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A new regioselective synthesis and ambient light photochemistry of quinazolin-1-oxides

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Abstract—Quinazolin-1-oxides were prepared by the oxidation of tetrahydroquinazolines with H_2O_2–tungstate and their ambient light photochemistry was investigated. Substituent effects on their photochemical cyclization and the reactions of the products 1a*H*-[1,2]oxazireno[2,3-*a*]quinazolines under photochemical and thermal conditions are reported. The cyclization of quinazolin-1-oxides and the reactions of 1a*H*-[1,2]oxazireno[2,3-*a*]quinazolines show pronounced solvent isotope and solvent effects.

1. Introduction

The quinazoline ring system is a frequently encountered moiety in organic syntheses as well as in medicinal chemistry.[1] Many alkaloids possess a quinazoline skeleton.[2] Quinazolines are an important class of compounds, which exhibit anticonvulsant, antibacterial, antidiabetic, and anticancer activities.[1a,3] The chemistry of parent quinazoline and the synthesis of different quinazoline derivatives are well established and a number of methods to prepare quinazolines are known.[4–6]

Herein we report the oxidation of in situ formed 2-substituted-1,2,3,4-tetrahydroquinazolines to quinazolin-1-oxides[7] **2** and the photochemical cyclization of the latter compounds. The substituent effects on the reactions of 1a*H*-[1,2]oxazireno[2,3-*a*]quinazolines **4** under photochemical and thermal conditions are also reported. The cyclization of quinazolin-1-oxides **2** and the reactions of 1a*H*-[1,2]-oxazireno[2,3-*a*]quinazolines **4** show pronounced solvent isotope and solvent effects.

2. Results and discussions

2.1. Oxidation of 2-substituted-1,2,3,4-tetrahydroquinazolines to quinazolin-1-oxides 2

As a continuation of our previous work[8] we have treated in situ formed tetrahydroquinazolines, obtained from the reaction of compound **1** with different aldehydes in methanol at room temperature, with H_2O_2–tungstate to give the corresponding quinazolin-1-oxides **2** (see Scheme 1 and Table 1 for the yields and mps). In the cases of **2a–d**, initially formed quinazolin-1-oles precipitated and gradually converted to the corresponding products within 25 h. In these cases, shorter reaction times were achieved by evaporating the initial reaction solvent (methanol) and subsequently suspending the residue in chloroform and stirring at room temperature in the presence of H_2O_2 and tetrabutylammonium hydrogen sulfate (TBAHS).

Despite the precautions to avoid direct exposure to light, the deoxygenated compounds **3** were detected in the crude reaction mixtures by ^{1}H NMR and in some cases isolated. The yields of the by products **3** were higher in the cases of phenyl rings having electron-withdrawing groups. The column chromatography of the reaction mixtures of **2** in 5 mmol scale afforded indazole in 7–28% yields in all cases. Indazole is assumed to be a product of oxidative intramolecular coupling of amine **1**, which formed from the hydrolysis of the corresponding tetrahydroquinazoline. The oxidation of pure **1** in methanol under the conditions of the reaction in Scheme 1 confirmed this assumption.

The singlet for C-4 hydrogen in the ^{1}H NMR spectra of quinazolines **3** in $CDCl_3$ appears at ca. 9.50 ppm, however, the same proton in compounds **2** appears at ca. 9.0 ppm (see Table 4 for the characteristic C-4H chemical shifts). The shift to higher field by ca. 0.5 ppm is ascribed to the positive resonance effect of the oxygen at N-1. The C-4 hydrogen in 2-chloromethylquinazolin-3-oxides was reported to appear at 9.50 ppm in DMSO-d_6.[9] The same shift to higher field is also observed for C-4. Detailed inspection and comparison of the ^{1}H NMR spectra of **2a** and its deoxygenation product **3a** allow further distinction between 1- and 3-oxide. In the

Keywords: *N*-Oxides; Quinazoline; Quinazolin-1-ol; Quinazolin-1-oxide; Quinazolin-3-oxide; Quinazolin-4(3*H*)-one; Ambient light photochemistry; Rearrangement; Photochemical deoxygenation; Solvent effect; Solvent isotope effect.
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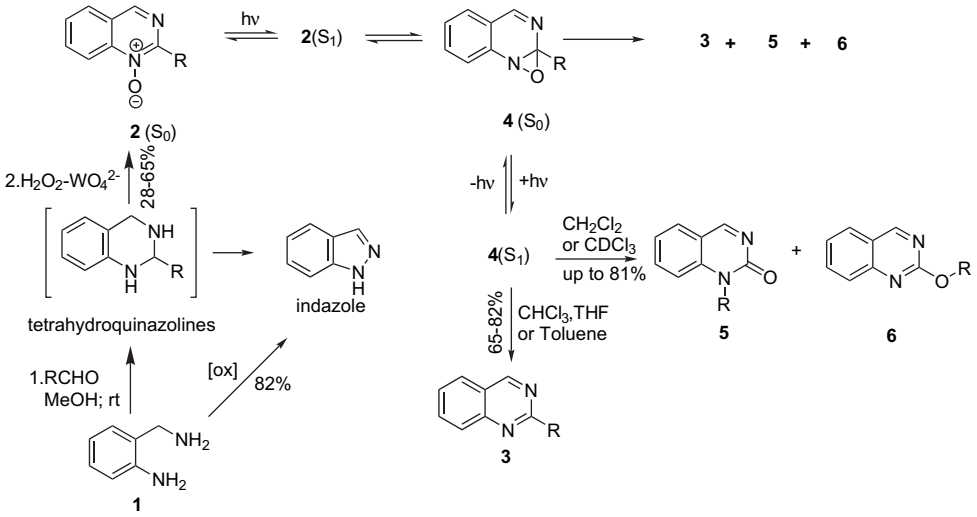


Scheme 1. The synthesis of compounds **2**–**6**: (**a**) R=Ph; (**b**) R=2-furyl; (**c**) R=4-MeOC$_6$H$_4$; (**d**) R=4-ClC$_6$H$_4$; (**e**) R=2-NO$_2$C$_6$H$_4$; (**f**) R=3-NO$_2$C$_6$H$_4$; (**g**) R=3,4-(MeO)$_2$C$_6$H$_3$; (**h**) R=ethyl.

Table 1. Synthesis of Quinazolin-1-oxides **2**

Entry	Yield (%)	RT (h)	Mp (°C)	Entry	Yield (%)	RT (h)	Mp (°C)
2a	40[a] (40)[b]	25	100–101	**2e**	50[c]	16	203–204
2b	38 (36)	25	154–155	**2f**	44	16	227–228
2c	41 (38)	25	151–152	**2g**	60	16	152–153
2d	28 (36)	25	140–141	**2h**	65	2.5	75–76

[a] Isolated 2-phenyl-1,2,3,4-tetrahydroquinazolin-1-ol was treated with H_2O_2–tungstate in the presence of TBAHS in chloroform for 1 h at room temperature to give the corresponding **2a** in 80% yield.

[b] Compounds **2a–d** were prepared in a shorter reaction time, when the residue, after evaporation of the methanol, was dissolved in chloroform and treated with the oxidant system in the presence of phase transfer catalyst. The yields in the parentheses are according to this method.

[c] The yields of the isolated by-product quinazolines are 7% for **3a**, 17% for **3d**, and 19% for **3f**.

^{1}H NMR spectrum of **3a**, the proton at C-8 and the *ortho* protons of the phenyl at C-2 resonate at 8.10 (1H) and 8.60 ppm (2H), respectively. However, the same protons for **2a** are at 8.72–8.74 (C-8 and an *ortho* proton) and the other *ortho* proton is at 8.79 ppm. It is clear that the oxygen is affecting both the mentioned protons at C-8 and the C-2 phenyl's *ortho* protons, confirming that it is at the N-1 position of the quinazoline system. Additional evidence for the structure **2** and its isomer 3-oxide could be deduced from their mass spectra. The fragment ion, which is derived from the molecular ion by loss of HCNO is characteristic for the 3-oxide. The same fragmentation pattern is absent in the mass spectra of the 1-oxides.

2.2. Ambient light photochemistry of quinazoline oxides 2

2.2.1. Substituent effects on the cyclization of quinazolin-1-oxides 2 and the reactions of 1a*H*-[1,2]oxazireno[2,3-*a*]quinazolines 4. A 0.014 M $CDCl_3$ solution of a series of 1-oxides **2** was exposed to ambient light in Pyrex NMR tubes for 100 min and the product distribution (see Scheme 1) was determined by ^{1}H NMR (see Table 4 for the protons characteristic of the compounds determined quantitatively using the integral areas). After exposure, the samples were kept in dark for 50 min and the change in the product distribution was monitored (see Table 2). It was not surprising that the decrease in the concentration of **4** was equal to the sum of the increase in the corresponding **2**, **3**, **5**, and **6**. This undoubtedly proves that thermal deoxygenation and rearrangements of **4** could produce the starting material **2**, the quinazolines **3**, and the rearrangement products **5** and **6**. The comparison of the total conversions (TC) of **2** within 100 min (see Table 2) shows that the order of reactivity in the photochemical cyclization of compounds **2** is a substituent dependent process and is as follows: 3,4-(MeO)$_2$C$_6$H$_3$>4-MeOC$_6$H$_4$>Ph>ethyl>2-furyl>4-ClC$_6$H$_4$>2-NO$_2$C$_6$H$_4$. This order of reactivity could be rationalized by assuming that the excited state of the 1-oxides **2**(S$_1$) is stabilized by electron-withdrawing substituents while in the case of electron-donating groups the latter prefer to cyclize to the corresponding oxaziridines **4**.

Comparison of the underlined TC values shows that **4** with electron-rich aromatic rings are more reactive than those with electron-poor ones at thermal conditions. The order of reactivity is: 3,4-(MeO)$_2$C$_6$H$_3$>2-furyl>4-MeOC$_6$H$_4$>ethyl>Ph>4-ClC$_6$H$_4$.

The rearrangement of **4** to **5** and **6** predominates over their deoxygenations to **3** under both photochemical and thermal conditions, however, it is much more pronounced under the thermal conditions except in the case of 4-methoxyphenyl substituted **4**. It is not clear to define a general rule for the substituent effects on the *R*/*D* value, however, generally we can say that under both conditions electron-rich substituents favor the rearrangements to **5** and **6**.

Comparison of the **4**/*R* ratios reveals that quinazolines **2** with electron-donating substituents easily form oxaziridines, which with the same ease rearrange to compounds **5** and **6**. The electron-withdrawing substituents at C-2 neither prevent the oxaziridine formation nor support their rearrangement. Compound **2e** having a 2-nitrophenyl group did not undergo any photochemical reaction probably due to the high stabilizing effect of the nitro group on the exited singlet state of **2e**. **4**/*R* ratios imply the stabilizing order for the

Table 2. Effect of substituents on the product distribution in the photochemical reactions of quinazolin-1-oxides **2** and the rearrangements of 1a*H*-[1,2]-oxazireno[2,3-*a*]quinazolines **4** in $CDCl_3$

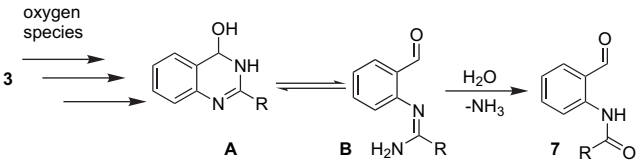
Entry	Product distribution (%)					TC (%)		*R*/*D*[d]		**5**/**6**		**4**/*R*	
	2	**3**	**4**	**5**	**6**	**2**	**4**	*hν*[a]	*Δ*[b]	*hν*	*Δ*	*hν*	*Δ*
2a	*13*	*2*	*73*	*8*	*4*	*87*		*6*		*2*		*6.08*	
4a	19 (6)[c]	3 (1)	55	14 (6)	9 (5)		25[e]		11		1.2		1.63
2b	*34*	*24*	*18*	*4*	*20*	*66*		*1*		*0.2*		*0.75*	
4b	34	30 (6)	0	11 (7)	25 (5)		100		2		1.4		1.5
2c	*3*	*2*	*44*	*15*	*36*	*97*		*25.5*		*0.42*		*0.86*	
4c	9 (6)	4 (2)	20	16 (1)	51 (15)		55		8		0.07		1.5
2d	*43*	*3*	*51*	*1*	*2*	*57*		*1*		*0.5*		*17*	
4d	45 (2)	4 (1)	45	2 (1)	4 (2)		12		3		0.5		2
2e	*100*	*0*	*0*	*0*	*0*	*0*		*0*		*0*			
4e	100	0	0	0	0		0		0				
2g	*0.5*	*16*	*7*	*34*	*42.5*	*99.5*		*4.8*		*0.8*		*0.09*	
4g	3 (2.5)	16	0	36 (2)	45 (2.5)		100		∞		0.8		
2h	*18*	*18*	*42*	*7*	*15*	*82*		*1.22*		*0.5*		*1.91*	
4h	24 (6)	22 (4)	25	8 (1)	21 (6)		40		1.75		0.2		2.42

[a] The ambient light exposure time was 100 min. The average light intensity was 150 lux.
[b] The reaction time for the thermal rearrangements was 50 min in the dark at 20 °C.
[c] The values in the brackets are the yields of the products from the thermal reactions of the 1a*H*-[1,2]oxazireno[2,3-*a*]quinazolines **4**.
[d] *R*/*D* is the rearrangement/deoxygenation ratio, TC=total conversion, and **4**/*R* is the ratio of the yields of the oxaziridine **4** to the sum of the yields of **5** and **6**.
[e] The ratio of the sum of the yields of all **4** transformation products to the yield of initial **4** multiplied by 100.

substituents at C-8a of oxaziridines **4** in the excited state to be: 4-ClC_6H_4>Ph>ethyl>4-$MeOC_6H_4$>2-furyl>3,4-$(MeO)_2C_6H_3$. It could be deduced from the **4**/*R* ratios that thermal rearrangements of **4** to **5** and **6** (see Table 2) are favored by electron-donating substituents at C-8a.

The formation of compounds **5** and **6** under photochemical conditions may result exclusively from the rearrangements of the excited states of oxaziridine **4**, exclusively from the rearrangements of ground state **4** or may involve both ways. If only the thermal rearrangement of **4**(S_0) was the source of **5** and **6** then their ratios should be close to the ratios under the thermal reaction conditions where we assume that the only rearranging product is **4**(S_0). This is true only in the case of 4-chlorophenyl substituted **4d**. In the other cases there are changes in the ratios of **5** and **6** under photochemical and thermal conditions. Under photochemical conditions, the shift to oxygen predominates in the case of aromatic rings having substituents with a positive resonance effect. The heteroaromatic electron-rich 2-furyl ring also accelerates the 2-aryloxyquinazoline formation (see Table 2). The reverse is true for the unsubstituted phenyl where the predominating shift is to nitrogen. 3-Nitro-substituted phenyl does not support at all any rearrangement to **5** and **6**; the only rearrangement is to the starting **2**.

It is highly possible that the oxygen formed under photochemical conditions could be different from the type formed under thermal conditions. Products isolated from the reaction mixtures of **2b** and **2h** in THF were proven to be *N*-(2-formylphenyl)furan-2-carboxamide **7b** and *N*-(2-formylphenyl)propionamide **7h** by spectral means. The formation of these compounds may be rationalized by the addition of oxygen species to the main product **3** of the reaction, the transformations of which could give dihydroquinazolines **A** (see Scheme 2). The hydrolysis of their ring-opened tautomer **B** could produce compounds **7**.



Scheme 2. Probable formation pathway for compounds **7**.

2.2.2. Solvent isotope and solvent effects on the cyclization of quinazoline 1-oxides 2 and the reactions of 1a*H*-[1,2]oxazireno[2,3-*a*]quinazolines 4. The comparisons of the yields of cyclization in $CHCl_3$ and $CDCl_3$ reveal that the reaction is faster in the deuterated solvent. An inverse solvent isotope effect is observed with the formation of **4a**. The deoxygenation products **3** predominate in $CHCl_3$, while the rearrangement processes predominate in $CDCl_3$.

The illumination of **2a** in THF chemoselectively gave compound **3a**. The rate of cyclization in CCl_4 was of the same magnitude as in $CDCl_3$, THF, and CH_2Cl_2. The deoxygenation predominates in toluene and CCl_4, while rearrangement is the main process in CH_2Cl_2 (Table 3).

2.2.3. Structural elucidation of the rearrangement products of oxaziridines 4. We were able to record, probably for the first time, the ^1H NMR spectrum of the fused oxaziridine

Table 3. Solvent isotope and solvent effects on the photochemical reactions of **2a**

Solvent	%[a]				%[b]			
	2	**4**	*D*	*R*	**2**	**4**	*D*	*R*
$CHCl_3$	92	0	8	0	44	0	43	8[c]
$CDCl_3$	16	58	9	17	2	29	21	48
THF	8	0	82	0[d]	0	0	82	0[e]
CH_2Cl_2	16	0	18	66	0	0	27	73
CCl_4	5	27	30	38	0	18	52	30
Toluene	24	0	58	18	15	0	70	15

[a] The product distribution after 100 min exposure.
[b] The product distribution after 200 min exposure.
[c] Also compound **7** with 5% integral area.
[d] A new product having singlet at 9.45 ppm with 9.8% integral area.
[e] Beside the previous at 9.45 ppm (7%) a singlet corresponding to the carboxamide **7** (11%). *D* is the yield of **3a** and *R* is the total yield of the rearrangement products **5a** and **6a**.

4a (76% pure), obtained from the ambient light irradiation of compound **2a**. The spectrum was elicited from the total spectrum and is as follows: ($CDCl_3$, 400 MHz) δ 7.42–7.50 (3H, m), 7.52–7.66 (4H, m), 7.85–7.88 (2H, m), 8.72 (1H, s).[10] The singlet at 8.72 ppm is assigned to the C-4 proton and is shifted to higher field in comparison with the values for the same protons in the aromatic derivatives **2**, **3**, **5**, and **6**. These protons range from 8.52 ppm for the ethyl-substituted oxaziridines **4h** to 8.79 ppm for the 3-nitrophenyl-substituted oxaziridine **4f** (see Table 4). Attempts to record the ^{13}C NMR spectrum failed as the compound gradually converted, in the dark, to the products shown in Table 2. The photoisomerization of 2-methylquinazolin-1-oxide was reported to give benzooxadiazepines, where the intermediate oxaziridine formation is assumed.[12] Compound **5a**, contaminated with 11% of carboxamide **7a**, was characterized as a representative of the 1-substituted quinazolin-2(1*H*)-ones. The presence of a carbonyl peak at 1670 cm^{-1} in its IR spectrum is in accordance with the proposed quinazolone structure (Fig. 1). The ^{13}C NMR spectrum of quinazolone contains 12 peaks. The HSQC spectrum revealed that eight carbons are CH and four are quaternary. Some of the characteristic assignments are shown in Figure 1. The most characteristic peaks are the singlet at 9.26 ppm, which correlates with the carbon at 168.2 ppm, assigned to the C4 proton, together with the doublet at 6.69 ppm, J=8.8 Hz, which was assigned to the C-8 proton. The latter proton was shown to belong to a spin system consisting of four protons by TOCSY1D experiment. All other quinazolones in the investigated reaction mixtures have the same signals with nearly the same chemical shifts. Table 4 summarizes the ^1H NMR chemical shift values for the characteristic C-4 proton of the compounds, which were used in the quantification of the product distribution of the investigated reactions.

Compound **6a** was isolated and characterized as the representative of the second rearrangement product series. The structure was deduced from the spectral data, some of which are shown in Figure 2. There is no carbonyl stretch in the IR spectrum of the compound. Beside the peaks arising from the stretching of the aromatic parts of the molecule, there are strong peaks at 1199 and 1281 cm^{-1} due to the diaryl ether's C–O–C stretching vibrations. These peaks are not so pronounced in the spectrum of **5a**. The compound has a characteristic singlet at 9.30 ppm, which corresponds to C-4 proton as all other 2-aryloxyquinazolines have. The same proton of the 2-ethoxyquinazoline resonates at 9.12 ppm (see Table 4).

The mass spectra of compounds **5a** and **6a** are nearly the same. The molecular ion (M^+) peaks are the base peaks in the spectra. The (M^+-1) peaks are the second most intense peaks.

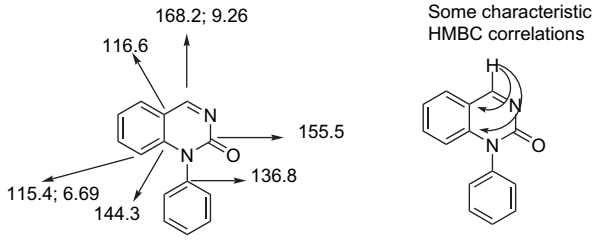


Figure 1. Characteristic NMR data for compound **5a**.

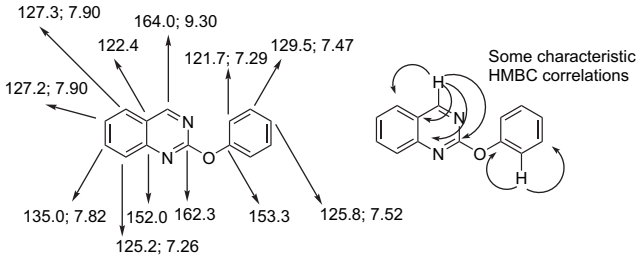


Figure 2. Some assignments for compound **6a** based on 1D and 2D experiments.

3. Conclusions

A convenient regioselective method for the oxidation of 2-substituted-1,2,3,4-tetrahydroquinazolines with H_2O_2–tungstate to quinazolin-1-oxides **2** has been developed. An excellent method, namely ambient light, proved to be efficient for the deoxygenation and the rearrangements of quinazolin-1-oxides **2**, if the appropriate solvent is chosen. The effect of substituents on the cyclization of compounds **2** as well as on the photochemical and thermal reactions of compounds **4** was investigated in detail. The intermediates of cyclization of a heterocyclic *N*-oxide were detected and in some cases their ^1H NMR spectra were recorded. For the first time, these reactions were shown to display solvent isotope and solvent effects. Structural elucidation of representative deoxygenation and rearrangement products of oxaziridines **4** (e.g., **3a–g**; **5a** and **6a**) was achieved by 1D and 2D NMR spectral methods. On the other hand, compounds **7** can be regarded as products from the reactions of **3** with the reactive oxygen species from the deoxygenations of **4**.

4. Experimental

4.1. General

All ambient light photochemical transformations of quinazolin-1-oxides were performed in Pyrex NMR tubes of the same quality in the same location in the laboratory.

Table 4. C-4H chemical shifts values of compounds **2**, **3a–h**, **4–6a–h**

Entry	2	3	4	5	6	Entry	2	3	4	5	6
a	9.01	9.48	8.72[a]	9.26[b]	9.30[b]	**e**	9.03				
b	9.03	9.39	8.63	9.21	9.31	**f**	9.04	9.52	8.79		
c	8.97	9.42	8.69	9.23	9.27	**g**	8.90	9.42	8.70	9.24	9.28
d	8.98	9.46	8.70	9.24	9.29	**h**	8.82	9.35	8.52	9.22	9.12

[a] See Section 2 for the full ^1H NMR spectrum of compound **4a**.
[b] The compounds' full characterization data are available in Section 4.

The samples were illuminated only by the light coming from the laboratory windows. The light intensity was measured with a Pasco high-sensitivity photometer Model OS-8020 (Pasco Scientific, Roseville, CA, USA). The solvents and reagents used in the synthesis and photochemical reactions of quinazolines were Aldrich or Merck quality and were used without additional purification. Melting points were taken on an Electrothermal Digital melting point apparatus. Infrared spectra were recorded on a Mattson 1000 FTIR. ^{1}H and ^{13}C NMR as well as 2D NMR experiments such as COSY, HMQC, HMBC, and NOESY 1D were performed on a Varian Mercury Plus 400 MHz spectrometer. The mass spectra were recorded on a Fisons VG Platform II instrument. Elemental analyses were performed on a EuroEA 3000 CHNS analyzer.

4.2. Synthesis of 2-substituted-quinazolin-1-oxides

4.2.1. One-pot procedure for the oxidation of 2-substituted-1,2,3,4-tetrahydroquinazolines to quinazolin-1-oxides 2a–h. *General procedure*: to a solution of 2-aminobenzylamine **1** (5 mmol, 0.610 g) in MeOH (20 mL), aldehyde (5 mmol) was added and the reaction mixture stirred for 1 h at room temperature. H_2O_2 (20 mmol, 30%, 2.266 g) and $Na_2WO_4\cdot 2H_2O$ (0.25 mmol, 0.082 g) were added and the mixture was stirred for a specified time. The precipitated **2e** from the reaction of **1** with 2-nitrobenzaldehyde was isolated by filtration. In the case of **2f** the product precipitated together with the corresponding 2-(3-nitrophenyl)quinazoline **3f**, which was purified by preparative TLC. In the other cases, the solvent was evaporated, water was added (15 mL), the mixture was basified with 10% NaOH, and then extracted with chloroform (3×15 mL). The extracts were combined and dried over anhydrous Na_2SO_4, filtered, and the solvent was evaporated. The residue was subjected to flash column chromatography using silica gel as an adsorbent and ethyl acetate–petroleum ether (1:9) as eluent mixture. The isolated products were crystallized from hexane or petroleum ether.

4.2.1.1. 2-Phenylquinazolin-1-oxide 2a. Tan colored crystals. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53–7.57 (3H, m), 7.75–7.79 (1H, m), 7.99–8.04 (2H, m), 8.71–8.73 (2H, m), 8.79 (1H, dd, J=8.8, 0.8 Hz), 9.01 (1H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 119.6, 124.8, 127.2, 128.1, 129.4, 130.2, 130.3, 130.9, 132.4, 134.6, 144.8, 146.2. Anal. Calcd for $C_{14}H_{10}N_2O$ (222.24), MS m/z 222 (M^+): C, 75.66; H, 4.54; N, 12.60. Found: C, 76.12; H, 4.60; N, 12.65.

4.2.1.2. 2-Furan-2-yl-quinazolin-1-oxide 2b. Light orange crystals. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.73 (1H, dd, J=3.6, 2.0 Hz), 7.72–7.78 (2H, m), 7.98–8.04 (2H, m), 8.35 (1H, d, J=3.2 Hz), 8.72 (1H, d, J=8.4 Hz), 9.03 (1H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 112.8, 118.7, 119.5, 123.9, 127.5, 129.1, 134.9, 143.4, 144.0, 145.5, 145.8, 147.1. Anal. Calcd for $C_{12}H_8N_2O_2$ (212.06), MS m/z 212 (M^+): C, 67.92; H, 3.80; N, 13.20. Found: C, 68.42; H, 3.81; N, 13.12.

4.2.1.3. 2-(4-Methoxyphenyl)quinazolin-1-oxide 2c. Gold colored crystals. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.91 (3H, s), 7.04–7.08 (2H, m), 7.70–7.74 (1H, m), 7.96–8.01 (2H, m), 8.77 (1H, d, J=8.0 Hz), 8.88–8.98 (2H, m), 8.98 (1H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.4, 113.4, 119.4, 124.4, 124.9, 127.2, 128.9, 132.3, 134.6, 144.8, 146.5, 149.8, 161.7. Anal. Calcd for $C_{15}H_{12}N_2O_2$ (252.27), MS m/z 252 (M^+): C, 71.42; H, 4.79; N, 11.10. Found: C, 71.31; H, 4.75; N, 10.80.

4.2.1.4. 2-(4-Chlorophenyl)quinazolin-1-oxide 2d. Light orange crystals. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49–7.52 (2H, m), 7.75–7.90 (1H, m), 7.98–8.04 (2H, m), 8.75–8.81 (3H, m), 8.98 (1H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 119.5, 124.8, 125.5, 127.3, 128.3, 129.6, 130.7, 131.7, 134.8, 136.9, 144.7, 146.4. Anal. Calcd for $C_{14}H_9ClN_2O$ (256.69), MS m/z 256 (M^+): C, 65.51; H, 3.53; N, 10.91. Found C, 65.62; H, 3.60; N, 10.80.

4.2.1.5. 2-(2-Nitrophenyl)quinazolin-1-oxide 2e. Yellow crystals. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67–7.71 (1H, m), 7.79–7.84 (3H, m), 7.98–8.03 (1H, m), 8.08 (1H, d, J=8.0 Hz), 8.17 (1H, d, J=7.6 Hz), 8.67 (1H, dd, J=8.0, 0.8 Hz), 9.03 (1H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 119.5, 124.0, 125.6, 127.4, 128.0, 130.1, 130.8, 132.2, 133.4, 134.9, 143.7, 146.4, 148.9, 149.6. Anal. Calcd for $C_{14}H_9N_3O_3$ (267.24), MS m/z 267 (M^+): C, 62.92; H, 3.39; N, 15.72. Found C, 63.08; H, 3.43; N, 15.68.

4.2.1.6. 2-(3-Nitrophenyl)quinazolin-1-oxide 2f. Yellow crystals. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (1H, t, J=7.6 Hz), 7.84 (1H, t, J=7.2 Hz), 8.04–8.09 (2H, m), 8.38 (1H, dt, J=8.4, 1.2 Hz), 8.79 (1H, d, J=9.2 Hz), 9.04 (1H, s), 9.24 (1H, dd, J=8.0, 1.2 Hz), 9.70 (1H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 119.8, 125.4, 125.5, 125.6, 127.6, 129.3, 130.3, 134.2, 135.2, 136.0, 145.1, 146.5, 147.9, 148.4. Anal. Calcd for $C_{14}H_9N_3O_3$ (267.24), MS m/z 267 (M^+): C, 62.92; H, 3.39; N, 15.72. Found C, 62.85; H, 3.40; N, 15.60.

4.2.1.7. 2-(3,4-Dimethoxyphenyl)quinazolin-1-oxide 2g. Light orange crystals. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.91 (3H, s), 3.95 (3H, s), 6.95 (1H, d, J=9.1 Hz), 7.65 (1H, t, J=7.4 Hz), 7.92 (2H, m), 8.49–8.56 (2H, m), 8.68 (1H, d, J=8.6 Hz), 8.90 (1H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 56.4, 56.4, 110.7, 113.6, 119.7, 124.8, 125.0, 125.5, 127.6, 129.4, 135.0, 145.3, 146.8, 148.5, 150.0, 151.8. Anal. Calcd for $C_{16}H_{14}N_2O_3$ (282.29), MS m/z 282 (M^+): C, 68.07; H, 5.00; N, 9.92. Found: C, 67.58; H, 4.9; N, 9.76.

4.2.1.8. 2-Ethylquinazolin-1-oxide 2h. Light orange crystals. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.39 (3H, t, J=7.4 Hz), 3.25 (2H, q, J=7.4 Hz), 7.64 (1H, t, J=7.6 Hz), 7.87–7.93 (2H, m), 8.59 (1H, d, J=8.7 Hz), 8.82 (1H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.1, 26.2, 119.2, 125.2, 127.6, 129.2, 134.9, 143.7, 146.5, 158.0. Anal. Calcd for $C_{10}H_{10}N_2O$ (174.20), MS m/z 174 (M^+): C, 68.95; H, 5.79; N, 16.08. Found C, 68.90; H, 5.85; N, 16.00.

4.2.2. Improved one-pot procedure for the oxidation of 2a–d in the presence of phase transfer catalyst. To a solution of 2-aminobenzylamine (2 mmol, 0.244 g) in methanol (10 mL), aldehyde (2 mmol) was added and the mixture stirred at room temperature for 1 h. H_2O_2 (8 mmol, 35%, 0.776 g) and $Na_2WO_4\cdot 2H_2O$ (0.1 mmol, 0.033 g) were added to the mixture and stirring continued for further 1 h. The solvent was evaporated under vacuum and then the residue was suspended in chloroform (15 mL). TBAHS

(0.12 mmol, 0.042 g) and H_2O_2 (1.8 mmol, 35%, 0.175 g) were added and the mixture stirred for 3 h at room temperature. The mixture was filtered and water was added to the mixture. The organic phase was separated and dried over anhydrous Na_2SO_4. Upon filtration the solvent was evaporated. The isolation procedure is as in the previous general method.

4.2.3. Conversion of 2-phenyl-1,2,3,4-tetrahydroquinazolin-1-ol to 2a. To a suspension of 2-phenyl-1,2,3,4-tetrahydroquinazolin-1-ol (0.2 mmol, 0.045 g) in chloroform (10 mL), TBAHS (0.1 mmol, 0.035 g), H_2O_2 (0.8 mmol, 35%, 0.078 g), and $Na_2WO_4\cdot 2H_2O$ (0.01 mmol, 0.003 g) were added successively and the mixture stirred at room temperature for 1 h. Water (10 mL) was added to the mixture and the organic phase was separated, dried over anhydrous Na_2SO_4, and filtered. The solvent was evaporated and the residue recrystallized from hexane or petroleum ether.

4.3. Deoxygenation of quinazolin-1-oxides

4.3.1. Synthesis of 3a–g.

4.3.1.1. 2-Phenylquinazoline 3a. The compound was obtained from the exposure of the solution of **2a** (0.23 mmol, 0.05 g) in THF (15 mL) to ambient light for 72 h. The compound was isolated by preparative TLC using ethyl acetate–petroleum ether (1:4) as an eluent system. Light yellow powder. Yield (38 mg, 80%). Mp 97–98 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49–7.57 (3H, m), 7.61–7.65 (1H, m), 7.90–7.95 (2H, m), 8.10 (1H, J=8.4 Hz), 8.61 (2H, dd, J=8.0, 2 Hz), 9.48 (1H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 123.6, 127.1, 127.3, 128.5, 128.6, 128.7, 130.6, 134.1, 138.1, 150.8, 160.5, 161.1. Anal. Calcd for $C_{14}H_{10}N_2$ (206.24), MS m/z 206 (M^+): C, 81.53; H, 4.89; N, 13.58. Found C, 81.47; H, 5.02; N, 13.62.

4.3.1.2. 2-(Furan-2-yl)quinazoline 3b. Compound **2b** (0.06 mmol, 0.013 g) in 6 mL of THF was exposed to ambient light in six Pyrex NMR tubes for 3.3 h. The yield determined by ^{1}H NMR is 65%. Isolated by means of preparative TLC. Brown powder. Yield (3 mg, 25%). Mp 113–114 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.63–6.64 (1H, m), 7.47–7.50 (1H, m), 7.60–7.64 (1H, m), 7.71 (1H, s), 7.91–7.95 (2H, m), 8.11–8.15 (1H, m), 9.40 (1H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 112.3, 114.1, 123.4, 127.3, 128.4, 134.5, 145.4, 150.5, 152.6, 154.2, 160.8. Anal. Calcd for $C_{12}H_8N_2O$ (196.2), MS m/z 196 (M^+): C, 73.46; H, 4.11; N, 14.28. Found C, 73.35; H, 4.01; N, 14.35.

4.3.1.3. 2-(4-Methoxyphenyl)quinazoline 3c. Compound **2b** (5 mg, 0.02 mmol) in 2 mL of THF was exposed to ambient light in two Pyrex NMR tubes for 3.3 h. The yield determined by ^{1}H NMR is 75%. Isolated by means of preparative TLC. Light yellow powder. Yield (0.002 g, 43%). Mp 82–84 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.91 (3H, s), 7.05 (2H, d, J=8.8 Hz), 7.59 (1H, t, J=7.6 Hz), 7.87–7.92 (2H, m), 8.06 (1H, d, J=8.8 Hz), 8.58 (2H, d, J=8.8 Hz), 9.43 (1H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.4, 114.0, 123.3, 126.9, 127.2, 128.3, 130.3, 134.2, 160.5, 160.8, 162.0. Anal. Calcd for $C_{15}H_{12}N_2O$ (236.27), MS m/z 236 (M^+): C, 76.25; H, 5.12; N, 11.86. Found C, 76.45; H, 4.95; N, 11.70.

4.3.1.4. 2-(4-Chlorophenyl)quinazoline 3d. The compound was isolated from the reaction mixture of **2d**. Yellow crystals. Mp 129–130 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48–7.51 (2H, m), 7.61–7.65(1H, m), 7.90–7.95 (2H, m), 8.07(1H, dd, J=9.6, 0.8 Hz), 8.55–8.59 (2H, m), 9.46(1H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 123.6, 127.2, 127.5, 128.6, 128.8, 129.9, 134.3, 136.5, 136.8, 150.7, 160.0, 166.0. Anal. Calcd for $C_{14}H_9ClN_2$ (240.69), MS m/z 240 (M^+): C, 69.86; H, 3.77; N, 11.64. Found C, 69.48; H, 3.88; N, 11.19.

4.3.1.5. 2-(3-Nitrophenyl)quinazoline 3f. The compound was isolated from the reaction mixture of **2f**. Light yellow powder. Mp 162–163 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67–7.74 (2H, m), 7.96–8.01 (2H, m), 8.14 (1H, dd, J=9.2, 0.8 Hz), 8.36 (1H, ddd, J=8.4, 2.4, 1.2 Hz), 8.99 (1H, dt, J=8.0, 1.2 Hz), 9.51 (1H, m) 9.52 (1H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 123.85, 124.19, 125.29, 127.49, 128.35, 129.00, 129.81, 134.48, 134.86, 140.11, 149.06, 150.85, 158.92, 161.04. Anal. Calcd for $C_{14}H_9N_3O_2$ (251.24), MS m/z 251 (M^+): C, 66.93; H, 3.61; N, 16.73. Found C, 66.50; H, 3.70; N, 16.53.

4.3.1.6. 2-(3,4-Dimethoxyphenyl)quinazoline 3g. Compound **2g** (0.04 mmol, 11 mg) in 4 mL of THF was exposed to ambient light in four Pyrex NMR tubes for 3.3 h. The yield determined by ^{1}H NMR is 80%. Isolated by means of preparative TLC. Light yellow powder. Yield (5 mg, 47%). Mp 73–75 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.99 (3H, s), 4.08 (3H, s), 7.02 (1H, d, J=8.4 Hz), 7.57–7.61 (1H, m), 7.88–7.92 (2H, m), 8.06 (1H, dd, J=8.4, 1.2 Hz), 8.20 (1H, d, J=2 Hz), 8.26 (1H, dd, J=8.4, 2 Hz), 9.43 (1H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.9, 56.0, 110.9, 111.1, 122.0, 123.4, 126.8, 127.1, 128.4, 134.0, 136.2, 136.4, 149.1, 150.8, 160.4, 160.8. Anal. Calcd for $C_{16}H_{14}N_2O_2$ (266.29): C, 72.16; H, 5.30; N, 10.52. Found: C, 72.00; H, 5.40; N, 10.52.

4.3.1.7. 2-Ethylquinazoline 3h. Compound **2h** (0.2 mmol, 0.034 g) in 10 mL of THF was exposed to ambient light in 10 Pyrex NMR tubes for 3.3 h. The yield determined by ^{1}H NMR is 74%. Attempts to isolate the compound by preparative TLC failed. The only isolable product from the reaction mixture was **7h**.

4.3.2. Synthesis of indazole. To a solution of 2-aminobenzylamine **1** (5 mmol, 0.611 g) in MeOH (20 mL), H_2O_2 (20 mmol, 35%, 1.94 g, 1.7 mL) and $Na_2WO_4\cdot 2H_2O$ (0.25 mmol, 0.082 g) were added and the mixture stirred for 1 h at room temperature. The solvent was evaporated, water was added (20 mL) to the mixture, and then extracted with chloroform (2×15 mL). The extracts were combined and dried over anhydrous Na_2SO_4, filtered, and the solvent was evaporated. The residue was recrystallized from ether–petroleum ether. Yield (482 mg, 82%). Mp 145–146 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11 (1H, t, J=7.5 Hz), 7.30 (1H, t, J=7.5 Hz), 7.43 (1H, d, J=8.4 Hz), 7.7 (1H, d, J=8.1 Hz), 8.05 (1H, s), 10.98 (1H, br s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 110.2, 121.3, 121.4, 123.6, 127.3, 135.1, 140.5. The spectral characteristics of the compound were compared with those of authentic sample.[13]

4.4. 2-(4-Chlorophenyl)quinazolin-3-oxide

The compound was isolated from the reaction mixture of **2d**. Light orange crystals. Yield (102 mg, 8%). Mp 161–162 °C

(with decomposition). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (2H, d, J=8.0 Hz), 7.63–7.79 (3H, m), 8.02 (1H, d, J=8.4 Hz), 8.39 (2H, d, J=8.0 Hz), 9.00 (1H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 123.9, 124.1, 128.3, 128.5, 129.9, 130.1, 131.8, 132.0, 137.4, 141.3, 142.1, 154.1. Anal. Calcd for $C_{14}H_9ClN_2O$ (256.69): C, 65.51; H, 3.53; N, 10.91. Found. C, 65.40; H, 3.60; N, 11.03.

4.5. 2-(4-Methoxyphenyl)quinazolin-4(3*H*)-one

From the reaction mixture of **2c**. Light yellow crystals. Yield (24 mg, 2%). Mp 237–239 °C. IR (KBr): $\nu_{C=O}$ 1678 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.91 (3H, s), 7.07 (2H, d, J=7.6 Hz), 7.45–7.49 (1H, m), 7.76–7.81 (2H, m), 8.15–8.18 (2H, m), 8.30–8.32 (1H, m), 11.0 (1H, br s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.5, 114.5, 120.6, 125.0, 126.3, 126.4, 127.7, 128.9, 134.9, 149.6, 151.3, 162.5, 163.5. Anal. Calcd for $C_{15}H_{12}N_2O_2$ (252.27), MS m/z 252 (M^+): C, 71.42; H, 4.79; N, 11.10. Found C, 71.37; H, 4.72; N, 11.07.

4.6. 1-Phenylquinazolin-2(1*H*)-one 5a

A solution of compound **2a** (0.1 mmol, 0.022 g) in $CDCl_3$ (4 mL) was exposed to ambient light for a day and then left overnight. The compound was isolated by preparative TLC. Yield (3 mg, 14%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.70 (1H, d, J=8.8 Hz), 7.26–7.35 (3H, m), 7.52–7.64 (4H, m), 7.79 (1H, dd, J=7.6, 1.6 Hz), 9.26 (1H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 115.4, 116.6, 122.9, 128.4, 128.8, 129.3, 130.4, 135.3, 136.8, 144.3, 155.5, 168.2. Anal. Calcd for $C_{14}H_{10}N_2O$ (222.24), MS m/z 222 (M^+): C, 75.66; H, 4.54; N, 12.60. Found: C, 75.22; H, 4.60; N, 12.17.

4.7. 2-Phenoxyquinazoline 6a

A solution of compound **2a** (0.1 mmol, 0.022 g) in $CDCl_3$ (4 mL) was exposed to ambient light for a day and left overnight. Light yellow crystals. Yield (6 mg, 27%). Mp 114–115 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26–7.30 (3H, m), 7.47 (2H, t, J=7.2 Hz), 7.51 (1H, t, J=8.0 Hz), 7.80–7.84 (2H, m), 7.90 (1H, d, J=8.0 Hz), 9.30 (1H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 121.7, 122.4, 125.2, 125.8, 127.2, 127.3, 129.6, 134.8, 152.0, 153.3, 162.3, 164.0. Anal. Calcd for $C_{14}H_{10}N_2O$ (222.24), MS m/z 222 (M^+): C, 75.66; H, 4.54; N, 12.60. Found: C, 75.34; H, 4.63; N, 12.30.

4.7.1. *N*-(2-Formylphenyl)furan-2-carboxamide 7b. Compound **2b** (0.06 mmol, 0.013 g) in 6 mL of THF was exposed to ambient light in six Pyrex NMR tubes for 3.3 h. The yield determined by ^{1}H NMR is 30%. Isolated by means of preparative TLC. Light yellow powder. Yield (2 mg, 14%). Mp 98–100 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.57–6.59 (1H, m), 7.27–7.30 (2H, m), 7.64–7.69 (2H, m), 7.73 (1H, dd, J=7.6, 1.6 Hz), 8.89 (1H, d, J=8.8 Hz), 10.01 (1H, s), 12.09 (1H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 112.4, 115.7, 120.1, 123.1, 136.1, 136.2, 145.2, 195.5, C=O. Anal. Calcd for $C_{12}H_9NO_3$ (215.2), MS m/z 215 (M^+): C, 66.97; H, 4.22; N, 6.51. Found: C, 66.85; H, 4.10; N, 6.35.

4.7.2. *N*-(2-Formylphenyl)propionamide 7h. Compound **2h** (0.2 mmol, 0.034 g) in 10 mL of THF was exposed to ambient light in 10 Pyrex NMR tubes for 3.3 h. Isolated by means of preparative TLC. Light yellow oil. Yield (3 mg, 9%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.29 (3H, t, J=7.2 Hz), 2.51 (2H, q, J=7.2 Hz), 7.22 (1H, dt, J=7.2, 0.8 Hz), 7.62 (1H, dt, J=7.2, 2 Hz), 7.68 (1H, dd, J=7.2, 2 Hz), 8.77 (1H, d, J=8.4 Hz), 9.93 (1H, s), 11.16 (1H, br s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 9.5 (CH_3), 31.59 (CH_2), 119.9 (C6H), 121.6 (C2), 122.7 (C5H), 136.1 (C4H), 136.2 (C6H), 141.1 (C1), 173.5 (amide C=O), 195.6 (aldehyde C=O). Anal. Calcd for $C_{10}H_{11}NO_2$ (177.2), MS m/z 177 (M^+): C, 67.78; H, 6.26; N, 7.90. Found: C, 67.40; H, 6.00; N, 7.30.

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References and notes

1. (a) Witt, A.; Bergman, J. *Curr. Org. Chem.* **2003**, *7*, 659–677; (b) Dyakonov, A. L.; Telezhenetskaya, M. V. *Khim. Prir. Soedin.* **1997**, *3*, 297–351; (c) Spence, G. G.; Taylor, E. C.; Buchardt, O. *Chem. Rev.* **1970**, *70*, 231–265.
2. (a) Michael, J. P. *Nat. Prod. Rep.* **1999**, *16*, 697–709; (b) Michael, J. P. *Nat. Prod. Rep.* **2002**, *19*, 742–760; (c) Michael, J. P. *Nat. Prod. Rep.* **2003**, *20*, 476–493.
3. (a) Touroutoglou, N.; Pazdur, R. *Clin. Cancer Res.* **1996**, *2*, 227–243; (b) Jackman, A. L.; Boyle, F. T.; Harrap, K. R. *Invest. New Drug* **1996**, *14*, 305–316; (c) Sielecki, T. M.; Johnson, T. L.; Liu, J.; Muckelbauer, J. K.; Grafstrom, R. H.; Cox, S.; Boylan, J.; Burton, C. R.; Chen, H.; Smallwood, A.; Chang, C. H.; Boisclair, M.; Benfield, P. A.; Trainora, G. L.; Seitza, S. P. *Bioorg. Med. Chem. Lett.* **2001**, *11*, 1157–1160; (d) Bonomi, P. E. *Expert Opin. Inv. Drug*. **2003**, *12*, 1395–1401.
4. (a) Armarego, W. L. F. *Advanced Heterocyclic Chemistry*; Academic: New York, NY, 1963; Vol. 1, pp 253–309; (b) Armarego, W. L. F. *Adv. Heterocycl. Chem.* **1979**, *24*, 1–61.
5. Gilchrist, T. L. Six-membered ring compounds with two or more heteroatoms. In *Heterocyclic Chemistry*; Pitman: London, 1985; pp 327–330.
6. (a) Sinkkonen, J.; Zelenin, K. N.; Potapov, A. A.; Lagoda, I. V.; Alekseyev, V. V.; Pihlaja, K. *Tetrahedron* **2003**, *59*, 1939–1950; (b) Göblyös, A.; Lázár, L.; Fülöp, F. *Tetrahedron* **2002**, *58*, 1011–1016.
7. Sternbach, L. H.; Kaiser, S.; Reeder, E. *J. Am. Chem. Soc.* **1960**, *82*, 475–480.
8. Coşkun, N.; Çetin, M. *Tetrahedron Lett.* **2004**, *45*, 8973–8975.
9. Stempel, A.; Douvan, I.; Sternbach, L. H. *J. Org. Chem.* **1968**, *33*, 2963–2966.
10. The photochemistry of the heteroaromatic *N*-oxides[11] is reviewed by Albini and Alpegiani and it is seen from the literature covered here that the rearrangements of the *N*-oxides are assumed to proceed through the intermediate oxaziridines, which are never isolated and their reactions are investigated.
11. Albini, A.; Alpegiani, M. *Chem. Rev.* **1984**, *84*, 43–71.
12. Field, G. F.; Sternbach, L. H. *J. Org. Chem.* **1968**, *33*, 4438–4440.
13. SDBSWeb: http://www.aist.go.jp/RIODB/SDBS/.