Electron-deficient Heteroaromatic Ammonioamidates.† Part 27.‡ Quinazolinioamidates.† Part 14.‡ *N*-Amination of some Quinazoline Derivatives and some Reactions of the Resulting Quinazolinioamides.

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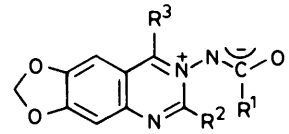
Treatment of the quinazolines (**4d**) and (**4e**) bearing no substituents at position 4 with *O*-mesitylenesulphonylhydroxylamine leads to amination of N-3 and formation of the mesitylenesulphonates of the corresponding (quinazolin-3-io)amides (**5a**) and (**5b**). Upon alkaline treatment these mesitylenesulphonates yield the free (quinazolin-3-io)amides (**5a**) and (**5b**) which exist predominantly in the form of the dimers (**6a**) and (**6b**), respectively. *O*-Mesitylenesulphonyl hydroxylamine aminates the 4-substituted quinazolines (**4f**)—(**4h**) at N-1, affording the mesitylenesulphonates (**7b**—**d**) of the corresponding (quinazolin-1-io)amides. The salts (**7b**) and (**7c**) undergo ring contraction to indazole derivatives of type (**10**) on alkaline treatment. All attempts to acylate the (quinazolin-3-io)amide (**5a**), its dimer, or its mesitylenesulphonate failed, whereas the mesitylenesulphonate of the (quinazolin-1-io)amide (**7b**) could be both benzoylated and ethoxycarbonylated. Irradiation studies of the (quinazolin-3-io)amides (**5a**) and (**5b**), respectively, of their dimers (**6a**) and (**6b**), and of the *N*-(quinazolin-1-io)amidate (**8c**) are also reported.

With the aim of studying their photochemistry,[2] we synthesized a series of *N*-(quinazolin-3-io)amidates (**2a**) [which, depending both on the conditions and the nature of the substituents R^1, R^2, and R^3, may exist, in the absence of nucleophiles HNu, as the dimers (**3**)[3,4]] by ring closure of the appropriate acylhydrazones of 2-acylaminobenzaldehydes and 2-acylaminoacetophenones (**1a**).[3] In order to devise an additional method of synthesis for type (**2**) compounds, the possibility of *N*-amination of type (**4**) quinazolines and of subsequent *N*-acylation of the expected (quinazolin-3-io)amides (**5**) has now been studied.

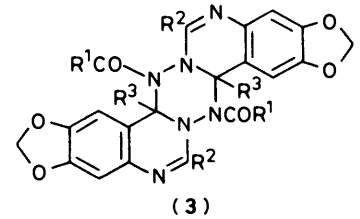
(**1**)

a; R^1 = OEt, OCH_2Ph, Ph, R^2, R^3 = H, Me
b; R^1 = OBu^t, R^2 = Me, R^3 = H
c; R^1 = OBu^t, R^2 = Pr, R^3 = H



(**2**)

a; R^1 = OEt, OCH_2Ph, Ph, R^2, R^3 = H, Me
b; R^1 = OBu^t, R^2 = Me, R^3 = H
c; R^1 = OBu^t, R^2 = Pr, R^3 = H
d; R^1 = OEt, R^2 = H, R^3 = Me
e; R^1 = OEt, R^2 = R^3 = Me
f; R^1 = R^2 = Me, R^3 = H



(**3**)

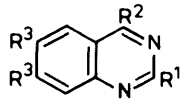
R^1 = OEt, OCH_2Ph, Ph, R^2, R^3 = H, Me

N-*Amination of the Quinazolines* (**4d**)—(**4h**).—Very little is known about the *N*-amination of quinazolines. Tamura *et al.* have obtained 1-amino-4-phenylquinazolin-1-ium mesitylenesulphonate (**7a**) *via* the amination of 4-phenylquinazoline (**4a**) with *O*-mesitylenesulphonyl hydroxylamine (MSH); benzoylation of the product and subsequent treatment with K_2CO_3 furnished the *N*-(quinazolin-1-io)benzamidate (**8a**).[5]

Treatment of the quinazoline (**4b**) with hydroxylamine-*O*-sulphonic acid (HAS), another aminating reagent, has led to the formation of a mixture of at least four products, *viz.* compounds (**4c**), (**9**), (**10a**), and (**11**).[6a] The formation of compounds (**4c**) and, particularly, (**9**) indicates that HAS is able to attack C-4 of the quinazoline ring as a nucleophile rather than one of the ring nitrogen atoms as an electrophile. *N*-Aminations of some related pyrimidines by MSH have also been observed[6b,7] as has the different behaviour of HAS (nucleophilic attack at C-4 of the pyrimidine ring).[6b]

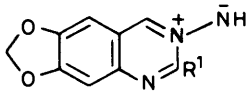
We have studied the reaction of quinazolines (**4d**)—(**4h**) with MSH. When a suspension of the quinazoline (**4d**) in dichloromethane was treated with MSH at 0 °C, the starting compound was aminated at N-3 to furnish the mesitylenesulphonate of the (quinazolin-3-io)amide (**5a**) which was converted by treatment with aqueous sodium carbonate or sodium hydroxide into a mixture of the free amide (**5a**) and its dimer (**6a**). The related free amide (**5c**) had previously been shown to exist in the crystalline state exclusively as the dimer (**6c**).[8] As shown by its ^1H n.m.r. spectrum, compound (**5a**)

† As a result of a revision in the 1979 IUPAC Organic Nomenclature Rules for the naming of ions, *etc.*, the presently accepted names *N*-ammonio- and *N*-quinazolinio-amidates will be changed to *N*-ammonio- and *N*-quinazolinio-amidides, respectively.
‡ For Parts 26 and 14, respectively, see ref. 1.



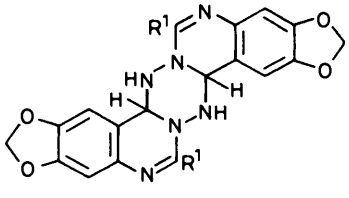
(4)

a; $R^1 = R^3 = H$, $R^2 = Ph$
b; $R^1 = R^2 = R^3 = H$
c; $R^1 = R^3 = H$, $R^2 = NH_2$
d; $R^1 = Me$, $R^2 = H$, $R^3—R^3 = —OCH_2O—$
e; $R^1 = Pr$, $R^2 = H$, $R^3—R^3 = —OCH_2O—$
f; $R^1 = R^2 = Me$, $R^3—R^3 = —OCH_2O—$
g; $R^1 = Me$, $R^2 = (CH_2)_2CO_2Et$, $R^3 = MeO$
h; $R^1 = (CH_2)_2CO_2Et$, $R^2 = Me$, $R^3 = MeO$
i; $R^1 = Me$, $R^2 = NH_2$, $R^3—R^3 = —OCH_2O—$
k; $R^1 = Pr$, $R^2 = NH_2$, $R^3—R^3 = —OCH_2O—$



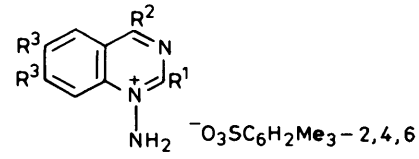
(5)

a; $R^1 = Me$
b; $R^1 = Pr$
c; $R^1 = (CH_2)_2CO_2Et$
d; $R^1 = (CH_2)_3CO_2Et$



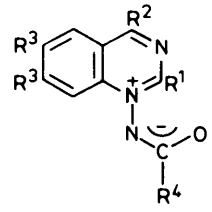
(6)

a; $R^1 = Me$
b; $R^1 = Pr$
c; $R^1 = (CH_2)_2CO_2Et$
d; $R^1 = (CH_2)_3CO_2Et$



(7)

a; $R^1 = R^3 = H$, $R^2 = Ph$
b; $R^1 = R^2 = Me$, $R^3—R^3 = —OCH_2O—$
c; $R^1 = Me$, $R^2 = (CH_2)_2CO_2Et$, $R^3 = MeO$
d; $R^1 = (CH_2)_2CO_2Et$, $R^2 = Me$, $R^3 = MeO$



(8)

a; $R^1 = R^3 = H$, $R^2 = Ph$
b; $R^1 = R^2 = Me$, $R^3—R^3 = —OCH_2O—$, $R^4 = Ph$
c; $R^1 = R^2 = Me$, $R^3—R^3 = —OCH_2O—$, $R^4 = OEt$

appears to exist in deuteriochloroform solution, even in the presence of TFA, in the form of a mixture with its dimer (**6a**), the equilibrium being considerably shifted towards the latter.* For the sake of simplicity, this compound [as well as the related propyl derivative, obtained similarly from quinazoline (**4e**)] will therefore henceforth be called dimers (**6a**) and (**6b**), respectively.

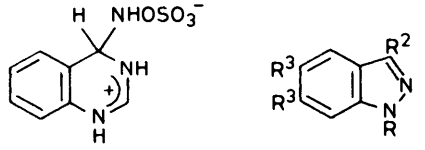
The site of amination of quinazolines (**4d**) and (**4e**) is established by the observation that refluxing of the hydrochlorides of the *N*-(quinazolin-3-io)amidates (**2b**) and (**2c**) [obtained by an unambiguous method, *viz.* cyclization of acylhydrazones (**1b**) and (**1c**)] with methanolic hydrogen chloride leads, after treatment with alkali, to the same products as were obtained by amination of the quinazolines (**4d**) and (**4e**), respectively. Further proof in favour of the (quinazolin-3-io)amide structures of these amination products is the observation that alkaline treatment of their mesitylenesulphonates leads to products in which the quinazoline rings are retained, *viz.* to type (**5**) compounds and their dimers (**6**), rather than, as is the case with the mesitylenesulphonates (**7**) of (quinazolin-1-io)amides (see below), by ring contraction to indazoles of type (**10**).

In contrast, the quinazolines (**4f**) and (**4g**) are aminated by MSH at N-1 to give the mesitylenesulphonates (**7b**) and (**7c**), respectively, of the corresponding (quinazolin-1-io)amides. Compound (**4h**) had been previously observed to behave similarly.[8] Whether this is a general rule of orientation in the reaction discussed and, in particular, whether the electronic effects of the C-4 substituent do exert an influence on the orientation, remains to be established. The structure assignments, (**7c**) and (**7d**), to the amination products of compounds (**4g**) and (**4h**), respectively, are based on their ^1H n.m.r. spectra taken in [$^2H_4$]methanol. The protons of the 4-methyl group and of the CH_2 group attached to C-4 exhibit intense signals [δ 3.08 (s) and 3.06 and 3.72 (2 t, CH_2CH_2), respectively] while the 4-methyl groups of the reference compounds (**2d**) and (**2e**) are not seen, owing to rapid ^1H–^2H exchange.[3] The considerable differences in the ^1H–^2H exchange rates most probably arise from different charge distributions, supporting the view that the formal positive charge of the amination products of compounds (**4g**) and (**4h**) is located at N-1, in contrast to N-3 of the reference compounds (**2d**) and (**2e**). Further proof in favour of structure (**7d**) for the amination product of compound (**4h**) comes from the observation that this product may be cyclized to yield compound (**13**) whose ^1H n.m.r. spectrum, taken in [$^2H_4$]-methanol, exhibits an intense singlet at δ 2.96 p.p.m. assigned to the C-methyl group.[8]

The evidence in favour of structure (**7b**) for the amination product of quinazoline (**4f**) comes from an examination of its reactivity towards acylating agents as well as to sodium hydroxide (see below).

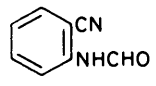
Catalytic Reduction.—Catalytic reduction of dimer (**6a**) in acetic acid furnished compound (**12**) which, together with its hydrochloride, proved identical with authentic samples.[3] Similarly, catalytic reduction of mesitylenesulphonate (**7b**) leads to a product to which structure (**14a**) or (**14b**) was assigned on the basis of its ^1H n.m.r. spectrum.

* For the analogous dimerization of quinolinio-, isoquinolinio-, and phenanthridinio-amides, see ref. 9.

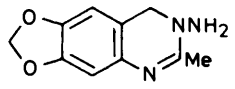


(9) (10)

a; R = R^2=R^3=H
b; R = Ac, R^2 = Me, R^3–R^3 = —OCH_2O—
c; R = Ac, R^2 = $(CH_2)_2CO_2Et$, R^3 = MeO
d; R = $CO(CH_2)_2CO_2Et$, R^2 = Me, R^3 = MeO
e; R = R^3=H, R^2= Ph



(11)



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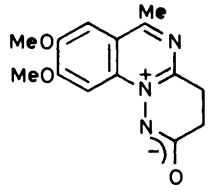

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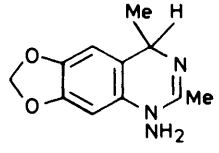
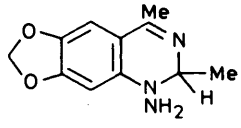
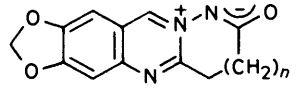


(14a)



(14b)

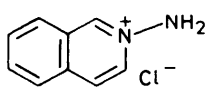


(15) a: n =1, b: n =2

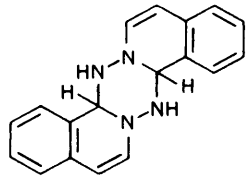
Acylations and Attempted Acylations of N-*Aminoquinazolinium Salts and the Corresponding Free Bases.*—The 1-aminoquinazolin-1-ium salts of type (7), and the isomeric 3-aminoquinazolin-3-ium salts and their corresponding free bases [(5) ⇌ (6)], differ considerably in their behaviour towards acylating agents. While all our attempts at acylation of the dimer (**6a**) met with complete failure, Tamura *et al.* succeeded in benzoylating the 1-aminoquinazolinium salt (**7a**) to (**8a**);[5] similarly, we were able to benzoylate and ethoxycarbonylate the salt (**7b**) to obtain, although in moderate to low yields, the amidates (**8b**) and (**8c**), respectively. These successful acylations are considered as proof in favour of structure (**7b**) for the amination product of the quinazoline (**4f**).

The successful application of the intramolecular version of this acylation reaction had enabled us earlier to cyclize compound (**7d**) to compound (**13**).[8] On the other hand, and in agreement with our unsuccessful attempts at acylating the dimer (**6a**), our attempts at cyclization of the dimers (**6c**) and (**6d**) to obtain compounds (**15a**) and (**15b**), respectively, met with complete failure.[8]

The reluctance of the dimers (**6**) as well as of the mesitylenesulphonates of (quinazolin-3-io)amides (**5**) to be acylated (both inter- and intra-molecularly) is somewhat surprising because the related isoquinoline derivatives (**16**) and (**17**) are easily acylated.[9c]



(16)

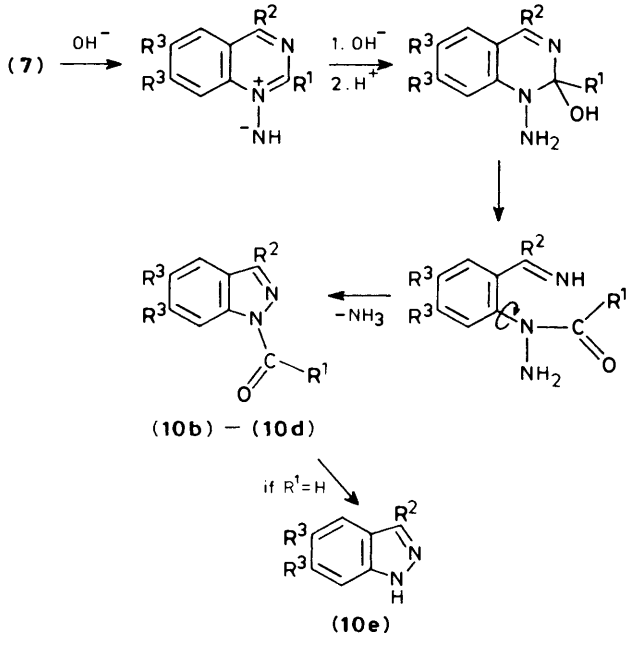


(17)

Ring Contraction of (Quinazolin-1-io)amides to Indazoles.—In contrast to the (quinazolin-3-io)amides of type (**5**) whose quinazoline rings are stable both in the mesitylenesulphonates and the free bases and, in particular, are retained in the course of dimerization to type (**6**) compounds,[3] the (quinazolin-1-io)-amides could not be obtained by treatment of the mesitylenesulphonates (**7b**) and (**7c**) with alkali, the free bases instead undergoing ring contraction to the corresponding indazole derivatives (**10b**) and (**10c**), respectively. This ring contraction of the amination product of compound (**4f**) is considered as further proof in favour of the structure (**7b**).

The same ring contraction has been observed when compound (**7d**) was treated with alkali; however, in this case the ring contraction was a minor side reaction leading to the formation of traces of compound (**10d**), competing with the main reaction of ring closure to give compound (**13**).[8]

The probable mechanism of these ring contractions is shown in the Scheme.



(10b) – (10d)

(10e)

Scheme.

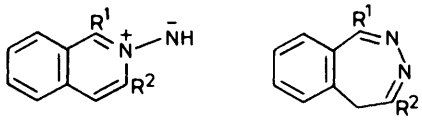
The *N*-(quinazolin-1-io)amidates of type (**8**) proved more stable than the corresponding amides liberated from their salts of type (**7**). For example, ring contraction of compound (**8a**) to yield the indazole (**10e**) requires prolonged refluxing with aqueous sodium hydroxide.[10] In the course of this reaction the benzoyl group is hydrolytically cleaved; however, it is not clear

whether the cleavage precedes the ring contraction reaction or takes place at an intermediate stage of the latter.

For the related ring contraction of a (pyrimidin-1-io)amide, see ref. 7.

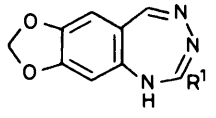
Photochemical Studies.—From the irradiation mixtures of the dimers (**6a**) and (**6b**), three compounds were isolated in both cases, *viz.* the parent quinazolines (**4d**) and (**4e**), respectively, and the 4-aminoquinazolines (**4i**) and (**4k**), respectively, as well as products of unknown structures, containing one carbon and one nitrogen atom more, and one hydrogen atom less than the monomers [(**5a**) and (**5b**)] of the starting compounds. Tsuchiya *et al.* had obtained 5*H*-2,3-benzodiazepines (**19**) by irradiation of isoquinolinioamides (**18**).[11] The 1,3,4-benzotriazepines (**20a**) and (**20b**), expected by analogy, could not be isolated from the irradiation mixtures of the dimers (**6a**) and (**6b**), respectively.

Irradiation of the *N*-(quinazolin-1-io)amidate (**8c**) furnished the parent quinazoline (**4f**) along with traces of a further product of unknown structure.



(**18**) (**19**)

(R^1, R^2 = H, Me)



(**20**)

a: R^1 = Me, b: R^1 = Pr

Experimental

Kieselgel $PF_{254+366}$ was used as the adsorbent in all t.l.c. separations. Light petroleum refers to the fraction of b.p. 40—60 °C. M.p.s are uncorrected. I.r. and mass spectra were obtained with Spektromom 2000 and Varian MAT 311A instruments* by electron impact (e.i.) (70 eV) and using the direct insertion system. ^{1}H N.m.r. spectra were recorded at 60 MHz with a Perkin-Elmer R-12 instrument or at 100 MHz with Varian XL-100A and JEOL PS-100 spectrometers in $CDCl_3$, $CDCl_3$—TFA, CD_3OD, or $(CD_3)_2SO$ solutions. $SiMe_4$ was used as the internal reference for the first two solvents while the peak of the monoprotio contaminant of the solvent was used as the reference signal for the spectra recorded in CD_3OD (δ = 3.35 p.p.m.) and $(CD_3)_2SO$ solutions (δ = 2.50 p.p.m.).

The irradiations were carried out under argon at room temperature, using high-pressure mercury immersion lamps (HPK-125) with Pyrex filters as the light sources.

Ether refers to diethyl ether.

Synthesis of Quinazolines (**4e**)—(**4g**).—(*a*) A suspension of 2-amino-4,5-methylenedioxybenzaldehyde[12] (1.65 g, 10 mmol) in a mixture of CH_2Cl_2 (10 ml) and pyridine (3 ml) was treated with butyryl chloride (1.30 g, 11 mmol) with cold water cooling. The mixture was stirred for 1 h, and the resulting solution washed with water. The organic layer was separated, dried ($MgSO_4$), and evaporated to dryness to give 2-butyryl-4,5-methylenedioxybenzaldehyde (1.55 g, 66%), m.p. 78 °C (crude); $\nu_{max.}$(KBr): 3 350, 1 695, and 1 650 cm^{-1}; this was used in the following step without further purification.

The above crude product (5 g, 21 mmol) was heated with an ethanolic NH_3 solution (60 ml; saturated at 0 °C) in a sealed tube for 5 h at 150 °C. The solution was evaporated to dryness under reduced pressure to give a tarry product from which, by sublimation at 150 °C (bath temperature) and 15 mmHg, 6,7-*methylenedioxy-2-propylquinazoline* (**4e**) (2.15 g, 47%), m.p. 78.5 °C, was obtained (Found: C, 66.6; H, 5.55; N, 12.75. $C_{12}H_{12}N_2O_2$ requires C, 66.65; H, 5.60; N, 12.95%). δ (60 MHz; $CDCl_3$) 1.02 (t, *J* 7 Hz), 1.6—2.1 (m), and 3.02 (t, *J* 7.5 Hz, 2-Pr), 6.10 (s, OCH_2O), 7.05 and 7.12 (2s, 5-H and 8-H), and 9.02 (s, 4-H); *m/z* (rel. intensity, %; 40 °C) 216 (47, $M^{+\cdot}$), 215 (16), 201 (38), 188 (100), 187 (5), 174 (7), 173 (5), 147 (6), and 120 (6).

(*b*) 2-Acetylamino-4,5-methylenedioxyacetophenone[13] (5 g, 23 mmol) was heated with an ethanolic NH_3 solution (60 ml; saturated at 0 °C) in a sealed tube for 5 h at 150 °C. The solution was allowed to cool to give 6,7-methylenedioxy-2,4-dimethylquinazoline (**4f**) (3.65 g, 80%), m.p. 185—186 °C (lit.,[14] 185—186 °C). For the mass spectrum of compound (**4f**) see ref. 3, and for its u.v. and n.m.r. spectra see ref. 14.

(*c*) A mixture of ethyl 3-(2-amino-4,5-dimethoxybenzoyl)-propionate[8] (25.6 g, 87 mmol), acetic acid (110 ml), acetic anhydride (11 ml, 120 mmol), and powdered zinc (0.1 g) was refluxed for 0.5 h and poured into ice–water (500 ml) to give the crystalline N-*acetyl derivative* (21.6 g, 76.5%), m.p. 100 °C (from EtOAc–hexane) (Found: C, 59.55; H, 6.6; N, 4.25. $C_{16}H_{21}NO_6$ requires C, 59.45; H, 6.55; N, 4.35%). $\nu_{max.}$(KBr): 3 130, 1 720, 1 680, and 1 620 cm^{-1}; δ (60 MHz; $CDCl_3$) 1.28 and 4.17 (t and q, CO_2Et), 2.20 (s, Ac), 2.71 and 3.31 (2 t, CH_2CH_2), 3.89 and 3.95 (2s, 2 × MeO), and 7.30 and 8.45 (2s, 2 × ArH).

A mixture of the above 3-(2-acetylamino-4,5-dimethoxybenzoyl)propionate (3.2 g, 10 mmol) and an ethanolic NH_3 solution (30 ml; saturated at 0 °C) was heated for 11 h in a sealed tube at 160 °C. The solvent was distilled off, and the oily residue triturated with hexane–ether (1:1 v/v) to give *ethyl* 6,7-*dimethoxy-2-methylquinazolin-4-ylpropionate* (**4g**) (1.45 g, 47%), m.p. 140 °C (from EtOH) (Found: C, 63.55; H, 6.6; N, 9.4. $C_{16}H_{20}N_2O_4$ requires C, 63.15; H, 6.60; N, 9.20%). $\nu_{max.}$(KBr) 1 730 cm^{-1}; δ (60 MHz; $CDCl_3$) 1.26 and 4.18 (t and q, CO_2Et), 2.78 (s, 2-Me), 2.97 and 3.50 (2 t, CH_2CH_2), 4.03 (s, 2 × MeO), and 7.25 and 7.29 (2s, 2 × ArH).

2-Acylamino-4,5-methylenedioxybenzaldehyde t-Butoxycarbonylhydrazones (**1b**) *and* (**1c**).—(*a*) t-Butyl carbazate (3.70 g, 28 mmol) was added to a refluxing ethanolic solution (80 ml) of 2-acetylamino-4,5-methylenedioxybenzaldehyde[12] (2.90 g, 14 mmol). The mixture was refluxed for 3 h, and allowed to cool slowly with continuous scratching of the reaction vessel to obtain *2-acetylamino-4,5-methylenedioxybenzaldehyde t-butoxycarbonylhydrazone* (**1b**) (3.32 g, 74%), m.p. 227 °C (from BuOH) (Found: C, 56.3; H, 6.2; N, 12.8. $C_{15}H_{19}N_3O_5$ requires C, 56.05; H, 5.95; N, 13.10%).

(*b*) Starting with an ethanolic solution (50 ml) of 2-butyrylamino-4,5-methylenedioxybenzaldehyde (3.30 g, 14 mmol), t-butoxycarbonylhydrazone (**1c**) (1.57 g, 32%), m.p. 163 °C (from EtOH), was similarly obtained (Found: C, 58.7; H, 6.4; N, 12.35. $C_{17}H_{23}N_3O_5$ requires C, 58.45; H, 6.65; N, 12.05%). $\nu_{max.}$(KBr) 3 400, 3 200, 1 745, 1 670, and 1 635 cm^{-1}.

(6,7-Methylenedioxyquinazolin-3-io)amides (**5a**) *and* (**5b**): *Preparation of Authentic Samples.*—(*a*) Thionyl chloride (0.08 ml, 1.05 mmol) was added dropwise to a solution of compound (**1b**) (321 mg, 1 mmol) in CH_2Cl_2 (6 ml) with continuous stirring and ice cooling. Stirring was continued for 3 h. The mixture was evaporated to dryness, and the residue was taken up in

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anhydrous methanol (2 ml). The suspension was acidified (pH 1) with methanolic HCl, refluxed until the evolution of CO_2 and isobutene ceased (*ca.* 1.5 h), and evaporated to dryness. The residue was taken up in water (5 ml), and the resulting suspension made alkaline (pH 8—9) by adding 10% aqueous NaOH. The mixture remained heterogeneous but both its colour and its appearance changed. The crystalline product was filtered off and thoroughly washed with water to give practically pure (i.r., ^{1}H n.m.r.) (*2-methyl-6,7-methylenedioxyquinazolin-3-io)amide* (**5a**) (197 mg, 97%) which, as shown by its ^{1}H n.m.r. spectrum, exists in $CDCl_3$ solution even in the presence of TFA, and almost certainly in the crystalline state also, mainly as the dimer (**6a**), m.p. 283 °C (decomp.) (Found: C, 58.95; H, 4.7; N, 20.9. $C_{20}H_{18}N_6O_4$ requires C, 59.10; H, 4.45; N, 20.70%). δ (100 MHz; $CDCl_3$—TFA) 2.62 (s, 2 × Me, dimer), 3.05 (s, Me, monomer), 6.08 (s, 2 × OCH_2O, dimer), 6.3 (s, 2 × 4-H, dimer), 6.35 (s, OCH_2O, monomer), 6.6 and 6.8 (2s, 4 × ArH, dimer), and 7.28 and 7.45 (2s; 2 × ArH, monomer); the intensity ratio of the corresponding signals of the dimeric and monomeric forms was *ca.* 15:1—20:1.

Because of its very low solubility the product could not be recrystallized. However, the m.p. could be raised to 293 °C (decomp.) by rapidly heating a sample (0.1 g) in dry DMF (0.5 ml) to the b.p. and immediately cooling the suspension back to room temperature; $\nu_{max.}$(KBr): 3 150, 1 610, 1 575vs, 1 495vs, 1 475vs, and 1 445 cm^{-1}.

Prolonged heating (refluxing) with DMF caused darkening of the suspension, and the m.p. of the resulting product was somewhat lower (*e.g.* DMF treatment of 1—2 g samples led to products of m.p.s not higher than 285 °C).

Alternatively, a solution of the crude product (1.0 g, 2.5 mmol) in hot acetic acid (12.5 ml) was treated with a solution of mesitylenesulphonic acid dihydrate (2.4 g, 10 mmol) in acetic acid (3 ml). The resulting colourless crystals were filtered off (while the mixture was still hot), and washed with hot acetic acid (3 × 2 ml) and methanol (3 × 5 ml) to give compound (**5a**)·$HO_3SC_6H_2Me_3$-2,4,6 (1.25 g, 62%), m.p. 247.5 °C. An aqueous (10 ml) suspension of the salt (100 mg) was made alkaline by the addition of 10% aqueous NaOH, and stirred for 1 h at room temperature. The insoluble product was filtered off and washed with water and methanol to give the dimer (**6a**) (43 mg, 85%), m.p. 295 °C (decomp.); *m/z* (rel. intensity, %; 280 °C) 406 (20, $M^{+\cdot}$), 218 (5), 204 (100), 203 (97), 189 (28), 188 (54), 187 (32), 174 (20), 162 (10), 161 (10), and 120 (21).

When the purification procedure *via* the mesitylenesulphonate was carried out with 1—10 g samples, the m.p. was not raised above 285 °C.

(*b*) Similarly obtained was (*6,7-methylenedioxy-2-propylquinazolin-3-io)amide* (**5b**) (210 mg, 91%) [which also exists predominantly in the form of the dimer (**6b**), m.p. 255—256 °C (from DMF)] starting with the hydrazone (**1c**) (349 mg, 1 mmol) (Found: C, 62.15; H, 5.6; N, 18.15. $C_{12}H_{13}N_3O_2$ requires C, 62.30; H, 5.65; N, 18.15%). $\nu_{max.}$(KBr) 3 400, 3 130, 1 630, 1 595vs, 1 510, and 1 480vs cm^{-1}; δ (100 MHz; $CDCl_3$–TFA) 1.08 (t, *J* 7.5 Hz, 2 × CH_2Me), 1.82 (sext., *J* 7.5 Hz, 2 × CH_2CH_2Me), 2.7 (t, *J* 7.5 Hz, ⩾ CCH_2CH_2, monomer), 2.91 (t, *J* 7.5 Hz, ⩾ CCH_2CH_2, dimer), 6.09 (s, 2 × OCH_2O, dimer), 6.30 (s, OCH_2O, monomer), 6.32 (s, 2 × 4-H, dimer), 6.63 and 6.75 (2s, 4 × ArH, dimer), and 7.28 (s, 2 × ArH, monomer, + $CHCl_3$); *m/z* (rel. intensity, %; 260 °C) 462 (17, $M^{+\cdot}$), 232 (100), 231 (19), 217 (24), 216 (49), 215 (64), 203 (27), 201 (14), 188 (34), 174 (10), 162 (5), and 161 (6).

Amination of the Quinazolines (**4d**)—(**4h**).—(*a*) A CH_2Cl_2 solution (90 ml) of MSH[15] (*ca.* 70% purity; 13.7 g, *ca.* 45 mmol) was added to a suspension of the quinazoline (**4d**)[3] (8.3 g, 45 mmol) in CH_2Cl_2 (80 ml) with continuous stirring at −5 to 0 °C (bath temperature). Stirring was continued for 1 h at 0 °C and for 5 h at room temperature. The mixture remained heterogeneous throughout but its colour and appearance changed. The mixture was allowed to stand overnight and diluted with ether (100 ml). The insoluble material was filtered off and washed with ether (2 × 50 ml) to give the crude mesitylenesulphonate of compound (**5a**) (12.8 g, 83%, based on the amount consumed of the starting quinazoline), m.p. 210—213 °C. The crude product was still contaminated by either the starting quinazoline or its mesitylenesulphonate since the quinazoline could be detected by t.l.c. in the mixture resulting from the treatment of an aqueous suspension of the crude product with 10% aqueous NaOH. The crude product (1 g) was purified by boiling with acetic acid (4 ml) and immediately cooling the mixture back to room temperature. The insoluble material was filtered off and washed with methanol (2 × 1 ml) and ether (2 × 1 ml) to give the pure mesitylenesulphonate of compound (**5a**) (*ca.* 0.7 g), m.p. 248 °C, which proved identical (m.p., i.r.) with an authentic sample (see above).

Treatment of the pure mesitylenesulphonate with NaOH as described above for the authentic sample of this product furnished the dimer (**6a**) (85—90%), m.p. 279—283 °C, and which proved identical (i.r.) with an authentic sample (see above).

The combined filtrate and washings of the crude mesitylenesulphonate were evaporated to dryness to give almost pure (m.p., i.r.) unchanged starting quinazoline (**4d**) (1.1 g, 13.3%), m.p. 176 °C (lit.,[3] 180 °C).

(*b*) A CH_2Cl_2 solution (10 ml) of MSH[15] (*ca.* 70% purity, *ca.* 4.7 mmol) was added to a suspension of quinazoline (**4e**) (1.0 g, 4.65 mmol) in CH_2Cl_2 (10 ml) with continuous stirring at 0 °C (bath temperature). The resulting clear solution was stirred for 10 min at room temperature, and evaporated to dryness under reduced pressure to give a crystalline mesitylenesulphonate. This was taken up in a small amount of acetone, filtered off, washed with acetone, and dried in air. An aqueous suspension (10 ml) of the mesitylenesulphonate was made alkaline by the addition of 10% aqueous Na_2CO_3. The mixture remained heterogeneous but its appearance changed. The insoluble material was filtered off, washed with water and methanol, dried, and recrystallized from DMF to give the dimer (**6b**) (0.32 g, 30%), m.p. 258 °C, identical (m.p., i.r.) with an authentic sample prepared as described above.

(*c*) A CH_2Cl_2 solution (20 ml) of MSH[15] (70% purity; 3.1 g, *ca.* 10 mmol) was added dropwise to a suspension of the quinazoline (**4f**) (2.0 g, 10 mmol) in CH_2Cl_2 (20 ml) with continuous stirring at 0 °C (bath temperature). Stirring was continued for 2 h at 0 °C. The mixture remained heterogeneous throughout but its appearance changed. Colourless crystals of compound (**7b**) (2.2 g, 53%), m.p. 225—228 °C, were filtered off. Recrystallization from MeCN raised the m.p. to 228—229 °C (Found: C, 57.8; H, 5.8; N, 10.05. $C_{20}H_{23}N_3O_5S$ requires C, 57.55; H, 5.55; N, 10.05%). δ [60 MHz; $(CD_3)_2SO$] 2.18 (s, *p*-Me, anion), 2.48 (s, 2 × *o*-Me, anion), 2.97 and 3.03 (2s, 2-Me and 4-Me), 6.50 (s, OCH_2O), 6.68 (s, 2 × ArH, anion), 7.15 br s, NH_2), and 7.88 and 7.95 (2s; 5-H and 8-H).

(*d*) A CH_2Cl_2 solution (4 ml) of MSH[15] (*ca.* 70% purity; 0.61 g, *ca.* 2 mmol) was added dropwise to a solution of the quinazoline (**4g**) (0.61 g, 2 mmol) in CH_2Cl_2 (4 ml) with continuous stirring at 0 °C (bath temperature). Crystallization of the product soon started. The mixture was allowed to warm up to room temperature with stirring, when it was diluted with ether (25 ml) to give compound (**7c**) (0.90 g, 87%), m.p. 195 °C (from EtOH or EtOAc) (Found: C, 57.9; H, 6.7; N, 8.4; S, 6.35. $C_{25}H_{33}N_3O_7S$ requires C, 57.80; H, 6.40; N, 8.10; S, 6.15%). $\nu_{max.}$(KBr): 1 745 cm^{-1}; δ (100 MHz; [$^2H_4$]methanol) 1.20 and 4.18 (t and q, CO_2Et), 2.21 (s, *p*-Me, anion), 2.52 (s, 2 × *o*-Me, anion), 3.06 and 3.72 (2t, CH_2CH_2), 3.10 (s, 2-Me), 4.14 and

4.20 (2s, 2 × MeO), 6.70 (s, 2 × ArH, anion), 7.56 (s, 5-H), and 7.78 (s, 8-H).

(*e*) Compound (**7d**) was similarly obtained, starting with the quinazoline (**4h**)[8] (0.61 g, 2 mmol); (**7d**), (0.55 g, 53%), m.p. 220 °C (decomp.) (from ethanol) (Found: C, 57.95; H, 6.55; N, 8.3; S, 6.35. $C_{25}H_{33}N_3O_7S$ requires C, 57.80; H, 6.40; N, 8.10; S, 6.15%). $\nu_{max.}$(KBr) 1 720 cm^{-1}; δ (100 MHz; CD_4) 1.21 and *ca.* 4.2 (t and q, CO_2Et), 2.23 (s, *p*-Me, anion), 2.59 (s, 2 × *o*-Me, anion), 3.08 (s, 4-Me), 3.09 and 3.75 (2t, CH_2CH_2), 4.13 and 4.21 (2s, 2 × MeO), 6.78 (s, 2 × ArH, anion), 7.55 (s, 5-H), and 7.83 (s, 8-H).

Reduction of the Dimer (**6a**).—An authentic sample of dimer (**6a**) (3.0 g, 7.5 mmol) was reduced in acetic acid solution (60 ml) in the presence of a 10% Pd/C catalyst (0.8 g) at normal pressure and ambient temperature. After uptake of the calculated amount of H_2 the catalyst was filtered off, and the filtrate was evaporated to dryness under reduced pressure. The residue was taken up in 10% aqueous Na_2CO_3 (30 ml) and CH_2Cl_2 (35 ml), and the aqueous layer was extracted with CH_2Cl_2 (2 × 30 ml). The combined organic solutions were dried ($MgSO_4$) and evaporated to dryness to give compound (**12**) (1.1 g, 32%), which proved identical (m.p., i.r.) with an authentic sample.[3]

Compound (**12**) (1.1 g) was dissolved in a small amount of methanol and treated with ethereal HCl to give (**12**)·HCl (1.2 g, 94%), which proved identical (m.p., i.r.) with an authentic sample.[3]

Reduction of the Mesitylenesulphonate (**7b**).—Compound (**7b**) (2.45 g, 5.9 mmol) was similarly reduced to obtain an oily product which crystallized when triturated with ether. The pink crystals were recrystallized from benzene–light petroleum to give 1-*amino*-2,4-*dimethyl*-6,7-*methylenedioxy*-1,4- (**14a**) (0.52 g 40%) or -1,2-*dihydroquinazoline* (**14b**), colourless crystals, m.p. 148—149 °C (Found: 60.3; H, 6.05; N, 19.0. $C_{11}H_{13}N_3O_2$ requires C, 60.25; H, 6.00; N, 19.15%). δ (60 MHz; $CDCl_3$) 1.35 (d, *J* 7.1 Hz, CH*Me*), 2.33 (s, ≷C–Me), 3.93 (br s, exch., NH_2), 4.38 (q, *J* 7.1 Hz, C*H*Me), 5.88 (s, OCH_2O), and 6.50 and 6.68 (2s, 2 × ArH).

Acylations of the Mesitylenesulphonate (**7b**).—(*a*) A mixture of the title compound (1.5 g, 3.6 mmol) and benzoyl chloride (10 ml) was stirred for 3 h at 100—105 °C (bath temperature). The resulting dark-red solution was allowed to cool and poured into ether (40 ml) to give the yellow crystalline mesitylenesulphonate of the benzamidate (**8b**) (1.6 g). This was taken up in CH_2Cl_2 (50 ml), and methanol (a few ml) was added to give a clear solution which was vigorously stirred with 3% aqueous Na_2CO_3 (20 ml). Conventional work-up of the organic phase and purification of the crude product (0.68 g) by t.l.c. (benzene–acetone 1:1; eluant MeOH), gave the benzamidate (**8b**) (0.25 g, 21.5%), m.p. 215—216 °C (benzene–light petroleum) (Found: C, 67.4; H, 4.65; N, 13.2. $C_{18}H_{15}N_3O_3$ requires C, 67.30; H, 4.70; N, 13.10%); δ (60 MHz; $CDCl_3$) 2.86 and 2.89 (2s, 2 × Me), 6.10 (d, probably the inner peaks of an AB spectrum, OCH_2O), 7.15—7.45 (m, 5-H and Ph, *p*-H and 2 × *m*-H), 7.65 (s, 8-H), 8.05–8.35 (m, Ph, 2 × *o*-H); *m/z* (rel. intensity, %; 200 °C) 321 (14, $M^{+\cdot}$), 306 (100), 244 (7), 202 (25), 187 (10), 120 (9), 105 (20), and 77 (31).

(*b*) The mesitylenesulphonate (**7b**) (6.10 g, 14.6 mmol) was dissolved in an anhydrous methanolic solution (50 ml) of metallic sodium (0.29 g, 14.6 mmol). The solution was evaporated to dryness at reduced pressure, and the residue was taken up in CH_2Cl_2 (25 ml). Diethyl dicarbonate (2.85 g, 17.5 mmol) was added. The mixture was refluxed for 5 h and poured into water (50 ml). The organic layer was washed with water (2 × 10 ml), dried ($MgSO_4$), and evaporated to dryness. The residue was worked up by column chromatography (Kieselgel 60; benzene–acetone, 10:1) to give compound (**8c**) (0.85 g, 20%), m.p. 196—197 °C (from CH_2Cl_2–acetone) (Found: C, 58.25; H, 5.15; N, 14.35. $C_{14}H_{15}N_3O_4$ requires C, 58.10; H, 5.25; N, 14.50%). δ (60 MHz; CCl_3) 1.33 and 4.12 (t and q, *J* 7.2 Hz, CO_2Et), 2.84 and 2.89 (2s, 2 × Me), 6.13 (s, OCH_2O), 7.20 (s, 5-H), and 7.73 (s, 8-H); *m/z* (rel. intensity, %; 160 °C) 289 (78, $M^{+\cdot}$), 274 (7), 246 (10), 244 (37), 217 (30), 202 (100), 201 (18), 187 (14), 176 (13), 175 (34), and 120 (12).

(*c*) The mesitylenesulphonate (**7b**) (0.42 g, 1.0 mmol) was similarly treated with ethanolic sodium ethoxide. The dry residue of the mixture was taken up in CH_2Cl_2 (10 ml); ethyl chloroformate (0.1 ml, 1.05 mmol) was added, and the mixture stirred for 0.5 h at room temperature. Work-up as described in (*b*) yielded compound (**8c**) (30 mg, 10%), m.p. 196 °C.

(*d*) DBU (220 mg, 1.4 mmol) was added dropwise to a solution of the mesitylenesulphonate (**7b**) (300 mg, 0.7 mmol) in anhydrous THF with continuous stirring at 0 °C (bath temperature). Stirring was continued for 10 min, and then ethyl chloroformate (86 mg, 0.8 mmol) was added to the mixture. The bath was removed, and the mixture was stirred for 1.5 h, and evaporated to dryness under reduced pressure. The residue was taken up in CH_2Cl_2 (20 ml). The solution was washed with water (2 × 5 ml), dried, and evaporated to dryness. The oily residue (82 mg) was worked up by t.l.c. (EtOAc–MeOH, 8:2) to give 14 mg (7%) of compound (**8c**), m.p. 195 °C, which proved identical (i.r.) with the samples prepared as described in (*b*) and (*c*).

Attempted Acylations of the Dimer (**6a**) *and of the Mesitylenesulphonate of the Monomer* (**5d**).—(*a*) The dimer (**6a**) could neither be benzoylated (PhCOCl, CH_2Cl_2, Na_2CO_3, room temperature; or PhCOCl, pyridine, reflux), nor acetylated (Ac_2O, 60 h, room temperature; refluxing with Ac_2O caused profound decomposition).

(*b*) Treatment of the mesitylenesulphonate of the (quinazolin-3-io)amide (**5d**) with benzoyl chloride or diethyl dicarbonate under the conditions described above for the analogous reactions of the isomeric 1-aminoquinazolin-1-ium mesitylenesulphonate (**7b**) did not afford the expected acyl derivatives.

Ring Contractions of the Mesitylenesulphonates (**7b**) *and* (**7c**).—(*a*) A suspension of the mesitylenesulphonate (**7b**) (recrystallized, see above; 0.5 g, 1.2 mmol) in 5% aqueous $NaHCO_3$ solution (10 ml) was stirred for 20 h at room temperature; the mixture remained heterogeneous but its appearance changed. The crystalline material (0.25 g, 94%) was isolated by conventional extraction with CH_2Cl_2 and proved (i.r.) to be practically pure. Further purification by t.l.c. (benzene–acetone, 1:1) furnished a pure sample of 1-*acetyl*-3-*methyl*-5,6-*methylenedioxyindazole* (**10b**), m.p. 175 °C (Found: C, 60.75; H, 4.5; N, 13.05. $C_{11}H_{10}N_2O_3$ requires C, 60.55; H, 4.60; N, 12.80%). $\nu_{max.}$(KBr) 1 720 cm^{-1}. δ (60 MHz; $CDCl_3$) 2.42 (s, Me), 2.67 (s, Ac), 6.02 (s, OCH_2O), 6.82 (s, 4-H), and 7.78 (s, 7-H); *m/z* (rel. intensity, %; 70 °C) 218 (32, $M^{+\cdot}$), 176 (100), 175 (26), 147 (3), 146 (2), 118 (3), 79 (4), 77 (5), 63 (5), and 43 (8).

(*b*) 10% Aqueous NaOH (1.2 mmol) was added dropwise to an aqueous (5 ml) suspension of the mesitylenesulphonate (**7c**) (0.52 g, 1 mmol) with continuous stirring. The mixture remained heterogeneous but the colour of the suspension changed. Ethanol (10 ml) was added (no clear solution resulted), and stirring was continued for 1 h. The bulk of the ethanol was removed by distillation under reduced pressure, and the insoluble material was filtered off and washed with water to give *ethyl* 1-*acetyl*-5,6-*dimethoxyindazol*-3-*ylpropionate* (**10c**) (0.30 g, 94%), m.p. 159—160 °C (from ethanol) (Found: C, 60.2; H, 6.35; N, 9.0. $C_{16}H_{20}N_2O_5$ requires C, 60.00; H, 6.25; N, 8.75%). $\nu_{max.}$(KBr) 1 740 and 1 700 cm^{-1}; δ (100 MHz; $CDCl_3$) 1.34 and 4.28 (t and q, CO_2Et), 2.83 (s, Ac), 3.02 and 3.35 (2t, CH_2CH_2), 4.07 and 4.11 (2s, 2 × MeO), 7.00 (s, 4-H), and 7.85 (s, 7-H); *m/z*

(rel. intensity, %; 115 °C) 320 (100, $M^{+\cdot}$), 278 (81), 277 (10), 247 (7), 233 (22), 205 (53), 204 (12), 191 (32), 189 (7), 161 (5), and 147 (6).

Irradiation Experiments.—(*a*) A suspension of the dimer (**6a**) (450 mg, 2.2 mmol) in a mixture of CH_2Cl_2 (400 ml) and AcOH (15 ml) was irradiated for 30 h. The mixture was evaporated to dryness under reduced pressure. The dry residue was taken up in CH_2Cl_2 (3 ml), the insoluble material was filtered off, and the filtrate was worked up by t.l.c. (benzene–acetone, 1:1) to give, in decreasing order of their R_F values, the following products: quinazoline (**4d**)[3] (41 mg, 10%), a compound of unknown structure (8 mg; m.p. >265 °C), and the aminoquinazoline (**4i**)[4b] (48 mg, 11%).

The $M^{+\cdot}$ peak of the unknown compound (*m/z* 228) probably corresponds to $C_{11}H_8N_4O_2$ [*cf.* the analogous product obtained in (*b*)], *i.e.* contains one carbon and nitrogen atom more, and one hydrogen atom less than the monomer (**5a**) of the starting compound.

(*b*) The dimer (**6b**) (900 mg, 3.9 mmol) was similarly irradiated, and the irradiation mixture was similarly worked up to give the following products in the order of their decreasing R_F values: the quinazoline (**4e**) (221 mg, 26%), the 4-aminoquinazoline (**4k**) (135 mg, 15%), m.p. 232 °C, and a compound of unknown structure (13.5 mg; m.p. 160—163 °C).

Compound (**4k**), *m/z* (rel. intensity, %; 115 °C) 231 (24, $M^{+\cdot}$), 230 (16), 216 (33), 203 (100), 189 (9), 188 (4), 173 (6), and 163 (10).

A compound of unknown structure (Found: $M^{+\cdot}$, 256.0943. $C_{13}H_{12}N_4O_2$ requires *M*, 256.0960), *i.e.* the compound contains one carbon and one nitrogen atom more, and one hydrogen atom less than the monomer (**5b**) of the starting compound; *m/z* (rel. intensity, %; 120 °C) 256 (100, $M^{+\cdot}$), 255 (11), 241 (14), 228 (92; M–C_2H_4), 227 (14), 214 (6), 213 (9), and 174 (6).

(*c*) Compound (**8c**) (410 mg, 1.4 mmol) was irradiated in methanolic solution (100 ml) for 34 h under the conditions described in (*a*). The mixture was evaporated to dryness, and the residue was worked up by preparative t.l.c. (benzene–acetone, 1:1) to give, in order of decreasing R_F values, a small amount (16 mg) of a compound of unknown structure, m.p. 174 °C and the parent quinazoline (**4f**) (168 mg, 58%), m.p. 185—186 °C, which proved identical (m.p., i.r., ^{1}H n.m.r.) with an authentic sample prepared as described above.

A compound of unknown structure, *m/z* (rel. intensity, %; 80 °C) 218 (100, $M^{+\cdot}$, $C_{11}H_{10}N_2O_3$), 217 (64), 189 ($C_{10}H_9N_2O_2$, 43), 188 (20), 187 (8), 147 ($C_8H_5NO_2$, 22), 120 (6), 104 (7), 76 (9), and 56 (10).

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