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Electron Deficient Heteroaromatic Ammonioamidates. XVII.* *N*-(3-Quinazolinio)amidates. VI.* The Photochemistry of *N*-(3-Quinazolinio)amidates in the Presence of α-Toluenethiol

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Irradiation through Pyrex of the *N*-(3-quinazolinio)amidates *1c*—*1f* and of the dimers *2a* and *2b* in chloroform—α-toluenethiol mixtures furnishes complex mixtures of the type *4*—*10* photoproducts. The relative amounts of the products depend on the nature of the substituents R, R^2 and R^4 of the starting compounds. The photochemistry of the amidates and their dimers can be rationalized on the basis of the observation that under the conditions of the irradiations these compounds exist as the free amidates if R^4=Me, and as the toluenethiol adducts *11* if R^4=H.

The photochemistry of the *N*-(3-quinazolinio)-amidates *1a*—*1f* and/or of their type *2* dimers [2,3] in primary alcohols has recently been rationalized [2] on the basis of equilibrium mixtures of two photoactive species: The amidate forms *1* and their adducts *3* formed with one molecule of the nucleophilic solvent, present in alcoholic solutions of both the amidates and their dimers. In continuation of this work we report here on the photochemistry of the type *1* and type *2* compounds in the presence of α-toluenethiol which is a much stronger nucleophile than the alcohols.***

* For Parts XVI and V, see Refs. 1a and 1b, respectively.

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*** Part of the results of these studies has been described in a preliminary communication.[4]

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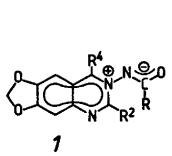
RESULTS AND DISCUSSION

The starting compounds: Compound *1c* is known [3] to exist in $CDCl_3$ solution almost entirely as such. When α-toluenethiol was added to a $CDCl_3$ solution of compound *1c*, the signals corresponding to *1c* were gradually replaced in the ^1H NMR spectrum by those of the adduct *11c*, and at concentrations corresponding to the starting conditions of the irradiations only the adduct form could be detected. The dimers *2a* and *2b* (where R^4 is hydrogen), too, may be assumed to exist under similar conditions as the practically pure type *11* adducts. The ^1H NMR spectra of the amidates *1e* and *1f* in $CDCl_3$—α-toluenethiol mixtures corresponding to irradiation conditions, on the other hand, suggest that these compounds and, presumably, also compound *1d* (where R^4 is also methyl) exist mainly as the free amidates *1* with only traces of the adducts *11* present. Apparently, the nucleophilicity of α-toluenethiol is insufficient to overcome the destabilization of the adduct *11* (R^4=Me) caused by crowding of the bulky groups around C-4. (*Cf.* the inability of the amidates *1a*—*1c* to form stable adducts with isopropyl and *tert*-butyl alcohols.[3])

The photoproducts. As seen from Table 1, the 4-benzylthio derivatives *4* could be detected as photoproducts only of those starting compounds having R^4=H. They may be derived by assuming a Norrish Type II cleavage



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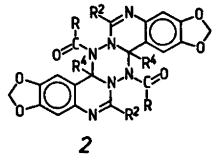

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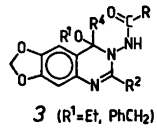

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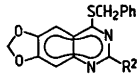

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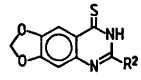

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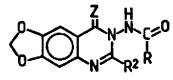
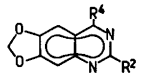


6: Z=S 7: Z=O



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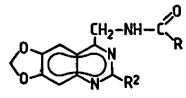

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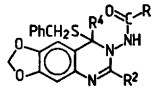

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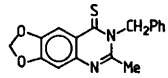

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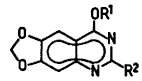
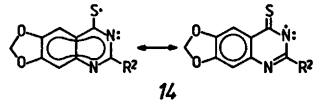


13

1-11, 13-15

	R^2	R^4	R
a	H	H	OEt
b	Me	H	OEt
c	Me	H	Ph
d	H	Me	OEt
e	Me	Me	OEt
f	Me	Me	Ph



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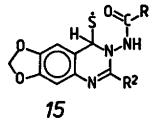

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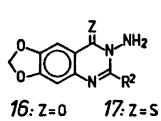

16: Z=O 17: Z=S

of the adducts *11*, the second product of this cleavage being the unstable imidic acid tautomer of the amide *9*. Since the structural prerequisite for the Norrish Type II cleavage to occur is R^4=H, no type *4* products could be expected from the irradiations of compounds *1d*–*1f* even if substantial amounts of their type *11* adducts were present in the reaction mixtures.

In contrast to the 4-ethoxy- and 4-benzyloxyquinazolines *13* (which are analogously formed through the adducts *3* on irradiation of alcoholic solutions of the amidates *1a*–*1c* or of the corresponding dimers [2]), the 4-benzylthioquinazolines *4* are photo-*un*stable. This is shown by separate irradiation of *4b* in pure $CHCl_3$ solution, whereby it is slowly debenzylated to yield the corresponding thione *5b* and, in addition, minor amounts of compound *12*. The formation of both the thiones *5* and *12* may be explained by assuming photo-induced homolysis of the benzyl-C–S bond of the compounds *4*, leading to the formation of 4-quinazolinylthiyl (*14*) and benzyl radicals which by recombination may give compound *12*. Alternatively, the radicals *14* may abstract hydrogen from the solvent to yield the corresponding thiones *5*.[5] It was not possible to detect any traces of type *12* products of *2a*, *2b* or *1c*.

Formation of compounds *6a*–*6c* may be rationalized by assuming similar photo-induced homolysis of the benzyl-C–S bonds of the adduct *11* (whereby the >C=O group possibly acts as an intramolecular sensitizer; for related reactions see, *e.g.*, Refs. 6 and 7), and subsequent stabilization of the resulting radicals *15* by *loss* of hydrogen from position 4. Accordingly, the necessary requirement for the

Table 1. Irradiation products of the *N*-(3-quinazolinio)amidates *1* (or their dimers *2*), their adducts *11* [a] and of some of their phototransformation products [b].

Starting compound [a]	Irradiation time/h	Products and yields [c,d] 4	5	6	7	8	9	10	1,2-Diphenylethane
2a	50	+	+	48–55 (*A*+*F*)	16 (*E*+*F*)	0	+	–	(*B*) [e]
2b	30	6.6 (*E*+*F*)	5.7 (*C*+*E*)	31 (*E*+*F*)	0	0	+	–	[e]
1c	6	1.8 (*D*)	+	56 (*A*+*C*+*D*)	0	18 (*D*)	26 (*D*)	–	[e]
1d	6	–	–	–	0	98 (*C*+*D*)	+	0	[e]
1e	4	–	–	–	0	66 (*C*+*D*)	+	6 (*D*)	(*B*) [e]
1f	5	–	–	–	0	83 (*C*+*D*)	81 (*D*)	0	[e]
11a	20	+	+	53 (*C*+*D*)	0	7 (*D*)	+	–	48 (*B*)
11b [f]	20	+ [g]	3.4 (*D*) [g]	27–30 (*D*) [g]	3.6 (*D*)	6 (*D*)	+	–	42 (*B*) [h]
4b [f,i]	200	39 (*C*+*D*)	18 (*D*)	–	–	0	–	–	11 (*B*) [h]
5b	100	0	94 (*A*)	–	–	0	–	–	[e]
6a	100	0	0	16 (*D*)	74 (*C*+*D*)	0	0	–	[e]
6a [j]	12				66 (*D*) [h]				
6b	30	0	0	2 (*D*)	53 (*D*)	0	0	–	[e]

[a] The quinazolinioamidates *1a*–*1c* exist under the conditions of the irradiations, *i.e.* in the presence of excess α-toluenethiol, exclusively as the type *11* adducts (irrespectively of whether they had been introduced as such or as their type *2* dimers), while the amidates *1d*–*1f* exist under the same conditions mainly as such with only traces of the adducts *11* present. The adducts *11a* and *11b* exist in $CHCl_3$ solution, even in the absence of α-toluenethiol, as such. [b] HPK-125 (Philips) high-pressure mercury immersion lamp, Pyrex filter, argon-flushed $CHCl_3$–α-toluenethiol (10:1 vol/vol) solutions. [c] +: Traces detected by TLC and identified by the IR spectrum. 0: Nothing detectable by TLC. –: In principle impossible products and not detected by TLC. [d] The letters *A*–*F* in parentheses after the yield data refer to the methods of isolation, see Experimental. [e] Irrelevant since this product may come either exclusively or in part from the solvent. [f] Irradiations performed in pure $CHCl_3$. [g] In some cases the irradiation mixtures were evaporated to dryness *in vacuo*, the residues taken up in THF and 2 μl aliquots of the resulting solutions analyzed by liquid chromatography (Du Pont Type 830 chromatograph, XLL-X column, length 25 cm, i.d. 2.1 mm, particle size 27–37 μm; solvent: hexane–dioxane, 95:5; pressure 13.8 MPa/m²; detection with a Du Pont T 837 spectrophotometer at 28 nm). The following yields were obtained: 1.7–2.3 % of *4b*, 2.7–6.0 % of *5b* and 24–37 % of *6b*. [h] In addition, toluene and stilbene were detected by GLC. [i] In addition, 4 % (*C*; *cf.* [d]) of 3-benzyl-2-methyl-6,7-methylenedioxy-4(3*H*)-quinazolinethione (*12*) was isolated. [j] Irradiated under oxygen. [k] No other products (except tars) were formed, according to TLC.

formation of the type *6* compounds is $R^4 = H$, and no such products could be expected from the irradiations of compounds *1d*–*1f* even if appreciable amounts of their type *11* adducts were present in the reaction mixtures.

The benzyl radicals formed in processes *4*→*5* and *11*→*6* should subsequently become stabilized by recombination and hydrogen abstraction processes, thereby yielding 1,2-diphenylethane, toluene and stilbene. 1,2-Diphenylethane was isolated from the irradiation mixtures of compounds *2a*, *2b* and *1c*, and all three hydrocarbons were detected by GLC in the irradiation mixtures of compound *2b*.*,**

1,2-Diphenylethane was isolated as a by-product in the irradiations of compounds *4b*, *11a* and *11b* as well and, along with toluene and stilbene, detected by GLC in the irradiation mixture of compound *11b*; in these cases the hydrocarbons clearly come from the benzylthio groups of the substrates since the irradiations were carried out in the absence of α-toluenethiol.

Two possibilities may be envisaged for the formation of compound *7a*. (1): Photooxidation by traces of oxygen (present in the solvent and/or the argon, used for flushing the reactor) of the hydrate *3a* (R′ = H). The latter may be formed as a result of the presence of traces of water, as has been described for the formation of the type *7* products in the irradiations carried out in ethanol.[2] (2): Photooxidation of primarily formed compound *6a*. That the latter possibility is real has been shown by separate irradiation of compounds *6a* and *6b*, and by the considerable acceleration of the conversion *6a*→*7a* by performing the irradiation under oxygen (Table 1). It is noteworthy that the photooxidations in all cases take place in the presence of excess α-toluenethiol.

The type *8* and *10* photoproducts are thought to be derived from the free amidate forms *1* as has been described for the formation of these products in the irradiations carried out in ethanol and acetone.[1a,2,12] Interestingly, small amounts of type *8* products were obtained also in the irradiations of compounds *1c*, *11a* and *11b* which, under the conditions of the irradiations, exist at least mainly in the form of adducts *11* (see above). The amides *9* may be formed, in addition to the pathway mentioned above, as by-products together with the compounds *8*.

Identification and proof of structure of the photoproducts. Compounds *7a*,[2] *7b*,[2] *8a*,[2] *8b*,[2] *8c*,[2] *8d*–*8f*,[2] *10e*,[12] as well as *9* (R = OEt), *9* (R = Ph) and 1,2-diphenylethane were identified by comparison (m.p., IR, R_F) with authentic samples. The structures of the new compounds *4a*, *4b* (= *4c*), *5a*, *5b* (= *5c*), *6a*, *6b*, *6c* and *12* were derived from their IR, mass, ^{1}H NMR and UV spectra and substantiated by synthesis or chemical transformations into known compounds (see Experimental).

Structure proving synthesis of compound *6b* was attempted by thiation of compound *16*[13] with P_2S_5 and ethoxycarbonylating the resulting thione *17*, but all experiments with the purpose of obtaining *6b* failed. The photoproduct *6b* was therefore converted by treatment with HgO into compound *7b*.

EXPERIMENTAL

IR, ^{1}H NMR and UV spectra were recorded with Spektromom 2000 IR (Hungarian Optical Works, Budapest), Perkin-Elmer R-12 60 MHz NMR and MOM 201 (Hungarian Optical Works, Budapest), Unicam Type SP-700 and Specord (Carl Zeiss, Jena, GDR) UV spectrometers, respectively. 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 the direct insertion system.

^{1}H NMR spectra of the amidates 1c, 1e *and* 1f *taken in the presence of α-toluenethiol*. (a) ^{1}H NMR spectrum of *1c* in pure $CDCl_3$: δ 3.08 s (2-Me), 6.34 s (OCH_2O), 7.21 s and 7.4 s (5-H and 8-H). 7.55 m and 8.3 m (*m*+*p*, and *o*-protons, respectively, of the benzoyl group), 9.62 s (4-H). ^{1}H NMR spectrum of *1c* + excess $PhCH_2SH$ in $CDCl_3$: δ 1.7 t (J = 8 Hz, SH; merged with s of 2-Me of adduct *11c*), 3.7 d (J = 8Hz, CH_2 of free $PhCH_2SH$; merged with CH_2 of $PhCH_2S$ of *11c*), 5.95 s (OCH_2O + 4-H of *11c*, 6.7 s and 6.8 s (5-H and 8-H of *11c*), 7.3 s (Ph of $PhCH_2SH$ and of $PhCH_2S$ of *11c*), 7.55 m and 8.15 m (*m*-+*p*-, and *o*-protons, respectively, of the benzoyl group of *11c*). The upfield shifts of the signals of *1c* caused by

* For the possibility of formation of these hydrocarbons by photo-induced decomposition of α-toluenethiol and dibenzyl disulfide, *cf.* Refs. 8 and 9.

** Further volatile products detected by GLC were dibenzyl sulfide and disulfide. However, the latter was a contaminant of the α-toluenethiol used and both could be photoproducts of α-toluenethiol as well. For relevant papers on the photochemistry of thiols, see, *e.g.*, Refs. 9–11.

adduct formation with α-toluenethiol are completely analogous to those caused by adduct formation with CD_3OD.[3]

(b) ^1H NMR spectrum of *1e* in pure $CDCl_3$: δ 1.37 t + 4.24 qu (COOEt), 2.9 s and 2.95 s (2-Me and 4-Me), 6.3 s (OCH_2O), 7.34 s and 7.36 s (5-H and 8-H). Addition of excess $PhCH_2SH$ did not cause any of these signals to shift; the only new signals were those of $PhCH_2SH$: δ 1.75 t, 3.7 d ($J = 8$ Hz) and 7.3 s.

(c) ^1H NMR spectrum of *1f* in pure $CDCl_3$: δ 2.85 s and 2.95 s (2-Me and 4-Me), 6.2 s (OCH_2O), 7.25 s (5-H and 8-H), 7.4 m and 8.2 m (*m*- + *p*-, and *o*-protons, respectively, of the benzoyl group). Addition of excess $PhCH_2SH$ had no effect, except for the appearance of its own signals.

Synthesis of the α-toluenethiol adducts 11a *and* 11b. (a) A suspension of compound *1a* (0.52 g; 2.0 mmol) in anhydrous benzene (5 ml) was stirred for 90 min with α-toluenethiol (0.26 ml; 2.2 mmol) at room temperature. A clear yellow solution was formed after 30 min. Light petroleum (5 ml) and ether (2 ml) were added to precipitate the light yellow crystals (0.57 g; 75 %) of the adduct *11a*, m.p. 122–123 °C (dec). Anal. $C_{19}H_{19}N_3O_4S$: C, H, N, S. IR (KBr): 3200–2700, b, vs; 1730 cm^{-1}, vs. ^1H NMR ($CDCl_3$): δ 1.2 t + 4.2 qu (COOEt) 3.6 s (S-CH_2); 5.95 s (OCH_2O); 6.0 s (4-H); 6.65 s, 6.7 s, 6.8 s (2-H, 5-H + 8-H); 7.2 s (Ph); very weak signal at 9.0 ppm (2-H of the free amidate *1a*).

(b) The adduct *11b* (76 %), m.p. 123–124 °C (dec), was obtained similarly. Anal. $C_{20}H_{21}N_3O_4S$: C, H, N, S. IR (KBr): 3200–2900 with local maxima at 3160, 2970 and 2890; 1730 cm^{-1}, vs. ^1H NMR ($CDCl_3$): δ 1.3 t + 4.3 qu (COOEt); 1.7 s (2-Me); 3.6 s (S-CH_2); 6.1, 2 × s, total intensity 3 H (OCH_2O + 4-H); 6.75 s, 6.8 s (5-H + 8-H); 7.4 s (Ph). Mass spectrum (125 °C): as a result of thermal instability of the adduct, identical with that of compound *1b*.[3]

Irradiations and work-up of the irradiation mixtures. The dimers *2a* and *2b* (2.8 mmol) or the amidates *1c–1f* (5.0 mmol) were dissolved in mixtures of $CHCl_3$ (150 ml) and α-toluenethiol (15 ml); the solutions were flushed with argon and irradiated under argon with a high-pressure mercury immersion lamp (HPK-125, Philips) through Pyrex, until the starting compounds were, according to TLC (Kieselgel G; solvents: benzene–MeOH, 10:1, or benzene–acetone, 1:1; detection: UV light or I_2 vapour), completely used up. The irradiations of compounds *5b* (2.25 mmol) in $CHCl_3$ (150 ml) + α-toluenethiol (15 ml), of compound *6a* (1.3 mmol) in $CHCl_3$ (100 ml) + α-toluenethiol (15 ml), of compound *6b* (0.6 mmol) in $CHCl_3$ (100 ml) + α-toluenethiol (10 ml) as well as of compounds *11a* and *11b* (3.8 mmol) and *4b* (4.8 mmol) in pure $CHCl_3$ (150 ml) were carried out similarly. In addition, compound *6a* (0.65 mmol) in $CHCl_3$ (100 ml) + α-toluenethiol (10 ml) was irradiated also under oxygen. For the necessary reaction times, see Table 1. The initially faint yellow solutions gradually darkened, and some insoluble material was deposited on the wall of the reactor. Before work-up the insoluble material was dissolved in anhydrous MeOH or $CHCl_3$ and added to the main solution which then was evaporated to dryness *in vacuo*. In most cases the excess α-toluenethiol was removed by keeping the residue for some time at 60 °C/0.4 mmHg.

The residue was taken up in MeOH (in the case of *1c* in benzene) and the occasionally formed crystalline product (*A*) collected. Kieselgel 60 (Merck, 0.063–0.200; 3 g) was added to the filtrate of *A* (or, if no product *A* was formed, to the clear solution) and the mixture was evaporated to dryness. The residue was transferred onto a column (prepared from Kieselgel 60 (60 g) with benzene) and chromatographed first with pure benzene and then with benzene–MeOH (or, in the case of *1f*, with benzene–acetone) mixtures in which the relative amount of the polar component was gradually increased to finish up with 10:1 benzene–MeOH (2:1 benzene–acetone) mixtures. The individual fractions were examined by TLC (as above) and those containing the same product combined and evaporated to dryness *in vacuo*. Any α-toluenethiol which had not been removed earlier, as well as any ethyl carbamate formed was found in the first benzene fractions and discarded. The dry residues of the benzene (*B*) and benzene–MeOH or benzene–acetone eluates (*C*) were recrystallized or, if the attempts of recrystallizing them failed, worked up, depending on their quantities, either by TLC (Kieselgel $PF_{254+366}$; benzene–MeOH, 10:1; *D*) or by a second column chromatography followed either by recrystallization (*E*) or TLC (Kieselgel $PF_{254+366}$; *F*).

R_F values (adsorbent: Kieselgel; solvent: benzene–MeOH, 10:1): *4a* 0.65, *5a* 0.40, *6a* 0.60, *7a* 0.45, *8a* 0.50; *4b* = *4c* 0.70, *5b* = *5c* 0.40, *6b* 0.60, *7b* 0.40, *8b* = *8c* 0.45, *12* 0.80; *6c* 0.60; *8d* 0.60; *8e* = *8f* 0.50,* *10e* 0.6; benzamide (*9c* = *9f*) 0.40;* 1,2-diphenylethane 0.90 (with solvent benzene).

New compounds which have not been obtained by independent synthesis. *6a*, m.p. 194 °C (from MeOH). Found C 49.63; H 4.23; N 14.29; S 10.67. Calc for $C_{12}H_{11}N_3O_4S$: C 49.14; H 3.78; N 14.33; S 10.93. UV [ethanol (log ε)]: 226 (sh, 4.25), 231 (2.48), 255 (sh, 3.91), 273 (4.03), 330 (sh, 3.52), 346 (sh, 3.87), 355 (sh, 3.96), 363 (4.06), 372 (sh, 3.99), 379 (4.00).** IR (KBr): 3350, b, 1750 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.22, 2 H (2-H + NH); 8.05 s (5-H); 7.1 s (8-H); 6.2 s (OCH_2O); 4.15 qu + 1.3 t ($J = 7.2$ Hz; COOEt). MS (85 °C), *m/z* (% rel. int.): 293 (100, $M^{+\cdot}$), 260 (17), 248 (13), 232 (6.2), 221

* Same with solvent benzene–acetone, 2:1.

** *Cf.* the spectra of the reference compounds *5a* and *5b* below.

(25), 207 (10), 206 (6.2), 205 (8.0), 192 (43), 191 (11), 190 (11), 173 (30), 164 (30), 162 (19).

6b, m.p. 170–171 °C (from MeOH). Found C 50.41; H 4.34; N 13.60; S 10.48. Calc for $C_{13}H_{13}N_3O_4S$: C 50.85; H 4.27; N 13.68; S 10.43. UV [ethanol (log ε)]: 205 (4.16); 227 (sh, 4.45), 231 (4.46), 256 (sh, 4.24), 274 (4.25), 352 (sh, 3.98), 366 (4.21), 377 (4.11), 386 (4.18).* IR (KBr): 3250, 1750 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.1 s (NH); 7.98 s (5H); 7.05 s (8-H); 6.18 s (OCH_2O); ~4.3 m + 1.35 t ($J = 7.3$ Hz; COOEt); 2.68 s (2-Me). MS (110 °C), *m/z* (% rel. int.): 307 (100, $M^{+\cdot}$), 274 (15), 262 (12), 246 (6.8), 235 (18), 220 (15), 206 (15), 205 (13), 204 (4.5), 187 (21), 164 (20), 162 (8.4).

6c, m.p. 244 °C (from EtOH). Anal. $C_{17}H_{13}N_3O_3S$: C, H, N. UV [ethanol (log ε)]: 226 (sh, 4.47), 230 (4.51), 255 (sh, 4.12), 271 (4.21), 322 (sh, 3.53), 348 (sh, 3.87), 362 (4.11), 378 (4.02), 387 (4.06).* IR (KBr): 3250, 1695 cm^{-1}. ^1H NMR (DMSO-d_6, reference signal: DMSO-d_5 = 2.50): δ 8.0 m (*o*-protons of Ph); 7.82 s (5-H); 7.5 m (other protons of Ph); 7.1 s (8-H); 6.2 s (OCH_2O). MS (150 °C), *m/z* (% rel. int.): 339 (34, $M^{+\cdot}$), 322 (23), 306 (15), 262 (2.2), 234 (2.5), 220 (4.3), 204 (5.7), 187 (7.5), 164 (5.2), 121 (4.3), 105 (100), 103 (6.5), 77 (42).

12, m.p. 188–191 °C (non-recrystallized). Anal. $C_{17}H_{14}N_2O_2S$: N. UV [ethanol (log ε)]: 228 (sh, 4.60), 233 (4.62), 256 (sh, 4.37), 273 (4.29), 3.25 (sh, 3.75), 350 (sh, 4.05), 365 (4.26), 387 (4.20).* ^1H NMR ($CDCl_3$): δ 8.2 s (5-H); 7.2 m (Ph); 6.9 s (8-H); 6.1 s and 6.05 s, total 4 H (OCH_2O and CH_2 of benzyl group); 2.55 s (2-Me). MS (125 °C), *m/z* (% rel. int.): 310 (100, $M^{+\cdot}$), 309 (22), 295 (6.7), 277 (71), 276 (13), 233 (13), 220 (6.6), 219 (11), 189 (11), 188 (35), 187 (18), 165 (6.0), 147 (23), 91 (83).

Attempted synthesis of compound 6b. (a) A mixture of 3-amino-2-methyl-6,7-methylenedioxy-4(3*H*)-quinazolinone (*16*;[13] 0.44 g; 2 mmol), P_2S_5 (0.44 g) and pyridine (10 ml) was refluxed for 2 h; a yellow oily product deposited. The mixture was poured into water (30 ml). On scratching, the yellow oil turned into 0.22 g (47 %) of the crude crystalline thione *17* which was recrystallized from BuOH to yield 0.15 g (31 %) of pure *17*, colourless needles, m.p. 257–258 °C. Anal. $C_{10}H_8N_2O_2S$: N, S. UV [ethanol (log ε)]: 226 (sh, 4.32), 230 (4.34), 254 (sh, 4.08), 276 (4.17), 342 (sh, 3.91), 358 (4.07), 370 (sh, 4.03), 375 (4.05).

(b) All attempts to convert the above product with ethyl chloroformate in pyridine or by refluxing with diethyl pyrocarbonate into *6b* failed.

Conversion of compound 6b *into* 7b. A mixture of compound *6b* (0.1 g), red HgO (0.3 g), dioxane (5 ml) and 10 % aqueous NaOH (1 ml) was refluxed for 24 h. The hot mixture was filtered and poured into water (10 ml). The aqueous mixture was extracted with CH_2Cl_2 and the extract worked up by TLC (Kieselgel $PF_{254+366}$, Merck; solvent: benzene–acetone, 1:1) to yield, in addition to considerable amounts of unchanged starting material, 5 mg of compound *7b* which proved identical (m.p., IR, R_F values) with an authentic sample.[3]

Synthesis of authentic samples of the photoproducts 4a, 5a, 4b (=4c) *and* 5b (=5c). (a) A mixture of 6,7-methylenedioxy-4(3*H*)-quinazolinone[3] (0.95 g; 5 mmol), P_2S_5 (1.3 g; 5.8 mmol) and anhydrous pyridine (15 ml) was refluxed for 2 h and poured into water (40 ml). The mixture was made alkaline by adding aqueous NaOH, filtered and acidified during ice-water cooling with AcOH to obtain 0.76 g (74 %) of *5a*, m.p. 276 °C (from a large amount of EtOH). Anal. $C_9H_6N_2O_2S$: C, H, N, S. UV [ethanol (log ε)]: 226 (sh, 4.35), 228 (4.36), 258 (sh, 3.95), 272 (4.03), 346 (sh, 3.66), 353 (sh, 3.99), 365 (4.17), 377 (4.10).

(b) Compound *5b* (=*5c*), m.p. 289–290 °C (from a large volume of EtOH), was similarly obtained in 73 % yield starting with 2-methyl-6,7-methylenedioxy-4(3*H*)-quinazolinone.[3] Anal. $C_{10}H_8N_2O_2S$: N, S. UV [ethanol (log ε)]: 223 (sh, 4.47), 228 (4.49), 260 (sh, 4.12), 271 (4.18), 354 (sh, 4.04), 370 (4.22), 381 (4.15), 385 (4.15).

(c) Sodium (46 mg; 2 mmol) was dissolved in anhydrous MeOH (10 ml); compound *5a* (0.41 g; 2 mmol) and then benzyl chloride (0.25 ml; 2.2 mmol) were added, and the solution was refluxed for 5 h. The product was worked up by preparative TLC (Kieselgel $PF_{254+366}$; solvent: benzene–MeOH, 10:1) to obtain 0.12 g (20 %) of compound *4a*, colourless needles, m.p. 131–132 °C (from EtOH). (Found: C 64.44; H 4.02; N 9.36. Calc. for $C_{16}H_{12}N_2O_2S$: C 64.86; H 4.08; N 9.45.) UV [ethanol (log ε)]: 205 (sh, 4.32), 214 (4.33), 234 (4.32), 263 (sh, 4.20), 270 (sh, 3.75), 318 (sh, 3.90), 327 (4.05), 340 (4.14).

(d) Compound *4b*, colourless needles, m.p. 170–171 °C (from EtOH), was similarly obtained in 68 % yield. The product crystallized directly after cooling, work-up by TLC was unnecessary. (Found: C 65.29; H 4.52; N 8.83; S 10.34. Calc. for $C_{17}H_{14}N_2O_2S$: C 65.78; H 4.54; N 9.02; S 10.31.) UV [ethanol (log ε)]: 203 (4.26), 214 (sh, 4.30), 234 (4.26), 242 (sh, 4.24), 281 (sh, 3.74), 315 (sh, 3.74), 329 (3.99), 342 (4.05). ^1H NMR ($CDCl_3$): δ 7.6–7.2 m, 7 H (5-H, 8-H and Ph); 6.15 s (OCH_2O); 4.7 s (CH_2 of benzyl group); 2.8 s (2-Me). MS (110 °C), *m/z* (% rel. int.): 310 (100, $M^{+\cdot}$), 309 (9.8), 295 (3.6), 277 (57), 276 (11), 233 (14), 220 (3.0), 219 (11), 189 (13), 188 (38), 187 (12), 147 (30), 91 (48).

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* *Cf.* the spectra of the reference compounds *5a* and *5b* below.

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