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Photochemical Studies

XIII.* The Liquid Phase Photolysis of Quinoline *N*-Oxides Unsubstituted in the 2-Position**

OLE BUCHARDT, PHILIP L. KUMLER***

Chemical Laboratory II (General and Organic Chemistry), University of Copenhagen, The H. C. Ørsted Institute, Copenhagen, Denmark

and

CHRISTIAN LOHSE

The Chemical Institute, University of Odense, Odense, Denmark

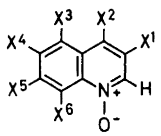
The photolysis, in various solvents, of a series of quinoline *N*-oxides (I) without substituents in the 2-position, is reported. The product distribution shows a remarkable solvent dependence. In protic solvents the isomeric carbostyrils (II) are formed; in aprotic solvents carbostyril formation is decreased, and *N*-formyl-2-indolinols (III) or their open-chain tautomers (III′) are produced. Minor amounts of other products were observed in most photolyses. A mechanistic rationalization of these findings is presented.

In a preliminary communication,[2] we described the light-induced formation of some *N*-formyl-2-indolinols (IIIa, e, o) from quinoline *N*-oxides (Ia, e, o) in ether or benzene solution (*cf.* Ref. 3). Previously, the formation of carbostyrils (II) from type I quinoline *N*-oxides in aqueous [4] and methanolic [5] solution had been reported. To further investigate the light-induced reactions

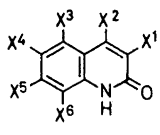
* For the previous paper see Ref. 1.

** A preliminary communication of part of this work has appeared.[2] The experimental details of the previous work are included in the present paper.

*** NATO Research Fellow, 1967–68. Present address: Department of Chemistry, University of Chicago, Chicago, Illinois 60 637, U.S.A.



I



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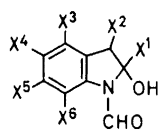
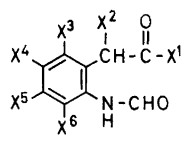


III



III′

	X^1	X^2	X^3	X^4	X^5	X^6
a	H	H	H	H	H	H
b	C_2H_5	H	H	H	H	H
c	H	CH_3	H	H	H	H
d	H	H	CH_3	H	H	H
e	H	H	H	CH_3	H	H
f	H	H	H	H	CH_3	H
g	H	H	H	H	H	CH_3
h	Br	H	H	H	H	H
i	H	Cl	H	H	H	H
j	H	Br	H	H	H	H
k	H	H	H	F	H	H
l	H	H	H	Cl	H	H
m	H	H	H	Br	H	H
n	H	H	H	H	Cl	H
o	H	H	H	OCH_3	H	H
p	H	CH_3	H	OCH_3	H	H
q	H	H	H	H	H	OCH_3

of type I quinoline *N*-oxides we have irradiated an extended series of these (Ia—q) in various solvents.*

* We have found acetone to be the preferred solvent for formation of benz[d][1,3]oxazepines, the presumed precursors of the *N*-formyl-2-indolinols (III) or their open-chain tautomers III′, in the photolysis of quinoline *N*-oxides.[6] Therefore, we have used this aprotic solvent instead of ether or benzene in our recent studies.

Table 1. Summary of product distribution in photolyses of 2-unsubstituted quinoline *N*-oxides.

Compound	Solvent	Ref.[a]	% Quinoline[b]	% Carbostyril	% Dimer	% Indolinol or chain tautomer	Other products[c]
Quinoline *N*-oxide (Ia)	Water	4	TLC	91	—	—	—
	Ether	2	TLC	30	—	50	—
	Ethanol	17	—	49	13	—	—
	Methanol	5	5—6	60—70	—	—	*N*-Formylindole (2.5)
	Acetone	3	7	15	—	41	*N*-Formylindole (3)
3-Ethylquinoline *N*-oxide (Ib)	Water	—	TLC	90	—	—	
	Acetone	—	—	17	—	68[d]	
3-Methylquinoline *N*-oxide	Water	4	—	90	—	—	—
4-Methylquinoline *N*-oxide (Ic)	Water	4	—	80	—	—	—
	Benzene	—	TLC	42	—	4[e]	Skatole(10), 2-Formamidoacetophenone(4) [f]
	Ether	—	TLC	25	—	25[e]	Skatole(TLC)[b]
	Methanol	5	1—2	70—75	—	—	Skatole(5)
5-Methylquinoline *N*-oxide (Id)	Water	4	—	88	—	—	—
6-Methylquinoline *N*-oxide (Ie)	Water	4	—	80	—	—	—
	Ether	2	TLC	30	—	33	2-Formamido-5-methylbenzaldehyde(5)[f]
	Ethanol	—	—	—	90	—	—
7-Methylquinoline *N*-oxide (If)	Water	4	—	98	—	—	—
	Ethanol	—	—	—	70	—	—
8-Methylquinoline *N*-oxide (Ig)	Water	4	—	80	—	—	—
	Acetone	—	—	41	—	23	2-Formamido-3-methylbenzaldehyde(9)[f]
3-Bromoquinoline *N*-oxide (Ih)	Ethanol	—	TLC	50	—	—	—
	Acetone	—	TLC	57	—	—	5 Other components (TLC)[b]
4-Chloroquinoline *N*-oxide (Ii)	Methanol	5	2—3	75—80	—	—	—
	Acetone	—	5	50—70	—	0—20[g]	5 Other components (TLC)[b]

Table 1. Continued.

4-Bromoquinoline *N*-oxide (Ij)	Water	—	—	50	—	—	—
	Ethanol	—	—	50	—	—	—
6-Fluoroquinoline *N*-oxide (Ik)	Water	—	—	70	—	—	—
	Acetone	—	4	29	4	45	2 Other components (TLC)[b]
6-Chloroquinoline *N*-oxide (Il)	Water	—	—	95	—	—	—
	Ethanol	—	—	—	70	—	—
6-Bromoquinoline *N*-oxide (Im)	Water	—	—	80	—	—	—
	Acetone	—	TLC	39	—	33	3 Other components (TLC)[b]
7-Chloroquinoline *N*-oxide (In)	Acetone	—	6	31	—	50	—
4-Methoxyquinoline *N*-oxide	Methanol	5	4—5	60—70	—	—	—
6-Methoxyquinoline *N*-oxide (Io)	Benzene	2	—	45	—	11	2-Formamido-5-methoxybenzaldehyde (0.5)[f]
	Methanol	5	—	—	63	—	—
	Methanol	5	5	50—55	—	—	—
	Ethanol	—	—	—	50	—	—
4-Methyl-6-methoxyquinoline *N*-oxide (Ip)	Water	—	—	85	—	—	—
	Benzene	—	TLC	30	—	—	7 Other components (TLC)[b]
	Ethanol	—	—	90	—	—	—
8-Methoxyquinoline *N*-oxide (Iq)	Water	—	—	—	50	—	—
4-Azidoquinoline *N*-oxide	Various	9	—	—	—	—	4,4′-Azidoquinoline-1,1′-dioxide(21—78)
4-Nitroquinoline *N*-oxide	ROH	8	—	—	—	—	2,4-Dihydroxyquinoline(7)
3-Methyl-4-nitroquinoline *N*-oxide	ROH	8	—	—	—	—	2,4-Dihydroxy-3-methylquinoline(30)

[a] If no reference is given, the data are new.
[b] TLC means detected by thin layer chromatography but not isolated.
[c] The yield is given in parentheses.
[d] This compound exists as the open-chain tautomer (*e.g.* III′b).
[e] Too unstable for complete characterization but identified by IR spectroscopy.
[f] Identified by IR and NMR spectroscopy.
[g] Very unstable but identified by IR and UV spectroscopy.

IRRADIATIONS

In each case the irradiation of quinoline *N*-oxides in aqueous solution led to the formation of carbostyrils in high yields. In some cases minor amounts of the parent quinolines and other byproducts were observed by thin layer chromatography (TLC). The results of these experiments are summarized in Table 1. If 96 % ethanol was used as solvent, carbostyril formation again dominated. However, if the time of irradiation was prolonged in this solvent, photodimers of carbostyrils could be isolated in high yield. The structure of these dimers is not known with certainty, but we suppose they are analogous to those from carbostyril and *N*-methylcarbostyril.[7] Only when $X^1=X^2=H$ was photodimerization observed. The results of these photolyses are also summarized in Table 1.

The photolyses of quinoline *N*-oxides in aprotic non-polar solvents have been studied most extensively. In most cases the isomeric carbostyrils (II) could be isolated directly from the photolysis mixtures by concentration and filtration. Preparative layer chromatography (PLC) of the filtrates from the photolysis of Ia, c—e, g, k, l, n, o yielded the *N*-formyl-2-indolinols (IIIa, c—e, g, k, l, n, o). Irradiation of 3-ethylquinoline *N*-oxide (Ib) in acetone gave 3-ethylcarbostyril and 1-(2-formamidophenyl)-2-butanone (III'b), whereas irradiation of Ih, i, p gave complex reaction mixtures from which only the corresponding carbostyrils (IIh, i, p) were isolated and identified (see, however, the experimental section and Table 1, where all of the presently as well as previously reported [2–5,7–9] results obtained upon photolysis of type I quinoline *N*-oxides are tabulated). In most of the presently described photolyses small amounts of the parent quinolines and other, unidentified, compounds were observed (Table 1). In some cases *o*-formamidobenzaldehydes were observed as minor products. These are believed to be due to photooxidation of thermal degradation products of the *N*-formyl-2-indolinols (III) or their open-chain tautomers III' (*cf.* Ref. 10a).

IDENTIFICATION OF PRODUCTS

The carbostyrils (II), except for 3-ethylcarbostyril (IIb), are all known compounds. They were identified by their melting points and by their characteristic IR, UV, and NMR spectra (Table 2). The photodimers were characterized by their IR and NMR spectra (Table 2) and by their easy thermal conversion to the monomeric carbostyrils. The *N*-formyl-2-indolinols (IIIa, c—e, g, k, l, n, o) and the open chain tautomer III'b were identified by comparing their IR and UV spectra with those of the previously described [10] *N*-acetyl-2-indolinols (Table 3). The NMR-spectra of compounds III and III'b, which are all in excellent agreement with the assigned structures, will be reported separately.[11] The mass spectra of some of the *N*-formyl-2-indolinols, which also support the structure assignment, are discussed elsewhere.[12]

Table 2. Spectral data and melting

Compound		IR[a] C=O	UV[b]						Arom.
			mμ	log ε	mμ	log ε	mμ	log ε	
Carbostyril	(IIa)	1665	229	4.54	268	3.86	329	3.81	2.0
3-Ethyl-	(IIb)	1660	229	4.45	269	3.87	324	3.87	2.1
3-Methyl-		1655	220	4.25	269	3.91	324	3.91	2.1
4-Methyl-	(IIc)	1655	230	4.58	268	3.82	327	3.84	2.0
5-Methyl-	(IId)	1660	234	4.51	281	3.97	333	3.76	2.2
6-Methyl-	(IIe)	1655	233	4.61	271	3.88	337	3.81	2.3
7-Methyl-	(IIf)	1650	232	4.61	276	3.95	329	3.99	2.3
8-Methyl-	(IIg)	1660	233	4.64	276	4.05	332	3.88	2.2
3-Bromo-	(IIh)	1660	233	4.49	280	3.93	336	4.07	2.4
4-Chloro-	(IIi)	1650	234	4.45	272	3.81	335	3.78	2.3
4-Bromo-	(IIj)	1660	231	4.48	273	3.74	335	3.70	2.1
6-Fluoro-	(IIk)	1670	229	4.37	264	3.83	336	3.73	2.3
6-Chloro-	(IIl)	1670	234	4.50	275	3.47	336	3.52	2.2
6-Bromo-	(IIm)	1660	239	4.56	277	3.56	338	3.61	2.2
7-Chloro-	(IIn)	1700	231	4.52	280	3.69	327	3.92	2.3
6-Methoxy-	(IIo)	1670	234	4.43	268	3.73	349	3.50	2.6
4-Methyl-6-methoxy-	(IIp)	1650	235	4.51	278	3.62	347	3.67	2.4
8-Methoxy-	(IIq)	1655	235[g]	4.01	273	3.56	336	3.15	2.5
Dimer of IIa		1715	—	—	—	—	—	—	2.8
Dimer of IIe		1715	—	—	—	—	—	—	2.8
Dimer of IIf		1710	—	—	—	—	—	—	3.0
Dimer of IIk		1720	—	—	—	—	—	—	3.1
Dimer of IIl		1710	—	—	—	—	—	—	—
Dimer of IIo		1690	—	—	—	—	—	—	3.2
Dimer of IIq		1710	—	—	—	—	—	—	3.0

[a] Spectra recorded in KBr discs; position reported in cm^{-1}.
[b] Spectra recorded in 96 % ethanol.
[c] Spectra recorded in trifluoroacetic acid solution with tetramethylsilane as internal standard. Chemical shifts are reported in τ units and coupling constants (J) in cps. s=singlet, d=doublet, t=triplet, and q=quartet.
[d] Reference in parentheses.
[e] Calc. for $C_{11}H_{11}NO$: C 76.27; H 6.40; N 8.09. Found: C 76.15; H 6.51; N 8.16.
[f] Calc. for C_9H_6NOF: C 66.25; H 3.71; N 8.59. Found: C 66.49; H 4.06; N 8.59.

points for carbostyrils and dimers.

NMR[c]				Melting point (°C)	
H(3)	H(4)	Other	Ratio	Obs.	Lit.[d]
2.55(d), $J=9$	1.23(d), $J=9$	—	4:1:1	192–193	192–193(4)
—	1.48(s)	CH_3,8.53(t) CH_2,7.00(q)	4:1:3:2	173–174[e]	—
—	1.50(s)	CH_3,7.45(s)	4:1:3	238–239	235(18)
2.67(s)	—	CH_3,7.03(s)	4:1:3	221–222	222–224(19)
2.65(d), $J=9$	1.13(d), $J=9$	CH_3,7.22(s)	3:1:1:3	227–228	228(20)
2.60(d), $J=9$	1.33(d), $J=9$	CH_3,7.37(s)	3:1:1:3	236–238	237(21)
2.75(d), $J=9$	1.43(d), $J=9$	CH_3,7.37(s)	3:1:1:3	198–199	198(22)
2.63(d), $J=9$	1.37(d), $J=9$	CH_3,7.22(s)	3:1:1:3	221–222	218–219(23)
—	1.45(s)	—	4:1	259–261	253(24)
2.72(s)	—	—	4:1	249–250	245–247(25)
2.53(s)	—	—	4:1	261–263	265(26)
2.82(d), $J=9$	1.63(d), $J=9$	—	3:1:1	268–271[f]	—
2.73(d), $J=9$	1.58(d), $J=9$	—	3:1:1	266–267	267(27)
2.80(d), $J=9$	1.63(d), $J=9$	—	3:1:1	269–271	268–269(28)
2.83(d), $J=9$	1.57(d), $J=9$	—	3:1:1	285–287	287–292(29)
3.17(d), $J=9$	1.52(d), $J=9$	CH_3O,6.02(s)	3:1:1:3	219–220	215–217(5)
2.87(s)	—	CH_3O,5.97(s) CH_3,7.15(s)	3:1:3:3	272–273	268–270(30)
2.70(d), $J=9$	1.45(d), $J=9$	CH_3O,5.87(s)	3:1:1:3	102–103	105(22)
5.88(s)		—	2:1	*ca* 300[h,i]	—
5.95(s)		CH_3,7.70(s)	3:2:3	>300[h,j]	—
5.92(s)		CH_3,7.62(s)	3:2:3	>275[h,k]	—
5.93(s)		—	3:2	307–312[h,l]	—
—		—	—	335–350[h]	—
5.92(s)		CH_3O,6.10(s)	3:2:3	267–270[h]	268–269(5)
5.93(s)		CH_3O,6.05(s)	3:2:3	260–261[h,m]	—

[g] This spectrum shows an additional band at 256 mμ (log ε=4.04).
[h] Sublimes.
[i] Calc. for $C_{18}H_{14}N_2O_2$: C 74.47; H 4.86; N 9.65. Found: C 73.45; H 4.97; N 9.42.
[j] Calc. for $C_{20}H_{18}N_2O_2$: C 75.45; H 5.70; N 8.80. Found: C 75.12; H 5.70; N 8.80.
[k] Calc. for $C_{20}H_{18}N_2O_2$: C 75.45; H 5.70; N 8.80. Found: C 75.52; H 5.49; N 8.82.
[l] Calc. for $C_{18}H_{12}N_2O_2F_2$: C 66.25; H 3.71; N 8.59. Found: C 65.51; H 4.08; N 8.31.
[m] Calc. for $C_{20}H_{18}N_2O_4$: C 68.56; H 5.18; N 8.00. Found: C 68.00; H 5.22; N 8.08.

Table 3. Infrared and ultraviolet spectra of *N*-formyl-2-indolinols (III) and the open-chain tautomer III'b.

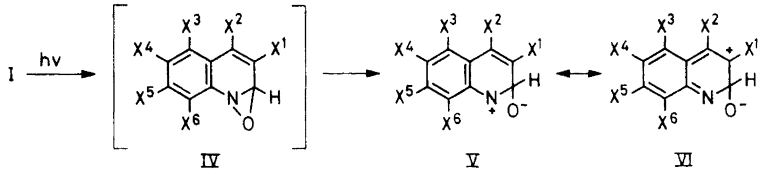
	IR(KBr), cm^{-1}		UV (96 % Ethanol)					
	OH	C=O	mμ	log ε	mμ	log ε	mμ	log ε
IIIa	3215	1665	248	4.13	278	3.61	287	3.60
IIIc	3260	1680	— [a]	—	—	—	—	—
IIIe	3210	1670	253	4.16	286	3.58	293	3.58
IIIg	3250	1660	249	4.05	281	3.45	302	3.28
IIIi	3200	1675	251	3.94	288	3.07	295	3.01
IIIk	3260	1670	250	3.90	287	3.33	294	3.28
IIIm	3280	1670	260	4.18	288	3.58	296	3.54
IIIn	3300	1660	250	3.97	288	3.37	295	3.41
IIIo	3355	1675	257	4.12	294	3.58	303	3.51
III'b	—	1720 1670	250	4.07	279	3.53	288	3.48

[a] See footnote *e*, Table 1.

DISCUSSION

The presence of oxygen seems to accentuate the formation of the parent amines in photolyses of quinoline *N*-oxides [5] and other aromatic amine *N*-oxides.[1] This fact suggests that the loss of oxygen from the amine oxide proceeds *via* a singlet excited state.* The other photoproducts probably arise from a triplet excited state.

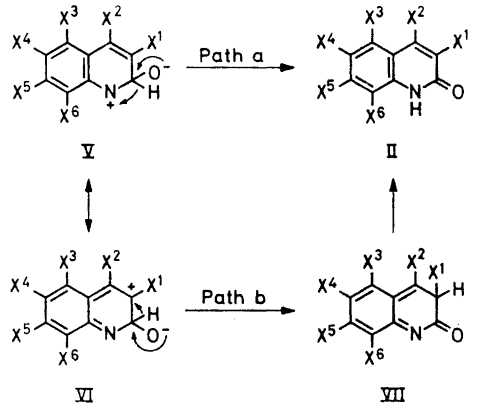
Although an oxaziridine (IV) has neither been isolated nor observed as a transient intermediate in any of the aromatic amine *N*-oxide photolyses, it is very attractive to regard oxaziridine formation as the primary step in



most of these photolyses.[1,6,14] We have previously suggested (see, *e.g.*, Ref. 14) the heterolysis of the intermediate oxaziridine to produce the zwitterion V—VI. This zwitterion can rearrange to a carbostyril derivative by either of the two intramolecular paths shown below.

We fully realize the possibility of other reaction paths (perhaps intermolecular) leading from the zwitterion V—VI to the carbostyril II and plan to investigate the fate of the proton in the 2-position of quinoline *N*-oxide during photolysis by deuterium labelling.

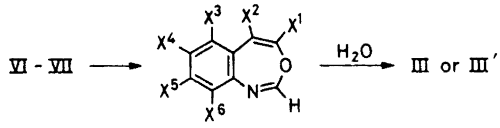
* For a discussion of triplet and singlet quenching by oxygen see, *e.g.* Ref. 13.



V II VI VII

In the photolysis of a series of 2-methylquinoline *N*-oxides in aprotic solvents we observed [10a] only a C(2) to C(3) shift (analogous to path *b*) and no *N*-methylcarbostyril was detected in the photolysis of an aqueous solution of 2-methylquinoline *N*-oxide.[10b] However, it has been reported [5] that 2-methyl- and 2,4-dimethylquinoline *N*-oxides rearrange to the corresponding *N*-methylcarbostyrils (analogously to path *a*) upon photolysis in methanol. Part of the reason for these somewhat contradictory results may be the influence of the different solvents used, but it is possible that both pathways can occur simultaneously.

The formation of the isomeric benz[d][1,3]oxazepines (VIII) from the zwitterions V—VI and the conversion of these seven-membered rings to the



VIII

corresponding *N*-formyl-2-indolinols (III) or the tautomers III′ has been previously discussed.[6]

It is possible that the oxaziridines (IV) undergo homolytic N—O bond cleavage, instead of the heterolytic cleavage that we have represented. If the cleavage takes place homolytically the resulting species should undergo some typical radical reactions. Preliminary experiments indicate that photolysis of quinoline *N*-oxides using cyclohexene as the solvent leads to no products incorporating the olefin. These results favor heterolytic cleavage.

The results obtained thus far show that the photolyses of quinoline *N*-oxides are subject to a pronounced solvent effect. This solvent dependence appears to be a general phenomenon; polar, protic media favor carbostyril formation and non-polar, aprotic media favor the production of benz[d][1,3]-oxazepines (VIII) or their solvolysis products, the *N*-formyl-2-indolinols (III) or the tautomers III′.

Finally, we would like to emphasize that the stability of the benz[d][1,3]-oxazepines seems to be dependent on the presence of electron-withdrawing substituents in the seven-membered ring.

The only benz[d][1,3]oxazepines thus far reported which are stable enough to be isolated and characterized are 2-cyano [6] and 2-phenyl [6] derivatives.

EXPERIMENTAL

Microanalyses were carried out in the microanalysis department of this laboratory by Mr. Preben Hansen and his staff.

Melting points (uncorrected) were determined on a Reichert melting point microscope.

Infrared spectra were recorded either on a Perkin Elmer "Infracord" or on a Perkin Elmer model 337 spectrophotometer. Ultraviolet spectra were recorded on a Perkin Elmer model 137 UV spectrophotometer. Nuclear magnetic resonance spectra were recorded on a Varian A60A or on a Varian HA 100 spectrometer.

Thin layer chromatograms (TLC). These were run on 8×10 cm plates with a 0.25 mm layer of silica gel (HF_{254}, Merck) or aluminium oxide ($PF_{254+366}$, Merck). The plates were visualized under UV light.

Preparative layer chromatography (PLC). The method described by Halpaap [15] was employed. The plates were 40×100 cm. They were developed 2—5 times with the appropriate solvent and the fractions separated were extracted using a Soxhlet apparatus.

Quinoline N-oxides. All of the quinoline *N*-oxides, except 4-chloroquinoline *N*-oxide, were prepared by oxidation of the corresponding quinolines using the previously described method.[4] 4-Chloroquinoline *N*-oxide was prepared from 4-nitroquinoline *N*-oxide by the reported method.[16]

Irradiations. The results are summarized in Table 1. All irradiations were performed through a Pyrex filter. The light source was either a Hanau Q-700 lamp or the 3600 Å lamps of a Rayonet reactor (Type RS). The irradiations were monitored by TLC and continued until no more starting material could be detected. All of the irradiations were carried out by one of the three methods described in detail below.

N-Formyl-2-indolinols. The melting points and analytical data for these compounds are summarized in Table 4.

Table 4. Physical constants and analytical data for *N*-formyl-2-indolinols (III) and the open-chain tautomer III'b.

	m.p. (°C)	% C		% H		% N		% Halogen	
		Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
IIIa	113—116	66.24	66.05	5.56	5.33	8.56	8.66		
IIIc	70—125[a]	—	—	—	—	—	—		
IIIe	108—109	67.78	67.80	6.26	6.10	7.91	7.93		
IIIg	128—130	67.78	67.78	6.26	6.36	7.91	7.98		
IIIi	110—112[b]	—	—	—	—	—	—		
IIIk	113—116	59.67	60.15	4.45	4.78	7.73	7.89		
IIIm	148—151	44.65	44.57	3.33	3.35	5.79	5.66	33.01(Br)	33.39
IIIn	155—156	54.69	54.87	4.08	4.23	7.09	6.86	17.94(Cl)	17.89
IIIo	151—152	62.13	62.35	5.74	5.79	7.24	7.43		
III'b	98—100	69.09	69.22	6.85	6.94	7.33	7.30		

[a] See footnote *e*, Table 1. [b] See footnote *g*, Table 1.

Photolysis of 4-methyl-6-methoxyquinoline N*-oxide in water.* A 200 mg sample of 4-methyl-6-methoxyquinoline *N*-oxide (Ip) was dissolved in 20 ml of water in a Pyrex test tube. The test tube was irradiated by placing it *ca.* 30 cm from a Hanau Q-700 lamp equipped with a reflector. After 20 h of irradiation all starting material was gone (TLC) and colorless crystals were present. Filtration of the mixture gave 4-methyl-6-methoxycarbostyril (IIp) as colorless needles (170 mg, 85 %), m.p. 272–273°.

Photolysis of 6-chloroquinoline N*-oxide in ethanol.* A 1.00 g sample of 6-chloroquinoline *N*-oxide (Il) was dissolved in 100 ml of 96 % ethanol and irradiated in Pyrex test tubes *ca.* 15 cm from the Hanau Q-700 lamp described above. After *ca.* 100 h irradiation the deposited dimer of 6-chlorocarbostyril was isolated by filtration as colorless crystals (700 mg, 70 %), m.p. 335–350° with sublimation. Sublimation of the dimer and recrystallization of the sublimate from ethanol gave 6-chlorocarbostyril (III), m.p. 269–270°.

Photolysis of 6-fluoroquinoline N*-oxide in acetone.* A 1.50 g sample of 6-fluoroquinoline *N*-oxide (Ik) was dissolved in 320 ml of acetone containing a small amount of water and irradiated with a Hanau Q-700 lamp contained in a Pyrex immersion well. After 3 h of irradiation no more starting material could be detected by TLC. Filtration of the solution gave the dimer of 6-fluorocarbostyril (126 mg, 4 %), which could be recrystallized from dimethylformamide to give colorless crystals, m.p. 307–312°. Sublimation of the dimer and recrystallization of the sublimate from ethanol gave 6-fluorocarbostyril (IIk), m.p. 268–271°.

The filtrate from the dimer was concentrated to a volume of *ca.* 50 ml and cooled in a dry ice-acetone bath. Filtration of the solution gave 6-fluorocarbostyril (IIk) as colorless crystals (243 mg, 16 %), m.p. 268–271°. An additional 195 mg of 6-fluorocarbostyril was isolated by PLC (see below), making the total yield of 6-fluorocarbostyril 439 mg (29 %).

The filtrate from the carbostyril was separated by PLC on silica gel using petroleum ether-benzene-acetone (7:7:1 by volume) as the eluent. From the PLC five fractions were isolated.

Fraction A: Colorless oil, 24 mg, unidentified.

Fraction B: Colorless oil identified as 6-fluoroquinoline (66 mg, 5 %) by IR, UV, and TLC comparison with an authentic sample.

Fraction C: White solid, m.p. 109–115°, which was recrystallized from benzene-cyclohexane to give *N*-formyl-5-fluoro-2-indolinol (IIIk) as colorless needles (754 mg, 45 %), m.p. 113–115°.

Fraction D: Tan solid, m.p. 263–267°, which was recrystallized from ethanol to give 6-fluorocarbostyril (IIk) as colorless needles (195 mg, 13 %), m.p. 268–271°.

Fraction E: Brown gum, 37 mg, unidentified.

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