; the peak is absent in the spectra of compounds (1) and (2). The longer wave absorptions of compounds (1), (2), (4), and (5) are similar, indicating the presence of the same chromophore.

Significant changes in the ^{1}H n.m.r. spectra of the rearrangement products are that the single proton resonances now appear at τ *ca.* 2, and that the ethyl signals appear as ABX_3 systems instead of the A_2X_3 type shown by the initial adducts. The ^{13}C n.m.r. spectra for (4) and (5) each show an sp^3 hybridised carbon atom, not attached to any hydrogen atom, at 75.9 and 76.1 p.p.m. Structures (4) and (5), which best accommodate these data, could be formed through protonation of N-6 and opening of the quinazoline ring to form the highly stabilised pyridinium derivative (3), followed by cyclization in the alternative mode. An exactly similar type of rearrangement has recently been demonstrated[6]

[1] Part LXI, R. M. Acheson and J. Woollard, *J.C.S. Perkin I*, 1975, 744.
[2] R. M. Acheson, M. W. Foxton, and J. K. Stubbs, *J. Chem. Soc.* (*C*), 1968, 926.
[3] R. M. Acheson and D. A. Robinson, *J. Chem. Soc.* (*C*), 1968, 1629.
[4] L. M. Jackson and S. Sternhell, 'Applications of N.m.r. Spectroscopy in Organic Chemistry,' Pergamon, Oxford, 1969, p. 184; H. A. Staab, F. Vögtle, and A. Mannschreck, *Tetrahedron Letters*, 1965, 697; K. Tabei and E. Saitou, *Bull. Chem. Soc. Japan*, 1969, **42**, 1440.
[5] H. C. Carrington, *J. Chem. Soc.*, 1955, 2027.
[6] P. J. Abbott, R. M. Acheson, U. Eisner, D. J. Watkin, and J. R. Carruthers, *J.C.S. Chem. Comm.*, 1975, 155.
[7] R. M. Acheson, *Adv. Heterocyclic Chem.*, 1963, **1**, 125.

TABLE 1

^{1}H N.m.r. spectra at 60 MHz; solvent $CDCl_3$; internal reference Me_4Si

Compound	MHz	τ Values (J in Ha)	Ester Me
(1)	60	4a-H, 4.22; 7-H, 2.31m; 8,9,10-H_3, 2.46—2.92m; OCH_2·CH_3, 5.79q; OCH_2·CH_3, 8.70t, J 7.5	1-OMe, 6.68; 2,4-$(OMe)_2$, 6.50, 6.58; 3-OMe, 6.34
(2)	60	4a-H, 4.25; 7-H, 2.50br, s; 8-Me, 7.59; 9,10-H_2, 2.65—3.00m; OCH_2·CH_3, 5.76q; OCH_2·CH_3, 8.64t, J 7.5	1-OMe, 6.32; 2,4-$(OMe)_2$, 6.19, 6.27; 3-OMe, 6.04
(4) [a]	270	1-H, 1.96; 7-H, 2.21dd; 8-H, 2.68t; 9-H, 2.43dt; 10-H, 2.61d; $J_{7,8} = J_{8,9} = J_{9,10} = 7.8$; $J_{7,9}$ 1.4; $J_{8,10} < 1$; OCH_aH_b·CH_3, 5.58dq; OCH_aH_b·CH_3, 5.73dq; OCH_aH_b·CH_3, 8.61t, $J_{a,b}$ 11.0, $J_{a,CH_3} = J_{b,CH_3}$ 7.3	2,4-$(OMe)_2$, 6.24, 6.24; 3-OMe, 6.07; 4a-OMe, 6.40
(4) [b]	60	1-H, 8.50; 7-H, −0.45; 8-H, −1.22; 9-H, −2.85; 10-H, −5.30; OCH_2·CH_3, 0.34; OCH_2·CH_3, 0.07	2-OMe, 8.54; 3-OMe, 1.94; 4-OMe, 0.74; 4a-OMe, 0.03
(5)	270	1-H, 2.00; 7-H, 2.44br, s; 8-Me, 7.61; 9-H, 3.65br, d; 10-H, 2.72d; $J_{9,10}$ 8.5; OCH_aH_b·CH_3, 5.58dq; OCH_aH_b·CH_3, 5.76dq; OCH_aH_b·CH_3, 8.60t; $J_{a,b}$ 10.7; $J_{a,CH_3} = J_{b,CH_3}$ 7.1	2,4-$(OMe)_2$, 6.24, 6.24; 3-OMe, 6.07; 4a-OMe, 6.40
(5) [b]	60	1-H, 9.26; 7-H, −0.42; 8-CH_3, −0.69; 9-H, −2.19; 10-H, −5.21; OCH_2·CH_3, 0.64; OCH_2·CH_3, 0.16	2-OMe, 9.11; 3-OMe, 2.23; 4-OMe, 0.98; 4a-OMe, 0.15
(6) [c]	270	1-H, 5.04br, s; 2-Me_2, 8.60; 4-SMe, 7.64; 5-H, 3.62dd; 6-H, 3.42t; 7-H, 3.88t; 8-H, 3.49d; $J_{5,6} = J_{6,7} = J_{7,8} = 7.8$, $J_{5,7}$ 1.3	
(7)	60	1-H, 2.05; 7-H, 1.95d, $J_{7,8}$ 8; 8,9,10-H_3, 2.35—2.92m; NH apparently obscured by ArH	2,4-$(OMe)_2$, 6.30, 6.32; 3-OMe, 6.14; 4a-OMe, 6.46
(8)	60	1-H, 3.37; 7-H, 1.65d, $J_{7,8}$ 8; 8,9,10-H_3, 2.15—2.7m; OCH_2·CH_3, 5.33q; OCH_2·CH_3, 8.51t, J 8	6.08, 6.11, 6.20, 6.25
(9)	60	1-H, 3.46; 5-NH, −3.06; 7-H, 1.65d, $J_{7,8}$ 8; 8,9,10-H_3, 2.4—2.7m	6.08, 6.11, 6.20, 6.25

[a] The multiplicity due to the CH_3·CH_2O protons is unchanged at 150 °C in $(CD_3)_2SO$ measured at 60 MHz. [b] LIS values for $Eu(dpm)_3$. [c] Solvent CCl_4.

TABLE 2

^{13}C N.m.r. chemical shifts (p.p.m. from internal Me_4Si; solvent $CDCl_3$) at 22 MHz[a]

Compound	C	CH	OCH_2	CH_3	OMe	C=O
(1)	124.0, 136.9, 139.5, 139.5; 6-C, 158.1	4a-C, 67.4; 121.1, 125.7, 128.2, 131.9	62.4	14.0	52.1, 52.1, 52.4, 52.9	162.9, 163.8, 164.5, 167.7
(4)	117.7, 119.9, 119.9, 133,8, 138.4; 6-C, 157.7; 4a-C, 75.9	117.0, 125.6, 126.1, 133.2, 141.7	62.6	14.0	51.7, 52.0, 52.6, 53.4	164.3, 164.9, 167.7, 167.7
(5)	117.7, 119.7, 119.7, 133.8, 136.1, 136.3; 6-C, 157.7; 4a-C, 76.1	116.9, 125.7, 133.8, 141.8	62.5	14.0, 21.0	51.6, 51.9, 52.5, 53.4	164.3, 165.0, 167.5, 167.8
(6) [b]	2-C, 70.4; 8a-C, 116.3; 4a-C, 143.3; 4-C, 159.4	113.7, 117.2, 124.9, 132.2		4-SMe, 11.8; 2-Me_2, 29.7		

[a] All ^{13}C—^{1}H attachments confirmed by off-resonance decoupling experiments. [b] Solvent CCl_4.

in the thiazole series, where the present 3- and 4-atoms of the quinazoline system are replaced by sulphur, but in this case acid is unnecessary, probably because the sulphur atom is more ready to accept a negative charge than the exocyclic nitrogen atom of (3). The methylene protons of the ethyl groups present in compounds (1), (2), (4), and (5) are diastereotopic, but this is only observed in the n.m.r. spectra for (4) and (5). This can be associated with the fact that these protons are relatively close to a large magnetoanisotropic group, the 4a-ester group, only in structures (4) and (5), for N-11 and the three carbon atoms which are attached are expected to be coplanar as in the case of corresponding thiazole adducts.[6] Adding large amounts of trifluoroacetic acid to solutions of (4) in [^{2}H]chloroform causes an immediate collapse of the multiplets of the AB part of the ABX_3 system to the quartet of the A_2X_3 type, this change being reversed by an excess of pyridine. This phenomenon can be associated with reversible protonation and ring opening to the dication derived from (3).

Aqueous methanolic acid hydrolysis of (4), and of (1) which presumably isomerises to (4) under the conditions used, removes the ethoxy-group to give the quinazolone (7).

Photolysis of (4) gives a more conjugated isomeric

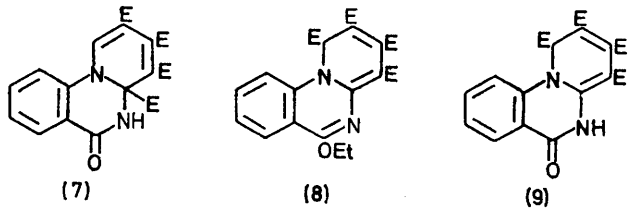
TABLE 3

U.v. spectra for methanolic solutions

Compound	$\lambda_{max.}$/nm (10^{-4} ε)
(1)	247br (2.2), 391 (0.83)
(2)	215 infl (1.77), 250br (2.30), 325infl (0.36), 393 (0.95)
(2) [a]	210 (2.09), 233infl (2.06), 253 (2.22), 270infl (1.70), 280infl (1.19), 400 (0.89)
(4) [b]	206 (2.18), 240br (2.25), 255infl (2.01), 270infl (1.43), 400 (0.85)
(5) [b]	208 (2.11), 232infl (2.18), 250br (2.27), 270infl (1.76), 280infl (1.47), 400 (1.09)
(8) [b]	236 (2.9), 294 (1.9), 345 (0.65), 435 (1.15)
(9)	226 (2.0), 289 (2.0), 385 (1.0)
(9) [c]	228 (2.0), 303 (2.1), 414 (1.5)

[a] Methanolic solution acidified with 5 drops of 72% $HClO_4$. [b] No change on acidification. [c] After basifying.

adduct (8) with a u.v. spectrum similar to that [8] of tetramethyl 1*H*-benzo[*c*]quinolizine-1,2,3,4-tetracarboxylate. The single proton resonance of (4) has now



moved upfield to a similar position (τ 3.37) to that of the 1-proton (τ 2.89) [9] of the above-mentioned benzo[*c*]-quinolizine, and the ABX_3 spectrum for the ethyl group has reverted to the A_2X_3 type. These changes are consistent with the bridgehead ester group of (4) undergoing a known type [10] of [1,5] shift to give structure (8). Hydrolysis of (8) gives the expected quinazolone (9), which shows a low-field signal due to the aromatic proton *peri* to the carbonyl group, and a very low-field amidic proton resonance, presumably a result of hydrogen bonding to the nearby ester group.

Lanthanide shift reagents (LSR) in chloroform complex poorly with the adducts (1) and (2), all signals moving downfield. In contrast, the rearrangement products (4) and (5) interact strongly. Most of the proton resonances move downfield (Table 1) but those due to the aromatic protons, particularly H-10, and the aromatic methyl group move upfield. The singlet due to H-1 is the most strongly shifted downfield. These

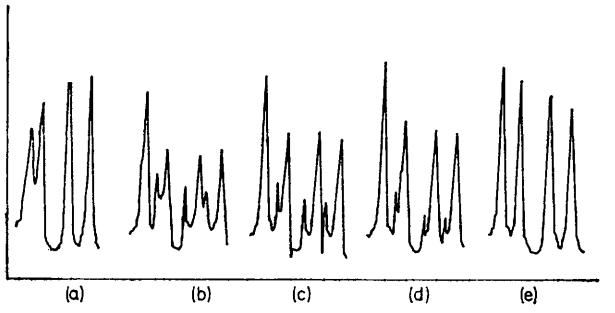


FIGURE 1 ^{1}H N.m.r. spectra (60 MHz) of the pyridoquinazoline (4) (*ca.* 0.05 mmol) with $Eu(tfc)_3$ (*ca.* 0.02 mmol) in $CDCl_3$ (0.33 ml) recorded (a) just after mixing solutions, (b) after *ca.* 2 min, (c) after *ca.* 4 min, (d) after *ca.* 6 min; (e) final spectrum

facts indicate that the LSR co-ordinates not to N-5 but to the 2-ester carbonyl oxygen atom, and that the preferred conformation is that indicated in Figure 2. This is confirmed by adding increasing amounts of the relaxation reagent $Gd(dpm)_3$. Only the 1-H signal broadens and disappears, the 10-H and 2-CO_2CH_3 signals broaden rapidly, and the width of the other signals remains unchanged.

The upfield shifts must be due to the protons concerned in the complex being outside the cone area in which the geometrical factor of the paramagnetic ion is positive.[11] Calculations of the position of the metal ion in the complex from (4) with $Eu(dpm)_3$ were made by a published procedure [12] on the basis of the lanthanide-induced shift (LIS) values (Table 1) for the single protons of the molecule, pure pseudocontact shifts being assumed. The probable location of the europium atom was *ca.* 3.08 Å from the carbonyl oxygen atom in the plane of the ring atoms N-11, C-1, and C-2 and the 2-carbonyl group the distance agreeing with the literature data.[11]

If the optically active shift reagent $Eu(tfc)_3$, tris-[3-(2,2,2-trifluoro-1-hydroxyethylidene)-(+)-camphorato]-europium(III), is used, splitting of the four ester-methyl

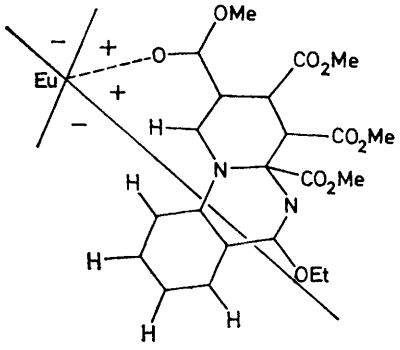


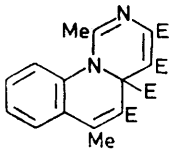
FIGURE 2 Projection of scale model of the adduct from (4) with $Eu(dpm)_3$, the calculated position of the europium atom and the magic angle of its dipolar field being shown

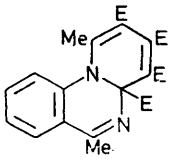
resonances is observed in a short time and this is attributed to the formation of two diastereoisomers. These splittings decrease as the distances between the chiral centre and the ester groups increase, and this is the reverse of the induced shifts as is expected of the illustrated structure (Figure 2). In a short space of time one set of four ester-methyl resonances gradually disappears while the other set increases correspondingly (Figure 1). The speed at which these processes occur varies, probably because of the presence of traces of moisture in the samples. The phenomenon could be due to the conversion of most of the initial racemate of (4) into the optical isomer, which gives the more stable diastereoisomer with the chiral shift reagent. The shift reagent, as a strong Lewis acid, will facilitate ring opening with inversion of the asymmetric centre. The optical activity of solutions of (4) and $Eu(tfc)_3$ changed after mixing over the same period of time as in the n.m.r. experiments. This change confirms the above conclusion.

In view of these results, structure (11) seems more

[8] R. M. Acheson, N. J. Earl, P. Higham, R. E. Richards, G. A. Taylor, and J. M. Vernon, *Proc. Chem. Soc.*, 1960, 281.
[9] R. M. Acheson, J. M. F. Gagan, and D. R. Harrison, *J. Chem. Soc.* (*C*), 1968, 362.
[10] R. M. Acheson, *Accounts Chem. Res.*, 1971, **4**, 177; I. Ninomiya, T. Kiguchi, and T. Naito, *J.C.S. Chem. Comm.*, 1974, 81.
[11] A. F. Cockerill, G. L. O. Davies, R. C. Harden, and D. M. Rackham, *Chem. Rev.*, 1973, **73**, 553.
[12] M. Y. Kornilov, A. V. Turov, and V. I. Zamkovoy, *Ukrain. khim. Zhur.*, 1975, **41**, 769.

likely than that (10) earlier proposed [2] for the adduct from 2,4-dimethylquinazoline and dimethyl acetylenedicarboxylate. The shifts induced by europium are


(10)


(11)

large for only one ester methyl and the higher field methyl (MeC=C) group. It it can be assumed, as for (4), that the co-ordination centre for the europium is the carbonyl oxygen atom, then the results are consistent with this hypothesis.

EXPERIMENTAL

The instruments and chromatographic procedures employed have been described. Optical rotation measurements were made on a Perkin-Elmer 141 polarimeter.

toluene, crystallized to give *tetramethyl* 6-*ethoxy*-4a*H*-*pyrido*[1,2-a]*quinazoline*-1,2,3,4-*tetracarboxylate* (1) as pale yellow prisms (7.15 g), m.p. 175—178°. The filtrate was chromatographed on alumina (200 ml) and eluted with toluene followed by ether to give more tetraester (1) (3.93 g).

(ii) A solution of the adduct (1) (5.0 g) in acetonitrile (50 ml) containing 2 drops of trifluoroacetic acid was refluxed (5 min), the solvent was removed *in vacuo*, and the residue was triturated with ether. *Tetramethyl* 6-*ethoxy*-4a*H*-*pyrido*[1,2-a]*quinazoline*-2,3,4,4a-*tetracarboxylate* (4) solidified, and was recrystallized (MeOH) to give yellow prisms, m.p. 175—176° (5.0 g).

(iii) Dimethyl acetylenedicarboxylate was added to 4-ethoxy-6-methylquinazoline in the same way as in (i), but after removing the reaction solvent *in vacuo* the residue was triturated with ether, and the adduct (2) then precipitated; it formed yellow microcrystals (from MeOH) (80%), m.p. 186°.

(iv) The adduct (5), m.p. 198° (yellow prisms), was prepared in quantitative yield from the adduct (2) as described in (ii) but was recrystallized by dissolving in the minimum volume of dimethylformamide and diluting with 5 volumes of methanol.

TABLE 4

Preparation of 4-ethoxyquinazolines

	2,3-H_2-4-one			4-Cl			4-EtO	
Substituents	Solvent	% Yield	M.p. (°C)	Solvent	% Yield	M.p. (°C)	% Yield	M.p. (°C)
None	MeOH	77	214—216	Light petroleum	85	97	90 [a]	48—50
6-Me	MeOH	42 [b]	Sublimed	Cyclohexane	80 [d]	105—106	53	63—64
8-Me	Sublimed	59 [c]	Sublimed	Cyclohexane	71 [e]	126	85	36—37

[a] M.p. 175—176° (picrate) for material from a different procedure (ref. 14). [b] M.p. 242° for material from a different procedure (ref. 15). [c] M.p. 250—251° for material from a different procedure (ref. 15). [d] M.p. 105—106° for material from a different procedure (ref. 16). [e] M.p. 129—130° for material from different procedure (ref. 16).

Analytical data (within accepted limits), i.r. and mass spectra for the new compounds, and n.m.r. and i.r. spectra for all additional quinazolines synthesized, are available as Supplementary Publication No. SUP 21572 (5 pp.).†

4-Ethoxyquinazolines.—The 3,4-dihydroquinazolinones were prepared by the method of Armarego,[13] and refluxed with stirring in phosphoryl chloride (20 mol. equiv.) containing phosphorus pentachloride (1.5—2.0 mol. equiv.) until the solid had dissolved (1—4 h). After 1 h more the mixture was evaporated *in vacuo* and the chloroquinazoline extracted from the residue with the recrystallization solvent.

The 4-chloroquinazoline was refluxed with sodium ethoxide [from sodium (1.5 mol. equiv.) in ethanol (150 mol. equiv.)] for 2 h, the solvent was removed, and the residue was sublimed (bath temperature *ca.* the m.p. of the product) at 0.2—0.3 Torr to give the 4-ethoxyquinazoline (Table 4).

Addition of Dimethyl Acetylenedicarboxylate to 4-Ethoxyquinazolines.—(i) 4-Ethoxyquinazoline (7.5 g) and dimethyl acetylenedicarboxylate (13.5 g) in acetonitrile (previously dried over CaH_2) were refluxed for 20 h. The solvent was removed *in vacuo* and the residue, in cold

Hydrolysis of the Quinazolines (1) *and* (2).—The quinazoline (1) or (2) (0.2 g) was dissolved in methanol (20 ml) containing 72% perchloric acid (0.1 g) and refluxed for 1 h. The solvent was removed *in vacuo* and the residue crystallized (2 : 1 v/v MeOH–MeCN) to give *tetramethyl* 5,6-*dihydro*-6-*oxo*-4a*H*-*pyrido*[1,2-a]*quinazoline*-2,3,4,4a-*tetracarboxylate* (7) (0.95 g) as yellow prisms, m.p. 241—243°.

Irradiation of the Quinazoline (1).—The quinazoline (1) (1.0 g) was irradiated in methanol (1 250 ml) under nitrogen with a Hanovia 450 W mercury-vapour lamp, for 1.75 h. The solvent was removed *in vacuo* and the residue chromatographed on alumina. Elution of the main orange band with benzene–chloroform (1 : 1 v/v) gave *tetramethyl* 6-*ethoxy*-1H-*pyrido*[1,2-a]*quinazoline*-1,2,3,4-*tetracarboxylate* (8) (0.3 g) as deep yellow platelets (from methanol–acetonitrile), m.p. 248—249°.

Hydrolysis of the Quinazoline (8).—The quinazoline (8) (0.2 g) was hydrolysed under the same conditions as for (1) and (2) to give *tetramethyl* 5,6-*dihydro*-6-*oxo*-1H-*pyrido*-[1,2-a]*quinazoline*-1,2,3,4-*tetracarboxylate* (9) (0.16 g) as pale yellow prisms, m.p. 224° [from methanol–acetonitrile (1 : 1 v/v)].

Lanthanide Shift Reagent Experiments.—The shifts

† For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1974, Index issue.

[13] W. L. F. Armarego, *J. Appl. Chem.*, 1961, **11**, 70.
[14] K. Adachi, *J. Pharm. Soc. Japan*, 1955, **75**, 1426.
[15] J. Maillard, M. Benard, M. Vincent, Vo-Van-Tri, R. Jolly, R. Morin, Mrs. Benazkate, and C. Menillet, *Chim. ther.*, 1967, **2**, 231.
[16] W. L. F. Armarego, *J. Chem. Soc.*, 1962, 561.

induced by $Eu(dpm)_3$ (LIS values) were measured for solutions in [^{2}H]chloroform containing the same amounts of the substrate (S) (*ca.* 0.05 mmol) and various proportions of the reagent up to the ratio [Eu] : [S] *ca.* 0.5 : 1 the LIS values being then reduced to the ratio 1 : 1 and averaged for 7—10 measurements (Table 1).

A 0.024mM-solution of $Eu(tfc)_3$ in [^{2}H]chloroform ($[\alpha]_D^{20}$ +15.4°) had an optical rotation of +3.252°. When the solution was made 0.036mM in (**4**) the rotation immediately became +2.840°, changing gradually to the constant value +2.902° after 5 min.

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