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ELECTRON DEFICIENT HETEROAROMATIC AMMONIOAMIDATES—XVI[a]

THE SYNTHESIS AND PHOTOCHEMISTRY OF ETHYL N-(2-METHYL-4-METHYLENE-6,7-METHYLENEDIOXY-3,4-DIHYDRO-3-QUINAZOLINYL)-N-PHENYLCARBAMATE

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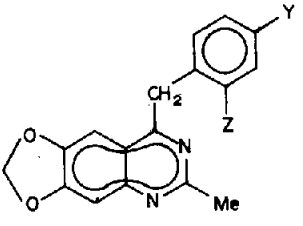
Abstract—Irradiation through Pyrex of the N-(dihydroquinazolinyl)carbamate **3c** in ethanol furnishes mixtures (Scheme 1) of two photoisomers (**2c** and **4a**), two dimeric products: the 1,2-bis(4-quinazolinyl)ethane **5** and the (*p*-phenylene)dicarbamate **6**, and of ethyl N-phenylcarbamate. The latter, as well as compounds **4a** and **5** are formed also on irradiation of compound **2c**. The radicals **9** and **10**, formed by homolysis of the N–N bond of **3c** as well as of the CH_2–N bond of **2c** are considered to be the primary photoproducts of both reactions, and to lead, by various recombination processes, to compounds **2c**, **4a**, **5** and **6**, and to ethyl N-phenylcarbamate by hydrogen abstraction. It is not clear at present whether concerted photochemical [1, 3] shifts contribute to the formation of **2c** and **4a**.

In Part XI[2] of the present series the unprecedented photoinduced rearrangements of the N - (4 - methyl - 6,7 - methylenedioxy - 3 - quinazolinio) - ethoxyformamidates **1a** and **1b** into the corresponding ethyl N - (6,7 - methylenedioxy - 4 - quinazolinylmethyl) - carbamates **2a** and **2b**, respectively, have been described. In the present work this novel rearrangement has been subjected to further investigation in order to determine its possible mechanism.

Since compounds **1a** and **1b** are, at least potentially, able to exist as the tautomeric methylene bases **3a** and **3b**, respectively, the related ethyl N - (2 - methyl - 4 - methylene - 6,7 - methylenedioxy - 3,4 - dihydro - 3 - quinazolinyl) - N - phenylcarbamate **3c**[b] which is incapable to tautomerize into the corresponding type **1** compound, was synthesised and subjected to irradiation.

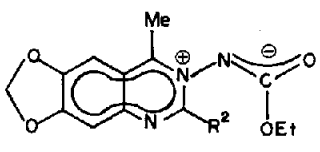
Argon purged ethanol and acetone solutions of compound **3c** were irradiated through Pyrex to furnish complex mixtures of products. These were worked up by chromatography to yield ethyl N - (2 - methyl - 6,7 - methylenedioxy - 4 - quinazolinylmethyl) - N - phenylcarbamate (**2c**), ethyl N - [*o* - (2 - methyl - 6,7 - methylenedioxy - 4 - quinazolinylmethyl)phenyl]carbamate (**4a**), 1,2 - bis(2 - methyl - 6,7 - methylenedioxy - 4 - quinazolinyl)ethane (**5**),[3] ethyl N-phenylcarbamate and diethyl N - phenyl - N,N′ - (*p* - phenylene)dicarbamate (**6**). The relative amounts of the products depended on



4

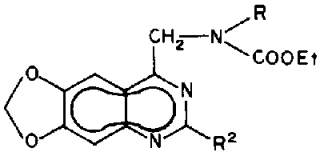
a: Y = H, Z = NHCOOEt
b: Y = H, Z = NH_2
c: Y = NHCOOEt, Z = H
d: Y = NH_2, Z = H
e: Y = NHAc, Z = H

[a] For Part XV, see Ref. 1.
[b] All attempts to obtain the related carbamate with a Me replacing the Ph group, failed.



1

a: R^2 = H
b: R^2 = Me



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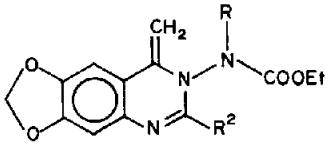
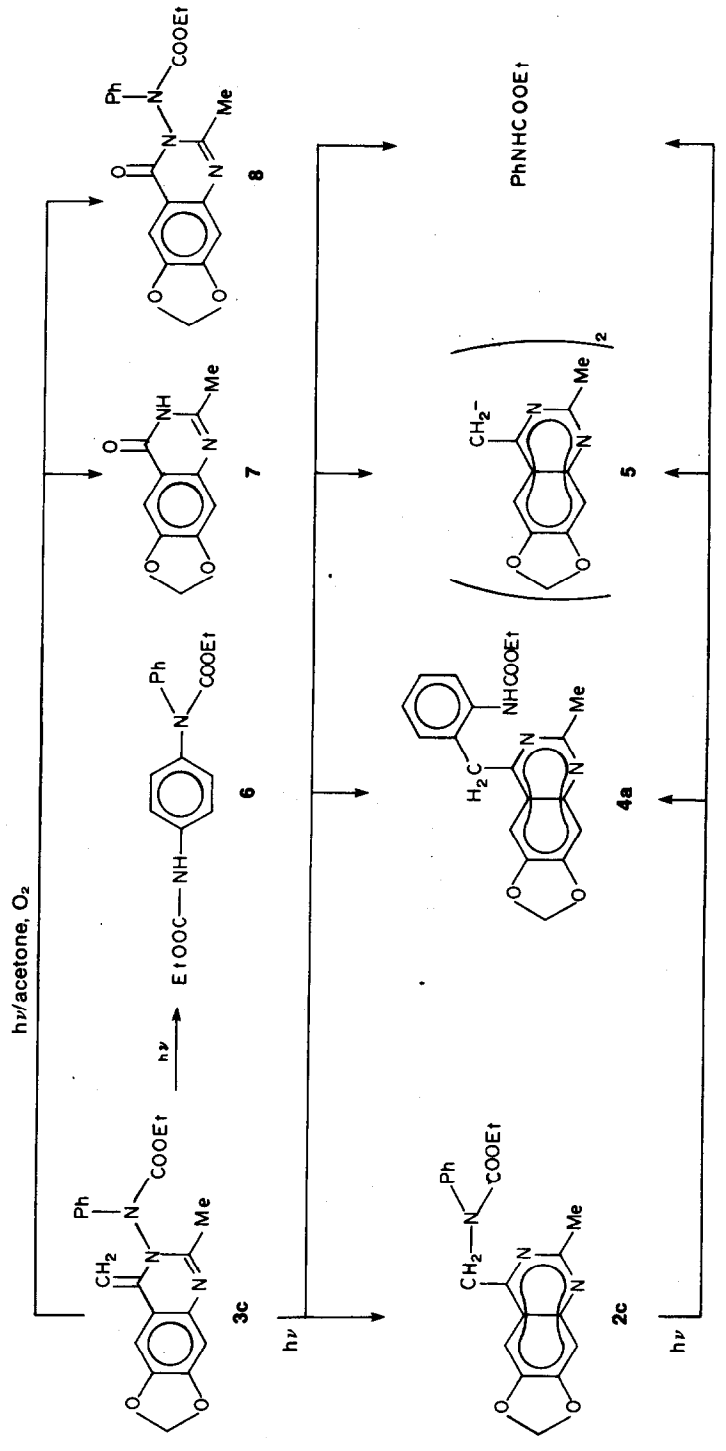


3

a: R = R^2 = H
b: R = H, R^2 = Me
c: R = Ph, R^2 = Me
d: R = Ph, R^2 = H



Scheme 1.

the solvent used. With ethanol the relative yields of compounds **2c** and **5** were significantly higher than with acetone, while the reverse was found for the yield of compound **4a**. In addition, 2 - methyl - 6,7 - methylenedioxy - 4 (3*H*) - quinazolinone (**7**)[3] and ethyl N - (2 - methyl - 6,7 - methylenedioxy - 4 - oxo - 3,4 - dihydro - 3 - quinazolinyl) - N - phenylcarbamate (**8**) were obtained when irradiation was performed in acetone solution.

The structures of the new compounds were deduced from their IR, mass, NMR and UV spectra, part of them was substantiated by synthesis, see below.

DISCUSSION

Two mechanisms were originally[2] considered for the photoisomerizations of compounds **1a** and **1b** into **2a** and **2b**, respectively: (a) photolysis of the N–N bond and insertion of the resulting *singlet* ethoxycarbonylnitrene into a C–H bond of the 4-Me group of the quinazoline fragment, and (b) tautomerization of the starting compounds into their 4 - methylene - 3,4 - dihydroquinazoline isomers (**3a, 3b**) and subsequent [1, 3] shifts (either concerted or stepwise) of the ethoxycarbonylamino groups from nitrogen to the exocyclic methylene C atom. Since (1) replacement of the solvent ethanol by acetone (which—if it has any effect—should favour the generation of *triplet* ethoxycarbonylnitrene) resulted in significant increase in the yield of **2b**, and (2) photolysis of N - (1 - pyridinio) - ethoxyformamidate has been reported to lead to almost exclusive generation of *triplet* ethoxycarbonylnitrene,[4] the first mechanism appears rather unlikely. The formation of compound **2c** on irradiation of **3c** is, on the other hand, consistent with both versions of the second of the above mechanisms.

Compounds **4a**, **5** as well as ethyl N-phenylcarbamate are in part secondary photoproducts of **3c**, formed via **2c**, as shown by irradiation experiments with a separately prepared sample of **2c**. (Another pathway for the reaction **3c**→**4a** which does not involve the intermediacy of compound **2c** is indicated by the observation that formation of compound **4a** from **2c** is considerably slower than from **3c**.) Compounds **5** and **6** are obviously the dimerization products[c] of radicals **9** and **10**, and ethyl N-phenylcarbamate may be derived from **10** by hydrogen abstraction from the solvent. [There is no indication of a corresponding hydrogen abstraction by **9**, since the expected reaction product, 2,4 - dimethyl - 6,7 - methylenedioxyquinazoline[3,5] could not be detected in the reaction mixture.] The formation of the radicals **9** and **10** strongly suggests that irradiation of **2c** may cause homolysis of its CH_2–N bond. Moreover, since homolysis of the N–N bond of compound **3c** should lead to the same primary products (i.e. radicals **9** and **10**) and (contrary to the homolysis of the CH_2–N bond of **2c**) result in gain of aromatic resonance energy, it appears highly probable that the N–N bond of compound **3c**, too, may suffer homolysis on irradiation.

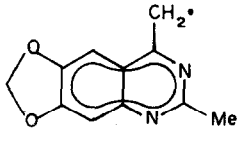
Recombinations of two unlike radicals **9** and **10** should lead to compounds **2c** and **4a**. The *p*-isomer (**4c**) of the latter could not be detected in the irradiation mixtures, which may be the result of the operation of the principle of least motion. Both isomerization steps **3c**→**2c** and **2c**→**4a** could, in principle, take place also as concerted photochemical [1, 3] sigmatropic shifts with retention at the migrating center.[d] Whether these additional concerted pathways do indeed operate or not, is not clear at present. It is hoped that a study of the wave-length dependence of the photochemistry of compound **3c** will help to clarify these problems.

Compounds **7** and **8** appear to be products of oxidation of the radical **9** and of compound **3c**, respectively, by traces of oxygen present in the reaction mixtures. The observation that compounds **7** and **8** were formed only when acetone was used as the solvent, strongly suggests that singlet oxygen is involved in these reactions.

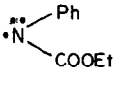
Synthesis of the starting compound **3c** *and chemical proof of structure of some of its phototransformation products*

4,5 - Methylenedioxy - 2 - nitroacetophenone[6] (**11**) was converted in three steps into 2 - acetylamino - 4,5 - methylenedioxyacetophenone phenylhydrazone; ring closure of the latter into the potentially tautomeric compound **13a** was brought about with $SOCl_2$ in CH_2Cl_2, and subsequent treatment with base. In $CDCl_3$ **13a** exists, according to its NMR spectrum, as the practically pure non-polar form **A**; no signals corresponding to the zwitter-ionic form **B** were detected. In methanol solution it exists, according to its NMR spectrum taken in CD_3OD, as a mixture of the non-polar form **A** and the methanol adduct **C**. Ethoxycarbonylation of compound **13a** furnished **3c**. Ethoxycarbonylation of the related compound **13b** (which was obtained similarly and which, too, exists as the non-polar tautomer in $CDCl_3$ solution) gave, in addition to several products whose structures have not yet been established, only minor quantities of **3d**.

The photosiomer **2c** was obtained from compound **11**[6] by successive bromination, anilinolysis, ethoxycarbonylation, reduction and acetylation to furnish **14** which, when heated with ethanolic ammonia, was smoothly transformed into **2c**. Attempts to synthesise the second photoisomer (**4a**) failed. [However, its *p*-isomer (**4c**) was obtained from **15a** *via* **15b**, **15c**, **15d**, **4e** and **4d**.[7]] The *ortho* position of the NHCOOEt group in **4a** was therefore established by hydrolysis and diazotization of

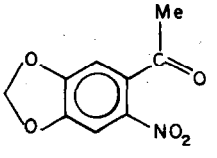


9*

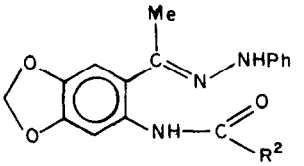


10*

*And further contributing resonance forms



11

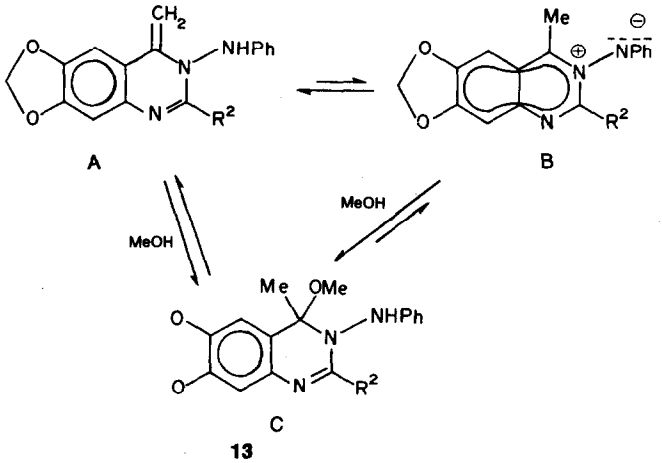


12

a: R^2 = Me
b: R^2 = H

[c] There is no indication whether the dimer **6** is formed directly or through the intermediacy of its symmetrical, hydrazobenzene type isomer.

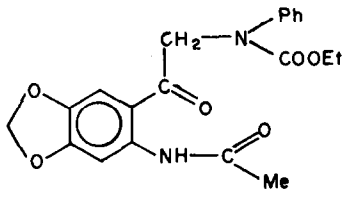
[d] No analogous concerted pathway would be conceivable for the formation of the *p*-isomer **4c** because of the geometrical impossibility of the transition state.



A B

C

13
a: $R^2 = Me$
b: $R^2 = H$



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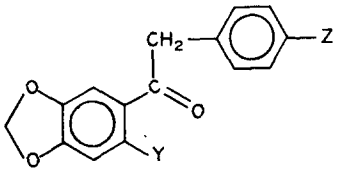
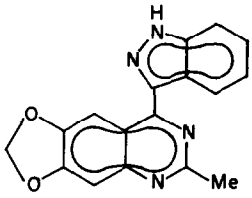


15

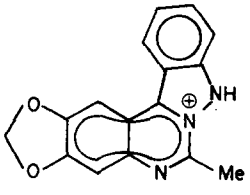
15
a: Y = H, Z = NO_2
b: Y = Z = NO_2
c: Y = Z = NH_2
d: Y = Z = NHAc



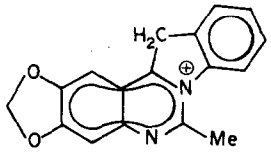
16

the resulting **4b** to yield the indazole **16**. Compound **6** was obtained by ethoxycarbonylation of *p*-aminodiphenylamine.

The mass spectrum of **3c** and those of the photoisomers **2c** and **4a** are shown in Fig. 1, together with the spectrum of **4c**. Figure 2 shows the mass spectra of **13a**, **4b** and **4d**. The ion at *m/e* 277 ($[M-NHCOOEt]^+$) in the spectrum of **3c** possesses the same composition ($C_{17}H_{13}N_2O_2$) as the $[M-NH_2]^+$ ion in the mass spectrum of **13a**. Although no significant daughter ions are formed from these ions, their metastable decompositions (DADI-spectra) are identical, suggesting the same ion structures for *m/e* 277 in the two spectra. Similar experimental evidence suggests that the *m/e* 278 ions ($C_{16}H_{12}N_3O_2$), too, are identical. Structures **a** and **b**, respectively, are



a: (*m/e* 278)



b: (*m/e* 277)

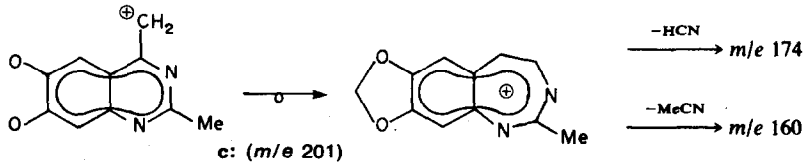
suggested for these ions. Great similarity is found between the spectra of **3c** and **13a** also in the lower mass regions. Thus, the ions at *m/e* 201 (**c**), together with their corresponding daughter ions, are identical in the two cases:

The abundances of these ions are significantly lower in the mass spectra of the photoproducts **2c** and **4a**, probably reflecting the absence of the 4-methylene group in the molecular ions of these compounds. Completely similar differences are observed when the spectra of **13a** and **4b** are compared (Fig. 2), whereas a high degree of similarity is found in the higher mass ranges. A corresponding resemblance is present in the spectra of **3c** and **4a** (Fig. 1), the compositions of the ions of the same masses being identical. Also the structures of the fragment ions *m/e* 278 and 277 of **4a** appear to be identical with those formed from **3c** (and **4b**).

In **4a** *m/e* 277 is generated by the direct elimination of the *ortho*-NHCOOEt substituent. This process parallels the loss of a hydrogen atom in the spectrum of **4c**, in which case direct elimination of the *para*-NHCOOEt substituent is completely absent. A corresponding behaviour is observed for **4b** and **4d**. While **4b** shows the direct loss of the *ortho*-NH_2 group, **4d** exhibits an abundant $[M-H]^+$ ion.

EXPERIMENTAL

IR and UV spectra were obtained with Hungarian Optical Works (Budapest) Type Spektromom 2000 and Unicam Type SP 700 spectrometers, respectively. The NMR spectra were obtained at 60 MHz on Perkin–Elmer Type R 12, at 90 MHz on Bruker (Karlsruhe) Type HFX-90, and at 100 MHz on Varian Type XL-100 VFT spectrometers. The mass spectra were obtained on a Varian Mat 311A (Grant No. 511-3809 from the Danish Natural Science Research Council) by electron impact (70 eV) and using



c: (*m/e* 201)

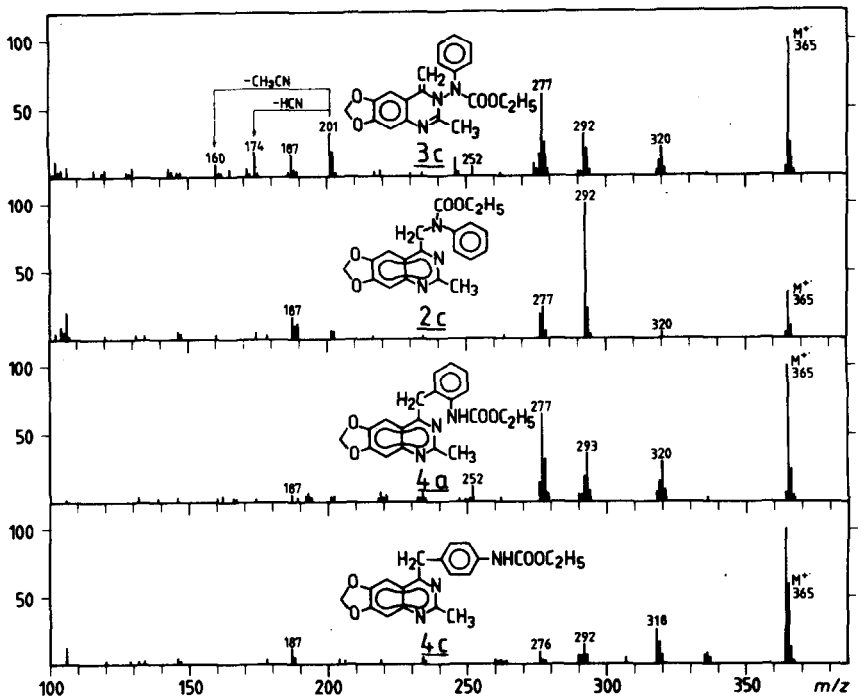


Fig. 1. Mass spectra of compounds **3c**, **2c**, **4a** and **4c**.

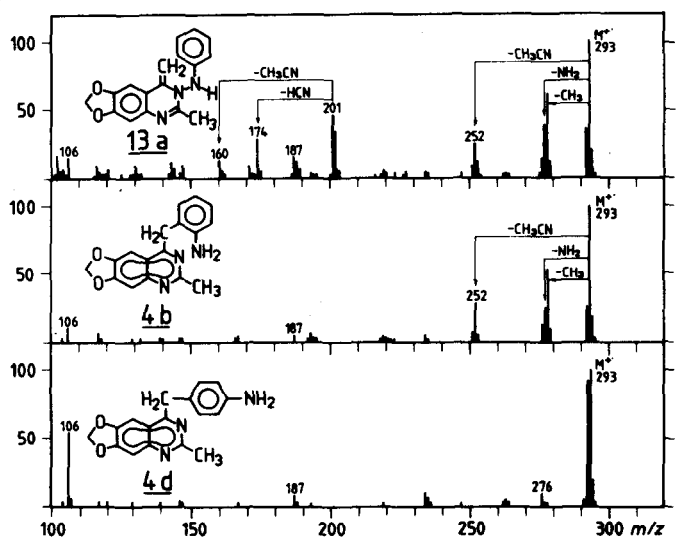


Fig. 2. Mass spectra of compounds **13a**, **4b** and **4d**.

direct insertion. For the spectra of reference compounds see Ref. 3.

4,5 - *Methylenedioxy* - 2 - *nitroacetophenone phenylhydrazone* was obtained by allowing **11**[6] to react with excess phenylhydrazine in the presence of AcOH in EtOH and treating the dark soln with Norite to yield 55% of the title compound m.p. 137–8° from EtOH. (Found: C, 59.91; H, 4.18; N, 14.07. Calc. for $C_{15}H_{13}N_3O_4$ (299.3): C, 60.20; H, 4.28; N, 14.04%).

2-Amino-4,5-methylenedioxyacetophenone phenylhydrazone. The aqueous (380 ml)–ethanolic (250 ml) suspension of the above compound (15.0 g; 50 mmoles) was treated at 60–65° with $Na_2S_2O_4$ (43 g; 250 mmoles) added in three portions. The purple colour of the suspension turned into yellow. After stirring for 30 min at 60–65° the mixture was allowed to cool to yield 10.2 g (76%) of the title compound, m.p. 180° from MeOH. (Found: C, 66.66; H, 5.63; N, 15.60. Calc. for $C_{15}H_{15}N_3O_2$ (269.3): C, 66.88; H, 5.61; N, 15.61%).

2 - *Acetylamino* - 4,5 - *methylenedioxyacetophene phenylhydrazone* (**12a**). A suspension of the above compound (1.5 g; 5.5 mmoles) in CH_2Cl_2 (20 ml) was treated with Ac_2O (0.6 ml; 6.1 mmoles). A yellow soln was rapidly formed from which the colourless title compound, 1.5 g (89%), m.p. 224–6° from MeOH. (Found: C, 65.35; H, 5.49; N, 13.59. Calc. for $C_{17}H_{17}N_3O_3$ (311.3): C, 65.58; H, 5.50; N, 13.50%) soon started to precipitate.

2 - *Formylamino* - 4,5 - *methylenedioxyacetophene phenylhydrazone* (**12b**). Acetic formic anhydride (15.4 ml; 20 mmole) was added under continuous stirring to the suspension of the amino compound (26.9 g; 0.10 mmole) in CH_2Cl_2 (100 ml) at r.t. From the resulting dark purple soln the cream-coloured product, 20.8 g (70%), m.p. 197° from EtOH (Found: C, 64.93; H, 5.17; N,

13.87. Calc. for $C_{16}H_{15}N_3O_3$ (297.3): C, 64.64; H, 5.09; N, 13.87%), soon started to precipitate.

3 - *Anilino* - 2 - *methyl* - 4 - *methylene* - 6,7 - *methylenedioxy* - 3,4 - *dihydroquinazoline* (**13a**). A suspension of **12a** (1.87 g; 6.0 mmoles) in CH_2Cl_2 (70 ml) was treated under stirring and ice-water-cooling with $SOCl_2$ (0.48 ml; 6.7 mmoles). The resulting clear brown soln was stirred for 2 hr and evaporated to dryness. The residue was dissolved in CH_2Cl_2 (15 ml) and treated with dry ether to yield a yellow gummy product (**13a** ·HCl) which, when separated and triturated with ether, turned into 1.9 g (97%) of a powder, m.p. 110° (dec). The crude salt was dissolved in CH_2Cl_2 (15 ml), and Et_3N (2 ml) was added with ice-cooling. The resulting suspension was evaporated to dryness and the residue washed with water to yield 1.1 g (60%) of the title compound, m.p. 161° from benzene–light petroleum. (Found: C, 69.16; H, 5.13; N, 14.57. Calc. for $C_{17}H_{15}N_3O_2$ (293.3): C, 69.61; H, 5.15; N, 14.33%).

UV (cyclohexane): 226 (4.54); 248 (4.19), sh; 329 (3.81); 334 (3.34), sh. NMR ($CDCl_3$ TMS): δ 2.30 (s, 3H, 2-Me); 3.8+4.2 (both d's, J = 2.6 Hz, exchangeable, 1H, each; 4-CH_2); 5.82 (s, exchangeable, 1H, N–H); 5.88 (s, 2H, OCH_2O); 6.6–7.3 (m, 7H, ArH's). NMR (CD_3OD; reference: CHD_2OD = 3.35): δ 1.24+2.27 (both s, total intensity 3H, 2-Me of form **A** and **C**, respectively); 6.0 (s, 2H, OCH_2O); 6.65–7.5 (m, 7H, ArH's). Mass spectrum (135°C) (see Fig. 2). NMR, HCl salt ($CDCl_3$, TMS): δ 3.0 and 3.2 (both s, 3H, each, 2-Me and 4-Me, respectively); 6.4 (s, 2H, OCH_2O); 6.6–7.3 (m, 5H, Ph); 7.35+7.55 (both s, 1H, each, 5-H+8-H); 12.2 (s, 1H, NH).

3 - *Anilino* - 4 - *methylene* - 6,7 - *methylenedioxy* - 3,4 - *dihydroquinazoline* (**13b**). The suspension of **12b** (14.9 g; 50 mmoles) in CH_2Cl_2 (230 ml) was treated with $SOCl_2$ (4.0 ml; 55 mmoles) and the resulting orange-yellow soln worked up as described for the preparation of **13a**. The suspension of the hydrochloride of the title compound in CH_2Cl_2 (80 ml) was treated with Et_3N (12 ml). A clear soln was first formed and turned rapidly into a thick paste which was diluted with light petroleum, filtered, dried, thoroughly washed with water and recrystallized from benzene to yield 6.7 g (48%) of **13b**, m.p. 158°. (Found: C, 69.00; H, 4.71; N, 15.13. Calc. for $C_{16}H_{13}N_3O_2$ (279.3): C, 68.80; H, 4.69; N, 15.05%). NMR ($CDCl_3$, TMS): δ 3.85 and 4.25 (both bs; 1H, each; 4-CH_2); 5.9 (s, 2H, OCH_2O); 6.1 (s, 1H, NH); 6.75 and 6.9 (both s, 1H, each, 5-H+8-H); 6.7–7.3 (m, 5H, Ph); 7.4 (s, 1H, 2-H). Mass spectrum (100°C), *m/e* (rel. int.): 279 ($M^{+\cdot}$, 100), 278 (36), 264 (45), 263 (70), 252 (51), 239 (8), 188 (39), 187 (36), 175 (7), 174 (10), 173 (7), 160 (92).

Ethyl - N - (2 - *methyl* - 4 - *methylene* - 6,7 - *methylenedioxy* - 3,4 - *dihydro* - 3 - *quinazolinyl*) - N - *phenylcarbamate* (**3c**). Ethyl chloroformate (15 ml) was added under continuous stirring to the suspension of **13a** (2.93 g; 10 mmoles) and Na_2CO_3 (3.0 g) in dry dioxane (20 ml). The mixture was stirred at r.t. until, according to TLC (Kieselgel $PF_{254+366}$; benzene–acetone, 1:1) the starting **13a** was completely used up (about 15 hr). The inorganic salts were filtered off, the filtrate evaporated to dryness, the residue dissolved in benzene and worked-up by column chromatography (Kieselgel 60, 0.063–0.200 mm; benzene–acetone 10:1) to yield 2.0 g (56%) of **3c**, m.p. 155–156° from gasoline (Found: C, 65.71; H, 5.36; N, 11.64. Calc. for $C_{20}H_{19}N_3O_4$ (365.4): C, 65.74; H, 5.24; N, 11.50%) as the main product.

UV (EtOH): 223 (4.63); 248 (4.35), sh; 340 (3.95). UV (cyclohexane): 224 (4.65); 250 (4.41), sh; 336 (4.00), very broad. NMR ($CDCl_3$, TMS): δ 1.3 (t, 3H)+4.35 (q, 2H), COOEt; 2.15 (s, 3H, 2-Me); 3.95+4.35 (both d, J = 2.9 Hz; 1H, each; 4-CH_2); 6.0 (s, 2H, OCH_2O); 6.75+7.0 (both s; 1H, each; 5-H+8-H), 7.15–7.50 (m, 5H, Ph). IR (KBr): 1740 cm^{-1}. Mass spectrum (90°) (see Fig. 1).

Ethyl - N - (4 - *methylene* - 6,7 - *methylenedioxy* - 3,4 - *dihydro* - 3 - *quinazolinyl*) - N - *phenylcarbamate* (**3d**). Ethyl chloroformate (0.53 ml; 5.5 mmoles) was added under ice-cooling to the soln of **13b** (1.4 g; 5.0 mmoles) in benzene (30 ml). Et_3N (0.8 ml; 5.5 mmoles) was added under stirring and ice-cooling. The starting **13b** was, according to tlc, completely used up after about 1 hr. The complex mixture was worked up by chromatography. The different products were examined by IR, and the crude gummy **3d** (0.29 g) was recrystallized from benzene–light petroleum to yield 0.15 g (8.5%) of the pure product, m.p. 134°. (Found: N, 11.68. Calc. for $C_{19}H_{17}N_3O_4$ (351.4): N, 11.96%). IR (KBr): 1740 cm^{-1}. NMR ($CDCl_3$, TMS): δ 1.3 (t, 3H)+4.3 (qu, 2H), COOEt; 3.95+4.3 (both d, J ≈ 3 Hz; 1H, each, 4-CH_2); 5.9 (s, 2H, OCH_2O); 6.75+6.95 (both s; 1H, each; 5-H+8-H); 7.3 (s, 1H, 2-H); 7.15–7.45 (m, 5H, Ph). Mass spectrum (100°), *m/e* (rel. int.): 351 ($M^{+\cdot}$, 84), 350 (7), 306 (17), 305 (12), 279 (16), 278 (23), 264 (27), 263 (100), 262 (24), 190 (15), 188 (17), 187 (20), 160 (65).

2 - *Bromo* - 4',5' - *methylenedioxy* - 2' - *nitroacetophenone*. Bromine (2.56 ml; 50 mmoles) was added under continuous stirring within 1 hr to the mixture of **11**[6] (10.5 g; 50 mmoles), CH_2Cl_2 (60 ml) and $AlCl_3$ (0.1 g). The mixture was stirred at r.t. until, according to tlc (Kieselgel $PF_{254+366}$; benzene) the starting ketone was completely used up (about 6 hr), and evaporated to dryness at r.t. The brown oily residue, when triturated with a small amount of MeOH, turned into a solid product (9.0 g; 62.5%) which was washed with ether and recrystallized from MeOH, m.p.: 102°. (Found: Br, 27.72; N, 5.15. Calc. for $C_9H_6BrNO_5$ (288.1): Br, 27.74; N, 4.86%). IR (KBr): 1715 cm^{-1}.

2 - *Anilino* - 4',5' - *methylenedioxy* - 2' - *nitroacetophenone*. A mixture of the above compound (2.9 g; 10 mmoles), aniline (3.6 ml; 40 mmoles) and dioxane (10 ml) was refluxed for 8 hr to yield a dark-brown soln from which 1.8 g (60%) of the title compound, m.p. 150–152° crystallized on cooling. (Found: C, 60.13; H, 4.18; N, 9.41. Calc. for $C_{15}H_{12}N_2O_5$ (300.2): C, 60.00; H, 4.03; N, 9.33%). IR (KBr): 3400, 1715 cm^{-1}.

Ethyl N - (4,5 - *methylenedioxy* - 2 - *nitrophenacyl*) - N - *phenylcarbamate*. A suspension of the above compound (1.5 g; 5 mmoles) in the mixture of anhyd benzene (15 ml) and anhyd pyridine (1.0 ml; 12.5 mmoles) was treated under ice-cooling and continuous stirring with ethyl chloroformate (1.1 ml; 12 mmoles). The mixture was subsequently refluxed for 10 min and evaporated to dryness *in vacuo*. The residue was washed with water, dried and recrystallized from MeOH (40 ml) to yield 1.3 g (69%) of the title compound, m.p. 148°. (Found: C, 58.15; H, 4.57; N, 7.64. Calc. for $C_{18}H_{16}N_2O_2$ (372.3): C, 58.06; H, 4.33; N, 7.53%). IR (KBr): 17400, 1700 cm^{-1}.

Ethyl N - (2 - *acetylamino* - 4,5 - *methylenedioxyphenacyl*) - N - *phenylcarbamate* (**14**). The above compound (1.9 g; 5 mmoles) was dissolved in EtOH (200 ml) and reduced in the presence of a 8% Pd–C catalyst at r.t. The mixture was heated to its b.p., filtered while hot and evaporated to dryness. The oily residue (which turned crystalline when allowed to cool) was dissolved in CH_2Cl_2 (20 ml). Ac_2O (0.52 ml; 5.5 mmoles) was added under continuous stirring, after which the mixture was stirred for 20 min and evaporated to dryness. The residue was recrystallized from benzene–light petroleum to yield 1.5 g (82%) of **14**, m.p. 159–160°. (Found: C, 62.61; H, 5.16; N, 7.37. Calc. for $C_{20}H_{20}N_2O_6$ (384.4): C, 62.49; H, 5.24; N, 7.29%). IR (KBr): 3250, 1740 (sh), 1700, 1655 cm^{-1}.

Ethyl N - (2 - *methyl* - 6,7 - *methylenedioxy* - 4 - *quinazolinylmethyl*) - N - *phenylcarbamate* (**2c**). Compound **14** (0.5 g; 1.3 mmoles) was heated with a saturated ethanolic NH_3 soln (10 ml) in a sealed tube for 5 hr at 150°. The mixture was treated with Norite and evaporated to dryness. The residue was recrystallized from EtOH to yield 0.35 g (73%) of **2c**, m.p. 159° from EtOH. (Found: C, 66.00; H, 5.30; N, 11.60. Calc. for $C_{20}H_{19}N_3O_4$ (365.4): C, 65.74; H, 5.24; N, 11.50%). IR (KBr): 1700 cm^{-1}; UV (EtOH): 232 (4.52), b; 320 (3.82), sh; 332 (3.91). NMR ($CDCl_3$, TMS): δ 1.2 (t, 3H)+4.15 (qu, 2H), COOEt; 2.7 (s, 3H, 2-Me), 5.25 (s, 2H, 4-CH_2–N), 6.05 (s, 2H, OCH_2O), 7.15+7.3 (both s's, 1H, each, 5-H+8-H), 7.2 (s, 5H, Ph). Mass spectrum (105°) (see Fig. 1).

Diethyl N - *phenyl* - N,N' - (p - *phenylene*)*dicarbamate* (**6**). The mixture of *p*-aminodiphenylamine (0.92 g; 5 mmoles), ethyl chloroformate (2.1 ml; 22 mmoles) and anhyd dioxane (10 ml) was refluxed for 2 hr, the resulting violet soln evaporated to dryness *in vacuo* and the residue triturated with a small amount of EtOH to yield 0.3 g (45%) of **6**, m.p. 141–142° from EtOH. (Found: C, 65.98; H, 6.12; N, 8.79. Calc. for $C_{18}H_{20}N_2O_4$ (328.4): C, 65.84; H, 6.14; N, 8.53%). IR (KBr): 3250, 1730, 1670 cm^{-1}, b. NMR ($CDCl_3$, TMS): δ 1.2 (t, 3H), 1.3 (t, 3H), 4.3 (qu, 4H), two COOEt groups; 6.55 bs (NH); 7.2+7.4 (both d's, J ≈ 9 Hz, 2H, each, *p*-phenylene); 7.3 (s, Ph). Mass spectrum (100°), *m/e* (rel. int.):

328 ($M^{+\cdot}$, 100), 300 (2.7), 282 (4.5), 256 (8), 255 (21), 228 (4.0), 227 (4.1), 183 (20), 182 (15), 181 (14), 167 (11), 166 (8).

Irradiations. The irradiations were carried out in Ar-flushed EtOH or acetone soln's using high-pressure mercury immersion lamps (Philips, HPK-125) and Pyrex filters. The rates of conversion were very different for compounds **2c** and **3c**. After irradiation of **2c** for 36 hr unchanged starting compound was still present, whereas **3c** was completely used up within a few hr at which time the irradiation was stopped. The soln's became gradually coloured and crystals of the photoproduct **5** were deposited. The filtrate was worked up by column chromatography (Kieselgel 60 Merck, particle size 0.063–0.200 mm; benzene–acetone, 10:1 or 1:1). Part of the eluated fractions were mixtures which were separated by tlc (Kieselgel $PF_{254+366}$, solvents as above).

Run 1. Starting compound **2c** (0.74 mmole), solvent: EtOH (100 ml), irradiation time: 36 hr. Products: unchanged **2c** (13.3%), **4a** (6.0%), **5** (4.5%), ethyl N-phenylcarbamate (26.5%).

Run 2. Starting compound **3c** (3.3 mmole), solvent: EtOH (150 ml), irradiation time: 4 hr. Products: **2c** (16.5%), **4a** (7.5%), **5** (34%), **6** (2.4%), ethyl N-phenylcarbamate (29%). Neither compound **7**, nor compound **8** were formed.

Run 3. Starting compound **3c** (2.2 mmoles), solvent: acetone (150 ml), irradiation time: 2 hr. Products: **2c** (4.7%), **4a** (14.2%), **5** (16%), **6** (3.0%), **7** (6.7%), **8** (3.4%), ethyl N-phenylcarbamate (26.8%).

Compounds **2c**, **5**,[3] **6**, **7**[3] and ethyl N-phenylcarbamate were identical with authentic samples.

Compound **4a**, m.p. 155–156° (gasoline); (Found: C, 65.45; H, 5.21; N, 11.34. Calc. for $C_{20}H_{19}N_3O_4$ (365.4); C, 65.74; H, 5.24; N, 11.50%). UV (EtOH): 226 (4.56), sh; 236 (4.62); 322 (3.81), sh; 334 (3.84). IR (KBr): 3200, 1740, sh at 1730 cm^{-1}. NMR ($CDCl_3$, TMS): δ 1.35 (t, 3H) + 4.2 (qu, 2H, J = 7.2 Hz), COOEt; 2.75 (s, 3H, 2-Me), 4.25 (s, 2H, 4-CH_2), 6.00 (s, 2H, OCH_2O), 7.05 + 7.15 (both s's, 1H, each, 8-H + 5-H), 6.90 + 7.85 (both dd's, J = 8.5 and 2 Hz, 1H, each, 3-H and 6-H of *o*-phenylene). Mass spectrum (135°) (see Fig. 1).

For comparison. **4c**, m.p. 169° (from EtOH). UV (EtOH): 228 (4.54), sh; 237 (4.58); 320 (3.98); 332 (3.99). IR (KBr): 3300, 1700 with sh at 1720, 800 cm^{-1}. NMR ($CDCl_3$, TMS): δ 1.26 (t, 3H) + 4.2 (qu, 2H, J = 7.1 Hz), COOEt; 2.8 (s, 3H, 2-Me); 4.4 (s, 2H, 4-CH_2); 6.07 (s, 2H, OCH_2O); 6.60 (bs, 1H, NH); 7.3–7.6 pm (m, 6H, ArH's). Mass spectrum (150°) (see Fig. 1).

Compound **8**, m.p.: 148° from ether. UV (EtOH): 242 (4.61); 288 (3.70); 314 (3.65); 328 (3.55), sh. IR (KBr): 1740, 1695 cm^{-1}. NMR ($CDCl_3$, TMS): δ 1.3 (t, 3H) + 4.3 (qu, 2H), COOEt; 2.5 (s, 3H, 2-Me), 6.2 (s, 2H, OCH_2O), 7.05 (s, 1H, 8-H), 7.35–7.50 (m, 5H, Ph), 7.6 (s, 1H, 5-H). Mass spectrum (115°), *m/e* (rel. int.): 367 ($M^{+\cdot}$, 100), 321 (14), 295 (75), 294 (33), 280 (34), 279 (17), 278 (48), 266 (13), 253 (12), 231 (11), 219 (9), 204 (56), 203 (32), 190 (60), 187 (37), 175 (22), 164 (17), 161 (40), 120 (95).

Hydrolysis of compound **4a**. A mixture of **4a** (0.55 g; 1.5 mmoles), 10% NaOH aq and EtOH (20 ml, each) was refluxed for 2 hr. The EtOH was distilled off *in vacuo* and the soln extracted with CH_2Cl_2. The CH_2Cl_2 soln was dried ($MgSO_4$) and evaporated to dryness and the residue triturated with ether to obtain 0.19 g (43%) of **4b**, m.p.: 138°. (Found: N, 14.18. Calc. for $C_{17}H_{15}N_3O_2$ (293.31): N, 14.32%). UV (EtOH): 226 (4.55), sh; 234 (4.60); 285 (3.75); 323 (3.95), sh; 333 (3.98). IR (KBr): 3250, 3150 cm^{-1}. NMR ($CDCl_3$): δ 2.75 (s, 3H, 2-Me), 4.3 (s, 2H, 4-CH_2), 4.75 (bs, 2H, NH_2), 6.1 (s, 2H, OCH_2O), 6.55–6.8 and 6.9–7.3 (m's, total 4H, *o*-phenylene), 7.2 + 7.55 ppm (both s's, 1H, each, 8-H and 5-H). Mass spectrum (115°) (see Fig. 2).

A further crop (0.2 g, 45%, m.p.: 130–135°) of compound **4b** was obtained by evaporation to dryness of the filtrate of the first.

For comparison. **4d**, m.p.: 211° (from Et_2O). UV (EtOH): 2.26 (4.49), sh; 236 (4.55); 286 (3.66); 322 (3.86), sh; 333 (3.89). IR (KBr): 3250, 3150 cm^{-1}. NMR ($CDCl_3$): δ 2.8 (s, 3H, 2-Me), 3.35 (bs, 2H, NH_2), 4.3 (s, 2H, 4-CH_2), 6.05 (s, 2H, OCH_2O), 6.6 and 7.05 (d's, J = 9 Hz, 2H, each, *p*-phenylene), 7.2 + 7.3 ppm (both s's, 1H, each, 8-H and 5-H). Mass spectrum (145°) (see Fig. 2).

Ethyl N-phenylcarbamate, m.p. 49–50°, lit.:[8] 52–53°; NMR ($CDCl_3$, TMS): δ 1.3 (t, 3H) + 4.2 (qu, 2H), COOEt; 6.7 (bs, 1H, NH); 7.1–7.35 (m, 5H, Ph).

4 - (3 - *Indazolyl*) - 2 - *methyl* - 6,7 - *methylenedioxyquinazoline* (**16**). Compound **4b** (0.2 g; 0.7 mmoles) was converted into its hydrochloride by dissolving it in excess methanolic HCl and evaporating the soln to dryness. The crystalline residue was taken up in water (10 ml). A slight excess (positive reaction with KI-starch) of $NaNO_2$ aq was added dropwise with ice-water cooling and continuous stirring to obtain 0.15 g (72%) of a yellow crystalline product, m.p. >300°. (Found: N, 18.23. Calc. for $C_{17}H_{12}N_4O_2$ (304.30): N, 18.41%). NMR ($CDCl_3$): δ 2.8 (s, 3H, 2-Me), 6.25 (s, 2H, OCH_2O), 7.26 (s, 1H, 8-H), 7.35–7.80 (m, 3H, indazole ring 5-H–7-H), 8.67 (d, 1H, indazole ring, 4-H), 8.79 (s, 1H, 5-H), 13.65 ppm (bs, 1H, NH). Mass spectrum (190°C), *m/e* (rel. int.): 304 ($M^{+\cdot}$, 75), 303 (100), 275 (8), 274 (4.7), 247 (7), 246 (20), 245 (6), 219 (3.7), 218 (4.0), 217 (5.2), 206 (3.4), 204 (4.2), 152 (M^{++}, 8), 151.5 ($[M-H]^{++}$, 3.6), 151 (5.6), 137 (274^{++}, 4.8), 123 (246^{++}, 9), 120 (9).

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